Photoluminescence Mechanism and Photocatalytic Activity of Organic–Inorganic Hybrid Materials Formed by Sequential Vapor Infiltration

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ABSTRACT: Organic–inorganic hybrid materials formed by sequential vapor infiltration (SVI) of trimethylaluminum into polyester fibers are demonstrated, and the photoluminescence of the fibers is evaluated using a combined UV–vis and photoluminescence excitation (PLE) spectroscopy approach. The optical activity of the modified fibers depends on infiltration thermal processing conditions and is attributed to the reaction mechanisms taking place at different temperatures. At low temperatures a single excitation band and dual emission bands are observed, while, at high temperatures, two distinct absorption bands and one emission band are observed, suggesting that the physical and chemical structure of the resulting hybrid material depends on the SVI temperature. Along with enhancing the photoluminescence intensity of the PET fibers, the internal quantum efficiency also increased to 5-fold from ~4–5% to ~24%. SVI processing also improved the photocatalytic activity of the fibers, as demonstrated by photodeposition of Ag and Au metal particles out of an aqueous metal salt solution onto fiber surfaces via UVA light exposure. Toward applications in flexible electronics, well-defined patterning of the metallic materials is achieved by using light masking and focused laser rastering approaches.

INTRODUCTION

Combination of organic and inorganic materials at molecular levels can stimulate synergetic properties superior to each of the components, assisting materials scientists to solve challenging problems of optical, electronic, catalysis, mechanical, and biomedical applications. Techniques such as sol–gel,¹ metal organic frameworks,² and molecular and atomic layer deposition^{3–5} have been proposed to create functional hybrid materials. Atomic layer deposition (ALD) is a thin film formation technique to deposit highly conformal thin films utilizing self-limiting reactions between substrate surface and vapor phase precursors. The free volume available in polymers provides for the diffusion of precursor vapors within the polymeric substrates during ALD.^{6–9} Organometallic precursors reacting with functional groups within the polymers form organic–inorganic hybrid materials in the subsurface regions of the polymer.⁸ The concept of precursor infiltration has inspired new techniques to create organic–inorganic hybrid materials, including techniques such as multiple pulsed vapor phase infiltration,^{10,11} sequential infiltration synthesis,^{12,13} and sequential vapor infiltration (SVI).¹⁴ Carbonyl (C=O) containing polymers such as polyamides,^{15,16} polyesters,^{14,17} polyacrylates,^{18,19} cellulose,²⁰ silk,^{10,21} and biopolymers²² have

been infiltrated with common organometallic ALD precursors such as trimethylaluminum (TMA),¹⁴ titanium tetrachloride,¹⁰ and diethylzinc^{20,23} for various applications. An important distinction between an SVI process and an ALD process is the sequence of precursor exposure. Whereas an ALD sequence is defined as a dose A/purge/dose B/purge cycle, where A and B are the precursors, an SVI sequence consists of a single repetitive precursor exposure (i.e., dose A/hold/purge). During the hold step the chamber is isolated from both the pump and nitrogen flow after the precursor dose, thus extending the precursor exposure. To replenish the precursor in the chamber, the system is purged and a new cycle is started with a precursor dose. After these cycles the second precursor (B) is cyclically exposed in a similar fashion to complete any internal reactions in the polymer. It is important to note here the term cycle is different than the ALD cycle and only meant to be used for one precursor's exposure with the pattern explained above.

In our previous works^{12,16} we have shown that SVI can change the optical properties of polyethylene terephthalate

Received: January 26, 2016

Revised: March 18, 2016

Figure 1. Optical images of PET fabrics treated with SVI at different temperatures and exposure conditions: (a) under ambient light and (b) under UV light (Blak-Ray B-100A (100 W) longwave UV lamp) in a dark room.

(PET).^{17,24} Upon SVI treatment the photoluminescence intensity of the PET polyester showed more than an order of magnitude increase.¹⁷ Virgin PET shows weak photoluminescence due to the presence of π electrons on the phenyl groups existing on the backbone of the polymer. These π electrons are excited by absorption of UV light, and electron recombination shows emission in the violet-blue region of the visible spectrum. This emission is studied in the literature to understand the space charge accumulation on these polymers during insulation applications, which can eventually result in degradation of the polymer.^{25,26} Polyesters showed two emission bands in these studies: (1) a band attributed to the monomeric emission, which can be explained by the excitation of mobile sp^2 electrons and their relaxation to ground state,²⁵ and (2) an emission attributed to dimeric interactions of the polymer.^{25–27} The mechanism of the second emission is believed to originate from an excited state dimer (excimer) emission which arises from interaction of excited species^{25,27} or from ground state dimers which are excited by photons.²⁶ Upon SVI treatment the emission spectrum also shifts slightly to the red,¹⁷ representative of the formation of AlO_x and linkages between the polymer chains increase the dimeric emission in the material.

Following the measured changes in the PL emission of the polymers, it is necessary to characterize the optical properties of the PET- AlO_x hybrid materials further to determine suitability for certain applications. The mechanism of PL, for example, needs to be studied further in order to understand the differences in the PL emission behavior observed with SVI temperature, as shown previously.¹⁷ Photoluminescence excitation spectroscopy can explain the PL mechanism by determining the relationship between the excitation and emission bands of the PET- AlO_x materials. Furthermore, understanding absorption mechanisms and photoluminescence internal quantum efficiency (IQE) of the optical materials is necessary for all optical applications in which these hybrid materials potentially can be used. For instance, the photocatalytic activity of a semiconductor material may be considered in relation to the PL performance of the material,^{28–30} the electronic band structure of the material, and the mobility and lifetime of the charge carriers.^{30–33} For high performance photocatalysis, a semiconductor should absorb strongly at the desired wavelength range, and after charge carriers are formed, they should have a lifetime long enough and mobility high

enough to diffuse to the surface and form radicals by redox reactions at the surface of the substrate.^{30–33}

In this report we analyze the dependence of optical emission, absorption, and IQE on the treatment temperature of SVI-processed PET fabrics using UV-vis and photoluminescence excitation (PLE) spectroscopy. We then investigate the photocatalytic activity of these materials in relation to this optical analysis. Increased IQE values are found to correlate with improved photocatalytic activity, as demonstrated with photodeposition of Ag and Au nanoparticles on PET- AlO_x fibers by UVA exposures in aqueous Ag and Au salt solutions.

EXPERIMENTAL METHODS

PET fabrics were obtained in the form of 2/1 woven twill structure, made of 330 denier multifilament 100% PET yarns. Fabrics are used as received, and no pretreatment is conducted. SVI treatments were performed using a flow tube type ALD reactor described elsewhere,¹⁵ using precursors of trimethylaluminum (TMA; STREM Chemicals; CAS No. 75-24-1; 98% purity) and high purity water (Sigma-Aldrich; biotechnology performance certified grade; CAS No. 7732-18-5). Precursor delivery and purging to the system were done via ultrahigh purity N_2 (Airgas National Welders, 99.999%) flow, and the pressure of the system was maintained at 1 Torr during purging. After the initial placement of the samples into the reactor, the chamber was purged for 5 min. TMA cycles were conducted with a sequence of 0.5 s dose/30 s hold/30 s purge, in which the chamber was isolated from the pump, and nitrogen flow was stopped during the hold step. After the TMA cycles were completed, the reactor chamber was evacuated for an additional 5 min before water cycles were conducted. H_2O cycles were carried with a 0.2 s dose/30 s hold/30 s purge sequence. At this point the samples were removed from the reactor after a final 2 min of inert gas purge.

X-ray photoelectron spectroscopy (XPS) analysis was conducted using a SPECS System with PHOIBOS 150 analyzer and Mg $K\alpha$ excitation (1254 eV). Prior to obtaining the XPS spectra, samples were pumped down in the vacuum chamber overnight to minimize effect of any outgassing from samples. Optical properties of samples were investigated using UV-vis and photoluminescence spectroscopy. A Thermo Scientific Evolution 300 BB UV-vis spectrometer with an integrating sphere was used to obtain absorbance and reflectance spectra of the fibrous samples. Photoluminescence (PL) spectra were obtained with a 30 cm grating spectrometer and a Princeton Instruments Spec-10 liquid nitrogen cooled detector, using a xenon lamp as a light source and a monochromator to adjust the wavelength while holding samples in air. For PLE measurements, the wavelength of the excitation was varied, and the PL strength was measured at each excitation wavelength. After determining the optimum wavelength for

Figure 2. High resolution XPS spectra of (a–c) carbon 1s, (d–f) oxygen 1s, (g–i) aluminum 2p peaks, for pristine PET and PET treated with 60-cycle SVI at 60 and 150 °C.

excitation, the absorption and IQE measurements were completed in a 10 cm integrating sphere attachment to the Spec-10 system.

For photoreduction experiments, 0.1 M AgNO_3 (Sigma-Aldrich; CAS No. 7761-88-8) and 10^{-3} M HAuCl_4 (Sigma-Aldrich; CAS No. 27988-77-8) solutions were prepared by using DI water. Cut fabrics of $25 \times 25 \text{ mm}^2$ dimension were embedded into 25 mL solution and exposed to UVA light source (Intelli-Ray 400 W UV Flood; 100 mW/cm²; 320–390 nm). After samples were taken out of the solution, they were rinsed with DI water and dried in an oven at 60 °C. SEM images were obtained using FEI Verios 460 L SEM. Patterning of the metal reduction was conducted using a nontransparent black plastic mask placed on top of the fabric in 25 mL solution and exposing it to the same UVA light source for 15 min. Patterning was also conducted by rastering a near UV laser ($\lambda = 405 \text{ nm}$) mounted on an X–Y gantry stage (Techno Inc.) while fabrics were embedded into the solution.

RESULTS AND DISCUSSION

Optical images of the SVI treated PET fabric samples under ambient and UV light (Blak-Ray B-100A (100 W) longwave UV lamp) conditions are presented in Figure 1. Upon SVI treatment at 60 and 90 °C, the color of the fabrics are visually observed to be the same as the pristine fabric. However, after SVI exposures at 120 and 150 °C, the samples start to show a yellow color, which intensifies as the temperature and exposure time increase. It is very interesting to see this color change for only the high temperature samples: we reported previously the extent of reaction during SVI at 60 and 90 °C, manifested by the mass gain of the samples, is higher than SVI at 120 and 150 °C.¹⁷ Therefore, the reason for the color change cannot be simply hybrid material formation during SVI; rather, it is a potentially new reaction mechanism occurring at higher temperatures as discussed below.

Another important observation after SVI processing is the enhancement of photoluminescence emission when these samples are exposed to UV excitation, as shown in Figure 1b. The weakest emission is observed from the sample treated with

Figure 3. UV–vis (a) absorbance and (b) reflectance spectra of the samples treated with 60 cycles of TMA SVI at various temperatures.

5 TMA cycles of SVI at 60 °C, which also shows the lowest mass gain among the samples. As the amount of hybrid material formation increases with increasing number of TMA cycles at 60 °C, the emission grows stronger. Similarly at 90 °C, photoluminescence of samples also increases with increasing exposure time; however, the stronger emission occurs in fewer TMA cycles as the SVI reaction extent increases more rapidly at 90 °C than at 60 °C.^{17,24} The color and intensity of the emission for the 60 and 90 °C samples are similar to the eye after 60 cycles. SVI processing at 120 °C shows a parallel change in the emission and optical color, while photo-

Figure 4. Photoluminescence excitation (PLE) spectroscopic analysis of SVI treated PET samples at (a) 90 and (b) 150 °C.

Figure 5. Absorption and internal quantum efficiency values of untreated control and 90 and 150 °C SVI treated samples at 355, 372, and 424 nm excitation wavelengths.

luminescence intensity and reaction extent rapidly increase in five cycles. The color of emission slightly changes as the exposure increases, as does the color of the samples. Color change with increasing exposure is even more rapid at 150 °C, and samples are less bright under UV illumination.

In order to understand the change in chemical structure of the materials after SVI processing, XPS analysis was conducted on pristine and 60-cycle SVI treated fabrics. The pristine sample shows a C:O ratio of 77:23, which is similar to the C:O ratio reported for PET in the literature.³⁴ Upon 60 TMA cycles

of SVI treatment at 60 °C, the concentration of C decreases to 37.6% while O increases to 43.8% and Al is 18.6%. The significant increase in the O concentration along with the observed Al formation is due to the aluminum oxide formation during SVI process. After 60 TMA cycle SVI treatment at 150 °C, the concentration of the C, O, and Al elements changes to 47.5, 33.5, and 19%, respectively. When the element ratios of the two SVI treated samples are compared, the amount of O in the higher temperature SVI samples is significantly lower than the low temperature SVI sample, indicating that the species forming at high temperatures has different stoichiometry. In order to further analyze the composition of the hybrid material, the high resolution spectra of C for pristine and SVI treated samples are provided in Figure 2a–c. Peak fittings of the C spectra of all three samples show peaks at 284.8, 286.4, and 288.7 eV due to C–C, C–O, and C=O bonds, respectively. In the pristine PET samples, the ratio of the three bonds is found as 65.1:21.5:13.3, respectively. The ratio changes to 64.8:24.1:11.1 upon 60 °C SVI treatment. The increase in the concentration of C–O bonds with a corresponding decrease in the C=O bond concentration suggests that aluminum oxide is attached to the polymer by attaching to the C=O group during which C–O–Al–O groups form as described in the literature.¹⁴ However, the concentrations of the bonds for the high temperature SVI sample are 75.3:13.2:11.5, showing a significant decrease in the C–O concentration. This result indicates that the reaction mechanisms of the SVI at high and low temperatures are significantly different. Previous FTIR analysis has demonstrated that higher temperature SVI samples show new peaks in the fingerprint region of the spectra and with a corresponding color change in the samples, these peaks were attributed to the quinone-like structures.¹⁷ These structures are likely to form by the chain scission reactions via catalysis effect of TMA, and the XPS data suggest that these reactions are occurring by transformation of C–O bonds. It is also known in the literature that one of the decay mechanisms for PET occurs due to the formation of quinone structures.³⁵ These structures can be the reason for PET yellowing during aging and recycling. The decreased concentrations of C–O and C=O in XPS, supports the idea of TMA accelerated chain scission reactions and the resulting yellow color. High resolution spectra of O and Al are also analyzed in order to understand the nature of the Al–O bands forming. O spectra of the pristine PET given in Figure 2d show that there are two peaks, for C=O bond at 531.86 eV and the C–O bond at 533.36 eV, both in good agreement with the literature. As shown in Figure 2e,f, after SVI processing at 60 and 150 °C, the samples each show one peak centering at 531.81 and 531.84 eV, respectively, along with a small peak at around 535 eV. The Al peak of the SVI treated samples in Figure 2h,i are centered at 74.3 eV. Both the O and Al peaks indicate that the aluminum oxide formed during SVI is different than Al₂O₃ and more similar to aluminum hydroxide as explained in the literature.³⁶ Overall, the XPS data suggest that, at low temperatures, SVI hybridization takes place by addition of Al–(OH)_x to the polymer backbone whereas at high temperatures the chain scission reactions also take place along with hybridizations. In either case the inorganic in the hybrid material is characterized as Al–(OH)_x.

In order to further understand the color changes in the samples, we conducted a comparative UV–vis spectroscopic absorbance and reflectance analysis utilizing an integrating sphere (Figure 3). PET is known for its UV absorption caused

Figure 6. Optical images of samples after 15 min of UVA exposure: (a) pristine PET, (b) SVI (30-cycle TMA at 90 °C) treated PET in AgNO_3 , (c) SVI (30-cycle TMA at 90 °C) treated PET in HAuCl_4 , and (d) SVI (30-cycle TMA at 150 °C) treated PET in AgNO_3 . SEM images of SVI (30-cycle TMA at 90 °C) treated PET samples after UVA exposure in (e) AgNO_3 and (f) HAuCl_4 solutions.

by the ring structures on the backbone of the polymer.²⁵ However, as with many conventional polymers, virgin PET does not show any significant absorption in the visible range, as confirmed in Figure 3a. After 60 cycles of TMA SVI treatment at 60, 90, 120, and 150 °C, samples begin absorbing in the 375–475 nm region, and the strength of the absorption increases with increasing SVI temperature. As the temperature increases, the long wavelength edge of the new absorption feature shifts to longer wavelengths and increases in strength. The edge moves from the 60 °C sample at 400 nm and increases to 475 nm for the 150 °C sample. This new absorption feature causes the yellow color observed in the material. The highest amount of absorption and the highest red shift is observed for SVI at 150 °C, in the range of 350–475 nm. After SVI at 120 °C, absorption still increases considerably in the range of 375–450 nm. As the SVI temperature decreases to 90 and 60 °C, absorbance drops substantially and the range of absorption decreases to 375–425 nm. Reflectance of the samples follow a very similar trend to absorbance in the range of 375–475 nm (Figure 3b), where the reflection shows a substantial drop whose extent increases with increasing SVI temperature. Since surface roughness and morphology are expected to be similar among these samples, this change in reflectance can be attributed to the absorption of the light. It is worth restating that even though the extent of the reaction is 3–4 times higher for SVI at 60 and 90 °C than for SVI at 120 and 150 °C, the higher absorption at 150 °C confirms that the chemical nature of the materials forming is different in these samples. Moreover, the change in the absorption spectral shape suggests that the band structure of the polymer is significantly altered upon SVI treatment.

The excitation and emission behavior in these samples was studied with PLE spectroscopy, as shown in Figure 4. The

temperature-dependent SVI treatments produce significant differences in the absorption and emission patterns. PLE mapping of PET treated with 90-cycle SVI at 90 °C (Figure 4a) shows that a single broad absorption band at 372 nm can excite two distinct emission bands at 424 and 452 nm. At 60 °C 60-cycle SVI treatments (not shown) produce a similar response. However, PET treated with 15-cycle SVI at 150 °C (Figure 4b) shows a significant change as excitation of two absorption bands, the original one at 372 nm and a new one at 424 nm, generate a single PL emission band centered at 472 nm. This change is attributed to different compositions of the hybrid material at different processing conditions (i.e., SVI temperatures). Specifically, the single absorption band observed at low temperatures suggests a single type of material modification takes place during SVI processing that is uniform throughout the cross-section of the fiber, just as was discussed in previous work.¹⁷ At higher temperatures the two absorption bands suggest two distinct phases in the material: one phase similar to the phase formed at low temperatures (absorbing at 372 nm) and the other representative of an altogether new phase (absorbing at 424 nm). Interestingly, the material formed at low temperature has an emission band at 424 nm that coincides with the strong absorption band for materials formed at high temperature. The possibility of increased reabsorption may explain why the emission intensity is an order of magnitude lower for the high temperature SVI-processed sample (Figure 4a,b). Furthermore, the high red shift in the emission along with the decrease in the emission intensity is attributed to the polymer degradation at higher temperature SVI in the polymer as suggested by the literature.³⁵ As explained previously, the XPS analysis suggests that polymer chains break and form quinone structures along with the hybridization at higher temperature SVI.

Figure 7. (a) Approach used for printing metal nanoparticles with a mask using a AgNO₃ solution. (b) Optical image of resulting patterns as prepared with masking approach. (c) Schematic of approach using a laser for printing metal nanoparticles with (d) resulting pattern.

To characterize these optical changes, the absorption and the PL IQE of the materials at these excitation bands were investigated using the techniques reported by de Mello et al.³⁷ As shown in Figure 5, pristine, untreated PET absorbs up to 70% of UV light when samples are excited at 355 nm but only ~30% at 372 nm. However, the IQE of the material is very low (~1.8% at 355 nm; ~4.5% at 372 nm), which means most of the electrons and holes excited by the absorption of photons recombine quickly via nonradiative decay to the ground state. After 90 -cycle SVI processing at 90 °C, absorption at 355 nm increases to ~90% and the IQE increases to ~25%. Upon 15-cycle 150 °C SVI, the sample shows even higher absorption at 355 nm, reaching almost 97%, but the IQE decreases to ~10%, which is most likely due to the new absorption edge which now overlaps the 424 nm emission pathway. When the samples are excited at the 372 nm, excitation band observed for both low and high temperature SVI treated samples, absorption values again reach ~90% for the 90 °C SVI sample and ~97% for the

150 °C SVI sample. IQE values are ~24% for 90 °C SVI and ~7% for 150 °C sample, also similar to the values for the 355 nm excitation. When excited at 424 nm, the 150 °C SVI sample absorbs 93%, as compared to 8% absorption by pristine PET.

The absorption behavior observed upon SVI treatment for low temperature samples is most likely caused by changes in the electronic band structure of the material, while the significant increase in absorption of the high temperature SVI samples is attributed to the two distinct structures of hybrid material formation. Most interesting is the fact that IQE increases after SVI processing compared to the pristine PET, suggesting that the additional absorption mechanisms introduced by SVI modify the electronic band structure and open an efficient radiative recombination pathway for the decay of photoexcited carriers. While the IQE values are not as high as more traditional semiconductor materials, certainly this work indicates that more efficient emission may be achieved by a simplistic modification of an inexpensive material.

We next demonstrate the utility of these hybrid materials as a photocatalytic agent for photodeposition of metal particles. It is well-known that PL performance of a semiconductor catalyst is closely related to its photocatalytic activity.^{28–30} We have already demonstrated the significant increase in the absorption and PL IQE values of the PET fibers upon SVI treatment, altering the electronic band structure and recombination pathways. This optical modification corresponds to more carriers being promoted to higher energy levels, altering their radiative pathways and lifetimes. Specifically, increased IQE indicates that a larger fraction of photoexcited carriers avoid rapid nonradiative decay and undergo slower, radiative decay, suggesting more carriers are available longer to increase the photocatalytic activity of these SVI treated samples. To test this hypothesis, pristine and 30-cycle 90 °C SVI treated samples are embedded into metal salt solutions and exposed to the UVA light source. Optical and SEM images of pristine and SVI (30-cycle TMA at 90 and 150 °C) treated samples after 15 min of UVA exposure in aqueous AgNO₃ and HAuCl₄ are provided in Figure 6. The pristine sample (IQE ~ 2–5%) shows very few stains on the fabric after the UVA exposures (Figure 6a) and remains relatively unchanged after 1 h of continuous UVA exposure. Conversely, samples treated with SVI at 90 °C (IQE ~ 20–25%) and exposed to AgNO₃ and HAuCl₄ solutions show a marked change in color upon 15 min of UVA exposure (Figure 6b,c), which is attributed to the deposition of metal nanoparticles onto the surface of the PET fibers. Although the sample treated with SVI at 150 °C (IQE ~ 7–10%) and exposed to AgNO₃ solution shows slightly more staining compared to the pristine PET (Figure 6d), it is not as covered with the Ag particles as the 90 °C samples, indicating that IQE efficiency of these samples can be related to the photocatalytic activity of them. The evolution of the Ag deposition is observed by the initial formation of black stains followed by a fully saturated black sample after ~10 min. During exposure to the HAuCl₄ solution, the SVI-modified PET fabric again starts black prior to evolving into a reddish color. This color difference is attributed to the composition of deposited particles as well as the particle size difference of Ag and Au particles, confirmed by the SEM micrographs in Figure 6e,f. Silver deposition produces very small nanoparticles with the size range < 100 nm, while gold deposition produces both large (>100 nm) and small particles (<100 nm).

Controlled reduction of nanoparticles selectively on a flexible, fabric substrate is of interest for many area-specific applications such as wearable devices. Two approaches are illustrated in Figure 7 to realize such patterning on the SVI treated fabric substrates: light masking and rastering of a high intensity UV laser light source. For the first approach, we prepared a black-dyed plastic mask and illuminated the fabric with UVA in select regions while submersed in a AgNO₃ solution. Optical imaging of the masked sample shows a well-defined pattern. The second approach utilizes a focused UV laser at 410 nm, and a well-defined pattern of photodeposited Ag is again observed.

CONCLUSIONS

In this work we present an analysis of the photoluminescent behavior and corresponding photocatalytic activity of organic–inorganic hybrid materials formed by sequential vapor infiltration of trimethylaluminum precursors into polyethylene terephthalate fibers. Upon formation of PET–Al(OH)_x hybrid structures, fibers show increased photoluminescence intensity,

absorption values, and internal quantum efficiency, a result of altered electronic band structure and multiple phases of the PET. Enhancement of the internal quantum efficiency correlates with improved photocatalytic activity of the fibers. Depositions of Ag and Au nanoparticles on the modified materials are carried out successfully by photoreduction in aqueous solutions of metal salts. Furthermore, photoreduction by selective excitation of the samples using simple masking and light rastering techniques is demonstrated. SVI shows promise as a simple material modification process to enhance the functionality of inexpensive polymers.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Authors acknowledge partial funding from the National Science Foundation Industry & University Cooperative Research Program: Center for Dielectrics and Piezoelectrics (CDP; Grant No. 1361503), the Army Competitive In-house Innovative Laboratory Research Grant, and the Ministry of National Education of Republic of Turkey.

ABBREVIATIONS

ALD, atomic layer deposition; DI, deionized; FT-IR, Fourier transform infrared; IQE, internal quantum efficiency; PET, polyethylene terephthalate; PL, photoluminescence; PLE, photoluminescence excitation; SEM, scanning electron microscopy; SVI, sequential organometallic vapor infiltration; TMA, trimethylaluminum; UVA, ultraviolet A; UV–vis, ultraviolet–visible

REFERENCES

- (1) Schubert, U.; Huesing, N.; Lorenz, A. Hybrid inorganic-organic materials by sol-gel processing of organofunctional metal alkoxides. *Chem. Mater.* **1995**, *7*, 2010–2027.
- (2) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keeffe, M.; Yaghi, O. M. Hydrogen storage in microporous metal-organic frameworks. *Science* **2003**, *300*, 1127–1129.
- (3) Parsons, G. N.; George, S. M.; Knez, M. Progress and future directions for atomic layer deposition and ALD-based chemistry. *MRS Bull.* **2011**, *36*, 865–871.
- (4) Brozena, A. H.; Oldham, C. J.; Parsons, G. N. Atomic layer deposition on polymer fibers and fabrics for multifunctional and electronic textiles. *J. Vac. Sci. Technol., A* **2016**, *34*, 010801.
- (5) Gregorczyk, K.; Knez, M. Hybrid nanomaterials through molecular and atomic layer deposition: Top down, bottom up, and in-between approaches to new materials. *Prog. Mater. Sci.* **2016**, *75*, 1–37.
- (6) Jur, J. S.; Spagnola, J. C.; Lee, K.; Gong, B.; Peng, Q.; Parsons, G. N. Temperature-Dependent Subsurface Growth during Atomic Layer Deposition on Polypropylene and Cellulose Fibers. *Langmuir* **2010**, *26*, 8239–8244.
- (7) Spagnola, J. C.; Gong, B.; Arvidson, S. A.; Jur, J. S.; Khan, S. A.; Parsons, G. N. Surface and sub-surface reactions during low temperature aluminium oxide atomic layer deposition on fiber-forming polymers. *J. Mater. Chem.* **2010**, *20*, 4213–4222.
- (8) Sun, Y.; Padbury, R. P.; Akyildiz, H. I.; Goertz, M. P.; Palmer, J. A.; Jur, J. S. Influence of Subsurface Hybrid Material Growth on the Mechanical Properties of Atomic Layer Deposited Thin Films on Polymers. *Chem. Vap. Deposition* **2013**, *19*, 134–141.

- (9) Wilson, C. A.; Grubbs, R. K.; George, S. M. Nucleation and growth during Al_2O_3 atomic layer deposition on polymers. *Chem. Mater.* **2005**, *17*, 5625–5634.
- (10) Lee, S.-M.; Pippel, E.; Goesele, U.; Dresbach, C.; Qin, Y.; Chandran, C. V.; Braeuniger, T.; Hause, G.; Knez, M. Greatly Increased Toughness of Infiltrated Spider Silk. *Science* **2009**, *324*, 488–492.
- (11) Lee, S.-M.; Ischenko, V.; Pippel, E.; Masic, A.; Moutanabbir, O.; Fratzl, P.; Knez, M. An Alternative Route Towards Metal-Polymer Hybrid Materials Prepared by Vapor-Phase Processing. *Adv. Funct. Mater.* **2011**, *21*, 3047–3055.
- (12) Peng, Q.; Tseng, Y.-C.; Darling, S. B.; Elam, J. W. A Route to Nanoscopic Materials via Sequential Infiltration Synthesis on Block Copolymer Templates. *ACS Nano* **2011**, *5*, 4600–4606.
- (13) Nam, C.-Y.; Stein, A.; Kisslinger, K. Direct fabrication of high aspect-ratio metal oxide nanopatterns via sequential infiltration synthesis in lithographically defined SU-8 templates. *J. Vac. Sci. Technol. B* **2015**, *33*, 06F201.
- (14) Gong, B.; Peng, Q.; Jur, J. S.; Devine, C. K.; Lee, K.; Parsons, G. N. Sequential Vapor Infiltration of Metal Oxides into Sacrificial Polyester Fibers: Shape Replication and Controlled Porosity of Microporous/Mesoporous Oxide Monoliths. *Chem. Mater.* **2011**, *23*, 3476–3485.
- (15) Akyildiz, H. I.; Padbury, R.; Parsons, G. N.; Jur, J. S. Temperature and Exposure Dependence of Hybrid Organic-Inorganic Layer Formation by Sequential Vapor Infiltration into Polymer Fibers. *Langmuir* **2012**, *28*, 15697.
- (16) Akyildiz, H. I.; Jur, J. S. Organometallic exposure dependence on organic–inorganic hybrid material formation in polyethylene terephthalate and polyamide 6 polymer fibers. *J. Vac. Sci. Technol., A* **2015**, *33*, 020604.
- (17) Akyildiz, H. I.; Lo, M.; Dillon, E.; Roberts, A. T.; Everitt, H. O.; Jur, J. S. Formation of Novel Photoluminescent Hybrid Materials by Sequential Vapor Infiltration into Polyethylene terephthalate Fibers. *J. Mater. Res.* **2014**, *29*, 2817–2826.
- (18) Tseng, Y.-C.; Peng, Q.; Ocola, L. E.; Czaplewski, D. A.; Elam, J. W.; Darling, S. B. Etch properties of resists modified by sequential infiltration synthesis. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* **2011**, *29*, 06FG01–06FG01–4.
- (19) Yu, Y.; Li, Z.; Wang, Y.; Gong, S.; Wang, X. Sequential Infiltration Synthesis of Doped Polymer Films with Tunable Electrical Properties for Efficient Triboelectric Nanogenerator Development. *Adv. Mater.* **2015**, *27*, 4938–4944.
- (20) Gregorczyk, K. E.; Pickup, D. F.; Sanz, M. G.; Irakulis, I. A.; Rogero, C.; Knez, M. Tuning the Tensile Strength of Cellulose through Vapor-Phase Metalation. *Chem. Mater.* **2015**, *27*, 181–188.
- (21) Lee, S.-M.; Pippel, E.; Moutanabbir, O.; Kim, J.-H.; Lee, H.-J.; Knez, M. In Situ Raman Spectroscopic Study of Al-Infiltrated Spider Dragline Silk under Tensile Deformation. *ACS Appl. Mater. Interfaces* **2014**, *6*, 16827–16834.
- (22) Lee, S.-M.; Pippel, E.; Moutanabbir, O.; Gunkel, I.; Thurn-Albrecht, T.; Knez, M. Improved Mechanical Stability of Dried Collagen Membrane after Metal Infiltration. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2436–2441.
- (23) Nam, C.-Y.; Stein, A.; Kisslinger, K.; Black, C. T. Electrical and structural properties of ZnO synthesized via infiltration of lithographically defined polymer templates. *Appl. Phys. Lett.* **2015**, *107*, 203106.
- (24) Akyildiz, H. I.; Mousa, M. B. M.; Jur, J. S. Atmospheric pressure synthesis of photoluminescent hybrid materials by sequential organo-metallic vapor infiltration into polyethylene terephthalate fibers. *J. Appl. Phys.* **2015**, *117*, 045301.
- (25) Takai, Y.; Mizutani, T.; Ieda, M. Photoluminescence study in polymers. *Jpn. J. Appl. Phys.* **1978**, *17*, 651–8.
- (26) Teyssedre, G.; Menegotto, J.; Laurent, C. Temperature dependence of the photoluminescence in poly (ethylene terephthalate) films. *Polymer* **2001**, *42*, 8207–8216.
- (27) Corrales, T.; Peinado, C.; Bosch, P.; Catalina, F. Study of secondary relaxations of poly (ethylene terephthalate) by photoluminescence technique. *Polymer* **2004**, *45*, 1545–1554.
- (28) Anpo, M.; Aikawa, N.; Kubokawa, Y.; Che, M.; Louis, C.; Giamello, E. Photoluminescence and photocatalytic activity of highly dispersed titanium oxide anchored onto porous Vycor glass. *J. Phys. Chem.* **1985**, *89*, 5017–5021.
- (29) Shi, J.; Chen, J.; Feng, Z.; Chen, T.; Lian, Y.; Wang, X.; Li, C. Photoluminescence characteristics of TiO_2 and their relationship to the photoassisted reaction of water/methanol mixture. *J. Phys. Chem. C* **2007**, *111*, 693–699.
- (30) Liqiang, J.; Yichun, Q.; Baiqi, W.; Shudan, L.; Baojiang, J.; Libin, Y.; Wei, F.; Honggang, F.; Jiazhong, S. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 1773–1787.
- (31) Ganguli, S.; Hazra, C.; Samanta, T.; Mahalingam, V. Photoluminescence and photocatalytic activity of monodispersed colloidal “ligand free Ln^{3+} -doped PbMoO_4 nanocrystals. *RSC Adv.* **2015**, *5*, 45611–45617.
- (32) Fox, M. A.; Dulay, M. T. Heterogeneous photocatalysis. *Chem. Rev.* **1993**, *93*, 341–357.
- (33) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. *Chem. Rev.* **1995**, *95* (3), 735–758.
- (34) Doren, A.; Genet, M. J.; Rouxhet, P. G. Analysis of poly (ethylene terephthalate) (PET) by XPS. *Surf. Sci. Spectra* **1994**, *3* (4), 337–341.
- (35) Edge, M.; Wiles, R.; Allen, N.; McDonald, W.; Mortlock, S. Characterisation of the species responsible for yellowing in melt degraded aromatic polyesters—I: Yellowing of poly (ethylene terephthalate). *Polym. Degrad. Stab.* **1996**, *53*, 141–151.
- (36) Crist, B. V. *Handbooks of monochromatic XPS spectra*; Wiley: New York, 1999.
- (37) de Mello, J. C.; Wittmann, H. F.; Friend, R. H. An improved experimental determination of external photoluminescence quantum efficiency. *Adv. Mater.* **1997**, *9*, 230–232.