# New Approach for Multilayered Microstructures Fabrication Based on a Water-Soluble Backing Substrate

Eunice Sok Ping Leong,* Sok Yee Yew, Tanu Suryadi Kustandi, Yan Jun Liu, Hendrix Tanoto, Qing Yang Wu, Wei Wei Loh, Siew Lang Teo, and Jinghua Teng

Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), 3 Research Link, Singapore 117602

ABSTRACT: We demonstrate a new approach for woodpile microstructure fabrication. The method involves the use of polyvinyl alcohol (PVA) as a sacrificial substrate for the transfer of SU-8 films to prepatterned structures. The surface activated PVA substrate allows good wettability of SU-8 film and its solubility in water eliminates the need of delaminating SU-8 structures from the substrate. This makes the fabrication process much simplified and we successfully demonstrate eight-layer stacking of gratings. Fourier transform infrared spectra of single-layer and four-layer grating structures show a broader transmission dip spectrum compared to their film counterparts, indicating their potential use as broadband terahertz (THz) absorbers.

KEYWORDS: woodpile, micropatterning, THz absorber, SU-8
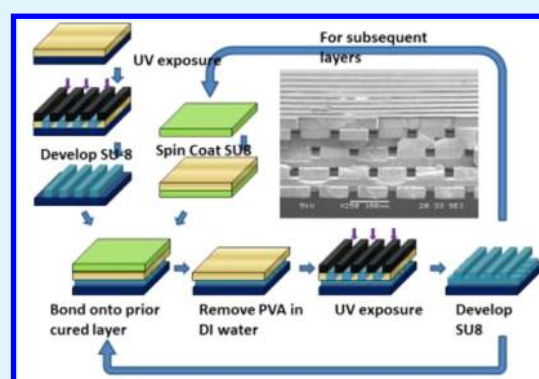
INTRODUCTION

Three-dimensional (3D) multilayered polymeric microstructures have attracted intense attention for a wide range of potential applications. In bioengineering, 3D scaffolds are needed for tissue engineering where different types of cells are grown and cultured, depending on the size of the pores that can range from a few to hundreds of micrometers.[1−3] Recently, it was demonstrated that 3D polyethylene glycol scaffolds can actually produce tunable negative Poisson's ratios, which is useful in tissue engineering.[4] In microfludics, multilayered SU-8 structures are stacked to form the microchannels.[5] In photonics, polymeric structures are either used as sacrificial templates, whereby they are calcinated after the infiltration of higher refractive index materials,[6] or doped with functional materials for photonic crystals.[7] Very recently, 3D polymeric structures have attracted intense interest in THz regime for potential applications as absorbers.[8] Therefore, fabrication of large 3D microstructures is of particular importance for THz applications.

Polymers such as poly(methyl methacrylate) (PMMA),[9] polydimethylsiloxane (PDMS)[2] and SU-8[6] are common materials for making multilayered structures. Among them, SU-8 is more attractive due to its high optical transparency, chemical resistance and mechanical stability. It is a negative resist that can be cross-linked by either heat or UV radiation. It can also be mixed with different materials to modify certain properties such as refractive index,[7] absorbance,[10] magnetic properties,[11] and hydrophobicity,[12,13] allowing direct use for mold fabrication and device applications. Furthermore, SU-8

films with thickness ranging from <1 μm to >300 μm are available commercially.

Various approaches have been employed to fabricate 3D multilayered SU-8 structures. Advanced techniques, such as holographic lithography[6,7] and proton beam lithography,[14] have shown the ease in making 3D structures with reduced steps. However these techniques are limited by their high cost and complexity. Alternatively, most researchers will apply the layer-by-layer patterning method. To form flat films for patterning, this is done either with the help of a planarization layer or layer-by-layer multiexposure followed by a one-time development.[15] Suitable planarization material may be difficult to find and the fabrication process can be time-consuming. This is especially so when fabricating large micrometer-size 3D structures. For the latter approach, nonuniform exposure may result in partial cross-linking of bottom layers during subsequent exposure.

Another common layer-by-layer fabrication method is to stack individual layers prepared on separate substrates, bond them together, and then remove the layer from the top substrate for repeated stacking.[2,16] Each single layer can be prepared using either soft lithography to form free-standing structures[2] or more commonly, standard photolithography technique on substrates.[16,17] For subsequent layers, SU-8 film spin-coated on another substrate can be UV cured either before or after in contact with the bottom layer. In both cases, there lies a contradictory issue about wettability of SU-8 on the
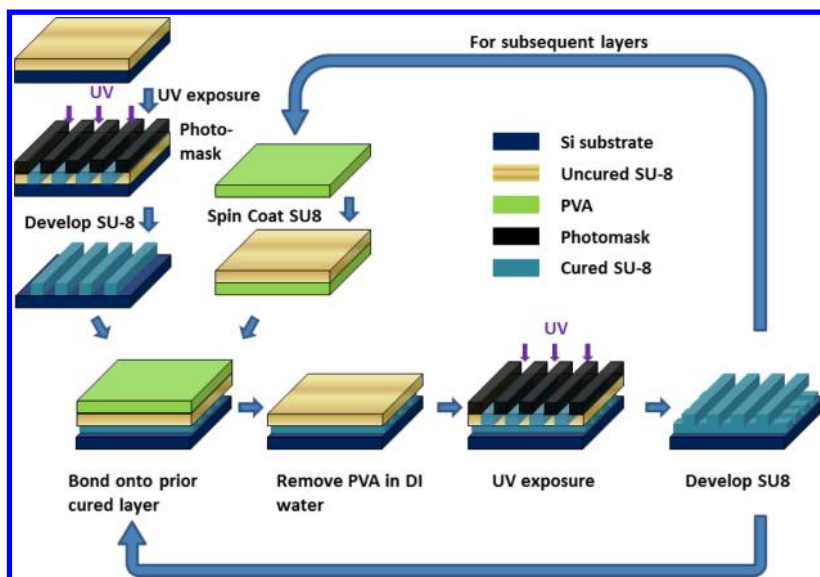
Figure 1. Schematic of fabricating multilayered SU-8 grating structures.

substrate[6] and release of SU-8 structures from the substrate after stacking. To tackle this problem, strong bonding of SU-8 layers have been demonstrated using adhesive layers[2,17,18] or by applying some pressure and heat.[16,19] These methods involve the release of the substrate, usually with razor blade, after the SU-8 film has been patterned. This can cause delamination of SU-8 and damage the structure. In addition, the transparency of these materials may affect the reliability of alignment and UV exposure dosage. As such, for stacking of multilayers, these requirements are highly desired: (1) good bonding force between the two layers, (2) easy release of SU-8 microstructures from its top substrate after UV exposure with minimal damage, and (3) transparent top substrate for easy alignment and UV exposure. On the other hand, we have also noticed that in nanoimprint lithography, PVA, a water-soluble material, is often used as a mold for subsequent transfer of imprint resins.[20,21] The imprint material is coated on the PVA mold and placed in contact with the desired pattern or substrate. Upon adhesion, the PVA mold is then dissolved in water. This process minimizes the release issue and allows stacking of several sealed channels.[21] In this work, we adopt similar idea by using PVA as a sacrificial backing substrate instead of an imprint mold to stack SU-8 3D scaffolds. Our method avoids the need to release the layer from substrate after UV exposure and makes the process less laborious and more cost-effective. We demonstrate eight layers of gratings stacked in an A−B−C−D manner (i.e., woodpile structure) to showcase the ease in alignment. We also compared the Fourier transform infrared (FTIR) spectra of single-layer and four-layer grating structures with their film counterparts, showing that the stacked SU-8 gratings are potentially useful for broadband THz absorbers.

■ EXPERIMENTAL SECTION

Fabrication. Figure 1 shows the schematic of the fabrication process. The first layer of SU-8 grating was fabricated using standard photolithography process. First, SU8−10 (a special formulation of SU-8 from MicroChem) was spin-coated onto an intrinsic silicon substrate at 1250 rpm for 34 s to form a 25 μm-thick film. After that, the film was prebaked at 65 °C for 3 min and softbaked at 95 °C for 7 min to remove the solvent.

UV exposure was done using a photomask and bond aligner (SUSS MicroTec, MA8/BA6) for 35.7 s at a power of 7 mW under hard contact mode. The photomask was a plastic sheet with 25 μm dark lines spaced 75 μm apart defined in an area of 2.5 × 2.5 cm². After exposure, the SU-8 film was post baked initially at 65 °C for 1 min and then at 95 °C for 3 min. Following that, the SU-8 film was developed with SU-8 developer (MicroChem) for 5 min. Finally, the substrate was rinsed with isopropyl alcohol (IPA) and dried with nitrogen.

Subsequent SU-8 layers were prepared on a sacrificial PVA film. For the preparation of PVA backing substrate, PVA in aqueous solution was casted onto a Si substrate, which was pretreated by a 1H,1H,2H,2H-perfluorodecyl-trichlorosilane (FDTS). After the PVA film was dried, it was exposed to oxygen plasma at a 30W electric power, 10 sccm oxygen flow rate, and 250 mTorr oxygen pressure for 60s in a RIE etcher, Sirus (Trion). After that, SU8−10 was spin-coated onto the surface activated PVA film at 1250 rpm for 34 s. Prebaking of the SU8−10 film on PVA/Si substrate was carried out in a vacuum oven at 60 °C for 1 h. The free-standing SU-8/PVA film was then obtained by peeling the PVA film from the Si substrate. To bond the prior SU-8 pattern with the SU-8 film on PVA backing substrate, we placed the SU-8 layers in contact with each other in the Obducat nanoimprinter (Sweden) at a pressure of 10 bar and at a temperature of 40 °C for 600 s. After that, the PVA backing substrate was removed by immersing the bonded sample in deionized (DI) water overnight. Note that the overnight removal of the PVA backing substrate is processed at the room temperature. It is possible to shorten the removal process in DI water at an elevated temperature[22] with stirring or sonication.

The SU-8 film on top of the SU-8 grating was again patterned using photolithography technique. The UV exposure, development and postbake conditions were the same as that for the first layer of SU-8 grating structure. The process was then repeated for subsequent addition of layers. Alignment with accuracy of ±1 μm could be achieved with the MA8/BA6 system. The second grating layer was defined to be 90° with respect to the first layer grating and the third (fourth) layer was offset by half pitch (i.e., 50 μm) from the first (second) layer to obtain an A−B−C−D stacking manner.
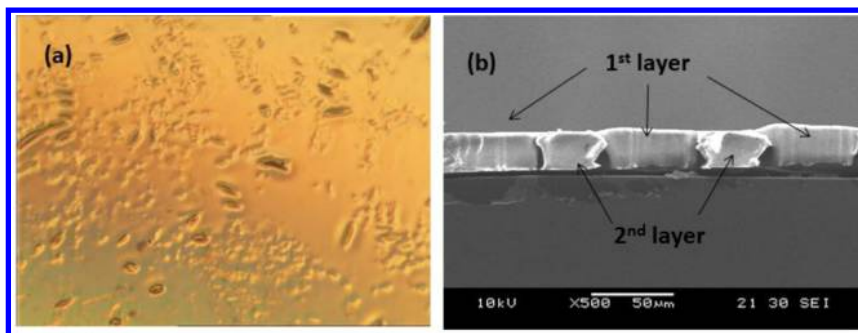
Figure 2. (a) Macroscopic view of PVA/SU-8 surface at softbaking temperature of 95 °C and (b) cross-sectional view of two-layer grating structure bonded near T_g of SU-8 at 55 °C.
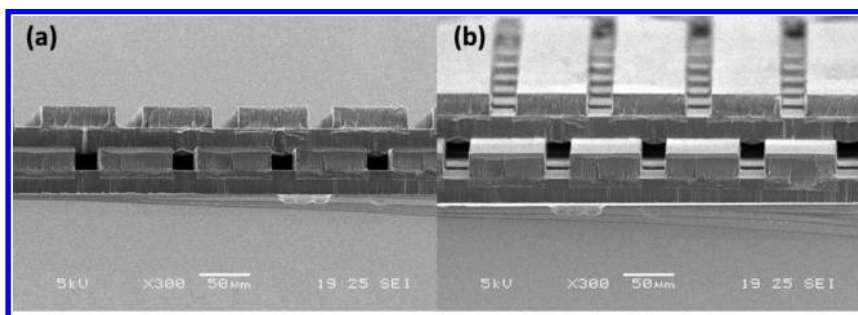

Figure 3. (a) Cross-sectional view and (b) tilted view of a four-layer grating structure bonded at 40 °C.
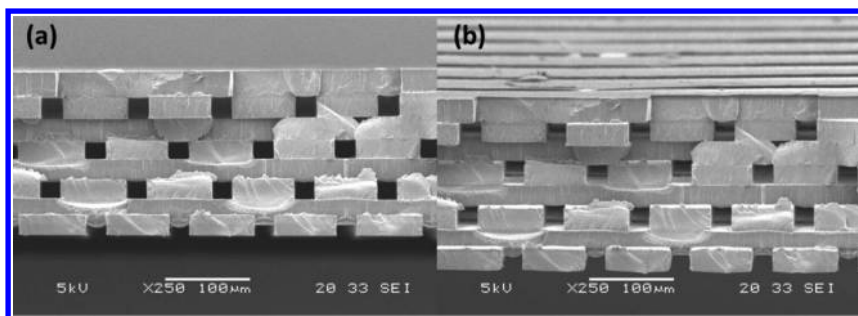

Figure 4. (a) Cross-sectional view and (b) tilted view of an eight-layer grating structure bonded at 40 °C.

Characterization. The cross-sections of the 3D structures were observed under a scanning electron microscopy (SEM) (JEOL JSM-5600) at low magnification. The top view of the structures was observed under an optical microscope (BX60, Olympus) using a 100× objective lens. The transmittance and absorbance of the structures were measured with a Bruker Vertex 80v FTIR spectrometer equipped with a room temperature DTGS. Unpolarized light was used in the measurement and the reference was air.

■ RESULTS AND DISCUSSION

The PVA backing substrate undergoes oxygen plasma to increase its surface energy such that SU-8 can wet readily and form a uniform film upon spin-coating. Because the glass transition temperature, T_g, of PVA is 85 °C,[23] the prebaking of SU-8 film on PVA substrate has to be done at a lower temperature compared to that (95 °C) for the first SU-8 layer on Si. As a control experiment, Figure 2a shows the case when SU-8 film coated on PVA substrate is softbaked at 95 °C. It is obvious that the sample surface appears rough, indicating the interdiffusion of polymers. During the bonding process, the temperature and pressure applied cannot be too high. Figure 2b

shows the cross-sectional view of a two-layer grating structure when the bonding condition is near the T_g of SU-8 film at 55 °C.[24] The applied pressure and time are 30 bar and 600 s, respectively. It is obvious that the top layer of uncured SU-8 has flowed into the cavities of the cured bottom grating layer. In our experiments, optimized prebaking for SU-8 on PVA backing substrate was 60 °C for 1 h, and the optimized bonding was 40 °C for 600 s at the pressure of 10 bar because the SU-8 just starts to flow and sticks to the cured layer at this temperature. The optimized bonding temperature also agrees well with the experimental process carried out in ref 24, which indicates that SU-8 will flow into cavities of bottom layers if the heating temperature exceeds 40 °C. As a demonstration, Figure 3 shows a typical four-layer grating structure under our optimized fabrication conditions.

The dissolving of PVA backing substrate in water after bonding of uncured SU-8 film with prior layers allows direct UV exposure on the uncured SU-8 film. This eliminates both the delamination and the transparency issue of backing substrate. Excellent control of alignment and UV exposure dosage can be achieved. Furthermore, the bonding strength between the SU-8 structure and SU-8 film is no longer critical
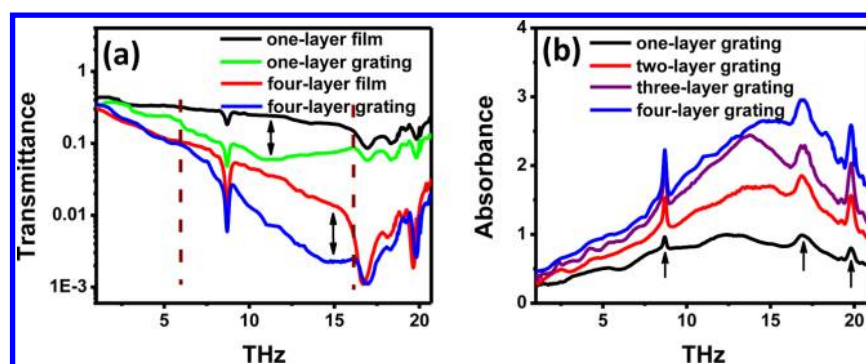
Figure 5. (a) Transmittance spectra of grating structures compared to film and (b) absorbance spectra of one- to four-layer grating structures. The grating resulted in a reduction in transmission in the frequency range denoted by the dashed lines and the transmission dips are indicated by the arrows in panel a. The intrinsic absorbance peaks corresponding to the transmission dips were indicated by the arrows in panel b.

for the release of the microstructures from the backing substrate. Therefore the amount of pressure and temperature applied to create the adhesion can be further reduced such that it lowers the chance of SU-8 film flowing into the cavities of the beneath grating layer.

In the stacking process, we had used a smaller piece of PVA/SU-8 film on top of the Si substrate with the grating structure during the bonding process. This resulted in a smaller area of SU-8 film being transferred to the bottom cured SU-8 gratings. Furthermore the flatness of both the PVA substrate and the underlying Si substrate limits the bonding area. In order to test if more than four layers of structures could be fabricated, we continued the process and managed to obtain repeatedly an area of 0.3×0.3 cm^2 with eight layers of grating structures stacked in A−B−C−D manner. Images a and b in Figure 4 show the cross-sectional view of the eight-layer structure. Technically, a larger area could be obtained by playing around with the size of the PVA/SU-8 substrate, which allows a uniform area of 0.8×0.8 cm^2 to be achieved. We believed that with further improvement in PVA preparation and bonding process, large area multilayer SU-8 structures could be realized.

The optical transmittance and absorbance of the SU-8 multilayered structures were further characterized in THz regime using FTIR. Figure 5a shows the transmittance spectra of a one-layer SU-8 film and a four-layer SU-8 film against a one-layer grating and a four-layer grating sample. In both cases, the thickness of each layer is equivalent to the grating height. We observe intrinsic transmission dips at around 8.68 THz, 16.9 THz and 19.8 THz. The dip at 18.3 THz is due to the absorption in intrinsic Si substrate. We can see from Figure 5a that compared to the film counterparts, the transmission is lower in the 6−16 THz range for the grating structures. The transmission spectra also have a broad line width with a dip at ~11 THz for the one-layer grating and at ~15 THz for the four-layer grating structures, which are mainly caused by the grating diffraction of the THz waves. Figure 5b shows the absorbance of the grating structure from one to four layers. A clear broad absorbance occurs and increases with the number of layers. This is in good agreement with the report in ref 25, which shows that the absorbance of SU-8 increases with thickness, though the reference shows for 0.3−10 THz range. In addition, we see that the absorbance peak red-shifts with the increase of numbers of the grating layers. From Figure 5a, the SU-8 material absorbs more at the higher frequencies in our interested region (0.3−20 THz). Therefore, the increased numbers of SU-8 grating layers will cause more absorption in

the higher frequency range, hence giving rise to a redshift of the absorbance peak, as shown in Figure 5b. These preliminary results show that it is possible to attain broadband absorption from SU-8 3D structures, which could be useful in the design of broadband THz absorbers.

CONCLUSIONS

An eight-layer SU-8 woodpile structure has been successfully fabricated using a novel fabrication technique. The fabrication combined the use of standard photolithography and PVA sacrificial backing substrate. Water-soluble property of PVA makes the PVA backing substrate easily removed upon bonding the SU-8 film to the prior SU-8 structure. The process allows a better control of the alignment and UV exposure process and does not pose critical requirement on the good wettability of SU-8 film and yet good release of the structure. The use of PVA simplifies the process of stacking multilayer structures and can be used for making scaffolds or sealed channels. Such a technology could also be applied for microelectromechanical systems (MEMS) and 3D scaffold fabrication for tissue engineering. FTIR studies show a broadening in transmission dip in the SU-8 gratings compared to the bare films and absorbance increases with the number of grating layers. Preliminary results have shown that SU-8 multilayered structures are potentially useful for broadband THz absorbers.

AUTHOR INFORMATION

Corresponding Author
*E-mail: leonge@imre.a-star.edu.sg.
Notes
The authors declare no competing financial interest.

REFERENCES

(1) Annabi, N.; Nichol, J. W.; Zhong, X.; Ji, C. D.; Koshy, S.; Khademhosseini, A.; Dehghani, F. *Tissue Eng. Part B: Rev.* **2010**, *16*, 371−383.
(2) Mata, A.; Kim, E. J.; Boehm, C. A.; Fleischman, A. J.; Muschler, G. F.; Roy, S. *Biomaterials* **2009**, *30*, 4610−4617.
(3) Choi, Y.; Powers, R.; Vernekar, V.; Frazier, A. B.; LaPlaca, M. C.; Allen, M. G. *Proceedings of the 2003 ASME International Mechanical Engineering Congress and Exposition (IMECE)*; ASME: New York, 2003; pp 651−654

(4) Fozdar, D. Y.; Soman, P.; Lee, J. W.; Han, L. H.; Chen, S. C. *Adv. Funct. Mater.* **2011**, *21*, 2712−2720.

(5) Chuang, Y. J.; Tseng, F. G.; Cheng, J. H.; Lin, W. K. *Sens. Actuators, A* **2003**, *103*, 64−69.

(6) del Campo, A.; Greiner, C. *J. Micromech. Microeng.* **2007**, *17*, R81−R95.

(7) Li, J. T.; Liang, B.; Liu, Y. K.; Zhang, P. Q.; Zhou, J. Y.; Klimonsky, S. O.; Slesarev, A. S.; Tretyakov, Y. D.; O'Faolain, L.; Krauss, T. F. *Adv. Mater.* **2010**, *22*, 2676−2679.

(8) Kim, D.-H.; Kim, D.-S.; Hwang, S.; Jang, J.-H. *Opt. Express* **2012**, *20*, 16815−16822.

(9) Yew, S. Y.; Kustandi, T. S.; Low, H. Y.; Teng, J. H.; Liu, Y. J.; Leong, E. S. P. *Microelectron. Eng.* **2011**, *88*, 2946−2950.

(10) Foulds, I. G.; Parameswaran, M. *J. Micromech. Microeng.* **2006**, *16*, 2109−2115.

(11) Damean, N.; Parviz, B. A.; Lee, J. N.; Odom, T.; Whitesides, G. M. *J. Micromech. Microeng.* **2005**, *15*, 29−34.

(12) Hong, L. F.; Pan, T. R. *J. Microelectromech. Syst.* **2010**, *19*, 246−253.

(13) Wu, C. L.; Chen, M. H.; Tseng, F. G. *Proc. MicroTAS* **2003**, 1117−1120.

(14) van Kan, J. A.; Bettiol, A. A.; Wee, B. S.; Sum, T. C.; Tang, S. M.; Watt, F. *Sens. Actuators, A* **2001**, *92*, 370−374.

(15) Mata, A.; Fleischman, A. J.; Roy, S. *J. Micromech. Microeng.* **2006**, *16*, 276−284.

(16) Agirregabiria, M.; Blanco, F. J.; Berganzo, J.; Arroyo, M. T.; Fullaondo, A.; Mayora, K.; Ruano-Lopez, J. M. *Lab Chip* **2005**, *5*, 545−552.

(17) Patel, J. N.; Kaminska, B.; Gray, B. L.; Gates, B. D. *J. Micromech. Microeng.* **2008**, *18*, 095028.

(18) Gadre, A. P.; Nijdam, A. J.; Garra, J. A.; Monica, A. H.; Cheng, M. C.; Luo, C.; Srivastava, Y.; Schneider, T. W.; Long, T. J.; White, R. C.; Paranjape, M.; Currie, J. F. *Sens. Actuators, A* **2004**, *114*, 478−485.

(19) Abgrall, P.; Lattes, C.; Conédéra, V.; Dollat, X.; Colin, S.; Gué, A. M. *J. Micromech. Microeng.* **2006**, *16*, 113−121.

(20) Schaper, C. D. *Nano Lett.* **2003**, *3*, 1305−1309.

(21) Han, K. S.; Hong, S. H.; Lee, H. *Appl. Phys. Lett.* **2007**, *91*, 123118.

(22) http://www.polyvinyl-alcohol.net/FAQ.html (accessed June 1, 2013).

(23) http://www.polymerprocessing.com/polymers/PVOH.html (accessed June 1, 2013).

(24) Hu, W.; Yang, B.; Peng, C.; Pang, S. W. *J. Vac. Sci. Technol., B* **2006**, *24*, 2225−2229.

(25) Perez, R.; Omictin, G.; Grbovic, D. (2012). http://www.nps.edu/Academics/Institutes/Cebrowski/STEM/doc/Rolando_George%20Poster.pdf (accessed Mar. 15, 2013).

5902

dx.doi.org/10.1021/am401397h | *ACS Appl. Mater. Interfaces* 2013, 5, 5898−5902