Impact of Particle Aggregation on Nanoparticle Reactivity

by

David Jassby

Department of Civil and Environmental Engineering
Duke University

Date:  7/19/11
Approved:

___________________________
Mark Wiesner, Supervisor

___________________________
Heileen Hsu-Kim

___________________________
Jerome Rose

___________________________
Adrienne Stiff-Roberts

Dissertation submitted in partial fulfillment of
the requirements for the degree of Doctor of Philosophy in the Department of
Civil and Environmental Engineering in the Graduate School
of Duke University

2011
ABSTRACT

Impact of Particle Aggregation on Nanoparticle Reactivity

by

David Jassby

Department of Civil and Environmental Engineering
Duke University

Date: 7/19/11
Approved:

__________________________
Mark Wiesner, Supervisor

__________________________
Heileen Hsu-Kim

__________________________
Jerome Rose

__________________________
Adrienne Stiff-Roberts

An abstract of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Civil and Environmental Engineering in the Graduate School of Duke University

2011
Abstract

The prevalence of nanoparticles in the environment is expected to grow in the coming years due to their increasing pervasiveness in consumer and industrial applications. Once released into the environment, nanoparticles encounter conditions of pH, salinity, UV light, and other solution conditions that may alter their surface characteristics and lead to aggregation. The unique properties that make nanoparticles desirable are a direct consequence of their size and increased surface area. Therefore, it is critical to recognize how aggregation alters the reactive properties of nanomaterials, if we wish to understand how these properties are going to behave once released into the environment. The size and structure of nanoparticle aggregates depend on surrounding conditions, including hydrodynamic ones. Depending on these conditions, aggregates can be large or small, tightly packed or loosely bound. Characterizing and measuring these changes to aggregate morphology is important to understanding the impact of aggregation on nanoparticle reactive properties. Examples of decreased reactivity due to aggregation include the case where tightly packed aggregates have fewer available surface sites compared to loosely packed ones; also, photocatalytic particles embedded in the center of large aggregates will experience less light when compared to particles embedded in small aggregates. However, aggregation also results in an increase in solid-solid interfaces between nanoparticles. This can result in increased energy transfer
between neighboring particles, surface passivation, and altered surface tension. These phenomena can lead to an increase in reactivity. The goal of this thesis is to examine the impacts of aggregation on the reactivity of a select group of nanomaterials. Additionally, we examined how aggregation impacts the removal efficiency of fullerene nanoparticles using membrane filtration.

The materials we selected to study include ZnS - a metal chalcogenide nanoparticle that photoluminesces after exposure to UV; TiO₂ and ZnO nanoparticles - photocatalytic nanoparticles that generate reactive oxygen species upon UV irradiation; and, fullerene nanoparticles used in the filtration experiments, selected for their potential use, small size, and surface chemistry. The primary methods used to characterize particle and aggregate characteristics include dynamic light scattering used to describe particle size, static light scattering used to characterize aggregate structure (fractal dimension), transmission electron microscopy used to verify primary particle sizes, and electrophoretic mobility measurements to evaluate suspension stability. The reactive property of ZnS that was measured as a function of aggregation was photoluminescence, which was measured using a spectrofluorometer. The reactive property of TiO₂ and ZnO that was studied was their ability to generate hydroxyl radicals; these were measured by employing a fluorescent probe that becomes luminescent upon interaction with the hydroxyl radical. To detect the presence of fullerene nanoparticles and calculate removal efficiencies, we used total organic carbon
measurements. Additionally, we used UV-vis spectroscopy to approximate the impact of particle shadowing in TiO$_2$ and ZnO aggregates, and Fourier transformed infrared spectroscopy to determine how different electrolytes interact with fullerene surface groups.

Our findings indicate that the impact of aggregation on nanoparticle reactivity is material and structure specific. ZnS nanoparticles exhibit a 2-fold increase in band-edge photoluminescence alongside a significant decrease in defect-site photoluminescence. This is attributed to aggregate size-dependent surface tension. Additionally, we used photoluminescence measurements to develop a new method for calculating the critical coagulation concentration of a nanoparticle suspension.

The ability of both TiO$_2$ and ZnO to generate hydroxyl radicals was significantly hampered by aggregation. The decline in hydroxyl radical generation could be attributed to two key parameters. First, increased aggregate size was associated with increased particle shadowing, as determined from the observed decrease in the rate of optically induced transitions. Secondly, aggregate structure was associated both with increased shadowing (denser aggregates exhibited more shadowing than similarly sized loose aggregates), and with an increase in radical quenching on neighboring particle surfaces in an aggregate.

Aggregation had a positive impact on hydroxylated fullerene membrane separation, increasing removal efficiency to around 80%, regardless of transmembrane
pressure. However, the type of electrolyte used determined whether aggregation was successful at increasing removal. Divalent ions, capable of forming strong covalent bonds with surface oxygen groups, increased removal efficiency and made it pressure insensitive. In contrast, monovalent ions increased removal efficiency slightly, but maintained the pressure dependence of the removal efficiency. Evidence is presented to support the hypothesis that divalently aggregated hydroxylated fullerenes deform under increased pressure and partially penetrate the membrane.

Finally, nanoparticle reactive properties depend on the primary particle aggregation state. Both size and structure are key factors when evaluating nanomaterial reactivity under aggregation-inducing conditions. However, the impact of aggregation is not easily predicted. Some materials exhibit a decreased reactivity while others experience an increase. Therefore, the impact of aggregation on nanoparticle reactive properties must be evaluated on a material-by-material basis, while considering all of the particle and aggregate characteristics as well as environmental ones.
Dedication

To my family, both near and far. Without your inspiration, love and support, I would have stopped long ago.
Contents

Abstract ........................................................................................................................................ iv

List of Tables ............................................................................................................................... xii

List of Figures ............................................................................................................................... xiii

Acknowledgements ...................................................................................................................... xvii

1. Introduction .............................................................................................................................. 1

1.1 Motivation ............................................................................................................................... 1

1.2 Particle Aggregation ................................................................................................................. 4

1.2.1 Particle stability .................................................................................................................. 4

1.2.2 Aggregation mechanisms ................................................................................................... 9

1.2.3 Aggregate Structure ......................................................................................................... 10

1.2.4 Attachment Coefficient and Critical Coagulation Concentration .................................. 12

1.2.5 Solid-solid interface .......................................................................................................... 15

1.2.6 Changes to surface area ..................................................................................................... 16

1.3 Photocatalytic Semiconducting Nanoparticles ................................................................... 16

1.3.1 ZnS Nanoparticles ............................................................................................................ 19

1.3.1.1 ZnS Nanoparticle Fabrication and Characterization .................................................. 21

1.3.1.2 Aggregation and PL Characteristics ............................................................................ 22

1.3.2 Photocatalytic ROS Generation ....................................................................................... 24

1.3.2.1 Aggregate Structure and ROS generation .................................................................... 27

1.4 Fullerene Aggregation and Membrane Filtration ................................................................. 28
1.4.1 Fullerene Nanoparticles ................................................................. 28
1.4.2 Fullerene Reactivity and Aggregate Structure .............................. 29
1.4.3 Membrane Filtration ................................................................ 30
1.4.4 Aggregation Assisted Membrane Filtration ................................. 31
1.4.5 Membrane Filtration of Nanomaterials ....................................... 32
1.5 Research Objectives .................................................................... 33

2. Characterization of ZnS Nanoparticle Aggregation using Photoluminescence (26) ... 36
2.1 Introduction .................................................................................. 36
2.2 Materials and Methods ............................................................... 40
  2.2.1 ZnS Fabrication .................................................................. 40
  2.2.2 Particle and Aggregate Characterization ................................. 40
  2.2.3 Aggregation Kinetics ......................................................... 42
  2.2.4 PL and Absorbance .......................................................... 43
2.3 Results and Discussion ............................................................... 44
2.4 Conclusions ............................................................................... 60

3. Impact of Aggregate Size and Structure on the Photocatalytic Properties of TiO2 and ZnO Nanoparticles ............................................................. 63
3.1 Introduction ................................................................................. 63
3.2 Materials and Methods ............................................................... 65
3.3 Results and Discussion ............................................................... 68

4. Membrane Filtration of Fullerene Nanoparticle Suspensions: Effects of Derivatization, Pressure and Electrolyte Concentration (99) ......................... 82
4.1 Introduction ................................................................................. 82
4.2 Materials and Methods ........................................................................................................ 85

4.2.1 Chemicals and Materials ............................................................................................... 85

4.2.2 Characterization of Fullerene Suspensions .................................................................. 85

4.2.3 FulleroL, C60, and Electrolyte Stock Solutions .............................................................. 87

4.2.4 Fullerene Suspensions for Membrane Filtration ............................................................ 87

4.2.5 Membrane Filtration ..................................................................................................... 88

4.3 Results and Discussion ....................................................................................................... 89

4.4 Conclusions ....................................................................................................................... 101

5. Summary, Conclusions, and Implications ......................................................................... 103

5.1 ZnS Nanoparticle Aggregation ......................................................................................... 103

5.2 Impact of Aggregation on Hydroxyl Radical Generation by TiO2 and ZnO Nanoparticles ......................................................................................................................... 106

5.3 Membrane Filtration of Fullerene Nanoparticle Suspensions: Effects of Derivatization, Pressure and Electrolyte Concentration ......................................................... 109

Appendix .................................................................................................................................. 112

Appendix A: Supporting Information for Chapter 2 .............................................................. 112

Appendix B: Supporting Information for Chapter 3 .............................................................. 115

Biography .................................................................................................................................. 142
List of Tables

Table 4.1: EPM and size measurements of fullerol and nC60 aggregates. Measurement ranges (±) correspond to 95% confidence intervals (borrowed from Jassby et al. 2009 (99))..................................................................................................................................................96

Table B.1: Estimated light intensity at a given wavelength. ......................................................... 120

Table B.2: Parameter values used in model..................................................................................... 123
List of Figures

Figure 1.1: Diagram relating free energy and particle separation distance. Particles will stick together when the net free energy is negative (borrowed from www.malvern.com). .............................................................................................................................................. 7

Figure 1.2: Log(I) vs. Log(q) over time of an aggregating ZnS sample. Plots generated using SAXS. .................................................................................................................................................. 12

Figure 1.3: Attachment coefficients as a function of NaCl concentration. The CCC is calculated from the intersection of the fitted lines through the diffusion and reaction limited regimes. Reaction-limited aggregation regime (■); diffusion-limited aggregation regime (◇) (borrowed from Jassby and Wiesner, 2011). .................................................................................................................. 14

Figure 1.4a,b: Figure 1.4a,b: Interaction of hydroxyl radical with hole leads to the creation of hydroxyl radicals. Slow electron-hole recombination leads to more radical generation (a); Increased electron-hole recombination lowers radial generation rate........................................................................................................................................ 18

Figure 2.1a,b: (a) Absorption (dotted line) and PL (solid line) of uncoated ZnS in methanol; (b) Absorption and PL of mercaptoethanol coated ZnS in methanol .......... 44

Figure 2.2: XRD patterns of the ZnS nanoparticles used in this study, along with reference ZnS patterns. ZnS nanoparticles (a); Wurtzite (b); Sphalerite (c). ...................... 45

Figure 2.3a,b: (a) TEM image of ZnS nanoparticles used in this work (scale bar=50 nm); (b) particle size distribution as measured from TEM image.................................................................................................................. 47

Figure 2.4: EPM of ZnS with varying concentrations of NaCl. ................................. 48

Figure 2.5: Attachment coefficients as a function of NaCl concentration. The CCC is calculated from the intersection of the fitted lines through the diffusion and reaction limited regimes. Reaction limited aggregation regime (■); Diffusion-limited aggregation regime (◇). ........................................................................................................................................ 49

Figure 2.6a,b: (a) Aggregation rate of ZnS nanoparticles with different electrolyte concentrations. (b) PL response to aggregation (0.01 M); lines are set at 10 minutes intervals. ........................................................................................................................................ 50
Figure 2.7: Evolution of the 284 (plain) and 425 (prime) nm PL peak. Lower NaCl concentration lead to consecutively longer times until the onset of PL enhancement. 0.01 M (a, a’); 0.005 M (b, b’); 0.0023 M (c, c’); 0.0025 M (d, d’); 0.002 M (e, e’). Error bars represent 95% confidence intervals. ................................................................. 51

Figure 2.8a,b: (a) The evolution of the PL signal over time from a stirred and unstirred sample with RLA conditions (0.00225 M NaCl). (b) ................................................................. 53

Figure 2.9: Attachment coefficients calculated using DLS (■) and PL (●). ......................... 58

Figure 3.1: TEM images of TiO2 (a) and ZnO (b). ................................................................. 68

Figure 3.2: Changes in the fractal dimension of aggregating TiO2 and ZnO suspensions with varying electrolyte concentrations................................................................. 70

Figure 3.3: Normalized (by number of primary particles in aggregate) PL vs. aggregate size................................................................. 74

Figure 3.4: Model schematic of reactions used in kinetic model. Values over arrows represent reaction rates. ................................................................. 75

Figure 3.5: Observed vs. expected results of OH• generation model. Within each material and ionic strength’s data series, results are relative to those obtained in t = 0. The dashed line represents the ideal situation where the observed results match the expected results perfectly. Solid lines are the 95% confidence intervals around the fitted slope, represented by the solid line running through the data points. Error bars around the data points represent the 95% confidence intervals around the PL measurements. ...79

Figure 4.1: Removal efficiency vs. pressure for fullerol and nC60 suspensions (no electrolyte). Dotted lines correspond to 95% confidence intervals. ........................................... 85

Figure 4.2a-d: FTIR absorbance spectra of fullerol suspensions. (a) fullerol + MgCl2; (b) fullerol + CaCl2; (c) fullerol + NaCl; (d) fullerol. ................................................................. 88

Figure 4.3a-c: TEM images of fullerol aggregates with different 0.1 M CaCl2 (a), 0.1 M MgCl2 (b), and 0.3 M NaCl (c). ................................................................. 91

Figure 4.4a: Removal efficiency vs. pressure for fullerol suspensions aggregated with different MgCl2 and CaCl2 concentrations. Error bars refer 95% confidence intervals. ...92
Figure 4.4b: Removal efficiency vs. pressure for fullerol suspensions aggregated with different NaCl concentrations. Error bars refer 95% confidence intervals.................92

Figure 4.5a-d: SEM images of post-filtration membrane with different pressures and electrolyte concentrations. The large image is of the membrane surface exposed to the fullerol suspension, while the inset is of the underside (permeate side) of the membrane. Arrows indicate flow direction. (a) 0.1 M MgCl₂, 0.05 bar; (b) 0.1 M MgCl₂, 0.15 bar; (c) 0.1 M MgCl₂, 0.3 bar; (d) 0.5 M MgCl₂, 0.3 bar.................................................................94

Figure A.1: Relative PL intensity of an electrolyte-free, non-aggregating sample under continuous irradiation. 284 nm band-edge PL (a); 425 nm trap-site PL (b).................112

Figure A.2: Changes in band-edge (284 nm, solid line) and defect-site (425 nm, dotted line) PL intensity of aggregating mercaptetoethanol coated ZnS particles (0.01 M) under unstirred (a) and stirred (b) conditions.................................................................112

Figure A.3: The relative absorbance at 277 nm at different time points and electrolyte concentrations...........................................................................................................113

Figure A.4: Uncoated ZnS absorbance at t=0 (a), after two hours of aggregation (before shaking) (b), and after 2 hours of aggregation + gentle shaking (c).........................113

Figure A.5: The slopes of the PL relative intensity (284 nm) over time for each electrolyte concentration. Slopes were determined by fitting a sigmoidal function to each PL relative intensity curve (as seen in Fig. 7) and then taking the derivative at each time point. .............................................................................................................114

Figure B.1a,b: Changes in R_b over time for aggregating TiO₂ and ZnO destabilized with varying concentrations of NaCl (a); changes in EPM as a function of ionic strength (b). .........................................................................................115

Figure B.2: Log(1/I) vs. LogQ of aggregating TiO₂ and ZnO nanoparticles with varying concentrations of NaCl .............................................................................................................116

Figure B.3: Log(1/I) vs. LogQ of two ZnO concentrations (20 ppm – blue, 40 ppm – red). As can be seen, the fitted line through both curves has a very similar slope, indicating that the fractal dimension observed is indeed a result of the aggregate structure, and not a result of the flattening of the curve due to a decrease in particle concentration..............117

Figure B.4a,b: Impact of aggregates size on the ability of photocatalytic nanoparticles to generate free hydroxyl radicals. TiO₂ aggregates (a); ZnO aggregates (b) ..............117
Figure B.5: Temporal changes in the absorbance of aggregating TiO$_2$ and ZnO nanoparticles. The wavelengths correspond to the excitation wavelengths of the UV bulb used in the experiments. ........................................................................................................ 118

Figure B.6: Emission spectra of the UV bulb used in experiment (provided by Koninklijke Philips Electronics N.V.) ................................................................................................................................................. 119

Figure B.7: Changes in the rate of optically induced transitions as a function of hydrodynamic radius in TiO$_2$ suspensions (a) and ZnO suspensions (b). ......................... 119

Figure B.8: Changes in $\epsilon^{D-1}$ as a function of aggregate size and structure for aggregating semiconducting nanoparticles .................................................................................................................. 119
Acknowledgements

Many thanks go out to the many people who helped me complete this work. In particular, I would like to thank my advisor, Professor Mark Wiesner, for the constant stream of advise, ideas, and encouragement. Also, I would like to thank Professor Heileen Hsu-Kim for always lending a patient listening ear for my never-ending questions. Other people who help drive my work forward include my lab mates and the people who sell coffee – without you this wouldn’t have been possible. Finally, I owe a huge debt of gratitude to my wife, Jenn, and my children Ayla and Vivian, who endured long dinner conversations about quantum dots and fractal dimensions. Without your love and support this wouldn’t have happened.
1. Introduction

1.1 Motivation

Nanoparticle properties will vary as a function of the surrounding matrix. The matrix surrounding nanoparticles is expected to change during environmental release. In particular, the presence of dissolved electrolytes is expected to reduce particle stability, leading to particle aggregation. The effects of aggregation on nanoparticle reactivity are poorly understood. While aggregation reduces the surface-area to volume ratio, it also brings nanoparticle surfaces closer to each other, resulting in their interaction and possibly altering the distinctive characteristics that make nanoparticles unique. To study this phenomenon, we have selected three different nanomaterials (ZnS, TiO$_2$, and ZnO) and studied the impact of aggregation on their unique properties.

ZnS is a semiconducting nanomaterial desired for its ability to fluoresce, and used in medical imaging; ZnO is widely studied for its photocatalytic ability and is used in many commercial applications; TiO$_2$ nanoparticles, arguably the most commonly used engineered nanomaterial, are found in numerous industrial products and applications (1-3). C$_{60}$ and fullerol are manufactured in increasing quantities, and offer special challenges due to their small size and aggregation behavior.

ZnS, ZnO and TiO$_2$ need an external light source to be activated. The interesting property of ZnS, namely fluorescence, does not require a donor molecule, and the
fluorescence reaction occurs internally within the particle itself. In contrast, the unique property of TiO$_2$ and ZnO, namely hydroxyl radical generation, requires interaction with an external molecule (H$_2$O or OH$^-$).

Thus, aggregation may influence the nano-properties of these materials differently; while they all require light to be activated, the reduced surface area of an aggregate will influence the ability of external molecules to react with TiO$_2$ and ZnO surfaces (there are less of them), while ZnS will likely not be affected by this decrease. Additionally, once the hydroxyl radical is formed, it can be quenched on surrounding particle surfaces.

Following previous work conducted in our group, relating singlet oxygen generation by various fullerene nanoparticles to the structure of fullerene aggregates, we set out to explore how different fullerene structures impact their removal efficiency through membrane separation. Our preliminary results suggested that changes in aggregate type impacted physical properties of fullerene aggregates, supporting the previous findings reported by our group. Aggregation-assisted filtration of nanomaterials is likely to play an increasingly important role in future efforts to separate these materials from waste streams. The distinctive properties of C$_{60}$ and its hydroxylated derivative, C$_{60}$OH$_{22-24}$ (fullerol), present special challenges to separation efforts, due to their unique surface chemistry and aggregation behavior. Thus, how
aggregation impacts the removal of C_{60} and fullerol via membrane filtration was also investigated in this work.

In this research effort we have striven to work with a representative selection of commonly used nanomaterials that have both environmental and commercial importance. Since we can expect these nanomaterials to find increased use in the coming years, we can also expect to find increasing concentrations of them in the environment. Since released nanoparticles are likely to undergo aggregation, it is important to understand what happens to their reactivity under such conditions. Additionally, when considering the use of these materials in practical settings, it is likely that they will be deposited in films or deployed as ensembles. This work hopes to provide insight into how nanoparticle ensembles influence their properties.

To explore the effects of aggregation on nanomaterial reactivity, we will measure particle and aggregate size, aggregate structure, and the reactive capabilities of each nanomaterial, and seek to establish a relationship between these elements. Additionally, we will explore the impact of aggregation on the ability of ultrafiltration units to effectively separate C_{60} and fullerol from aqueous suspensions.
1.2 Particle Aggregation

1.2.1 Particle stability

Particle aggregation can be considered as a two-step process. In the first step, particles approach and potentially collide with each other (transport step). In the second step, colliding particles can attach to each other (attachment step). To prevent nanoparticles from sticking together and settling out of suspensions, nanoparticles must be stabilized. There are two main stabilization mechanisms responsible for nanoparticle stability in suspensions - electrostatic repulsion, and steric hindrance. Electrostatic repulsion happens because certain nanoparticle surfaces tend to be electrically charged. The charged surfaces of two nanoparticles repel each other, resulting in a stable suspension. Sources of surface charge on mineral surfaces include (4):

- Isomorphous replacement - Replacing one species of atom with a lower-valence species in a crystal lattice. This results in a negative charge on the surface of metal-oxide particles.
- Structural imperfections – Imperfections in the crystal lattice and broken bonds (dangling) can lead to surface charges.
- Preferential adsorption of specific ions – Sorbed molecules on the surface of nanoparticles can have an associated charge (such as natural organic matter).
Ionization of inorganic groups - pH dependent inorganic groups (such as hydroxyl) will develop a different charge under different pH conditions. Below the point of zero charge (PZC), the group will acquire a positive charge due to the association of a proton. Above the PZC, the group will acquire a negative charge due to the loss of a proton.

The charged surface of the nanoparticle attracts a layer of counter ions tightly bound to the surface (Stern layer). Beyond the Stern layer, there is a zone where an overall excess of the counter-ions is present along with an overall net charge with the same sign as the surface charge. As the distance from the surface grows, the charge trends closer to zero (4). This charge structure is known as the electric double layer (EDL). As particles approach each other, their EDL begin to interact. The similar charges of the EDL repel the particles from each other, discouraging aggregation. One way to measure the EDL charge of a nanoparticle is through electrophoresis. In electrophoresis, an external electric field is applied to the particle suspension, and the movement of a particle in response to the external field is measured. The relationship between the particle velocity (U) and the external electric field (E) is given by (5):

\[ U = \mu E \]  
Equation 1.1

where \( \mu \) is the electrophoretic mobility (EPM). When particles migrate in response to an external field, they take with them their EDL. U values are very sensitive to the
concentration of ions in suspension (5). Hence, EPM values are a measure of the
difference between the charge of the EDL and the bulk solution. As the difference
between the charge of the EDL and the bulk diminishes, $\mu$ values approach zero.

Steric stabilization is a stability mechanism achieved through the sorption of
non-ionic molecules (usually large ones) onto the surface of nanoparticles. The surface-
grafted molecules have a tail that is soluble in the surrounding solvent, and an anchor
unit that is ideally non-soluble (6). These molecules keep particle surfaces away from
each other, nullifying the effects of attractive van der Waals forces (7). There are two
physical mechanisms at play in steric stabilization (6). The first occurs when stabilizing
molecules on different particles begin to interact with each other. When this happens,
there is an increase in local molecular concentrations. This results in fewer
conformational formations, and a decrease in entropy. Additionally, the local increase in
concentration results in local increase in osmotic pressure, and hence a repulsive force.
The second occurs when the particles are close enough to each other so that the
stabilizing molecules begin to deform, resulting in an elastic compression of the
stabilizing molecules. This too results in a decrease in entropy, and is therefore
energetically unfavorable (6). If a charged molecule is sorbed to the surface of a particle,
acting as a stabilizer, then a combination of steric and electrostatic forces contribute to
particle stabilization. This phenomenon is known as electrosteric stabilization (8).
The stability of nanoparticles is a function of the balance between attractive (van der Waals) and repulsive (electrostatic, steric, or both) forces. For uncoated particles, where the primary stabilizing mechanism is electrostatic repulsion, the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is a useful model used to predict particle stability in suspension. The DLVO theory describes the repulsive and attractive forces between particles as a function of the distance between particles. An example of a DLVO stability analysis can be seen in Figure 1.1.

![Diagram](image)

**Figure 1.1: Diagram relating free energy and particle separation distance.** Particles will stick together when the net free energy is negative (borrowed from www.malvern.com).

The electrostatic repulsive force dominates at greater distances. However, if particles get close enough (overcoming repulsive forces) then van der Waals attractive
forces can bind the particles together, forming an aggregate. The distance at which the electrostatic repulsive force dominates is dependant on the thickness of the EDL. The thickness of the EDL can be approximated by the following equation (9):

\[ \text{Thickness} = \frac{1}{\kappa} = 2.32 \times 10^9 (\Sigma c_i z_i^2)^{1/2} \]

Equation 1.2

where \( \kappa \) is the Debye-Huckel parameter, \( c_i \) is the electrolyte concentration, and \( z_i \) is the electrolyte valence. As can be seen, the thickness depends on the electrolyte concentration and valence. When either increases, the EDL compresses, lowering the repulsive electrostatic forces. The result of this compression is that the kinetic energy needed by the particles to overcome the electrostatic repulsion is lowered, allowing more particles to come together and be bound by attractive van der Waals forces. Thus, the addition of an electrolyte to a particle suspension will lead to particle aggregation through EDL compression. Changes to a suspension’s stability due to the addition of electrolyte can be monitored through EPM measurements.

The stability of sterically stabilized nanoparticle suspensions is less sensitive to monovalent counter-ion concentrations. One way to induce particle instability in a sterically stabilized suspension is to change solvent conditions (i.e change in temperature) so that the stabilizing molecules grafted to the surface of the particles become less soluble (10). Also, if there are charged groups on the stabilizing molecules,
the addition of divalent counter-ions can induce particle bridging and aggregation (9, 11).

1.2.2 Aggregation mechanisms

There are three physical mechanisms responsible for particle collisions in suspension – Brownian motion, fluid shear forces, and differential sedimentation.

- **Brownian motion**: The random movement of solvent molecules, due to thermal energy, causes random movement of suspended particles. The smaller the particle, the more it will be affected by Brownian motion. The random movement of particles can induce particle collision. Brownian motion is utilized in dynamic light scattering (DLS) where the instrument deduces the diffusion coefficient of suspended particles by measuring the frequency shift of scattered light from the particles. The diffusion coefficient is then converted to particle size through the Stokes-Einstein equation. The larger the frequency shift, the faster the particles are moving, and hence the size of the particle is smaller.

- **Fluid shear**: Particles in a layer of fluid moving at a certain speed can collide with particles in a different, slower moving, layer. Additionally, high fluid shear has been shown to induce particle breakup and a change in aggregate structure, when compared to suspensions created in a lower-shear environment (12-14).
• Differential sedimentation: Large particles settle faster than small particle. Therefore, a falling large particle can overtake and collide with a smaller particle during settling.

In un stirred nanoparticle suspensions, the primary aggregation mechanism is Brownian motion (15). However, in stirred systems, fluid shear can play a significant role. Increased fluid shear increases both nanoparticle aggregation rate (increased probability of collision) and aggregate breakup (due to shear forces acting on an aggregate) (16).

1.2.3 Aggregate Structure

Aggregating colloidal suspensions tend to form aggregates with a fractal, or self-similar, structure (17, 18). For fractal colloids, when the mass of a large number of colloids is plotted against the colloid size, the slope is linear. However, the slope can have non-integer values (10). This slope is known as the fractal dimension (D) of an aggregate. In general, the closer D is to 3, the more dense an aggregate is.

Rapid aggregation, where every collision results in particles sticking together, and where the limiting factor of the aggregation rate is the diffusion of the particles, is known as diffusion limited aggregation (DLA). In contrast, slower aggregation, where the rate limiting step is the low probability that colliding particles will stick together, is known as reaction limited aggregation (RLA). The aggregation regime (DLA or RLA)
has a significant impact on the D of aggregates. Shear rates have a significant impact on
the measured D of aggregates (14, 19, 20). A colloidal suspension of SiO2 nanoparticles
(40 nm) placed under shearing conditions, showed an increase in aggregate size and D,
indicating rearrangement of the monomers within the aggregate (21).

The fractal dimension of an aggregate can be determined by various scattering
techniques including static light scattering (SLS) and small angle x-ray scattering (SAXS)
(22, 23). All these technique utilize similar principles to measure D. To determine D, the
log-transformed intensity of scattered light (I) is plotted vs. the log-transformed
scattering vector (q) (Figure 1.2) defined as

\[ q = \frac{4\pi \sin(\theta/2)}{\lambda} \quad \text{Equation 1.3} \]

where \( \theta \) is the angle between the sample and the detector and \( \lambda \) is the incident light
wavelength. Fitting a linear trend-line through the curve will yield the fractal dimension
of an aggregate. However, the fitted line must span at least an order of magnitude of q
values (in \( \text{Å}^{-1} \) space).
Figure 1.2: Log(I) vs. Log(q) over time of an aggregating ZnS sample. Plots generated using SAXS.

The length scales that a measurement technique is able to probe, is a function of the scattering angles and incident wavelength. SLS, which utilizes lasers, probes larger length scales than SAXS. Therefore, the appropriate technique needed to effectively measure D is dependent on the primary particle size. Aggregates composed of larger primary particles (tens of nanometers) are more effectively probed with SLS.

1.2.4 Attachment Coefficient and Critical Coagulation Concentration

The probability that two colliding particles will stick is termed the attachment coefficient (α). In DLA, where each collision results in the particles sticking together, α = 1. In RLA, α can attain values anywhere between 0 and 1. The probability of particles sticking together after collision is a function of the repulsive and attractive forces between the particles (24). The addition of electrolyte lowers the electrostatic repulsive
forces, and increases \( \alpha \). To calculate \( \alpha \), one must determine the initial aggregation rate, or the rate of dimer formation (25). The initial increase in aggregate radius is dependent on particle concentration, and can be expressed as (25)

\[
\left( \frac{dR_h(t)}{dt} \right)_{t=0} \propto k_{11}N_0 \quad \text{Equation 1.4}
\]

where \( R_h \) is the hydrodynamic radius as measured by dynamic light scattering (DLS), \( t \) is time, \( k_{11} \) is the initial aggregation rate, and \( N_0 \) is the initial particle concentration. If all repulsive forces are eliminated (as through the addition of sufficient electrolyte), then the initial aggregation rate is controlled by diffusion only (DLA), and can be called “fast”. \( \alpha \) can be expressed as a ratio between the initial aggregation rate, and the initial aggregation rate in the “fast” scenario (25)

\[
\alpha = \frac{k_{11}}{k_{11,\text{fast}}} = \frac{1}{N_0} \left( \frac{dR_h(t)}{dt} \right)_{t=0} \quad \text{Equation 1.5}
\]

where \( k_{11,\text{fast}} \) correspond to the “fast” (DLA) aggregation rate.

As the electrolyte concentration increases, the repulsive forces between particles decrease (in an electrostatically stabilized suspension), and the aggregation rate and \( \alpha \) increase. However, the maximum value \( \alpha \) can attain is 1. Therefore, beyond a particular salt concentration \( \alpha = 1 \). The minimum salt concentration where \( \alpha = 1 \) is termed the critical coagulation concentration (CCC). CCC values can be inferred by plotting \( \alpha \)
values vs. electrolyte concentrations, and then fitting linear trendlines through DLA and RLA points; the intersection of these lines yields the CCC (Figure 1.3) (26, 27).

Figure 1.3: Attachment coefficients as a function of NaCl concentration. The CCC is calculated from the intersection of the fitted lines through the diffusion and reaction limited regimes. Reaction-limited aggregation regime (■); diffusion-limited aggregation regime (♦) (borrowed from Jassby and Wiesner, 2011).

In general, the CCC is electrolyte-species dependent. Di and tri-valent counter ions are more effective charge screeners than monovalent ions, and thus require smaller concentration to reach the CCC (28). The Schultz-Hardy law predicts an inverse sixth power relationship between CCC for each increase in electrolyte valence. Experimental results indicate a CCC value relationship of 1 : 0.013 : 0.0016 for counter-ions with the valence of 1, 2, and 3, respectively (28). Additionally, the larger the ion, the better it is at charge screening. Thus, less Na⁺ is needed to reach the CCC than Li⁺ (28).
1.2.5 Solid-solid interface

The result of uncoated nanoparticle aggregation is the formation of a solid-solid interface. In particles with a high D, one can expect a large number of these interfaces, compared to low D aggregates. This interface is thought to enhance the unique capabilities of nanoparticles (29). In particular, this interface can prolong the lifetime of an electron-hole pair, by facilitating electron transfer between neighboring particles, allowing these reactive species to exert their redox powers on surrounding molecules (30). When two touching semiconducting nanoparticles are irradiated, the electron-hole pair can migrate from one particle to another (31, 32). This migration can be exploited to increase the functionality of nanomaterials to longer wavelength of light, by coupling a material that absorbs longer wavelengths with a material that possesses desired characteristics but can only absorb short-wavelength light (31).

The presence of a solid-solid interface between ZnS nanoparticles was credited with the observed reduction in surface strain in ZnS aggregates (33). Increased surface strain has been attributed to a decrease in fluorescence intensity from single-walled carbon nanotubes (34). Additionally, lattice strain can form defect sites that can trap either electrons or holes, reducing the quantum yield and changing the photoluminescent properties of quantum dots (35).
1.2.6 Changes to surface area

Another result of particle aggregation is a decrease in the surface area to volume ratio. The reduction in surface area can lead to a decrease in active surface sites. Aggregated magnetite nanoparticles were found to possess a significantly reduced capacity to dechlorinate CCl₄ when compared to unaggregated monomers (36). Aggregated PbS nanoparticles exhibited a dissolution rate an order of magnitude smaller than non-aggregated PbS particles (37). The authors attributed this change to decreased diffusion in aggregate pores that stemmed from the increased viscosity of trapped water molecules within the pores. The porosity of aggregates is directly related to D. High D values indicate low porosity of an aggregate (15, 38). In another study, both Fe(II) adsorption and nitrobenzene reduction rates were found to be independent of monomer size in aggregated goethite nano and micro-rods (39). The authors argue that particle aggregation negates any size effect, and that monomer size should not be considered when discussing reaction rates in aggregated systems.

1.3 Photocatalytic Semiconducting Nanoparticles

Semiconducting nanoparticles are characterized by the presence of an energy gap between valence and conduction electron bands, known as the band gap. The energy required to excite an outer-shell electron in a semi-conducting material so that the electron becomes a mobile charge carrier is referred to as the band gap energy. The
energy required to promote an electron from the valence to the conduction band of the semiconducting material may be provided by a photon. The formation of a carrier electron also creates an electron hole. Once a valence-band electron absorbs a suitably energetic photon, the electron-hole pair is free to migrate throughout the crystal lattice of the nanoparticle, including to the particle surface. The electron-hole pair can recombine, dissipating the absorbed energy in the form of an emitted photon (photoluminescence). Alternatively, at the surface, the electrons or holes are capable of interacting with surrounding molecules. Examples of such interactions are when a hole interacts with a hydroxyl ion to form a hydroxyl radical or when an electron interacts with an oxygen molecule to form a superoxide radical. Both hydroxyl radicals and superoxide radicals are forms of reactive oxygen species (ROS).

In many respects, fluorescence and ROS generation are competing processes. When electron-hole recombination is efficient, then fluorescence intensity increases. In contrast, when the recombination is inefficient, the electron or hole has a greater probability of interacting with surrounding molecules. For a reaction occurring on the surface of a nanoparticle, such as ROS generation from an electron/hole, the reaction rate will depend on the availability of electron/hole pairs. Increased electron-hole recombination will lower the reaction rate.
Figure 1.4a,b: Interaction of hydroxyl radical with hole leads to the creation of hydroxyl radicals. Slow electron-hole recombination leads to more radical generation (a); Increased electron-hole recombination lowers radial generation rate.

The reaction rates associated with Figure 1.4a and 1.4b are

\[
\frac{d(OH^*)_a}{dt} = k[OH^-][h^+]_a \quad \frac{d(OH^*)_b}{dt} = k[OH^-][h^+]_b \quad \text{Equation 1.6a,b}
\]

where \( k \) is the reaction rate, \([OH^-]\) is the concentration of hydroxyl ions, and \([h^+]_a\) and \([h^+]_b\) are the concentrations of holes associated with the conditions depicted in Figure 1.4a and 1.4b, respectively. In Figure 1.4b, the increased electron-hole recombination leads to \([h^+]_a > [h^+]_b\). Therefore

\[
\frac{d(OH^*)_a}{dt} > \frac{d(OH^*)_b}{dt} \quad \text{Equation 1.7}
\]
1.3.1 Generalized Aggregation-Reactivity Model

We attempted to create a general model relating aggregation with reactivity.

Reactions involving nanoparticles are often surface reaction that depend on available surface sites on the faces of particles. Examples of reaction products include ROS from photocatalytic nanoparticles and reduced organic compounds from reactions with zero valent iron. An equation describing the change in reaction product concentrations can be written as

\[
\frac{d[P]}{dt} = k[S_i][R] \quad \text{Equation 1.8}
\]

where \( k \) is the reaction rate, \( S_i \) is the active surface site, and \( R \) is the reactant. Since the rate of product formation depends on the concentration of reactive surface site, an equation describing this property is necessary. An equation describing the change in active surface site concentrations can be written as

\[
\frac{d[S_i]}{dt} = \varepsilon_i k_i[\text{particles}] - \sum_j \varepsilon_j k_{i,j}[S_i][S_j] \quad \text{Equation 1.9}
\]

where \( S_i \) is the concentration of active surface sites of interest, \( \varepsilon_1 \) and \( \varepsilon_2 \) are structural parameters related to aggregate fractal dimension, \( k_i \) and \( k_{i,j} \) are reaction rate terms, [particles] is the concentration of particles, and \( S_j \) are other surface sites on neighboring particles in an aggregate that can quench the active surface sites of interest, including self quenching, if applicable. Assuming steady state, equation 1.8 can be solved as
\[
[S_i] = \frac{\varepsilon_2 \sum_{j=1}^{\text{particles}} k_{i,j}[S_j] + \sqrt{\varepsilon_1^2 \left( \sum_{j=1}^{\text{particles}} k_{i,j}[S_j] \right)^2 + 4\varepsilon_1 \varepsilon_2 k_{i,j}[\text{particles}]}}{2\varepsilon_2 k_{i,j}}
\]
Equation 1.10

The above equations can be applied to any conditions, as long as the parameters are known. A detailed example of the application of this model to hydroxyl radical generation can be found in Chapter 3.

1.3.2 ZnS Nanoparticles

ZnS nanoparticles are semiconducting nanocrystals capable, under certain conditions, of photoluminescence (PL). ZnS is a member of the important II-IV semiconductor family. ZnS nanocrystals have a wide band gap (3.6 eV), and emit PL in the Ultraviolet (UV) range (40). The source of PL in ZnS nanocrystals lies in quantum confinement, or size quantization. The energy required to excite an outer-shell electron in a semi-conducting material so that the electron becomes a mobile charge carrier is referred to as the band gap energy. The energy required to promote an electron from the valence to the conduction band of the semiconducting material may be provided by a photon. The formation of a carrier electron also creates an electron hole. PL in semiconductor nanocrystal is the result of a recombination of the electron-hole pair. When this recombination takes place, a photon is emitted. The emitted photon has lower energy then the exciting photon, causing the emitted light to be red-shifted.
When the size of the semiconducting crystal where this phenomenon is observed is comparable to the DeBroglie wavelength of the charge carrier (41), the excitation and electron-hole pair recombinations are constrained by the quantized nature of the energy transferred from photon to electron leading to PL over a narrow band of wavelengths. The onset of photo-absorption is shifted towards lower wavelengths (blue-shifted) as the size of the nanocrystal declines.

Strain inducing crystal lattice defects (vacant, doped, or interstitial sites), as well as dangling bonds at the surface of the crystal can cause the charge carriers to become “trapped”, leading to energy loss, and producing phonons within the lattice (42). When these charge carriers recombine, the emitted photon will have less energy, resulting in a greater red-shift. When a trapped electron-hole pair recombines, the red-shifted PL is termed “defect-site” PL. If the electron-hole pair recombine across the entire band gap, with no trapping of the charge carriers, the PL is termed “band-edge” PL.

1.3.2.1 ZnS Nanoparticle Fabrication and Characterization

Recently, several research groups have succeeded in creating ZnS nanoparticles that exhibit both band-edge fluorescence and defect-site PL (40, 43-45). The emission peak at 428 nm can be attributed to sulfur vacancies within the ZnS crystal lattice (45). Other emission peaks are assigned to other interstitial or vacant atoms (trap sites) in the crystal lattice, depending on the preparation method. Several studies have found that
traps within the crystal structure can significantly reduce the quantum yield of quantum dots (46, 47).

Many different ZnS fabrication routes have been developed (40, 43, 48-50). A simple method in which ZnS nanocrystals can be fabricated easily from simple precursors in both water and methanol was reported by (51). ZnS nanocrystals prepared by their technique exhibit a sharp absorption shoulder at 279 nm, and have an approximate diameter of 3 nm. ZnS nanocrystals (3.4 nm) have large internal strains caused by unsatisfied molecular bonds on the surface of the crystal (52). This phenomenon is observed despite the presence of strong surface-passivating ligands. In a later study, (53) note that the nature of surface chemical reactions govern internal strain in ZnS nanocrystals. In particular, the authors note that methanol causes significant strain in ZnS crystals, while surface oxidation reduces such strain.

1.3.2.2 Aggregation and PL Characteristics

Uncoated ZnS nanocrystals prepared in water have positive EPM in the absence of electrolyte, at pH values smaller than 5 (54). Additionally, EPM is not affected by the presence or absence of oxygen. Nanoparticle stability can be altered through the addition of salts (54-56). Various researchers have explored the effects of particle aggregation on qdots. It was found that after shaking a suspension of uncoated CdSe qdots, their band-gap increased, and the maximum PL both increased and blue-shifted
(57). The X-Ray Diffraction (XRD) pattern of these qdots did not change after shaking, and it was concluded that no change occurred in the crystal size. Also, CdSe aggregates in the shaken sample were described as loosely packed, when compared to the pre-shaken sample. Fast aggregating particles tend to form loosely packed aggregates, while slowly aggregating particles tend to form densely packed aggregates. (58) induced aggregation in a ZnS/methanol system through solvent evaporation at different rates. The authors found that fast-aggregating ZnS nanocrystals had a different XRD pattern than slowly aggregating ZnS. Small Angle X-Ray Scattering (SAXS) indicated that ZnS formed aggregates with a fractal dimension of 2.6±0.1 and 2.9±0.1, for rapid and slow aggregation, respectively. Also, ZnS aggregates are not trapped in a metastable state, and that the energy of aggregation is low in this system, allowing for easy disaggregation.

Prolonged irradiation of CdSe/ZnS core-shell qdots leads to increased photoluminescence (59). Also, the addition of methanol to the qdot suspension (in toluene and hexane) enhances this phenomenon. Methanol is commonly used to precipitate various qdots. However, no visible precipitation occurred due to methanol addition. Fluorescence enhancement in CdSe/ZnS core-shell qdots suspended in toluene is the result of photo-assisted water adsorption onto the surface of the qdots, resulting in surface passivation (60). Mn+2 doped ZnS qdots exhibit a 50% increase in quantum yield
when continually irradiated with UV light in an inert atmosphere (61); in the presence of air, quantum efficiency grows by 100%. It was concluded that oxygen is key for efficient photo-induced surface passivation, and that the 50% increase noted in the inert atmosphere is probably a result of residual oxygen bound to the surface of the crystal. Prolonged laser irradiation of CdTe qdots leads to particle aggregation and subsequent PL enhancement (62).

The ZnS nanoparticle is a compelling model nanomaterial that is easy to fabricate and monitor, making it a particularly useful tool for studying the role of the aggregation process in determining nanomaterial fate, transport, and reactivity in multiple systems. This work intends to evaluate the potential importance of aggregation in altering size-dependent properties of nanoparticles, possibly including reactivity. Aggregation will be a key process in many physiological and environmental systems that must be monitored if nanomaterial behavior is to be interpreted correctly.

1.3.3 Photocatalytic ROS Generation

TiO$_2$ and ZnO nanoparticles are of interest for their color, semiconducting properties, and their ability to generate ROS upon exposure to UV light. TiO$_2$ is among the most commonly used nanomaterials, found in paints, foods, sunscreen, and other consumer products (63, 64). ZnO can be found in rubber, cement, and paints. When a TiO$_2$ or ZnO nanoparticle is hit with a photon whose energy exceeds the material’s bang
gap (3.18 eV for bulk anatase, 3.34 eV for ZnO), a valance band electron can jump to the conduction band (65). The resulting electron-hole pair can then reduce or oxidize materials adsorbed to the surface of the particle or in the surrounding suspension. The generated hole can oxidize a water molecule or a hydroxyl ion to produce an OH• radical, and the electron can reduce a dissolved oxygen molecule to produce a superoxide anion (O2•-) (65-69). Furthermore, it has been found that the O2•- ion can recombine with a trapped hole to generate singlet oxygen (¹O₂) (70). The reactions responsible for generating ROS are (66-69, 71):

\[
\begin{align*}
\text{photocatalyst} + h\nu &\rightarrow \tilde{e} + h^+ \\
\tilde{e} + O_2 &\rightarrow O_2^• \\
h^+ + H_2O &\rightarrow OH^• + H^+ \\
h^+ + OH^- &\rightarrow OH^• \\
h^+ + (\text{photocatalyst})OH &\rightarrow \text{OH}^•_{\text{sorbed}} \\
O_2^• + h^+ &\rightarrow ^1O_2
\end{align*}
\]

where hv is the exciting photon, \(\tilde{e}\) is a generated electron, \(h^+\) is a generated hole, and \((\text{photocatalyst})OH\) represents a sorbed hydroxyl ion on the surface of a particle.

Direct hole oxidation may play a key role in oxidative degradation reactions (70, 72). There is some controversy regarding the quantum yield of OH• formation, and the significance these radicals play in photocatalytic oxidation reactions (73, 74). In one study, it was found that direct hole oxidation was responsible for the degradation of an azo dye (73). Another study found that either sorbed OH• radicals or trapped holes are
responsible for the oxidation of nitroxide radicals (75). The quantum yield of hole production was found to be three orders of magnitude greater than that of free OH• radicals (74). ROS generated by semiconducting nanoparticles can be either sorbed to the surface of the particle or released into the surrounding medium (72, 76). It was found that the ratio between sorbed and free ROS in a TiO₂ suspension is dependant on pH. When pH increases, the concentrations of O₂•- and OH• radicals in suspension increases (76). While there are many more oxidizing holes and sorbed hydroxyl radicals generated during the photocatalytic process, the redox potential of non-sorbed OH• radicals is significantly higher (1.5 V vs. 1.9 V) (77). Therefore, for certain recalcitrant contaminant remediation, the ability of a semiconducting nanoparticle to generate non-sorbed OH• radicals, and their fate in the surrounding suspension is of particular importance.

TiO₂ can be found in three crystalline forms: Brookite, rutile, and anatase. In nano-sized TiO₂ particles, the most common types of crystalline forms are rutile and anatase. The standard TiO₂ nanoparticle used in most photocatalytic studies is TiO₂ P25, made by Evonic, Inc. (formerly Degussa). This material consists of a mixture of rutile and anatase (1:3 ratio) (78). The average particle size in this powder is 25 nm for the anatase crystals and 85 nm for the rutile crystals (78). The mixture of the anatase and rutile phases enhances the photocatalytic activity of the material (78, 79). In this mixture,
the rutile, which is considered to be photocatalytically inert, acts as a photon antenna, funnelling energy towards the active anatase particles (79).

In some cases, ZnO has been found to be a superior photocatalytic material, when compared to TiO₂ (80, 81). Photocatalytic ZnO nanoparticles have a hexagonal wurtzite crystal structure (82).

1.3.3.1 Aggregate Structure and ROS generation

Commercially available nano TiO₂ powder (e.g. P25), when added to water, tends to form relatively large aggregates (83, 84). There has been relatively little work done on the effects of particle aggregation on the reactivity of TiO₂. One study found that TiO₂ aggregates exhibited a significant decrease in their ability to degrade 2-chlorophenol, although the authors did not characterize the aggregates beyond the average hydrodynamic radius, and only looked at 2 time points during the aggregation process (83). Another study examined the effects of TiO₂ sintered networks on charge separation. The sintered TiO₂ network had a significantly reduced capability of maintaining charge separation. The authors attribute this to charge annihilation resulting from the solid-solid contact points between sintered particles (85). Two other studies found that increased aggregate size results in decreased photocatalytic activity, but again, aggregate characterization (beyond Rh) is absent (86, 87). In contrast, several studies found that TiO₂ aggregation enhanced reactivity. One study found that the absorption
capacity of organic acids onto TiO₂ surfaces was virtually unchanged in TiO₂ aggregates of different sizes (88). Another study found that TiO₂ aggregation, due to changes in pH, led to a significant increase in H₂ production. However, the same study found that aggregation reduced the ability of TiO₂ to reduce/oxidize organic molecules (89). The authors attribute these differences to aggregate structure, which lowers available surface reactive sites. However, the authors also note that changes in pH can affect the ability of TiO₂ to generate ROS, and concede that they are not sure of the importance of this mechanism.

While there is some conflicting information regarding the effect of particle aggregation on photocatalytic nanoparticle reactivity, the majority of the literature points to decreased reactivity. However, there has been no systematic study following aggregate size, structure, and reactivity. Specifically, to the best of our knowledge, there has been no detailed study of the effect of aggregate size and structure on the ability of photocatalytic nanoparticles to free hydroxyl radicals.

1.4 Fullerene Aggregation and Membrane Filtration

1.4.1 Fullerene Nanoparticles

Fullerenes are a family of carbon-based nanomaterials (90, 91, 92) that include caged molecules such as C₆₀ as well as carbon nanotubes. These materials are of particular interest due to their structural and electronic properties, including their high
quantum yield, efficient electron harvesting, and ability to generate various ROS, including O$_2^-$ and O$_2$ under UV illumination (93, 94). Furthermore, it was found that fullerenes are efficient radical quenchers, as well (95, 96).

The underivatized form of C$_{60}$ is extremely hydrophobic (97). However, it is possible to create C$_{60}$ aqueous suspensions through either a solvent exchange or prolonged sonication and mixing (98). The suspensions formed in these ways are actually aggregates of C$_{60}$ primary particles, with average aggregate sizes in the tens of nanometers (98,99). Adding hydroxyl groups to the surface of C$_{60}$ particles (C$_{60}$(OH)$_{22-24}$ also known as fullerol) greatly enhances their aqueous solubility, requiring little more than stirring to create a stable suspension. However, fullerol particles in suspension also form large aggregates with size ranges in the tens to hundreds of nanometers (99, 100).

1.4.2 Fullerene Reactivity and Aggregate Structure

While theoretical predictions indicate that underivatized C$_{60}$ should have a quantum yield of almost 1, in practice, aqueous suspension of these materials do not generate any ROS (100, 101). In contrast, derivatized C$_{60}$ particles have a lower quantum yield, but do generate ROS (100, 102). It is thought that aggregate structure plays a significant role in the lack of ROS generation in C$_{60}$, where ROS generated by these aggregates is effectively quenched due to the tight packing of the particles. In contrast, the open fractal structure of fullerol allows for some ROS generation (100, 102).
However, fullerene aggregate structure was not verified experimentally, due to poor electron density in carbon structures. Ambiguities in membrane filtration of fullerene aggregates were attributed to aggregate structure (99). Removal efficiencies of fullerol aggregates were highly dependent on the applied pressure across the membrane, indicating that fullerol aggregates can be broken apart to pass through the membrane. In contrast, C₆₀ aggregates exhibited removal efficiencies that were independent of transmembrane pressure. The filtration experiments reinforce the theoretical predictions regarding the fundamental difference between C₆₀ and fullerol aggregates.

While exploring differences between C₆₀ and fullerol aggregates, we discovered that changes in aggregate character have a significant impact on the removal of fullerene materials from water. This result had implications for waste-stream remediation and material recovery, and was developed into an independent research project.

### 1.4.3 Membrane Filtration

Pressure-driven membrane filtration is a commonly used step in many water treatment trains (4). Membrane types can be delineated by their pore sizes and what they can remove, and include (4)

- Microfiltration (> 0.1 μm) – particles, sediment, algae, protozoa, bacteria
- Ultrafiltration (0.01 – 0.1 μm) – small colloids, viruses
- Nanofiltration (1 nm) – dissolved organic matter, divalent ions
• Reverse osmosis (<1 nm) – monovalent ions

Smaller pore sizes offer greater removal, but also demand higher pressures to push the water through, and also foul more readily. Therefore, there is an interest in using the largest pore-size possible to separate contaminants from the influent water.

Membranes generally consist of two layers, an active layer and a support layer. The active layer has a narrow pore range, low porosity, and is responsible for the size exclusion. The support layer has larger pores and is primarily there to offer mechanical support to withstand the pressure needed for filtration (4).

There are three mechanisms responsible for removing particles from solution through membrane filtration. The first is simple straining, where particles larger than the pore size are excluded from the stream passing through the membrane (4). The second is cake layer trapping, where large strained particles form a layer on the surface of the membrane that traps smaller particles and prevents them from passing through the membrane (4). The third mechanism is adsorption, where small particles are adsorbed to the surface and pores of the membrane (4).

1.4.4 Aggregation Assisted Membrane Filtration

Aggregating target particles prior to filtration offers the advantage of lower operational costs due to the use of larger pore membranes, as well as the simplicity of aggregation initiation (103). An aggregation step prior to filtration has been applied
towards the removal of metal ions by aggregating them with chitosan (103); recovery of
ionic liquids from wastewater streams (104); enhanced removal of F-specific RNA
phages (105).

The rigidity of a colloidal aggregate depends on both the electrolyte species and
electrolyte concentration (106, 107). In laser tweezing experiments, it was demonstrated
that aggregates formed with divalent ions, which formed inter-particle bridges,
exhibited stronger resistance to bending, when compared to monovalently destabilized
particle suspensions. Additionally, higher electrolyte concentrations yielded stiffer
aggregates (107). Thus, it is expected that the removal efficiency of aggregates formed as
the result of divalent ion addition would exhibit a lower dependence on transmembrane
pressure, as they are less likely to break and deform.

1.4.5 Membrane Filtration of Nanomaterials

There have been many studies published about nanoparticle membrane filtration
including a study of cake layer formation by silica nanoparticles in cross-flow membrane
filtration (108); a study of novel membrane materials for nanoparticle fractionation (109);
and, a comparison between centrifugation and ultrafiltration as a purification method
for nanoparticle suspensions (110).

There have been relatively few studies on the filtration of fullerene suspensions.
Filtration of fullerol through a nano filtration membrane achieved a removal efficiency
of 98% (111). The pore size of the membranes used in the study was found to be <0.3 nm, confirming size straining as the separation mechanism (fullerol primary particles are ~1 nm in diameter) (112). In another study, C60 suspensions were aggregated with alum and 50 ppm of Ca2+, and then filtered successfully through an 8 μm membrane filter with nearly 100% removal efficiency (113). However, removal efficiency was highly dependent on the pH of the suspension and alum concentration (113). In another study, it was observed that some fullerol could diffuse through a dialysis bag with a molecular weight (MW) cut-off of 100 Da (114). A conversion between molecular weight and hydrodynamic radius was performed for dextran, with the following relationship (115)

\[ 2 \times R_h = 0.11(MW)^{0.46} \]  

Equation 1.12

Based on equation 1.9, the cutoff size for the 100 Da dialysis bag is ~2 nm. Therefore, even though fullerol aggregates were definitely present, some fullerol still penetrated through the bag, perhaps due to the fact that some of the fullerol was unaggregated.

1.5 Research Objectives

The overriding objective of this work is to understand how aggregation impacts nanoparticle properties.

In Chapter 2 we describe the impact of aggregation on the PL spectra of ZnS nanoparticles. ZnS nanoparticles are a useful model due to their ease of preparation and non-toxicity. Additionally, their nano-characteristic (PL) is easy to monitor and allows
for high temporal resolution. Since semiconducting quantum dots are increasingly used in industrial applications, it is important to understand the impact of aggregation on their reactive properties. Additionally, we demonstrate how to utilize changes to the PL spectra to determine the attachment coefficient of PL particles. This work has been published in the journal Langmuir (26).

In Chapter 3 we investigate the impact of aggregation on photocatalytic nanoparticles, and in particular on their ability to generate free hydroxyl radicals. We utilize TiO$_2$ and ZnO as model photocatalytic nanomaterials, chosen for their wide use in many industrial and commercial applications, and for their superior reactive properties. We followed changes in aggregate size and structure using DLS and SLS, and correlated these results to OH$^-$ concentrations. Additionally, we developed a kinetic model that allowed us to evaluate the importance of various particle and aggregate properties to hydroxyl radical generation. The significance of this work is two-fold. First, photocatalytic nanomaterials will increasingly be found in the natural environment. Second, when applying these materials in water treatment applications, they will most probably be deposited in some form of thin-film. Understanding the interplay between size, structure and reactivity will allow for a better understanding of the impact of these materials in the environment, as well as design optimization in engineered settings. This work has been submitted to the journal Environmental Science and Technology.
In Chapter 4 we explore how nanoparticle membrane separation can be enhanced through aggregation. This line of investigation is important in waste-stream remediation, as well as in providing a fundamental understanding of how nanoparticles are held together in aggregates. The materials used in this chapter are two types of fullerenes, derivatized (18-24 hydroxyl groups) and underivatized. We used ceramic membranes with a narrow pore distribution and a pore size significantly smaller than the nanoparticle aggregate. Additionally, we utilized both mono and di-valnt counter ions to destabilize the nanoparticle suspension, and vacuum filtered the suspension using varying pressures. We attempted to demonstrate how inter-particle interactions govern the strength of nanoparticle aggregates, and how these interactions would impact the removal efficiency of nanoparticles using membrane filtration. This work has been published in the Journal of Colloid and Interface Science (99).

The final chapter of this dissertation (Chapter 5) discusses the importance of aggregation to nanoparticle processes, in light of the theoretical and experimental evidence put forward in this dissertation.
2. Characterization of ZnS Nanoparticle Aggregation using Photoluminescence (26)

2.1 Introduction

Semiconducting nanoparticles are capable, under certain conditions, of photoluminescence (PL). ZnS is a member of the important II-IV semiconductor family. ZnS nanoparticles have a wide band gap (3.6 eV), and photoluminesce in the ultraviolet (UV) range (40). The source of PL in ZnS nanoparticles lies in quantum confinement, or size quantization. The energy required to excite an outershell electron in a semiconducting material so that the electron becomes a mobile charge carrier is referred to as the band gap energy, and may be provided by a photon. The formation of a carrier electron also creates an electron hole. PL in semiconductor nanoparticles is the result of a recombination of the electron-hole pair. When this recombination takes place, a photon is emitted. The emitted photon has lower energy than the exciting photon, causing the emitted light to be red-shifted.

When the size of the semiconducting nanoparticle where this phenomenon is observed is comparable to the DeBroglie wavelength of the charge carrier (41), the excitation and electron-hole pair recombinations are constrained by the quantized nature of the energy transferred from photon to electron, leading to PL over a narrow band of wavelengths. The onset of photo-absorption is shifted towards lower wavelengths (blue-shifted) as the size of the nanoparticle declines. Strain inducing
crystal lattice defects (vacant, doped, or interstitial sites), as well as dangling bonds at the surface of the crystal can cause the charge carriers to become “trapped”, leading to energy loss, and producing phonons within the lattice (42). When these charge carriers recombine, the emitted photon will have less energy, resulting in a greater red shift.

Recently, several research groups have succeeded in creating ZnS nanoparticles that exhibit both band-edge and defect-site PL (40, 43-45). The defect-site PL peak located at 428 nm is attributed to sulfur vacancies within the ZnS crystal lattice (45). Other emission peaks are assigned to other interstitial or vacant atoms (trap sites) in the crystal lattice, depending on the preparation method. Several studies have found that traps within the crystal structure can significantly reduce the quantum yield of quantum dots (46, 47).

Many different ZnS fabrication routes have been developed (40, 43, 48-50). A method in which ZnS nanoparticles can be fabricated easily from simple precursors in both water and methanol was reported by Rosetti et al. (51). ZnS nanoparticles prepared by this technique exhibit a sharp absorption shoulder at 279 nm, and have an approximate diameter of 2 nm. ZnS nanoparticles (3.4 nm) were found to have large internal strains caused by unsatisfied molecular bonds on the surface of the crystal (52). This phenomenon is observed despite the presence of strong surface-passivating ligands. In a later study, the authors note that the nature of surface chemical reactions
govern internal strain in ZnS nanocrystals (53). In particular, the authors note that methanol causes significant strain in ZnS crystals, while surface oxidation reduces such strain.

Uncoated ZnS nanoparticles prepared in water have positive electrophoretic mobility (EPM) in the absence of electrolyte, at pH values smaller than 5 (54). Also, it was found that EPM is not affected by the presence or absence of oxygen. Nanoparticle stability can be altered through the addition of salts (54-56). Various researchers have explored the effects of particle aggregation on PL nanoparticles. One group found that after shaking a suspension of uncoated CdSe quantum dots, their band-gap increased, and the maximum PL both increased and blue-shifted (57). The x-ray diffraction (XRD) pattern of these nanoparticles did not change after shaking, and the authors conclude that no change occurred in the crystal size. Also, the authors note that CdSe aggregates in the shaken sample appear to be loosely packed, when compared to the pre-shaken sample.

Particle aggregation can be induced through the addition of an electrolyte. Rapid aggregation, where every collision results in particles sticking together, and where the limiting factor of the aggregation rate is the diffusion of the particles, is known as diffusion limited aggregation (DLA). In contrast, slower aggregation, where the rate limiting step is the low probability that colliding particles will stick together, is known
as reaction limited aggregation (RLA). The aggregation regime (DLA or RLA) has a significant impact on the fractal dimension of aggregates. In general, aggregates formed under DLA and RLA, in a zero-shear environment, have a fractal dimension of approximately 1.8 and 2.1, respectively (10). Shear rates have a significant impact on the fractal dimension of aggregates (14, 19, 20). Many studies have shown that electrolyte destabilized suspensions display faster aggregation rates and an increased fractal dimension when exposed to increasing shear forces (shear forces were induced by stirring) (21, 116, 117). When aggregation was induced in a ZnS/methanol system through solvent evaporation at different rates, it was found that fast-aggregating ZnS nanocrystals had a different XRD pattern than slowly aggregating ZnS (58). Also, the authors note that the ZnS aggregates are not trapped in a metastable state, allowing for easy disaggregation (58).

In this paper we describe the effects of particle aggregation on the PL characteristics of ZnS nanoparticles. Additionally, we demonstrate how to exploit PL data to derive a key aggregation characteristic – the attachment coefficient. Particle aggregation is a commonly observed process that is likely to affect nanoparticle persistence, reactivity, and bioavailability. The ZnS nanoparticle is a compelling model nanomaterial that is easy to fabricate and monitor, making it a particularly useful tool
for studying the role of the aggregation process in determining nanomaterial transport and fate in multiple systems.

### 2.2 Materials and Methods

#### 2.2.1 ZnS Fabrication

The procedure for fabricating uncoated ZnS in methanol has been described elsewhere (51). For uncoated ZnS nanoparticles, 6 ml of freshly prepared Na2S (6.6 mM) dissolved in methanol are rapidly injected into 100 ml of Zn(ClO4)2 (1.3 mM) and allowed to stir for several seconds. The resulting stock suspension had a ZnS concentration of 0.373 mM (as S). Mercaptoethanol coated ZnS nanoparticles were prepared in the same manner, except that the Zn(ClO4)2 solution had 50 mM of mercaptoethanol added to it. The suspension was prepared under aerobic conditions at room temperature (23 °C) and stored in the light.

#### 2.2.2 Particle and Aggregate Characterization

Particle size distributions were measured using dynamic light scattering (DLS) at 148°, on an ALV CGS-3 (ALV-GMBH, Langen, Germany). We found that this angle was best suited to capture the large variation of particle and aggregate sizes generated in the aggregation experiments described below. In particular, this large angle allowed us to accurately measure the presence of the ZnS monomers in suspension. The DLS instrument used in this study is equipped with a He-Ne laser (633 nm), and is capable of
conducting DLS measurements at angles ranging between 12 and 152°. The intensity-weighted average hydrodynamic radius (Rh) was calculated by second order cumulant analysis; the intensity weighted and number weighted particle size distributions were calculated by fitting an exponential function to the auto-correlation function (ALV software package). EPM measurements were performed using a Zeta Sizer Nano ZS (Malvern, Bedford, MA). This instrument employs a He-Ne laser (633 nm) and collects scattered light at a fixed angle of 173°. The instrument measures the frequency shift of the scattered incident beam, deducing the particle EPM. EPM measurements were done in triplicate. The EPM of ZnS nanoparticles with 0.01 M NaCl was measured in a different manner than the rest. When measuring EPM at this concentration, it was observed that at the beginning of the measurement the EPM was positive, but as the measurement wore on, the EPM became negative, indicating a charge reversal. It is important to note that chloride counter-ions were found to be indifferent to ZnS particle surfaces (54). It was observed elsewhere that charge reversal can occur in organic solvents in the presence of sufficient indifferent monovalent ion concentrations (118). To accurately measure EPM under such circumstances, it was suggested that only the first mobility measurement be used to determine the actual EPM (118). This methodology was adopted in this work for the 0.01 M NaCl EPM measurements. ZnS nanoparticles were visualized by a transmission electron microscope (TEM) (FEI Tecnai G2 Twin,
Hillsboro, OR) operating at 160 kV. TEM image analysis was performed using the ImageJ software package (ImageJ version 1.40G, National Institute of Health, USA). XRD measurements were performed on a Philips X’Pert PRO MRD HR X-Ray Diffraction System (PANalytical Inc., Westborough, MA).

2.2.3 Aggregation Kinetics

All aggregation kinetics measurements were done in triplicate. ZnS aggregation kinetics were determined using a method similar to the one described elsewhere (119). In short, 1 ml of ZnS suspension was added to varying volumes of 0.02 M NaCl (dissolved in methanol) and methanol, for a total volume of 2 ml. The Rh of ZnS particles (fixed ZnS concentration) was followed over time in the presence of varying concentrations of NaCl (0.0021 to 0.01 M) with DLS. Size measurements were taken every second. Linear trend-lines were fitted to the hydrodynamic radius data points. Aggregation kinetics experiments were stopped when Rh reached a value of 1.3xRh,0, where Rh,0 is the initial average hydrodynamic radius. In the DLA regime, due to extremely rapid aggregation, only the first three data points were used. In all cases, the intercept of the fitted line was within 4 nm of the original Rh. Aggregation rates were determined from the slope of the fitted line. The attachment coefficient (α) of the ZnS particles at different NaCl concentrations was determined from
\[ \alpha = \frac{\left(\frac{dR_h(t)}{dt}\right)_{t \to 0}}{\left(\frac{dR_h(t)}{dt}\right)_{t \to 0, \text{fast}}} \]  

Equation 2.1

where \( R_h(t) \) is the average hydrodynamic radius at time \( t \). The term with the “fast” designation refers to diffusion-limited aggregation, where there are no electrostatic repulsive forces between particles due to charge screening by the electrolyte.

### 2.2.4 PL and Absorbance

PL measurements were performed on a Varian Cary Eclipse Fluorescence Spectrophotometer (Varian Inc., Palo Alto, CA). Excitation wavelength was fixed at 250 nm, and slit width maintained at 5 nm for both excitation and emission. Absorbance measurements were performed on a Hitachi U-2810 (Hitachi High Technologies, Schaumburg, IL) Spectrophotometer in scanning wavelength mode. All PL/absorbance measurements were done using a 10 mm/10 mm (4 ml) quartz cuvette. Additionally, when following the evolution of the intensity of either the PL or absorbance over time, relative intensity was used. Relative intensity was calculated by

\[ I_{r,t} = \frac{I_t}{I_0} \]  

Equation 2.2

where \( I_{r,t} \) is the relative intensity at time \( t \), \( I_t \) is the PL intensity measured at time \( t \), and \( I_0 \) is the PL intensity at \( t=0 \).
PL of an Aggregating ZnS Suspension: All PL measurements were done in triplicate. 1.5 ml of ZnS stock suspension were added to varying volumes of a 0.02 M NaCl (in methanol) and methanol, for a total volume of 3 ml. Depending on the measurement, the suspension was then placed either in the DLS instrument, the UV-vis spectrophotometer, or the fluorometer. Three stirring regimes were used in this study – no stirring, slower stirring (180 rpm), and faster stirring (230 rpm). Stirring conditions were induced by a magnetic stirrer, using the built-in capability of the fluorometer. Stirring experiments were only performed on the fluorometer and could not be duplicated using DLS or UV-vis absorbance.

**2.3 Results and Discussion**

Absorption and PL spectra of uncoated and coated (mercaptoethanol) ZnS nanoparticles are shown in Figure 2.1a and 2.1b, respectively.

![Figure 2.1a](image1.png) ![Figure 2.1b](image2.png)

**Figure 2.1a,b:** (a) Absorption (dotted line) and PL (solid line) of uncoated ZnS in methanol; (b) Absorption and PL of mercaptoethanol coated ZnS in methanol.
The nanoparticles exhibit an absorption shoulder centered on 277 nm and 269 nm for the uncoated and coated ZnS, respectively (Figure 2.1a and 2.1b). This shoulder is indicative of a discrete electronic transition, commonly found in quantum-confined nanoparticles. For the uncoated ZnS nanoparticles, the PL spectra exhibits two peaks; a large, sharp peak centered around 284 nm (full width at half maximum (FWHM)=35nm) is associated with band-gap PL and a smaller, wide peak centered around 425 nm (FWHM=138 nm) associated with strain-inducing sulfur vacancies. The coated ZnS exhibit the same two peaks, although the 284 nm peak is not as well defined, and the 425 nm peak is sharper. The XRD patterns for the uncoated ZnS particles exhibit both cubic and hexagonal ZnS patterns (Figure 2.2).

![XRD patterns](image)

**Figure 2.2:** XRD patterns of the ZnS nanoparticles used in this study, along with reference ZnS patterns. ZnS nanoparticles (a); Wurtzite (b); Sphalerite (c).
The broad widths of the 40°, 47°, and 55° peaks of the ZnS nanoparticle XRD patterns indicate very small crystal size (Figure 2.2). Due to the sample preparation method, NaClO4 diffraction peaks are also evident. The Rh (intensity-weighted) of an unaggregated, uncoated ZnS sample, as measured by DLS, was 30 nm. However, fitting an exponential function (regularized fit – intrinsic software function on ALV instrument) to the auto-correlation function (intensity weighted) indicated the presence of 3.6 nm (2.5%) particles as well as a population of 37 nm particles (97.5%). A number weighted distribution put the population of 3.6 nm particles at 99.6%. Figure 2.3a shows a TEM image of the ZnS nanoparticles used in this work. As can be seen, the ZnS crystals are well separated, and can be found in either clusters or individual form. TEM image analysis (106 particles) indicated that the average ZnS particles were approximately 3.3 ± 0.68 nm in diameter (Figure 2.3b).
Figure 2.3a,b: (a) TEM image of ZnS nanoparticles used in this work (scale bar=50 nm); (b) particle size distribution as measured from TEM image.
Particle destabilization was achieved by introducing varying concentrations of NaCl. The EPM of the ZnS particles as a function of NaCl concentration is summarized in Figure 2.4.

![Graph showing EPM of ZnS with varying NaCl concentrations](image)

**Figure 2.4: EPM of ZnS with varying concentrations of NaCl.**

ZnS aggregation kinetics were studied over a range of NaCl concentrations (0.0021 – 0.01 M).
Figure 2.5: Attachment coefficients as a function of NaCl concentration. The CCC is calculated from the intersection of the fitted lines through the diffusion and reaction limited regimes. Reaction limited aggregation regime (■); Diffusion-limited aggregation regime (◆).

Changes in the attachment coefficient ($\alpha$) as a function of NaCl concentration indicate distinct diffusion-limited and reaction-limited aggregation regimes (Figure 2.5). In the diffusion-limited regime, $\alpha$ remains constant at 1. In the reaction limited regime, $\alpha$ changes with NaCl concentrations, declining in step with NaCl concentrations. These results are consistent with EPM measurements (Figure 2.4), as a lower EPM implies a more rapid aggregation rate. Indeed, when linear trend-lines were fitted through the data points of the reaction and diffusion limited regimes, the intersection of these lines indicated a critical coagulation concentration (CCC), of 0.0048 M which approximately corresponds to the electrolyte concentration that reduced the EPM to zero.
Growth of aggregate size was monitored using DLS. The growth rate of aggregate size increased with electrolyte concentration, until the CCC was exceeded (Figure 2.6a). Particle aggregation produced dramatic effects on the PL spectra of the ZnS nanoparticles. An example of the full spectrum PL response to aggregation (0.01 M) can be seen in Fig. 2.6b.

![Graph](image)

**Figure 2.6a,b:** (a) Aggregation rate of ZnS nanoparticles with different electrolyte concentrations. (b) PL response to aggregation (0.01 M); lines are set at 10 minutes intervals.

Changes in the aggregation regime produced by changes in ionic strength were expressed strongly in the evolution of the band-edge PL relative intensity (284 nm) over time as a function of electrolyte concentration (Figure 2.7). Additionally, Defect-site PL (425 nm) intensity decreased in-step with the increase in band-edge relative PL intensity (Figure 2.7).
Figure 2.7: Evolution of the 284 (plain) and 425 (prime) nm PL peak. Lower NaCl concentration lead to consecutively longer times until the onset of PL enhancement. 0.01 M (a, a'); 0.005 M (b, b'); 0.0023 M (c, c'); 0.00225 M (d, d'); 0.002 M (e, e'). Error bars represent 95% confidence intervals.

For each electrolyte concentration, there is an initial, gradual increase in band-edge PL intensity followed by a rapid increase in signal intensity. The PL intensity then asymptotically levels off. When the concentration of electrolyte exceeds the CCC, the rate of PL intensity increases more rapidly and at an earlier point in time compared with the increases in PL intensity observed at lower electrolyte concentrations (below the CCC). Above the CCC, aggregation is diffusion-limited, and PL enhancement occurs at the same time for both concentrations above the CCC threshold. The intensity of defect-site PL follows a mirror image path. However, in the early stages of the aggregation process, defect-site PL intensity increases slightly, followed by a rapid decline, which corresponds to the increase in band-edge PL (Figure 2.7). This increase in defect-site PL
can be attributed to surface oxidation brought on by UV exposure (120). To verify this, we repeated the experiment in an electrolyte-free environment. PL intensity measurements indicate that defect-site PL intensity increased over time, while band-edge PL intensity exhibited little change (Figure A.1). The fact that band-edge PL enhancement and defect-site PL quenching occur at the same time for all electrolyte concentrations above the CCC, and at consecutively later times for lower electrolyte concentrations, indicates that PL enhancement/quenching is a size-sensitive phenomenon.

In addition to aggregation processes driven by Brownian motion (non-stirred conditions), we conducted several time-resolved PL measurements with uncoated ZnS nanoparticles under stirred conditions (Figures 2.8a and 2.8b). In all stirred experiments, we used electrolyte concentrations identical to the ones used in the unstirred experiments, guaranteeing aggregation. All other conditions were kept identical to those in the unstirred samples.
Figure 2.8 a,b: (a) The evolution of the PL signal over time from a stirred and unstirred sample with RLA conditions (0.00225 M NaCl). (b) The evolution of the PL signal over time from a stirred and unstirred sample with DLA conditions (0.01 M NaCl). 284 nm, slower stirring (180 rpm) (c); 284 nm, faster stirring (230 rpm) (d); 284 nm, no stirring (e); 425 nm slower stirring (180 rpm) (e’); 425 nm faster stirring (230 rpm) (d’); 425 nm no stirring (e’). Error bars represent 95% confidence intervals.

As can be seen (Figure 2.8a) in the case of RLA, slower stirring decreases the time to PL enhancement when compared to faster stirring. Also, under both stirring conditions, PL enhancement occurs much sooner than under unstirred conditions, further strengthening the hypothesis that PL enhancement is influenced by aggregate size. However, under both stirring conditions, PL levels stabilize at values below those measured in the unstirred experiment. Stirring can cause significant shearing. This shearing leads to faster aggregation, but also results in increased particle breakup and re-aggregation. This, in turn, causes aggregates to be more compact, with a higher fractal dimension (12-14). As can be seen, there is a trend towards lower PL as aggregate density increases, from no stirring to fast stirring (Figure 2.8a and 2.8b). The mechanism behind this difference is still unclear. In the case of DLA (Figure 2.8b), PL enhancement
occurred at the same time for both the slow and faster stirring, but the enhancement was still hastened when compared to non-stirred conditions. Stirring would increase the collision frequency of particles, which under DLA consistions would result in aggregation. However, it is possible that the difference between the slow and faster stirring speeds was not enough to impact the aggregation rate, resulting in similar times to PL enhancement. Also, it can be seen that under the faster stirring conditions, the PL is lower than under slower stirring conditions, similarly to what was observed under lower ionic strength (Figure 2.8a vs. 2.8b). This trend is evident even under no stirring conditions, where slower aggregation processes lead to overall lower PL (Figure 2.7). It is known that slower aggregation processes lead to aggregates with a higher fractal dimension. The trends observed in Fig. 2.7, 2.8a and 2.8b indicate that fractal geometry plays a role in PL intensity increase.

To investigate whether PL intensity changes are observed in coated particles, we repeated some of the aggregation experiments with mercaptoethanol-coated ZnS particles. DLS measurements clearly indicate that the particles aggregate in response to the addition of NaCl (not shown). Under unstirred conditions, both band-edge and defect-site PL intensity remained constant for a significant period of time, followed by a decline (Figure A.2a). However, under stirred conditions (180 rpm), both band-edge and defect-site PL remained constant throughout the experiment (Figure A.2b). Therefore,
the decline in PL intensity observed under the unstirred conditions (Figure A.2a) can be attributed to particle settling. Stirring the aggregating suspension prevents particle settling, and eliminates the observed decline in PL intensity.

As mentioned, some of the ZnS particles used in this study were uncoated. Particle aggregation brings individual ZnS crystallites into close contact with each other, allowing for Coulombic and non-Coulombic forces between surface atoms of aggregating particles, and reducing surface tension in the crystal (58). Numerous studies have indicated that reduced surface tension increases PL intensity in semiconductor nanoparticles (121-123). Therefore, we speculate that the increase in band-edge PL is a result of a decrease in surface tension, which reduces the strain induced by sulfur vacancies in the crystal lattice, eliminating electron-hole traps. Significant reduction in surface strain only occurs when a critical number of particle-particle interactions occur (58). This observation fits well with our findings, namely that increased PL occurs once a certain aggregate size is attained. The coating present on the mercaptoethanol coated ZnS prevents adjacent particle surfaces from interacting, eliminating the drop in surface tension and the observed changes in PL intensity.

The maximum absorbance of the uncoated ZnS nanoparticles used in this study was at 277 nm (Figure 2.1a). The evolution of the 277 nm relative absorption intensity
over time was followed in aggregating uncoated ZnS suspensions with varying NaCl concentrations (Figure A.3).

In all cases, absorption decreased over time. As electrolyte concentrations increase, the time to the drop in absorption decreases. Analogous to the observations of PL intensity, 277 nm absorption evolves nearly identically at all electrolyte concentrations greater than the CCC. Additionally, greater electrolyte concentrations induce a greater decline in absorbance. However, No relationship between PL and absorbance was observed. It is possible that the drop in absorbance is more than offset by the aggregation-induced reduction of surface strain. Also, while the 425 nm PL intensity decreases, the point in time where the decrease becomes apparent occurs significantly later than the point where absorbance occurs.

To eliminate the possibility that particle settling caused the decrease in absorption, an aggregated sample was manually shaken and the absorption measured. A small increase was observed in absorbance, but the overall spectral signature is identical, and significantly different than at t=0, with no identifiable spectral shift (Figure A.4).

No spectral shift was detected due to particle aggregation (for an example, see Figure 2.6b). This fact was surprising, considering the abundance of studies reporting this phenomenon (57, 124, 125). However, one study reports that at room temperatures,
the Forster energy transfer is dampened in single-sized quantum dot solids (125).

Efficient energy transfer between quantum dots occurs only when there is a suitably-sized energy acceptor, so that the emission and absorption bands are in resonance (124). Additionally, the authors note that efficient energy transfer occurs between quantum dots of markedly different sizes. It is possible that this match-up does not occur with the ZnS nanoparticles used in this study, and therefore the red shift is negligible, and within instrument error.

Fitting a sigmoidal function using Matlab (MathWorks, Natick, MA) to each of the temporal PL data shown in Fig. 2.7 allowed us to explore these data and determine how PL relates to other aggregation phenomenon. In all cases, the fitted sigmoidal function had an R2 value of at least 0.98. Comparing the slope of the fitted function for different electrolyte concentrations was particularly informative (Figure A.5).

We found that dividing the maximum slope of the fitted line, the slope at the point of inflection, by the maximum slope calculated in the DLA case (0.01 M), yielded results very near the attachment coefficients measured using DLS (Figure 2.9).
Figure 2.9: Attachment coefficients calculated using DLS (■) and PL (◆).

This pattern was consistent when moving away from the maximum slope by a given standard deviation (SD). For example, by taking the slope of the line associated with 0.00225 M (RLA) one SD away from the peak, and dividing it by the slope of the 0.01 M (DLA) line one SD away from the peak, yields the attachment coefficient of ZnS nanoparticles destabilized with 0.00225 M. If the decrease in surface tension occurs when a critical number of particle-particle interactions are reached, and PL enhancement is the result of this drop in surface tension, then PL enhancement occurs once a critically-sized aggregate is formed. Therefore, the temporal progression of PL intensity follows the change in the number of critically sized ZnS aggregates over time. We can then write

\[
\alpha = \frac{\left(\frac{dR_h}{dt}\right)_{t \to 0}}{\left(\frac{dR_h}{dt}\right)_{t \to 0, fast}} \leq \frac{\left(\frac{dPL}{dt}\right)_{\text{max}}}{\left(\frac{dPL}{dt}\right)_{\text{max, fast}}} = \frac{\left(\frac{dN_c}{dt}\right)_{\text{max}}}{\left(\frac{dN_c}{dt}\right)_{\text{max, fast}}} \quad \text{Equation 2.3}
\]
where \( N_c \) is the number of critically sized aggregates, \( c \) is the critical size where PL enhancement occurs, \( \text{max} \) refers to the maximum slope of the fitted sigmoidal curve, and fast refers to DLA. Based on the Smoluchowski equation, we can write equations describing the rate at which aggregates equal or greater to the critical size are formed (126)

\[
\frac{dN_c}{dt} = \frac{1}{2} \alpha \sum_{i+j \geq c} N_i N_j \beta_{i,j}
\]

Equation 2.4a,b

\[
\left( \frac{dN_c}{dt} \right)_{\text{fast}} = \frac{1}{2} \sum_{i+j \geq c} N_i N_j \beta_{i,j}
\]

where \( i+j \geq c \) refers to two particles or aggregates (when \( i \) or \( j \) < \( c \) who when aggregated form an aggregate with a size equal or greater than the critical size needed for PL enhancement (\( c \)); \( N_i \) and \( N_j \) are the number of particles or aggregates of size \( i \) or \( j \); and \( \beta_{i,j} \) is the coagulation kernel. Then we can write

\[
\sum_{i+j \geq c} N_i N_j \beta_{i,j} = \left( \sum_{i+j \geq c} N_i N_j \beta_{i,j} \right)_{\text{fast}} \quad \text{Equation 2.5}
\]

Therefore, in a Brownian diffusion governed system, at a given standard deviation distance from the maximum slope describing the rate of creation of critically-sized aggregates, the particle size distribution (PSD) is invariant across electrolyte concentrations. Thus, The only thing that changes is the rate of aggregation; the particles
and aggregates that make up the PSD, as it evolves, are identical under different electrolyte concentrations.

**2.4 Conclusions**

Temporal changes in PL intensity can be used as a sensitive indicator of aggregation in uncoated ZnS nanoparticles. Aggregating uncoated ZnS nanoparticles exhibit a drop in trap-site PL and a simultaneous increase in band-edge PL. Band-edge PL enhancement and trap-site PL quenching are not observed in aggregating mercaptoethanol coated ZnS nanoparticles. We hypothesize that the drop in surface tension (caused by aggregation) reduces some of the strain associated with sulfur vacancies in the crystal lattice, which in turn eliminates some of the electron-hole traps. Additionally, neighboring particles in an aggregate possibly passivate each other’s surfaces, eliminating dangling bonds and surface traps. The elimination of these traps leads to a drop in the 425 nm PL peak. With the traps gone, more efficient electron-hole recombination can take place, leading to an increase in band-edge PL. The drop in surface strain has been reported to be sensitive to aggregate size. We observe that the increase in band-edge PL occurs at consecutively longer times, as electrolyte concentration decreases, leading to the conclusion that PL enhancement is dependent on aggregate size. This finding supports the previous findings regarding surface tension, and supports our hypothesis regarding the reason for the increase in band-edge PL.
Additionally, we found that the increase in band-edge PL and the drop in surface-trap PL was related to aggregate structure. Tightly packed aggregates exhibit a smaller increase in band-edge PL and a smaller decrease in trap-site PL than loosely packed aggregates. This phenomenon was observed in both stirred and unstirred conditions, but was more markedly seen under stirred conditions, most likely because stirring speeds can greatly influence aggregate density through a process of breakup and reformation. Finally, we found that dividing the rate of change of PL intensity in an aggregating uncoated ZnS suspension by the rate of change observed under DLA, yields the attachment coefficient measured using DLS. This finding indicates that PSDs of aggregating nanoparticles are invariant when measured at equal standard deviations from the time when the maximum rate of critically sized aggregates are formed. Unlike DLS, PL measurements are relatively simple, and do not require any assumptions about particle shape or data fitting to yield meaningful results. Hence, for uncoated, photoluminescent nanoparticles, monitoring changes in PL can yield the attachment coefficient independently of size monitoring using DLS, offering an alternative and independent measurement of attachment coefficients.

This work underscores the potential importance of aggregation in altering size-dependent properties of nanoparticles, possibly including reactivity. Aggregation will
be a key process in many physiological and environmental systems that must be monitored if nanomaterial behavior is to be interpreted correctly.
3. Impact of Aggregate Size and Structure on the Photocatalytic Properties of TiO₂ and ZnO Nanoparticles

3.1 Introduction

Photocatalytic semiconducting nanoparticles are being studied for a wide range of applications including water treatment, solar power, and self-cleaning surfaces (127-131). TiO₂ nanoparticles, arguably the most commonly used engineered nanomaterial, are found in numerous industrial products and applications (1-3). ZnO is widely studied for its photocatalytic ability and is used in many commercial applications. Because of the wide use of these materials, there is growing concern over their release into the environment (132-134). Once introduced to the environment, nanoparticles encounter conditions of ionic strength, pH and solution chemistry that may alter nanoparticle surface chemistry, leading to changes in stability with respect to aggregation (135, 136).

The aggregation of metal oxide nanoparticles has been found to decrease photocatalytic properties in generating reactive oxygen species (ROS) (87, 137-139). However, the roles that aggregate size and structure may play in producing this decrease have not been demonstrated. While mass transfer and shadowing effects can be expected to reduce ROS generation when nanoparticles aggregate, theory we have developed for surface-active nanoparticles also suggests that the very proximity of reactive surfaces may play a role in determining the net nanoparticle reactivity (102).
Aggregating particles may associate in a fractal, or self-similar, structure (17, 18). The mass of primary particles in a fractal aggregate plotted as a function of length scale is observed to be linear over intermediate length scales, with a non-integer value for slope (140) that describes the fractal dimension (D) of an aggregate. As D approaches a value of 3, aggregates approach their maximum density. Conditions favoring particle-particle attachment during aggregation, and therefore rapid aggregation, lead to aggregates with a lower D, compared to slower aggregation processes (140).

The primary form of ROS generated by semiconducting metal oxides is the hydroxyl radical (OH•) created when an electron hole (formed when the energy of absorbed photons exceeds the band-gap of the material) reacts with a water molecule or hydroxyl ion on the particle surface (1, 76). Processes such as aggregation affect the local concentration of one of the key reactants- particle surfaces- and may thereby alter ROS production.

In this work, we consider the effect of the size and structure of aggregates of TiO₂ and ZnO nanoparticles on the generation of free hydroxyl radicals. We find that the data are well described by theory that considers interactions between particle surfaces within an aggregate, analogous to previously developed theory published by our group that describes the impact of aggregation on the ability of C₆₀ to generate ROS in the form of singlet oxygen (102). The results of this study emphasize the importance of aggregate
size and structure beyond simple mass transport limitations, with significance for interpreting nanomaterial behavior in natural systems as well as in engineered applications where nanoparticles may aggregate or be deposited on substrates.

3.2 Materials and Methods

3.2.1 Materials

P25 TiO$_2$ powder was generously provided by Evonik (Evonik Industries, Essen, Germany). ZnO powder was purchased from Skyspring Nanomaterials Inc. (Houston, TX). NaCl, NaOH, K2HPO4, and KH2PO4 were purchased from Fisher Scientific (Pittsburgh, PA). Hydroxyl radical production was measured using Terephthalic Acid (TA, Sigma, St. Louis, MO), which has been found to be a selective free hydroxyl radical probe, producing 2-hydroxy terephthalic acid (TAOH), and has been used extensively to evaluate the ability of TiO2 to generate hydroxyl radicals (77, 141, 142). TiO2 stock suspension was prepared by adding 40 mg TiO$_2$ P25 powder to 1 L of deionized water (DIW) buffered to pH 7.8 using 10 mM phosphate buffer, followed by 30 minutes of probe sonication. ZnO stock suspension was prepared by adding 80 mg ZnO powder to 1 L of DIW adjusted to pH 10.8 with NaOH, followed by 30 minutes of probe sonication. TA stock solution was made at a concentration of 0.5 mM in DIW adjusted to pH 9.8 with NaOH. NaCl stock solution (1 M) was prepared by stirring NaCl in DIW.
3.2.2 Particle Characterization

Measurements of particle and aggregate electrophoretic mobility (EPM) were done using a Zeta Sizer Nano ZS (Malvern, Bedford, MA). TiO2 and ZnO nanoparticles were visualized by a transmission electron microscope (TEM) (FEI Tecnai G2 Twin, Hillsboro, OR) operating at 160 kV. Aggregate size and structure were determined using a light scattering set-up (ALV-CGS3, ALVgmbh, Langen, Germany) employing a He/Ne laser (632.8 nm) and a detector mounted on a goniometer. Dynamic light scattering (DLS) measurements were effected with this set-up to determine the average hydrodynamic radius (Rh) from time-variable light scattering at a scattering angle of 90°. Static light scattering (SLS) measurements at angles ranging from 60-140° using the same set-up were used to characterize aggregate structure.

3.2.3 Experimental Procedure

In the SLS/DLS experiments, 0.5 ml of stock TA solution, varying volumes of stock NaCl solutions, and enough DIW were added to 1 ml of stock nanoparticle suspension to make up a total volume of 2 ml. The suspension was placed in the SLS/DLS instrument and measurements were taken every 10 minutes. All aggregation experiments were done in triplicate.

The absorption cross section of an aggregating sample was determined using a Varian Eclipse UV-vis spectrophotometer (Agilent, Santa Clara, CA). In these
experiments, 4 ml disposable plastic cuvettes loaded with 1 ml of stock nanoparticle suspension, 0.5 ml of stock TA solution, varying volumes of stock NaCl solution and enough DIW to make up 2 ml were placed into the instrument. Absorption measurements were taken every 10 minutes between 340-390 nm. All absorption experiments were done in triplicate.

Measurements of hydroxyl radical generation were done using 4 ml disposable plastic cuvettes loaded with 1 ml of stock nanoparticle suspension, 0.5 ml of stock TA solution, varying volumes of stock NaCl solution and enough DIW to make up 2 ml. In these experiments, we exposed a single cuvette to UV irradiation for 1 minute, and did not expose each cuvette to UV more than once. Therefore, for each electrolyte concentration, a unique cuvette was prepared for each time point. Measurements were taken every 10 minutes. We initiated aggregation in all cuvettes simultaneously by adding NaCl to each one, but only exposed 1 cuvette to UV at a given time point. UV exposure was done in a UV box equipped with a low-pressure mercury fluorescent lamp (TL-D 15W BLB SLV, Philips, Eindhoven, Netherlands) with emission centered around 365 ± 25 nm. Following the UV exposure, 1.5 ml of the sample were centrifuged for 5 minutes at 18,000 rpm, and 1 ml of supernatant was removed. Photoluminescence (PL) of TAOH was measured using a Varian Eclipse fluorometer (Agilent, Santa Clara, CA),
with excitation wavelength set at 315 nm, and emission at 425 nm. All UV exposure experiments were done in triplicate.

### 3.3 Results and Discussion

TEM images of TiO$_2$ nanoparticles revealed an absence of individual primary particles (Figure 3.1a). In contrast, TEM images of ZnO nanoparticles showed well-separated primary particles (Figure 3.1b).

![Figure 3.1a,b: TEM images of TiO$_2$ (a) and ZnO (b).](image)

These images are consistent with many published observations of the TiO$_2$ used in this study (See for example (143, 144)) showing stable aggregates of fused primary particles despite sonication. By trial and error, we found that a 90° scattering angle for the DLS measurements angle exhibited the most consistent results for the range of particle sizes we were investigating. The Rh of both TiO$_2$ and ZnO dispersions showed a
clear dependence on both time and electrolyte concentration (Figure B.1a). DLS measurements of a stable TiO$_2$ suspension indicate the presence of particles with Rh = 125 nm. Data fits to the autocorrelation function (using ALV software package) yielded an intensity-weighted hydrodynamic radius of 116 nm, and no evidence of smaller particles in the suspension. DLS measurements of a stable ZnO suspension yielded Rh = 90 nm, however data fits indicated two peaks at hydrodynamic radii of 99 nm (99%) and 20 nm (1%) when weighted by intensity. A number-weighted fit indicated that 75% of the particles were near the smaller the 20 nm peak. As commonly observed, increasing electrolyte concentrations increased the aggregation rate. This phenomenon is consistent with measurements of EPM (Figure B.1b), where increasing electrolyte concentrations caused the EPM to approach zero.

Temporal changes to TiO$_2$ and ZnO fractal dimensions were followed using SLS. The fractal dimension of the aggregates in suspension was evaluated by determining the slope of a line formed by plotting the intensity of the scattered light (log(I)) vs. the scattering vector (log(Q)). Q values were in the range of 0.013-0.024 nm$^{-1}$. A complete set of scattering intensities vs. scattering vectors are shown in Fig. B.2. For aggregating TiO$_2$ nanoparticles, varying the aggregation rate did not significantly change the aggregate’s fractal dimension (Figure 3.2).
Figure 3.2: Changes in the fractal dimension of aggregating TiO2 and ZnO suspensions with varying electrolyte concentrations.

Values of fractal dimension ranged between 1.988 and 2.178, with no clear pattern emerging. In contrast, aggregation rate had a significant impact on ZnO aggregate fractal dimension (Figure 3.2). For the 0.05 M aggregation (rapid aggregation), fractal dimension values ranged between 2.074 and 2.120. However, 0.02 M aggregation (slow aggregation) yielded much denser aggregates as expressed by their significantly higher fractal dimension ranging between 2.335 and 2.401. To verify that changes in D were indeed a result of aggregation, and not simply an artifact resulting from multiple scattering by the particles, we aggregated 20 ppm of ZnO nanoparticles (half of the concentration used in the ROS generation experiments) using 0.02 M NaCl. The resulting fractal dimension of the aggregates was similar to that produced with 40 ppm ZnO, indicating that multiple scattering coupled with aggregation was not responsible for the observed change in structure (Figure B.3).
While the ZnO suspension begins as a stable suspension consisting of primary particles 10 to 30 nm in diameter, the TiO₂ suspension is made up of fused primary particles, with Rh = 125 nm. Light scattered from TiO₂ aggregates is dominated by scattering from fused TiO₂ primary particles. The packing of these primary particles is not affected by further aggregation as they are fused. Therefore, aggregation of these fused primary particles will preserve the structure of the fused aggregate at larger length-scales, resulting in an invariant fractal dimension, regardless of the aggregation rate. This is consistent with previously reported results about cluster-cluster aggregate structure (145, 146).

To monitor the effect of particle aggregation on the ability of TiO₂ and ZnO to generate free hydroxyl radicals, we employed a chemical probe (TA) that photoluminesces upon interaction with a free hydroxyl radical (77). TA is negatively charged at the pHs used in this study (pKa₂ = 4.8).

The experimental design ensured that the TA transformation to its hydroxylated form was not mass limited by using high concentrations of this marker (0.125 mM) relative to the nanoparticle concentrations, exposing the suspension to UV light for only brief periods (1 min), and by not re-exposing the same suspension to UV twice. Thus, as the aggregate grew, TA was included in the aggregate pores, and due to the brief UV exposure we can assume that no TA needed to diffuse from the bulk to replenish TA.
concentrations within the aggregate. No pH changes were observed in either the TiO2 or ZnO suspensions after the short exposure to UV. Furthermore, the high pH used in the ZnO suspensions ensured no particle dissolution (68, 147).

Dissolved ionic species have a detrimental impact on the ability of photocatalytic nanoparticles to generate ROS (148-150). Therefore, comparing the impact of aggregation on the ability of TiO2 and ZnO to generate hydroxyl radicals in suspensions with different ionic strengths is not practical due to the additional quenching inherent in the suspension with higher ionic strength. Thus, in our study, the impact of aggregation on hydroxyl radical generation was limited to a given ionic strength, i.e. changes in hydroxyl radical generation capacity (measured as changes in TAOH PL) of an aggregating suspension were compared to the capacity at time zero when the electrolyte was just added to the suspension, but little, if any, aggregation took place.

The process of aggregation had a detrimental impact on the photocatalytic activity of TiO2 nanoparticles, decreasing hydroxyl radical generation by over 15% for large aggregates (Figure B.4a). Comparing OH• generation relative to Rh yields conflicting results. In the case of TiO2 aggregates formed with 0.035 M NaCl, it appears that the slowly aggregating particles generate less OH• than rapidly aggregating particles (0.2 M) (Figure B.4a). In contrast, for some Rh values, it appears that the slightly faster aggregating TiO2 (0.04 M) generate more OH• than the rapidly
aggregating particles (0.2 M) (Figure B.4a). To account for this discrepancy, we normalized the PL by the number of primary particles in each aggregate. Since the TiO$_2$ aggregates exhibit mass fractal properties, the number of primary particles per aggregate can be calculated as (102)

$$n = \left(\frac{d_a}{d_m}\right)^D$$  \hspace{1cm} \text{Equation 3.1}

where $n$ is the number of primary particles in an aggregate at a given aggregate size, $D$ is the aggregate fractal dimension, and $d_a$ and $d_m$ are the average hydrodynamic diameter of the aggregate and primary particle, respectively. Therefore, the normalized PL can now be calculated

$$PL_{\text{mono}} = \frac{PL}{n}$$  \hspace{1cm} \text{Equation 3.2}

where $PL_{\text{mono}}$ is the normalized PL intensity. When comparing $PL_{\text{mono}}$ to the corresponding $Rh$ it becomes clear that TiO$_2$ aggregates have the same hydroxyl radical generation capability, regardless of the aggregation rate (Figure 3.3). This strengthens our previous claim that TiO$_2$ aggregate structure does not significantly change with changing aggregation rate.
Figure 3.3: Normalized (by number of primary particles in aggregate) PL vs. aggregate size.

When comparing PL to \( R_h \) in the aggregating ZnO suspension (Figure B.4b), it appears that the hydroxyl radical generation capacity is similar for both aggregation rates for aggregates up to 350 nm in diameter; larger aggregates formed under slower aggregation regime (0.02 M) displayed a decreased ability to generate hydroxyl radicals, when compared to aggregates formed in the fast aggregation regime (0.05 M; Figure B.4b). However, comparing PLmono to Rh under the two aggregation regimes revealed that \( \text{OH}^- \) generation in tightly packed aggregates formed during slow aggregation was significantly less than the ability of aggregates formed under rapid aggregation (Figure 3.3).

These observations can be described by a kinetic model that considers aggregate size, structure (fractal dimension), and photon absorption to predict the impact of
aggregation on OH• generation (Figure 3.4) in analogous form to a model we have previously presented to describe the effect of aggregation on fullerene reactivity (102).

![Diagram](image)

Figure 3.4: Model schematic of reactions used in kinetic model. Values over arrows represent reaction rates.

The model calculates the rate of hole (h+) creation:

\[
\frac{d[h^+]}{dt} = \phi R [\text{particles}] - k_1 [OH^-][h^+] - \epsilon D-1 k_2 [h^+][e^-]
\]

Equation 3.3

where \(\phi\) is the quantum yield of the material, \(R\) is the rate of optically induced transitions, [particles] is the molar concentration of primary particles of the semiconductor expressed per aggregate volume, \([e^-]\) is the molar concentration of surface electrons, \([h^+]\) is the molar concentration of surface holes, \(k_1\) and \(k_2\) are reaction rate constants (M^4S^-1), and \(\epsilon\) is the porosity of the aggregate (Equation 3.4). Reaction rate
constant values used in this model are listed in Table B.2. The first term on the right side of Equation 3.3 is a h\(^+\) generation term. It is important to note that this term represents changes in the concentrations of h\(^+\) on the surface of the particles. The second term is a OH\(^•\) generation term, and the third term is a h\(^+\) quenching term representing the case where electrons and holes on neighboring primary particles in an aggregate quench each other. \( \varepsilon \) represents an aggregate structural characteristic that depends on \( R_h \) and \( D \), and represents the solid fraction of an aggregate

\[
\varepsilon = \left( R_h^{D-3} r_m^{3-D} \right)
\]

Equation 3.4

where \( r_m \) is the radius of the monomer. A key parameter was found to be \( R \)

\[
R = \int \frac{I(\lambda)\sigma(\lambda)_{abs}}{hv(\lambda)} d\lambda
\]

Equation 3.5

where \( I(\lambda) \) is the excitation light intensity at a given wavelength, \( \lambda V \) is the energy of a photon at a given wavelength, and \( \sigma(\lambda)_{abs} \) is the absorption cross-section at a given wavelength. The extinction coefficient of a suspended material at a given wavelength can be expressed using the Beer-Lambert law

\[
extinction(\lambda) = \frac{Abs(\lambda)}{cl}
\]

Equation 3.6

where \( Abs(\lambda) \) is the photoabsorption measured using UV-vis spectroscopy, \( c \) is the concentration of the material, and \( l \) is the path length. The extinction cross section can be expressed as
\[ \text{extinction}(\lambda) = \sigma(\lambda)_{\text{abs}} + \sigma(\lambda)_{\text{scat}} \quad \text{Equation 3.7} \]

where \( \sigma(\lambda)_{\text{abs}} \) is the absorption cross section and \( \sigma(\lambda)_{\text{scat}} \) is the scattering cross section.

For particles much smaller than the incident beam wavelength, \( \sigma(\lambda)_{\text{scat}} \) can be neglected \((^{151})\). Additionally, while larger particles scatter more light, \( \text{Abs}(\lambda) \) decreases over time as aggregate size increases (Figure B.5). This indicates that if \( \sigma(\lambda)_{\text{scat}} \) does increase significantly due to aggregation, we would expect to see an overall increase in excitation(\(\lambda\)). However, this was not observed (Figure B.5). Thus, by following temporal changes to \( \text{Abs}(\lambda) \) in an aggregating sample, \( \sigma(\lambda)_{\text{abs}} \) was paired with a given aggregate size and structure. Radiometer readings of the UV light source indicated a total intensity of 2.1 mW/cm². The intensity of the excitation light source at each wavelength was estimated from lamp characteristics as specified by the manufacturer (Figure B.6) that indicated that the excitation light was centered around 365 ± 25 nm. We assumed a normal distribution around 365 nm, with 99% of the energy falling within ±25 nm of the mean (365 nm). By fitting a normal distribution function around the mean of 365 nm, we could estimate \( I(\lambda) \) at any given wavelength (Table B.1).

Assuming steady-state, and assuming that \([h^+] = [e^+]\), it is possible to solve Equation 3.3, resulting in

\[
[h^+] = \frac{-k_1[OH^-] + \sqrt{k_1^2[OH^-]^2 + 4e^{D-1}k_2\phi[R\text{monomers}]}}{2e^{D-1}k_2} \quad \text{Equation 3.8}
\]
Changes to the hydroxyl radical concentration can be expressed as

\[
\frac{d[OH^•]}{dt} = k_1[OH^-][h^+] - \frac{k_3}{2}[OH^•]^2 - \varepsilon^{d-1}k_4[OH^•][e^-] - \varepsilon^{d-1}k_5[OH^•][h^+] - k_6[OH^•][TA]
\]

Equation 3.9

where [TA] is the concentration of the terephthalic acid. Since [TA] >> [OH•], we assume that the self-quenching term \(k_3/2[OH^•]^2\) can be neglected. The first term of equation 3.9 is an OH• generation term, the second term is a self quenching expression, the third and fourth term describe the interaction of a free OH• with a surface electron or hole, respectively, and the fifth term describes the interaction of OH• with the PL marker (TA). \(\varepsilon\) in the third and fourth terms accounts for the increased probability of a free OH• to interact with a monomer surface in a tightly packed aggregate, leading to increased quenching in aggregates with a higher fractal dimension. Assuming steady state, we can solve equation 3.9 to yield

\[
[OH^•] = \frac{k_1[OH^-][h^+]}{\varepsilon^{d-1}k_4[h^+] + \varepsilon^{d-1}k_5[h^+] + k_6[TA]}
\]

Equation 3.10

Changes in the hydroxylated form of TA (TAOH) can be expressed as

\[
\frac{d[TAOH]}{dt} = k_6[OH^•][TA]
\]

Equation 3.11

For a given salt concentration, the impact of aggregation on OH• generation can be expressed as a ratio between the concentrations of TAOH. Therefore, we can write
\[
\frac{[\text{TAOH}]_1}{[\text{TAOH}]_2} = \frac{[\text{OH}^\bullet]_1}{[\text{OH}^\bullet]_2}
\]
Equation 3.12

where subtext 1 and 2 denote two distinct aggregation states within a given salt concentration. Using the rate constant values in Table B.2, we were able to reasonably recreate the ratios between TAOH concentrations obtained experimentally (Figure 3.5).

![Observed vs. expected results of OH• generation model. Within each material and ionic strength’s data series, results are relative to those obtained in \( t = 0 \). The dashed line represents the ideal situation where the observed results match the expected results perfectly. Solid lines are the 95% confidence intervals around the fitted slope, represented by the solid line running through the data points. Error bars around the data points represent the 95% confidence intervals around the PL measurements. Plotting the observed vs. expected values of \([\text{OH}^\bullet]_1/\square[\text{OH}^\bullet]_2\) and fitting a linear trendline forced through the zero intercept, yields a slope of 1.0004 (Figure 3.5). In an ideal model, the slope would be 1. The coefficient of determination (\( R^2 \)) was determined to be 0.68; 95% confidence intervals calculated for the slope of the fitted line indicate that the ideal case (slope = 1) falls within the area covered by the confidence intervals.}
Additionally, error bars surrounding the data points indicate that a portion of the uncertainty expressed in the relatively low $R^2$ value can be explained by variability in PL measurements.

Changes in $R$ as a function of aggregate size for TiO$_2$ and ZnO suspensions aggregated under different conditions can be seen in Fig. B.7a,b. $R$ values decrease with increasing $R_b$ in both TiO$_2$ and ZnO suspensions. Furthermore, for similar aggregate sizes, it is apparent that $R$ values are lower in the slower aggregating suspensions. As the aggregate grows, particle shadowing decreases the ability of primary particles buried within the aggregate to absorb incoming exciting photons. This leads to fewer electron-hole pairs, ultimately resulting in lower OH• generation.

Fig. B.8 demonstrates changes in $e^{D-1}$ as a function of $R_b$ for aggregating TiO$_2$ and ZnO suspensions. $e^{D-1}$ decreases with increasing aggregate size when the fractal dimension does not change greatly with aggregation (all TiO$_2$ suspensions, and ZnO 0.05 M). However, for ZnO 0.02 M aggregation, $e^{D-1}$ does not change much with aggregation. The structure of the aggregate plays a key role in the quenching of both holes and free hydroxyl radicals. When the local concentration of primary particles increases, as in a tightly packed aggregate, generated holes can recombine with electrons from adjacent particles. Also, there is an increased probability that free OH• will recombine with either electrons or holes on particle surfaces, increasing quenching.
Eliminating the structural component from the model decreased the accuracy of the model, causing an increase in the predicted amount of TAOH generated.

The experimental and computational results emphasize the importance of aggregation when discussing the fate of photocatalytic nanoparticles in the environment. Clearly, aggregate size and structure will determine how reactive these materials will remain in the environment. Simply assuming that aggregation will decrease their reactivity, and potential toxicity, could significantly underestimate the potential harm these materials can cause to aquatic life. Furthermore, the application of photocatalytic nanoparticles in engineered settings, either in suspension or deposited on a substrate, should consider aggregate structure. In particular, deposited photocatalytic nanoparticles used in water treatment processes should consider both the thickness and density of the deposited layer, to avoid shadowing, quenching, and mass-transport limitations.
4. Membrane Filtration of Fullerene Nanoparticle Suspensions: Effects of Derivatization, Pressure and Electrolyte Concentration (99)

4.1 Introduction

Fullerenes are a family of carbon-based nanomaterials (90, 91, 92) that include caged molecules such as C_{60} as well as carbon nanotubes. The unique properties of fullerenes inspire a wide range of promising applications that also imply a potential for long-term environmental release and exposure (152, 153). It is therefore important to understand the factors that control nanomaterial transport and transformation in the environment as well as the capabilities of current technologies to remove nanomaterials from air and water. This paper addresses the capability of porous membranes to remove C_{60} from water.

Non-derivatized C_{60} is extremely hydrophobic with a reported Kow of 6.67 (97). However, stable colloidal suspensions of C_{60} aggregates (nC_{60}) can be formed under conditions of extensive sonication, extended mixing, the introduction of surface-active agents such as humic materials, or through a solvent exchange process (98). The characteristics of these fullerene aggregates vary as a function of the preparation method, but typically range from several tens to several hundreds of nanometers in diameter. Hydroxylated C_{60} molecules (Fullerol), with between 18-24 hydroxyl groups per C_{60} molecule, readily disperse in water with gentle stirring and also form aggregates
(154, 155, 156). Fullerol aggregates have a more open, fractal structure compared with non-derivatized nC60 aggregates. Compared with the crystalline structure of aggregates of non-derivatized nC60, the more open aggregate structure of fullerol aggregates favors the production of reactive oxygen species in water (100). The particle size distributions (PSD) of fullerol suspensions, as measured by dynamic light scattering (DLS), is typically bimodal, with peaks at approximately 100 nm and between 1-5 μm, and a rather large polydispersivity index (PDI) – a measure of the variance of particle sizes in a suspension. A PDI value close to zero indicates a more monodisperse suspension. Transmission electron microscopy (TEM) indicates the presence of large clusters of particles with a broad distribution of sizes (154). Also, the authors observed large fullerol aggregates as measured by DLS after filtration through a 0.22 μm membranes.

While fullerol and nC60 suspensions remain quite stable in the absence of electrolyte, the addition of salt to these suspensions favors aggregation (98, 119). X-ray photoelectron spectroscopy and UV-visible measurements of fullerol destabilized with various di- and tri-valent counter-ions indicate that these electrolytes form chemical bonds with fullerol surface oxygen groups (157).

The physical and chemical properties of fullerenes have been the subject of numerous previous studies (98, 100, 119), and removal by conventional porous media filters has been examined (158). However, the conditions affecting the removal of these
materials via membrane filtration have received little attention. Filtering a fullerol suspension through a dense polyamide nanofiltration membrane (NF200, Dow-Filmtec, Midlad, MI) resulted in the removal of 98% of the fullerenes and attributed removal to simple size exclusion (111). This is consistent with an average pore size of 0.3 nm reported for the NF200 nanofiltration membrane as determined by atomic force microscopy (112) which is substantially smaller then the diameter of a single $C_{60}$ molecule. The propensity of fullerenes to form aggregates in aqueous solutions suggests that porous membranes might also remove these aggregates. The removal efficiency of $C_{60}$ flocculated with alum in the presence of 50 ppm of Ca$^{2+}$ and filtered through an 8 µm filter, was highly dependent on the pH of the suspension and alum concentration (159). The authors report removal efficiencies ranging between zero and nearly 100%, depending on the concentration of alum and pH. However, in a previous study, some fullerol nanoparticles were observed to diffuse through a dialysis bag with a molecular weight cut off of 100 Da (114). Although the fullerol molecules were present as aggregates with a mean diameter of 248 nm at pH 6.9, the possibility exists that a fine fraction of fullerol is not bound up in the aggregates (114). The addition of salts to fullerol suspensions is expected to reduce the amount of fullerol that is not bound up in aggregates (if any), increasing removal efficiency. Therefore, in this paper, we explore the circumstances that influence the removal of destabilized fullerene suspensions in
aqueous media, using ultrafiltration membranes under variable conditions of ionic strength, ionic composition, and pressure gradient.

### 4.2 Materials and Methods

#### 4.2.1 Chemicals and Materials

Fullerol (C_{60}(OH)_{22-24}) and C_{60} (99.9% pure) were purchased from MER (Tucson, AZ). MgCl₂ and CaCl₂ were purchased from Fisher Scientific (Pittsburgh, PA). NaCl was purchased from Mallinckrodt Chemicals (Boulder, CO). Anodized aluminum oxide ultrafiltration membranes, with a nominal pore size of 20 nm (Anodisc 47), were purchased from Whatman (Piscataway, NJ). The clean membrane resistance was measured to be 6.59x10¹¹ m⁻¹. Due to the small volume filtered (10 ml) and the low particle concentration (10 ppm), the average flux through the membrane did not change appreciably when filtering clean water or fullerol suspensions. Filtration was conducted under constant transmembrane pressure, which could be easily and accurately controlled.

#### 4.2.2 Characterization of Fullerene Suspensions

Fullerol and C_{60} concentrations (stock solutions, post-aggregation, post filtration) were determined as total carbon (TC) concentrations using high temperature oxidation at 680 °C after CO₂ stripping by adding H₃PO₄ and N₂ degassing (TOC-5050A, Shimadzu, Kyoto, Japan). Average hydrodynamic radius of particles was measured by
DLS at 90° (ALV CGS-3, Langen, Germany). This instrument is equipped with a He-Ne laser (632.8 nm), and is capable of conducting DLS measurements at angles ranging between 12 and 152°. The intensity-weighted average hydrodynamic radius was calculated by second order cumulant analysis (ALV software package). The intensity and mass weighted PSDs were calculated by the ALV software package. Electrophoretic mobility (EPM) measurements were performed on a Zeta Sizer Nano ZS (Malvern, Bedford, MA). This instrument employs a He-Ne laser (633 nm) and collects scattered light at a fixed angle of 173°. The instrument measures the frequency shift of the scattered incident beam, deducing the particle EPM. Surface morphology of the membranes after fullerol filtration was investigated using scanning electron microscopy (SEM) (FEI XL30 SEM-FEG, FEI, OR). Aggregate structure was visualized by using a TEM (FEI Tecnai G2 Twin, Hillsboro, OR) operating at 160 kV. Chemical bonds within fullerol aggregates were determined using Fourier-transformed infrared spectroscopy (FTIR). A fullerol suspension was stirred for two hours with 0.3 M NaCl, 0.1 M CaCl₂, or 0.1 M MgCl₂. Then, the suspension was spun in an ultra-centrifuge for 40 minutes at 40,000 rpm. The centrifuge tube was decanted and the resulting pellet was washed with DI water. This process was repeated three times. The resulting powder was dried at 80° C, and stored in a desiccator. The powder was then crushed with KBr, and the pellet was
placed in the FTIR spectrophotometer (Thermo Electron Nicolet 8700, Thermo Scientific, MA), operated in absorbance mode.

4.2.3 Fullerol, C60, and Electrolyte Stock Solutions

A stock suspension of C60 aggregates (nC60, where n indicates a theoretical number of C60 molecules per aggregate) was prepared by solvent substitution based on the method described by Deguchi et al. (2001) (160). A stock fullerol suspension (20 mg/L as TC) was prepared by stirring 30.8 mg of fullerol into 1 L of double de-ionized water (DDW) that had a minimum resistivity of 18.2 MΩ-cm and dissolved organic carbon concentration was less than 0.05 ppm. This resulted in a stable suspension of fullerol aggregates (nC60(OH)22·24 but referred to here as simply fullerol). Stock MgCl2, CaCl2, and NaCl at 1, 1, and 3 M, respectively, were prepared by dissolving the salts into 1 L of DDW.

4.2.4 Fullerene Suspensions for Membrane Filtration

Fullerene suspensions (nC60 and fullerol) were made without electrolyte and, in the case of the fullerol suspensions, with increasing concentrations of electrolyte followed by programmed stirring. In the case of the fullerol and nC60 suspensions without electrolyte, stock solutions were diluted to a concentration of 10 mg/L, with no additional stirring. Fullerol aggregation was evaluated by first adding 10 ml of electrolyte solution to 10 ml of the stock fullerol suspension to yield a final volume of 20
ml of 10 mg/L fullerol suspension with the desired electrolyte concentration and composition (0.5, 0.1, 0.01, and 0.001 M MgCl₂; 1.5, 0.3, and 0.03 M NaCl). These suspensions were then stirred for two hours at 700 rpm with a magnetic stir-bar.

4.2.5 Membrane Filtration

10 ml of post-aggregation suspension were placed in a dead-end vacuum filtration unit (without stirring), equipped with an unused 20 nm ultrafiltration membrane. A pressure differential across the membrane was provided by attaching the permeate line to an adjustable vacuum pump. Vacuum pressure was controlled via a needle-point valve, and monitored closely to maintain constant pressure throughout the filtration process. Transmembrane pressure was set at one of four values: 0.05, 0.1, 0.2, or 0.4 bar. The entire volume of permeate was collected (100% recovery), and an average particle removal efficiency was calculated as:

\[ R = 100 \times (1 - \frac{C_f}{C_i}) \]  

Equation 4.1

where R is the removal efficiency (% removal), Ci is the initial particle concentration (verified as 10 mg/L post-aggregation), and Cf is the final particle concentration (in the accumulated permeate), both measured as total carbon concentrations. This average does not take into account transient changes in membrane rejection, if any do occur.
4.3 Results and Discussion

Removal of nC60 by the membrane was observed to be largely independent of the transmembrane pressure applied (Figure 4.1). By comparison, the fullerol suspensions in the absence of electrolyte showed significant sensitivity to transmembrane pressure, exhibiting a marked decrease in removal efficiency when the transmembrane pressure exceeded the 0.05 bar threshold (Figure 4.1). The fullerol was removed by these membranes to a lesser degree despite having a larger radius as measured by DLS (Table 4.1). Intensity-weighted PSD (measured by DLS) measurements in pre-filtered fullerol do not indicate the presence of a size fraction smaller than the nominal membrane pore size (20 nm). In contrast, Intensity-weighted PSD measurements in nC₆₀ suspensions reveal a fraction of aggregates with a radius of 8.5 nm (0.5%) (Table 4.1). Mass-weighted PSD measurements increase the fraction of the 8.5 nm population in nC60 to 17%. This value is in close agreement with the removal rate measured by TC (~20%, Figure 4.1). Therefore, it is likely that nC₆₀ aggregates are removed from suspension by a simple size exclusion mechanism, where the larger aggregates are either too strong or not flexible enough to pass through the membrane pores. A lower removal of the fullerol aggregates might be attributed to either greater polydispersivity (and thus a possible population of aggregates with diameters significantly smaller than the average, even though non was observed by DLS) and/or a
weaker aggregate binding strength that allowed for deformation or breakup at the entrance to membrane pores. Interestingly, for both fullerol and nC\textsubscript{60} suspensions, the average hydrodynamic radius of the permeate suspension was larger than the pore size, and often larger than the original suspension (Table 4.1). Intensity-weighted PSD measurements indicate that nC\textsubscript{60} aggregates in the permeate are larger than the nominal pore size of the membrane (Table 4.1). We speculate that C\textsubscript{60} accumulates as small deposits on the permeate side of the membrane, similar to drop formation on a membrane surface, and detaches as an nC\textsubscript{60} aggregate as filtration proceeds. In contrast with the nC\textsubscript{60}, intensity-weighted PSD measurements of fullerol aggregates filtered at 0.4 bar indicate the presence of a substantial (14\%) population of 5 nm particles. On a mass-weighted basis, this 5 nm population accounts for 74\% of the total mass in the permeate. The permeate generated after filtration at 0.05 bar does not show the presence of a smaller-than-pore size population (Table 4.1). Therefore, for fullerol, it is possible that at sufficiently high pressures, aggregates break up and pass through the membrane without reforming on the permeate side. At lower pressures, aggregates may be deforming and passing through the membrane, without particle breakup. However, there is a possibility that a smaller than pore size fraction exists in the permeate of the 0.05 bar suspension, but its presence is masked by a substantially larger population of larger aggregates. DLS measurements are biased towards larger particles due to their tendency
to scatter significantly more light. Therefore, if the population of small particle is relatively small, observing it with DLS is extremely difficult. The presence of a fraction of fullerol particles smaller then the pore size in the permeate, coupled with the fact that fullerol removal efficiency does depend on transmembrane pressure, indicates that the removal mechanism for fullerol is different than that found in nC60.

![Graph](image.png)

**Figure 4.1: Removal efficiency vs. pressure for fullerol and nC60 suspensions (no electrolyte). Dotted lines correspond to 95% confidence intervals.**

Destabilization of fullerol aggregates using electrolytes was examined as a basis for enhancing particle removal. The average hydrodynamic radius of fullerol aggregates, as measured by DLS, stabilized after 2 hours of mixing when using MgCl₂ or CaCl₂ as the destabilizing electrolyte. CaCl₂ produced a more rapid aggregation of fullerol compared with MgCl₂ or NaCl. However, in all cases, aggregate size did not increase measurably after a period of 2 hours. Moreover, despite the more rapid initial rate of aggregation produced by Ca²⁺ ions, the aggregates produced in the presence of 0.1 M of
Mg$^{2+}$ ions were comparatively larger than aggregates produced by CaCl$_2$ or NaCl (0.1 M and 0.3 M, respectively). The larger aggregates obtained using MgCl$_2$ were attributed to a stronger attachment between the initial fullerol aggregates that reduced break-up. Di- and tri-valent metal counter-ions are capable of binding strongly to fullerol molecules (157). While the higher charge density of Mg$^{2+}$ would lead to stronger aggregates when compared to aggregates formed in the presence of Ca$^{2+}$, the hydration shell surrounding the Mg$^{2+}$ ion would be more tightly bound, making it more difficult for Mg$^{2+}$ to form bonds with fullerol. This added bond strength, provides a possible explanation for the difference in aggregate size. Counter-ions are hypothesized to function as bridging agents between two particles by exchanging two of its water of hydration with particulate surface hydroxyl groups (161). The energy required to separate a water molecule from a Mg$^{2+}$ ion was calculated to be greater than that required for a Ca$^{2+}$ ion (162). Thus, a possible explanation to the observed phenomenon would be that it is easier for a Ca$^{2+}$ ion to exchange one of its hydrated water molecules for a fullerol hydroxyl group, resulting in faster aggregation. However, once a Mg$^{2+}$ ion exchanges its hydrated water for a fullerol hydroxyl, the fullerol hydroxyl would be more tightly bound, resulting in a stronger aggregate. Previous research has noted that Mg$^{2+}$ ions do not form bridges between organic molecules (16). However, using FTIR we have observed the Mg-O bond in a Mg$^{2+}$ destabilized fullerol suspension, as evident by the
peak at 451 cm\(^{-1}\) (163, 164) (Figure 4.2a). Also, examination of the FTIR spectra generated from a Ca\(^{2+}\) destabilized fullerol suspension revealed a peak at 417 cm\(^{-1}\), corresponding to the Ca-O bond (164, 165) (Figure 4.2b). The FTIR spectra of a Na\(^+\) destabilized fullerol suspension does not differ substantially from the spectra obtained from an electrolyte-free fullerol suspension (Figure 4.2c,d). The peaks at 3420 cm\(^{-1}\), 1640 cm\(^{-1}\), 1380 cm\(^{-1}\), and 1060 cm\(^{-1}\) are associated with O-H stretching, C=C, C-OH, and C-O bonds, respectively (166) (Figure 4.2d). The peak at 515 cm\(^{-1}\) and 540 cm\(^{-1}\) in the fullerol + NaCl and fullerol suspensions, respectively is possibly associated with the C=C bond. Therefore, it can be concluded that Mg\(^{2+}\) and Ca\(^{2+}\) ions are capable of forming chemical bonds with oxygen atoms on the surface of fullerol molecules, and can be expected to function as bridging elements between fullerol molecules.
Figure 4.2a-d: FTIR absorbance spectra of fullerol suspensions. (a) fullerol + MgCl₂; (b) fullerol + CaCl₂; (c) fullerol + NaCl; (d) fullerol.

Measurements of electrophoretic mobility indicated that the fullerol was negatively charged in water, with a mobility of -3.523 μmcm/Vs in the absence of electrolyte (Table 4.1). Fullerol aggregates formed in the presence of NaCl retained a negative charge even at very high electrolyte concentrations. In contrast, Mg²⁺ greatly reduced the surface charge of these aggregates even at very low concentrations. At a concentration of 10 mg C/L the fullerol suspensions would have approximately 3×10⁻⁴ eq/L of OH groups. Thus the cations present in these solutions were substantially in excess of the OH groups on the fullerol. Charge reversal was observed at the highest
concentration (0.5 M) of MgCl₂. While all the tested electrolytes produced significant aggregation, the extent of aggregation was greater for the CaCl₂ and MgCl₂ destabilized suspensions. These data suggest differences in the nature and strength of bonds between fullerol molecules produced by mono and divalent ions, with divalent ions hypothesized to initiate particle bridging or “polymerization” (157) that would favor removal of fullerol aggregates by porous membranes.
Table 4.1: EPM and size measurements of fullerol and nC60 aggregates. Measurement ranges (±) correspond to 95% confidence intervals (borrowed from Jassby et al. 2009 (99)).

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte conc.</th>
<th>EPM (mN cm⁻¹ m/²)</th>
<th>Average hydrodynamic radius (nm) after 2 h of stirring (PSD)</th>
<th>Intensity-weighted PSD (nm) after 2 h of stirring</th>
<th>Average hydrodynamic radius (nm) after filtration at 0.05 and 0.4 bar (PDI)</th>
<th>Intensity-weighted PSD (nm) after filtration at 0.05 and 0.4 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fullerol</td>
<td>0.5 M MgCl₂</td>
<td>0.174 ± 0.047</td>
<td>Too large (not meaningful)</td>
<td>Too Large</td>
<td>0.05 bar: 1.38 ± 0.38 (0.163)</td>
<td>0.05 bar: 3.96 (0.136)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>0.1 M MgCl₂</td>
<td>−0.494 ± 0.037</td>
<td>2975 ± 1695 (0.325)</td>
<td>2405 (100%)</td>
<td>0.05 bar: 1.21 ± 0.29 (0.084)</td>
<td>0.05 bar: 3.85 (0.136)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>0.001 M MgCl₂</td>
<td>−0.750 ± 0.051</td>
<td>424 ± 640 (0.143)</td>
<td>525 (100%)</td>
<td>0.05 bar: 1.50 ± 0.45 (0.084)</td>
<td>0.05 bar: 5.48 (0.136)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>0.001 M MgCl₂</td>
<td>−1.331 ± 0.060</td>
<td>218 ± 146 (0.48)</td>
<td>132 (57%), 131 (41%)</td>
<td>0.4 bar: 3.49 ± 0.94 (0.084)</td>
<td>0.4 bar: 3.49 ± 0.94 (0.084)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>0.1 M CaCl₂</td>
<td>0.0069 ± 0.001</td>
<td>1805 ± 725 (0.161)</td>
<td>357 (35%), 291 (61)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>0.001 M CaCl₂</td>
<td>−1.294 ± 0.173</td>
<td>97 ± 61 (0.42)</td>
<td>21 (8%), 106 (92%)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>1.5 M NaCl</td>
<td>−0.584 ± 0.098</td>
<td>1120 ± 525 (0.22)</td>
<td>1200 (100%)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>0.3 M NaCl</td>
<td>−1.246 ± 0.060</td>
<td>417 ± 275 (0.32)</td>
<td>327 (50%), 154 (58%)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>0.03 M NaCl</td>
<td>−2.562 ± 0.144</td>
<td>180 ± 116 (0.416)</td>
<td>123 (55%), 120 (35%)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
</tr>
<tr>
<td>Fullerol</td>
<td>0</td>
<td>−3.533 ± 0.357</td>
<td>126 ± 66 (0.277)</td>
<td>102 (100%)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
</tr>
<tr>
<td>nC60</td>
<td>0</td>
<td>−4.077 ± 0.137</td>
<td>80 ± 32 (0.157)</td>
<td>8.3 (0.53), 91 (9.60)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
<td>0.4 bar: 3.47 ± 0.94 (0.084)</td>
</tr>
</tbody>
</table>
TEM images of fullerol aggregates formed in the presence of 0.1 M MgCl₂, 0.1 M CaCl₂, and 0.3 M NaCl can be seen in Figure 4.3. In all cases it is clear that fullerol does indeed form large aggregates in the presence of electrolytes. However, due to the sample preparation method, which involves a drying step, it is difficult to draw any conclusions regarding aggregate structure.

In the following section, we report the results of membrane filtration experiments performed with fullerol suspensions that had been aggregated using the range of NaCl, CaCl₂, and MgCl₂ concentrations summarized in Table 4.1. It should be noted that removal efficiencies of Ca²⁺ destabilized suspensions were only measured at 0.05 and 0.4 bar. In all cases, DLS measurements indicate that for all electrolyte concentrations, the average hydrodynamic radius as well as all size classes in the PSD of aggregated fullerols, exceed the nominal pore size of the membrane (Table 4.1).

Figure 4.3: TEM images of fullerol aggregates with different 0.1 M CaCl₂ (a), 0.1 M MgCl₂ (b), and 0.3 M NaCl (c).

The results of the filtration experiments can be seen in Figure 4.4.
Figure 4.4a: Removal efficiency vs. pressure for fullerol suspensions aggregated with different MgCl$_2$ and CaCl$_2$ concentrations. Error bars refer 95% confidence intervals.

Figure 4.4b: Removal efficiency vs. pressure for fullerol suspensions aggregated with different NaCl concentrations. Error bars refer to 95% confidence intervals.

Aggregation of fullerol suspensions destabilized with MgCl$_2$ and CaCl$_2$ resulted in a pressure-independent removal of these fullerenes (Figure 4.4a), similar to that observed for nC$_{60}$ (Figure 4.1). Removal efficiencies were nearly identical over the entire range of CaCl$_2$ and MgCl$_2$ concentrations evaluated, ranging between 70-85% (Figure 4.4a). No clear relationship between removal efficiency and transmembrane pressure
was observed. However, when NaCl is added as the destabilizing electrolyte, removal efficiencies show a marked decrease with an increase in transmembrane pressure. As the NaCl concentration decreases from 1.5 M to 0.03 M, there is a noticeable decrease in removal efficiency with increasing pressure. However, for all NaCl concentrations, removal efficiencies at low pressure (0.05 bar) are well above those achieved with fullerol alone (Figure 4.4b). The aluminum oxide membranes used in this work have a point of zero charge in the range of pH 8.75 to 9.4 (167). The pH of our suspension was below these values (6.51). Therefore, it is possible that some of the removal efficiency can be attributed to adsorption of the negatively charged fullerol on the positively charged membrane. However, adsorption of fullerol to the membrane is not sufficient to explain differences observed between the suspensions destabilized by mono and di-valent ions, nor the pressure-dependent behavior. Moreover, the maximum difference in charge between fullerol aggregates and the membrane occurs for fullerol suspensions in the absence of electrolyte where removals were relatively low.

SEM images of post filtration membranes (MgCl:\textit{only}) indicate that electrolyte concentrations and transmembrane pressure both play a significant role in cake layer formation (Figure 4.5). For the same electrolyte concentration, low-pressure filtration (0.05 bar) yields a visible cake layer, while increasingly higher pressures (0.15 bar and 0.3 bar) produce progressively thinner depositions, and in the case of 0.3 bar, little material appears to be deposited at all (Figure 4.5c). Higher electrolyte concentrations
appear to cause large aggregates to be deposited on the membrane surface, rather then a uniform cake layer. Interestingly, large aggregates appear on the under-side of the membrane, indicating that either filtered fullerol re-aggregates on the bottom surface of the membrane after passing through and adheres there, or that fullerol aggregates can deform due to the pressure gradient and partially pass through the membrane (Figure 4.5d).

Figure 4.5a-d: SEM images of post-filtration membrane with different pressures and electrolyte concentrations. The large image is of the membrane surface exposed to the fullerol suspension, while the inset is of the underside (permeate side) of the membrane. Arrows indicate flow direction. (a) 0.1 M MgCl₂, 0.05 bar; (b) 0.1 M MgCl₂, 0.15 bar; (c) 0.1 M MgCl₂, 0.3 bar; (d) 0.5 M MgCl₂, 0.3 bar.

The SEM imagery is consistent with the hypothesis that Mg²⁺ ions form ionic bridges between fullerol molecules, causing these aggregates to be effectively retained by the membrane filter. Low transmembrane pressures may not be strong enough to
deform these aggregates and force them through the membrane, thus cake layer formation would be favored as observed in the SEM images of membrane surfaces following filtration at low transmembrane pressures (Figure 4.5a). High transmembrane pressure may deform aggregates and drive them into the membrane, causing them to “poke out” of the other side, as seen in the SEM images (Figure 4.5d). However, these aggregates do not go all the way through the membrane, keeping the removal efficiency steady. In contrast, the Na+ ion does not mediate the polymerization of fullerol, and aggregates simply break apart and pass through the membrane once a critical pressure is exceeded.

4.4 Conclusions

In this paper, we describe our experimental results pertaining to fullerene separation under different solution and pressure conditions. The results indicate that derivatization, transmembrane pressure, electrolyte species, and electrolyte concentrations all play roles in the separation efficiency of fullerene from aqueous suspensions. There may be analogies with the conditions controlling the rejection of suspensions of oil drops by membranes (168) and those for fullerol suspensions. The removal efficiency of oil from an oil/water emulsion is affected by transmembrane pressure and there is a critical pressure, beyond which oil droplets deform and pass through a porous membrane. This pressure depends on the interfacial tension between the oil and water. Molecular interactions that determine interfacial tension may play an
analogous role to that of bond strength between fullerol molecules in an aggregate.

Beyond a critical pressure, ties between fullerol molecules might be weakened, allowing for aggregate deformation or break-up, and possible passage through the membrane. In this model, electrolytes that favor stronger bonds in aggregates (e.g. Mg$^{2+}$ or Ca$^{2+}$) will exhibit greater removal by membranes.

The results of this work highlight the difficulties encountered when tackling the separation of nanomaterials from suspension using conventional membranes. In cases where water sources contain fullerene nanomaterials that must be removed (such as processing plant effluents), porous membrane filters may not always serve as an adequate barrier. Laboratory separations or size fractionations using porous membranes must be executed with care, considering the interplay between pressure, aggregate strength, and membrane pore size.
5. Summary, Conclusions, and Implications

The overall research goal was to investigate the impact of particle aggregation on nanoparticle reactivity and membrane filtration. To that end, we explored how aggregation impacts the ability of ZnS nanocrystals to PL; how aggregate size and structure changes the ability of photocatalytic nanoparticles (TiO$_2$ and ZnO) to generate hydroxyl radicals; and how surface derivatization, electrolyte concentration, species, and transmembrane pressure influence membrane separation of fullerene suspensions.

5.1 ZnS Nanoparticle Aggregation

In Chapter 2, we describe the influence of particle aggregation on ZnS PL, as well as describe a new method to determine the attachment coefficient of PL nanoparticles. In our work, we added varying concentrations of NaCl as the destabilizing agent, which induced aggregation at varying rates. We show that the EPM of ZnS particles draws closer to zero as the concentration of NaCl increases, and as a result the aggregation rate increases as well. Furthermore, we used DLS to follow the evolution of $R_0$ over time, as a function of NaCl concentrations. To assess the impact of aggregation on reactivity, we measured the changing PL intensity of an aggregating sample using a spectrofluorometer.

As can be seen in Chapter 2, aggregation had a significant impact on the PL characteristics of ZnS nanoparticles. In particular, we determined that once aggregates reach a critical size, there is an increase in band-edge PL intensity and a corresponding
decrease in defect-site PL. By calculating the maximum rate of PL increase for each electrolyte concentration, we were able to develop a novel method of attachment coefficient calculation. This method utilizes changes in PL, rather than aggregate diameter. PL is easier to determine, and is subject to less assumptions regarding particle and aggregate properties such as morphology, when compared to size measurements obtained from DLS. Additionally, current attachment coefficient calculation methodology requires the initial aggregation rate to be determined, and in particular the dimer formation rate. In contrast, to use PL for attachment coefficient determination, all one needs is to determine the maximum rate of PL enhancement.

Several implications arise from the work presented in Chapter 2. The first implication is that aggregation can increase the reactivity of certain nanoparticles. Contrary to some reports linking aggregation with declining reactivity (20, 83, 85-87), we find that aggregation can enhance certain reactive properties. Due to their extremely small size (~3 nm), ZnS nanoparticles experience strong surface strains. Additionally, the presence of sulfur vacancies in the crystal lattice contribute to these strains, as bond lengths in the lattice are distorted to accommodate these defect. These strains manifest as PL at a wavelength of ~425 nm. Once ZnS aggregates reach a critical size, these strains relax (as manifested in the drop in 425 nm PL intensity) (33). Therefore, for any nanoparticle system where large surface strains impact the reactivity of the material, aggregation could mitigate these strains and enhance the material’s reactivity.
A possible example is the case of pyrite (FeS$_2$) nanoparticles used in solar energy applications. FeS$_2$ has the appropriate photoabsorption spectra useful for solar energy harvesting, but the presence of numerous crystal lattice defects (sulfur vacancies) result in excessive electron trapping, reducing the open-circuit voltage (169).

Another implication of this research is in the field of medical imaging. There is a large body of research detailing how PL from semiconducting nanoparticles can be used to target cells, organelles and molecules (170, 171). The PL intensity is used to quantify the concentration of the target molecule. However, if aggregation of uncoated semiconducting nanoparticles results in an increase in band-edge PL, then it is possible that the observed increase in PL is the result of aggregation.

One future research question that arises from the work presented in Chapter 2 includes examining commercially available quantum dots used in medical imaging for the possibility of aggregation induced enhanced PL. A thorough examination of a range of quantum dots would also indicate whether the phenomenon observed in Chapter 2 are unique to ZnS, or are a common characteristic to all PL semiconductor nanoparticles.

Another research question that arises is how to improve the performance of applications that incorporate semiconducting nanoparticles, and whose performance is compromised by the presence of strain-inducing crystal lattice defects.

Finally, in Chapter 2 we demonstrate how to measure the attachment coefficient using an alternative method to the one currently used, namely PL instead of aggregation
rate. We speculate that once aggregates attain a critical size, enhanced PL occurs. Thus, by following PL intensity we are essentially following the concentration of critically sized aggregates. However, the drawback of this method is that it is relevant only to small PL nanoparticles. Therefore, a potential future project would be to identify an easily measureable physical trait (optical, electronic or other) that can be attributed to a critically sized aggregate, and explore whether following this trait allows for the determination of the attachment coefficient, in a similar way that we demonstrated in Chapter 2.

5.2 Impact of Aggregation on Hydroxyl Radical Generation by TiO$_2$ and ZnO Nanoparticles

In Chapter 3 we describe the impact of aggregate size and structure on the ability of TiO$_2$ and ZnO nanoparticles to generate hydroxyl radicals under UV illumination. To accomplish this task, we suspended commercially available TiO$_2$ (P25) and ZnO powders in DIW by sonication, and then added varying concentrations of NaCl to destabilize the suspensions. We followed aggregate size through DLS, and aggregate fractal dimension by using SLS. To measure hydroxyl radical generation, we employed a fluorescent marker (TA) that only fluoresces when it interacts with a hydroxyl radical. In addition to the above measurements, we also used UV-vis spectroscopy to measure the absorbance of the suspension as it aggregated. Our experimental design ensured that the hydroxyl radical detection method was not mass-limited, and was thus able to isolate the hydroxyl radical generation/quenching mechanism, and measure it effectively.
Our results indicate that, overall, aggregation decreases the ability of TiO₂ and ZnO to generate hydroxyl radicals. Additionally, both aggregate size and structure play key roles in hydroxyl radical generation. Our experimental results show that while there is an overall decrease in hydroxyl radical generation with increasing aggregate size, aggregates with a higher fractal dimension (more densely packed) generate less hydroxyl radicals than aggregates with lower fractal dimensions (loosely packed).

In Chapter 3 we describe a predictive model that takes into account both aggregate size and fractal dimension to calculate both the concentration of the electron-hole pairs, and of free hydroxyl radicals. One of the key parameters of this model was determined to be \( R \), the rate of optically induced transitions. We approximated \( R \) by using UV-vis absorption measurements, and determined that increasing aggregate size led to enhanced shadowing of particles embedded in the center of an aggregate, leading to decreased UV absorption, and hence to less hydroxyl radicals being generated. A second key parameter of the model was determined to be \( \varepsilon^{D-1} \), and represents the solid fraction of an aggregate. An increase in this term led to an increase in radical quenching on neighboring particle surfaces, decreasing the availability of these radicals to interact with our fluorescent marker.

The results presented in Chapter 3 point to several important implications. First, they indicate that as aggregates grow, their ability to generate ROS diminishes. This has important implications for nanoparticles released into the environment, and for
nanoparticle applications utilizing nanoparticle ensembles, such as thin film depositions. Many studies predict that as more photocatalytic nanomaterials find their way into consumer and industrial products, their prevalence in the environment will increase (172, 173). For example, it has been observed that engineered TiO2 nanoparticle aggregates are found in runoff from painted surfaces (174). Our results indicate that while the reactivity of the aggregates is diminished, they are still reactive, and can still generate ROS. Thus, while aggregation could reduce the toxicity of photocatalytic nanomaterials, the extent of toxicity reduction will depend on the final aggregate size and structure.

Many applications utilizing photocatalytic nanoparticles have these materials deposited or embedded in thin films (175-178). The advantage of using thin-film depositions over suspensions in water treatment processes is that in suspensions the photocatalytic materials must be removed, usually by filtration – an additional costly step. In Chapter 3 we show that as aggregates increase in size there is a corresponding increase in shadowing, as expressed by a decrease in photo absorbance. Thus, when creating thin-films from nanoparticles, it is important to consider film thickness. Too thick of a film will decrease photo absorption deep in the film, reducing material utilization. Additionally, since the reactive species generated by photocatalytic nanomaterials are either found on the surface of the material itself (holes, bound hydroxyl radicals) or exist in free form for extremely short time periods (hydroxyl
radicals, superoxides, singlet oxygen), it is imperative to maximize the available surface area on the thin-film. Tightly packed depositions decrease the available surface area as well as increase the probability of free reactive species quenching on surrounding surfaces. Therefore, controlling both the thickness and structure of thin-film depositions is critical for process optimization.

As direct hole oxidation is the primary oxidation route in photocatalytic reaction (74), it is important to obtain direct experimental verification of the impact of aggregation on hole production. There are multiple chemical markers capable of probing hole concentrations that could be used. The results of this research could also be important for water splitting applications that rely on resilient electron-hole separation for high efficiency hydrogen production (179). Additionally, further work is warranted on the impact of aggregation on other free reactive species such as superoxide radicals and singlet oxygen.

5.3 Membrane Filtration of Fullerene Nanoparticle Suspensions: Effects of Derivatization, Pressure and Electrolyte Concentration

In Chapter 4 we report our findings regarding the separation of fullerene aggregates using membrane filtration. Both derivatized fullerenes \( \text{C}_{60}(\text{OH})_{18-22} \) a.k.a fullerol) and underivatized fullerenes \( \text{nC}_{60} \) form aggregates when dispersed in water. We found that fullerol removal efficiency through a ceramic ultrafiltration membrane (pore size of 20 nm) was highly dependant on the transmembrane pressure. In contrast,
nC₆₀ removal efficiency was independent of pressure. We tested whether inducing aggregation through the addition of an electrolyte (NaCl, MgCl₂, CaCl₂) would improve removal efficiencies of both derivatized and non-derivatized fullerene suspensions. Our results indicate that both electrolyte concentration and species play an important role in enhancing removal efficiencies of fullerol suspensions. Divalent ions formed covalent bonds with surface oxygen groups (verified with FTIR), resulting in strong bonds between fullerol particles. These strong aggregates resulted in elevated removal efficiencies that were independent of transmembrane pressure, much like nC₆₀ aggregates. In contrast, removal efficiencies of fullerol aggregates formed after the addition of NaCl were still sensitive to transmembrane pressure, even though higher NaCl concentrations resulted in elevated removal efficiencies. SEM images suggest that when aggregates formed with divalent ions are subjected to increased pressure they deform and partially penetrate the membrane.

As nanomaterials increasingly find their way into waste streams, it is important to develop comprehensive treatment strategies that specifically address their unique characteristics. By taking advantage of these characteristics, significant cost savings may be attained. Since filtration is a commonly used step in water treatment trains, and using the largest pore-size possible reduces operational costs, each target nanoparticle contaminant should be assessed based on its unique characteristics, and an appropriate aggregation strategy developed.
Other nanomaterials, such as metal oxides, often have unsatisfied oxygen bonds on their surface, a fact that imparts them a negative surface charge in basic pH conditions (180). Therefore, the findings reported in Chapter 5 may be relevant towards the remediation of waste streams contaminated with metal oxide nanoparticles.
Appendix

Appendix A: Supporting Information for Chapter 2

Figure A.1: Relative PL intensity of an electrolyte-free, non-aggregating sample under continuous irradiation. 284 nm band-edge PL (a); 425 nm trap-site PL (b).

Figure A.2a,b: Changes in band-edge (284 nm, solid line) and defect-site (425 nm, dotted line) PL intensity of aggregating mercapt ethanol coated ZnS particles (0.01 M) under un stirred (a) and stirred (b) conditions.
Figure A.3: The relative absorbance at 277 nm at different time points and electrolyte concentrations.

Figure A.4: Uncoated ZnS absorbance at t=0 (a), after two hours of aggregation (before shaking) (b), and after 2 hours of aggregation + gentle shaking (c).
Figure A.5: The slopes of the PL relative intensity (284 nm) over time for each electrolyte concentration. Slopes were determined by fitting a sigmoidal function to each PL relative intensity curve (as seen in Fig. 7) and then taking the derivative at each time point.
Appendix B: Supporting Information for Chapter 3

Figure B.1: Changes in $R_h$ over time for aggregating TiO$_2$ and ZnO destabilized with varying concentrations of NaCl (a); changes in EPM as a function of ionic strength (b).
Figure B.2: Log(1/I) vs. LogQ of aggregating TiO₂ and ZnO nanoparticles with varying concentrations of NaCl.
Figure B.3: Log(1/I) vs. LogQ of two ZnO concentrations (20 ppm – blue, 40 ppm – red). As can be seen, the fitted line through both curves has a very similar slope, indicating that the fractal dimension observed is indeed a result of the aggregate structure, and not a result of the flattening of the curve due to a decrease in particle concentration.

Figure B.4a,b: Impact of aggregates size on the ability of photocatalytic nanoparticles to generate free hydroxyl radicals. TiO2 aggregates (a); ZnO aggregates (b).
Figure B.5: Temporal changes in the absorbance of aggregating TiO$_2$ and ZnO nanoparticles. The wavelengths correspond to the excitation wavelengths of the UV bulb used in the experiments.
Figure B.6: Emission spectra of the UV bulb used in experiment (provided by Koninklijke Philips Electronics N.V.)

Figure B.7a,b: Changes in the rate of optically induced transitions as a function of hydrodynamic radius in TiO₂ suspensions (a) and ZnO suspensions (b).

Figure B.8: Changes in $\varepsilon^{D-1}$ as a function of aggregate size and structure for aggregating semiconducting nanoparticles.
Table B.1: Estimated light intensity at a given wavelength.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Energy (watts/cm^2) (joules/cm^2/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>0.0000021</td>
</tr>
<tr>
<td>341</td>
<td>3.57509E-06</td>
</tr>
<tr>
<td>342</td>
<td>4.61162E-06</td>
</tr>
<tr>
<td>343</td>
<td>5.8859E-06</td>
</tr>
<tr>
<td>344</td>
<td>7.43303E-06</td>
</tr>
<tr>
<td>345</td>
<td>9.28777E-06</td>
</tr>
<tr>
<td>346</td>
<td>1.14829E-05</td>
</tr>
<tr>
<td>347</td>
<td>1.40469E-05</td>
</tr>
<tr>
<td>348</td>
<td>1.70023E-05</td>
</tr>
<tr>
<td>349</td>
<td>2.03622E-05</td>
</tr>
<tr>
<td>350</td>
<td>2.41288E-05</td>
</tr>
<tr>
<td>351</td>
<td>2.82904E-05</td>
</tr>
<tr>
<td>352</td>
<td>3.28198E-05</td>
</tr>
<tr>
<td>353</td>
<td>3.76727E-05</td>
</tr>
<tr>
<td>354</td>
<td>4.27868E-05</td>
</tr>
<tr>
<td>355</td>
<td>4.80824E-05</td>
</tr>
<tr>
<td>356</td>
<td>5.34632E-05</td>
</tr>
<tr>
<td>357</td>
<td>5.8819E-05</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------</td>
</tr>
<tr>
<td>358</td>
<td>6.40285E-05</td>
</tr>
<tr>
<td>359</td>
<td>6.89639E-05</td>
</tr>
<tr>
<td>360</td>
<td>7.34959E-05</td>
</tr>
<tr>
<td>361</td>
<td>7.74993E-05</td>
</tr>
<tr>
<td>362</td>
<td>8.08585E-05</td>
</tr>
<tr>
<td>363</td>
<td>8.34731E-05</td>
</tr>
<tr>
<td>364</td>
<td>8.52629E-05</td>
</tr>
<tr>
<td>365</td>
<td>8.61722E-05</td>
</tr>
<tr>
<td>366</td>
<td>8.61722E-05</td>
</tr>
<tr>
<td>367</td>
<td>8.52629E-05</td>
</tr>
<tr>
<td>368</td>
<td>8.34731E-05</td>
</tr>
<tr>
<td>369</td>
<td>8.08585E-05</td>
</tr>
<tr>
<td>370</td>
<td>7.74993E-05</td>
</tr>
<tr>
<td>371</td>
<td>7.34959E-05</td>
</tr>
<tr>
<td>372</td>
<td>6.89639E-05</td>
</tr>
<tr>
<td>373</td>
<td>6.40285E-05</td>
</tr>
<tr>
<td>374</td>
<td>5.8819E-05</td>
</tr>
<tr>
<td>375</td>
<td>5.34632E-05</td>
</tr>
<tr>
<td>376</td>
<td>4.80824E-05</td>
</tr>
<tr>
<td>377</td>
<td>4.27868E-05</td>
</tr>
<tr>
<td>378</td>
<td>3.76727E-05</td>
</tr>
<tr>
<td>379</td>
<td>3.28198E-05</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>380</td>
<td>2.82904E-05</td>
</tr>
<tr>
<td>381</td>
<td>2.41288E-05</td>
</tr>
<tr>
<td>382</td>
<td>2.03622E-05</td>
</tr>
<tr>
<td>383</td>
<td>1.70023E-05</td>
</tr>
<tr>
<td>384</td>
<td>1.40469E-05</td>
</tr>
<tr>
<td>385</td>
<td>1.14829E-05</td>
</tr>
<tr>
<td>386</td>
<td>9.28777E-06</td>
</tr>
<tr>
<td>387</td>
<td>7.43303E-06</td>
</tr>
<tr>
<td>388</td>
<td>5.8859E-06</td>
</tr>
<tr>
<td>389</td>
<td>4.61162E-06</td>
</tr>
<tr>
<td>390</td>
<td>3.57509E-06</td>
</tr>
</tbody>
</table>
### Table B.2: Parameter values used in model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_{\text{ZnO}}$</td>
<td>1.30E-02</td>
<td>181</td>
</tr>
<tr>
<td>$\Phi_{\text{TiO}_2}$</td>
<td>2.00E-02</td>
<td>141</td>
</tr>
<tr>
<td>$k_1$</td>
<td>4.00E+9 M$^{-1}$S$^{-1}$</td>
<td>Assumed (Diffusion Limited)</td>
</tr>
<tr>
<td>$k_2$</td>
<td>1.66E+9 M$^{-1}$S$^{-1}$</td>
<td>182</td>
</tr>
<tr>
<td>$k_4$</td>
<td>3.00E+10 M$^{-1}$S$^{-1}$</td>
<td>183</td>
</tr>
<tr>
<td>$k_5$</td>
<td>7.00E+9 M$^{-1}$S$^{-1}$</td>
<td>183</td>
</tr>
<tr>
<td>$k_6$</td>
<td>3.30E+9 M$^{-1}$S$^{-1}$</td>
<td>142</td>
</tr>
</tbody>
</table>
References


130


95. Markovic, Z.; Trajkovic, V., Biomedical potential of the reactive oxygen species generation and quenching by fullerenes (C-60). Biomaterials 2008, 29, (26), 3561-3573.


111. Pickering, K. D. Photochemistry and environmental applications of water-soluble fullerene compounds. Rice, Houston, **2005**.


134


emission from exterior facades into the aquatic environment. *Environmental Pollution* 2008, 156, (2), 233-239.


139. Siedl, N.; Elser, M. J.; Bernardi, J.; Diwald, O., Functional Interfaces in Pure and Blended Oxide Nanoparticle Networks: Recombination versus Separation of 136


149. Mascolo, G.; Ciannarella, R.; Balest, L.; Lopez, A., Effectiveness of UV-based advanced oxidation processes for the remediation of hydrocarbon pollution in


Biography

David Jassby was born on a sunny summer day, in Tel-Aviv, Israel. Mr. Jassby obtained a B.Sc. in Biology from Hebrew University in Jerusalem, Israel (2002); a M.Sc. in Civil and Environmental Engineering from UC Davis (2005); and a Ph.D. in Civil and Environmental Engineering from Duke University (2011).