ACS Macro Letters

Letter

pubs.acs.org/macroletters

Chemically Driven, Water-Soluble Composites of Carbon Nanotubes and Silver Nanoparticles as Stretchable Conductors

Hangil Ki,[†,⊥] Jaewon Jang,[†,⊥] Yejin Jo,[‡] Dong-Yong Kim,[†] Sang-Soo Chee,[†] Byeong-Yun Oh,[†] Changsik Song,[§] Sun Sook Lee,[‡] Sungho Choi,[‡] Youngmin Choi,[‡] Sunho Jeong,[*,‡] and Moon-Ho Ham[*,†]

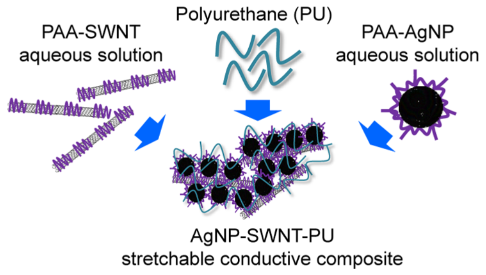
[†]Center for Emerging Electronic Devices and Systems, School of Materials Science and Engineering, Gwangju Institute of Science & Technology, 123 Cheomdangwagi-ro, Buk-gu, Gwangju 500-712, Republic of Korea

[‡]Division of Advanced Materials, Korea Research Institute of Chemical Technology, 19 Sinseongno, Yuseong-gu, Daejeon 305-600, Republic of Korea

[§]Department of Chemistry, Sungkyunkwan University, Suwon, Gyeonggi 440-746, Republic of Korea

Supporting Information

ABSTRACT: In the past decade, hybrid materials for highly stretchable, conductive electrodes have received tremendous attention in the fields of emerging wearable electronic, optoelectronic, and sensing devices. Here, we present a previously unrecognized aqueous route to producing stretchable conductors composed of silver nanoparticles (AgNPs) and single-walled carbon nanotubes (SWNTs) embedded in a polyurethane (PU) matrix, in contrast to ones dispersed in toxic organic solvents reported to date. The intact chemical interaction between one-dimensional SWNTs, for endowing the capability of establishing conductive pathways even in stretching conditions, and AgNPs, for enabling high conductivity of the composites, is achieved in an aqueous medium with an anionic polyelectrolyte, poly(acrylic acid), that undergoes pH-dependent conformational evolution. With this aqueous approach, we demonstrate that AgNP−SWNT−PU composites supported on PDMS substrates have the conductivities of 620 and 120 S cm^{-1} in unstrained and 90% elongated conditions, respectively, and display repeatable reversibility at a strain of 60%.



Electrically conductive materials that can both stretch and deform while being formed into complex curvilinear shapes, have received a great deal of attention for future applications including flexible displays, wearable computers, smart clothing, medical implants, and dielectric elastomer actuators.[1−5] Considerable effort has been focused on the simultaneous incorporation of excellent mechanical robustness and stable electrical conductivity into one material, for which two major strategies have been suggested.[2] One method involves using new structural layouts such as waves or nets with conventional materials, and the other involves the use of new materials in conventional layouts. However, structuring metal strips with wavy geometries involves time-consuming, sequential lithography and etching processes that are not easily scalable.[6−8] Most applications of stretchable conductors require the ability to make arbitrary patterns over large areas, which can be accomplished with direct printing techniques using printable composite inks.[5] To date, a variety of conductive materials (e.g., metals, carbon nanomaterials (carbon nanotubes (CNTs) and graphene), and conducting polymers) have mostly been placed in a rubbery matrix to make solution-processable, elastic, conductive composites.[3,9−13]

Since rubber-like conductive composites were reported from a mixture solution of single-walled carbon nanotubes (SWNTs), an ionic liquid, and a fluorinated copolymer in 2008,[3] CNTs have received much interest as conductive fillers. This is because of their large aspect ratios and because of conducting pathways that can bridge cracked regions while being subjected to large strains.[3,9,14] However, these systems (including SWNTs) have relatively low conductivities (~60 S cm^{-1} when unstrained[3,15]). This deficiency needs to be improved if SWNTs are to compete with metals (~10^3 S cm^{-1} for silver nanoparticles (AgNPs)[12] or flakes[9]) regarding conductivity. To increase electrical conductivity while retaining stretchability, the composites could be hybridized with metal particles or flakes, in which case good electrical contacts between SWNTs and metals would be indispensable. More recently, Baik et al. fabricated polymer composites comprising silver flakes and multiwalled carbon nanotubes (MWNTs) decorated with AgNPs, which exhibited conductivities of 3100 and 706 S cm^{-1} at 0% and 30% strains, respectively, but ruptured at 35% strain.[9] This method required additional processes of curing and hot rolling at elevated temperatures to obtain maximum conductivities of 5710 and 20 S cm^{-1} at 0% and 140% strains, respectively. Additionally, most studies reported to date have used organic solvents and/or ionic liquids to uniformly disperse CNTs in the polymer matrix.[3,9,16]

Received: June 4, 2015
Accepted: July 2, 2015
Published: July 6, 2015

DOI: 10.1021/acsmacrolett.5b00374
ACS Macro Lett. 2015, 4, 769−773

In this study, we developed an environmentally friendly, low-cost, facile route to producing highly stretchable and conductive, water-soluble composites comprising AgNPs and SWNTs in a polyurethane (PU) matrix without any additional treatment. Both AgNPs and SWNTs are uniformly dispersed with poly(acrylic acid) (PAA) in an aqueous medium instead of in organic solvents, the mixture solution of which is subsequently incorporated into a PU aqueous solution. The AgNP−SWNT−PU hybrid composites exhibit electrical conductivities of 620 and 280 S cm^{-1} at 0% and 30% strains, respectively, and can be stretched by 90% while retaining an electrical conductivity of 120 S cm^{-1}. This demonstration of stretchable conductive composites made from water-based mixture solutions is a significantly meaningful scientific finding in the quest to realize low-cost, large-area, stretchable, and bioimplantable electronics that cannot be achieved using traditional electronic technologies.

Figure 1a shows the schematic diagram for a chemical hybridization approach to making AgNP−SWNT−PU composites. To fabricate an aqueous solution of the AgNP−SWNT−PU composites via a scalable chemical method, each component solution was prepared and mixed using simple physical agitation. The surfaces of the AgNPs used in this work were tailored with a water-soluble polyelectrolyte, PAA, to allow for compatibility with an aqueous solution. The PAA is an anionic polyelectrolyte, in which the carboxyl acid, present in each monomer unit, is deprotonated in a basic aqueous environment,[17] resulting in the formation of negatively charged repeated moieties. This electrostatically functionalized polymeric structure endows the capability of electrosteric repulsion, a combination of an electrostatic repulsion and a steric repulsion, for the AgNPs in an aqueous medium. The surface zeta potential of the PAA-capped AgNPs was −45 mV at a pH of 7.3, allowing for the good dispersion stability. There was no morphological variation after a sonication process (Figure S1, Supporting Information); the spherical morphology was preserved, and agglomeration was not observed even after an intensive sonication process.

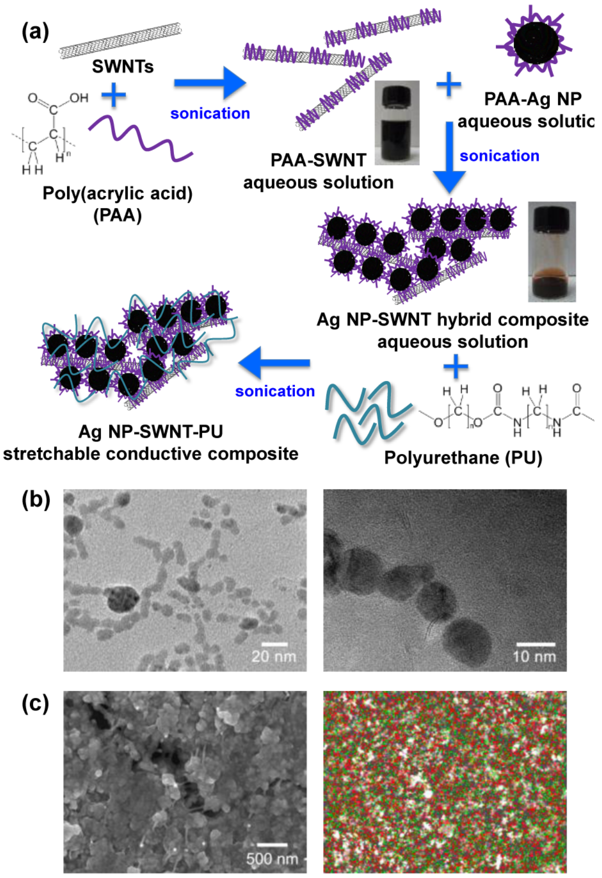


Figure 1. (a) Schematic diagram showing the procedural sequence for preparing AgNP−SWNT−PU hybrid materials. (b) HRTEM images of AgNP−SWNT hybrid materials. (c) SEM and EDS mapping images for AgNP−SWNT−PU hybrid materials. In the condition of 90% elongation, the sample for SEM observation was highly stretched out to demonstrate that the SWNTs bridge the AgNP assemblies to form conducting pathways. In the EDS mapping image, the green and red dots represent the presence of carbon (from SWNTs and PU) and silver elements, respectively.

The PAA also acts as a dispersion agent for SWNTs. In an aqueous solution containing both PAA and SWNTs, the polymeric chains of the PAA undergo conformational change depending on pH. It is known that the PAA chains are strongly bound to the nanotube surface due to hydrophobic interaction, enabling for CNT dispersion over a wide range of pH (2−9 for SWNTs[18] and 4−7 for MWNTs[19]). In this pH range, the PAA chains are partially deprotonated and exhibit a coiled conformation by intramolecular hydrogen bonding. The coiled PAA chains are absorbed to the nanotube surface due to hydrophobic interaction and lead to electrosteric repulsion required to overcome the van der Waals interaction between the nanotubes.[18,19] At pH > 9, the completely deprotonated PAA chains are not capable of being adsorbed to CNTs.[19] The loading of SWNTs was 1 mg/mL, and the pH of the PAA−SWNT suspension was ∼2.5, producing good dispersion of SWNTs in water. Whereas most of the SWNTs settled after a centrifugation process in a PAA-free SWNT aqueous suspension, the PAA−SWNT suspension remained stable over several months (Figure S2, Supporting Information).

After addition of the AgNP suspension to the SWNT suspension was completed, the pH remained acidic, at a sufficiently low value of ∼3.3; the conformation of the PAA chains adsorbed to the surface of the AgNPs was changed to a coiled structure, being adsorbed to the suspending SWNTs. The pH-dependent change in a conformation of carboxyl acids present along PAA can be verified with the observation of rheological properties of PAA-capped AgNP inks. As reported in our previous study,[20] the carboxyl groups are entangled by intermolecular hydrogen bonding under an acidic environment, resulting in the severe shear thinning behavior. High-resolution transmission electron microscopy (HRTEM) images revealed that the AgNPs were completely loaded along the SWNTs (Figure 1b). Meanwhile, the AgNPs underwent instantaneous sedimentation at pH < 4, due to loss of the driving force for electrosteric repulsion (Figure S3, Supporting Information);[21] this would not occur if the chemically driven physical interaction with PAA−SWNTs was involved. In this experiment, no noticeable precipitates were observed for over one month (Figure S4, Supporting Information). For the aqueous solution of AgNP−SWNTs, the plasmonic resonance of AgNPs indicates the excellent suspension behavior of wet-chemically prepared composite materials (Figure S5, Supporting Information). The interaction between PAAs anchored to the SWNTs and the AgNPs gives rise to facile hybridization of the different types of conductive materials.

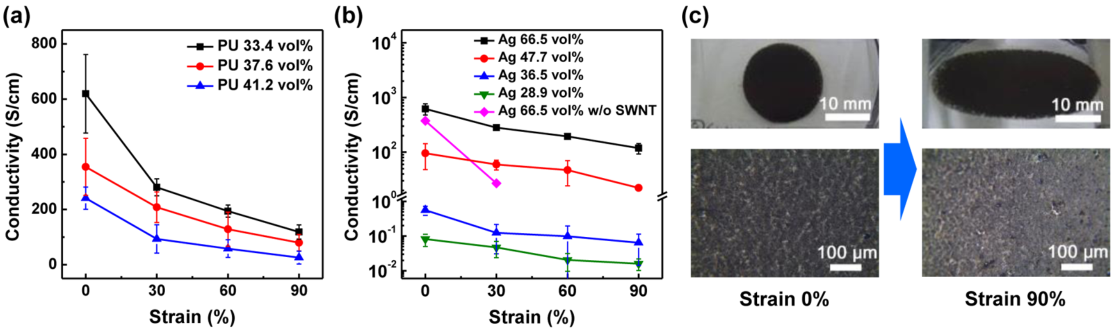


Figure 2. Variation of conductivity as a function of the applied strains for AgNP−SWNT−PU composites as a function of concentration of (a) PU (33.4, 37.6, and 41.2 vol %; the volumetric ratio of Ag to SWNT was kept at 540) and (b) AgNPs (28.9, 36.5, 47.7, and 66.5 vol %; the volumetric ratio of PU to SWNT was kept at 270). (c) Photographs and optical images demonstrating the mechanical stability under highly strained conditions (up to 90% for a composite with 66.5 vol % Ag).

When the AgNP−SWNTs were incorporated into a PU matrix that is a soft and elastomeric polymer, the conductivity of the composite film was ∼620 S cm^{-1}, and the film structure was maintained well at a strain of 30% without any mechanical rupture or crack generation. This could be interpreted as resulting from the homogeneous spatial distribution of each component. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS)-based elemental mapping images show that the AgNPs were interconnected uniformly with one-dimensional SWNTs, reflecting the effective entanglement between SWNTs with large aspect ratios and spherical AgNPs (Figure 1c). In contrast, a AgNP−PU film suffered from significant crack propagation along the overall film surface under an elongation strain of 30%, even with a high conductivity of 375 S cm^{-1} in an unstrained state (Figure S6, Supporting Information). A SWNT−PU film accommodated the applied stress but had low conductivities (5 and 1 S cm^{-1} at 0% and 90% strains, respectively) because of the absence of highly conductive AgNPs. These results reveal that the hybridization of AgNPs and SWNTs resolves the drawbacks of each conductive component.

To investigate the role of each component material on both electrical conductivity and elastomeric stretchability, the conductivities of the AgNP−SWNT−PU composites were measured according to the relative compositions of each component, at an elongation strain of up to 90%. The compositional details for preparing all the composites are summarized in Table S1 (Supporting Information). As shown in Figure 2a, as the elastomeric polymer, PU, which is inactive in providing electrically conductive pathways in a composite, decreased from 41.2 to 33.4 vol % (the volumetric ratio of Ag to SWNT was kept at 540), the conductivity gradually increased from 240 to 620 S cm^{-1} in an unstrained state. Note that the conductivity still evolved well with an R_c (ratio of conductivities at 0% to 90% strains) of 5.2 for the composite with a PU content of 33.4 vol %. Here, R_c represents the degree of conductivity reduction in a highly strained condition. This confirms that the presence of an elastomeric structure in well-designed composites endows the capability of maintaining the electrical properties when mechanically stretched, although slightly restricting the percolation-based electrical conduction. In the composites with PU content of less than 33.4 vol %, the reproducibility in evolving conductivities was not obtained in repeated stretching tests due to an insufficient amount of elastomeric matrix. The AgNP content also plays a significant role in determining the conductivity of the composites containing them (Figure 2b). When the AgNP content increased from 28.9 to 66.5 vol % (the volumetric ratio of PU to SWNT was kept at 270), the conductivity increased over all the strain ranges up to 90%, with an abrupt increment between 36.5 and 47.7 vol %. This was caused by enhanced electrical percolation due to additional incorporation of highly conductive metallic components, a condition that is commonly observed in metal-NP-based stretchable conductors.[9,12] When AgNP volumetric content reaches >66.5 vol %, the incorporation of insufficient elastomeric polymer leads to unstable stretching behavior of composite films. Thus, it is speculated that the conductivity obtained from the composite film with 66.5 wt % AgNP content was the best achievable value among those for PAA-decorated AgNP−SWNT−PU composite systems. Note that the conductivity of AgNP−PU film prepared without CNTs was 375 S cm^{-1} and had poor stretchability. The significant degradation in conductivity evolved after stretching at a strain of 30%, and the films became electrically inactive when strain exceeded 60%. This suggests the importance of optimizing the composition of composites to achieve both high electrical conductivity and excellent mechanical stretchability, by allowing spherical metallic NPs, one-dimensional CNTs, and elastomeric polymers to fulfill their characteristic roles in stretchable conductors. Figure 2c shows photographs showing no mechanical failure under applied strains from 0% to 90% for a composite film with Ag content of 66.5 vol %. When it comes to cost effectiveness of Ag nanomaterials, the economic issue could be addressed by replacing AgNPs with CuNPs.[22,23] However, in synthesizing the CuNPs in aqueous medium, the suppression of surface oxidation is extremely demanding and essential for obtaining a highly conductive system. Research is now underway to develop CuNPs suitable for the PAA-based stretchable conductors suggested in this study.

We compared the electrical conductivities of AgNP−SWNT−PU composite films with other previously reported systems (Figure 3). The conductivity of our samples was an order of magnitude higher than those of previous CNT-based composites.[3,15,16,24,25] Ag-flake−CNT-based composites in a previous study exhibited maximum conductivities of 5710 and 20 S cm^{-1} at 0% and 140% strains, respectively, after post-treatments of curing and hot rolling at elevated temperatures.[9] However, as-prepared composites showed a conductivity of 3100 S cm^{-1} at 0% strain in the initial state. The application of 30% strain resulted in a decrease of conductivity to 706 S cm^{-1}, and the composites ruptured at a 35% strain before additional

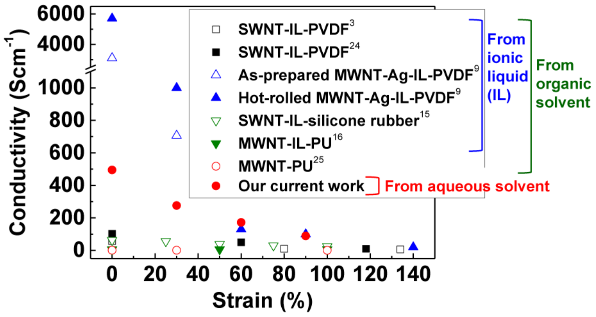


Figure 3. Variations of conductivities as a function of applied strains for our composite (Ag composition of 66.5 vol %) and solution-processable stretchable conductors reported to date.

processes. However, our films had a conductivity of 120 S cm^{-1} at 90% strain while maintaining the continuous film structure, without any further treatment (Figures 2c and 3). This value was approximately four times higher than those of CNT-based composites at 100% strain[15] and was similar to that of hot-rolled Ag-flake–CNT-based composites at 90% strain.[9] It is important to note that in contrast to most previous studies, which used ionic liquids and/or organic solvents to disperse CNTs,[3,9,15,16,24,25] a water-soluble polymer, PAA, was employed in this work. It facilitated preparation of highly stretchable and conductive composite films from aqueous mixture solutions of AgNPs and SWNTs. To further evaluate the reversibility of the AgNP–SWNT–PU composite film, we made electrical measurements during 1000 stretching cycles, at between 0% and 60% strain, and at a frequency of 0.8 Hz. Figure 4 shows the variation ratio in resistance (R_{strain}/R_0) at 0% and 60% strains as a function of the number of stretching cycles. In the first stretching cycle, the electrical resistance increased at 60% strain, then recovered its initial value when the strain was released. The R_{strain}/R_0 of the AgNP–SWNT–PU composite film remained almost constant over 1000 stretching cycles, showing an R_{strain}/R_0 of 1.7–2.1. From these results, it is believed that the composite films are highly stable and reversible without any significant degradation, when they are repeatedly stretched and released at a high strain level. This meets the requirements for practical, stretchable, electronic applications.

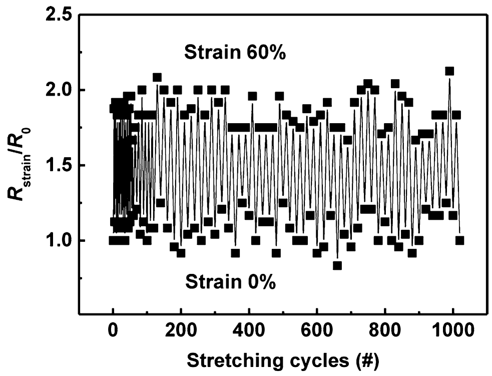


Figure 4. Relative ratio of resistances at 0% and 60% strain during 1000 cycles, for a composite with a Ag content of 66.5 vol %.

In summary, we developed highly stretchable and conductive water-soluble composites through chemical hybridization of AgNPs and SWNTs, with the aid of an anionic polyelectrolyte, PAA. We demonstrated that the PAA plays significant roles in the dispersion of AgNPs and SWNTs in an aqueous medium, as well as in the intact interaction of the two conductive components. Thus, it facilitates a nontoxic, aqueous route to producing stretchable conductors. By incorporating the elastomeric polymer, PU, the resulting AgNP–SWNT–PU composite films exhibited an electrical conductivity approaching 620 S cm^{-1} in an unstrained condition and maintained a relatively high conductivity (120 S cm^{-1}) even at a strain of 90%, without any structural degradation. In addition, our study confirmed that our stretchable composites are reversibly active, even after repeated stretching tests under a strain of 60%, and only show a variation in resistance ratio of 1.7–2.1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods, experimental conditions for preparing AgNP–SWNT–PU composites, SEM images of AgNPs, dispersion stability of SWNTs and AgNP–SWNT aqueous solutions, UV–vis–nIR spectra, and mechanical stability of AgNP–PU composite film. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00374.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: sjeong@krict.re.kr (S.J.).
*E-mail: mhham@gist.ac.kr (M.H.H.).

Author Contributions

$^{\perp}$These authors contributed equally (H.K. and J.J.). The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2013R1A1A1011215), Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2013M3A6B1078873), and the Korea Research Institute of Chemical Technology (KRICT).

■ REFERENCES

(1) Pelrine, R.; Kornbluh, R.; Pei, Q.; Joseph, J. *Science* **2000**, *287*, 836–839.

(2) Rogers, J. A.; Someya, T.; Huang, Y. *Science* **2010**, *327*, 1603–1607.

(3) Sekitani, T.; Noguchi, Y.; Hata, K.; Fukushima, T.; Aida, T.; Someya, T. *Science* **2008**, *321*, 1468–1472.

(4) Park, S. I.; Xiong, Y.; Kim, R. H.; Elvikis, P.; Meitl, M.; Kim, D. H.; Wu, J.; Yoon, J.; Yu, C. J.; Liu, Z.; Huang, Y.; Hwang, K. C.; Ferreira, P.; Li, X.; Choquette, K.; Rogers, J. A. *Science* **2009**, *325*, 977–981.

(5) Yang, C.; Wong, C. P.; Yuen, M. M. F. *J. Mater. Chem. C* **2013**, *1*, 4052–4069.

(6) Wang, X.; Hu, H.; Shen, Y.; Zhou, X.; Zheng, Z. *Adv. Mater.* **2011**, *23*, 3090–3094.

(7) Kim, D. H.; Choi, W. M.; Ahn, J. H.; Kim, H. S.; Song, J.; Huang, Y.; Liu, Z.; Lu, C.; Koh, C. G.; Rogers, J. A. *Appl. Phys. Lett.* **2008**, *93*, 044102.
(8) Gray, D. S.; Tien, J.; Chen, C. S. *Adv. Mater.* **2004**, *16*, 393−397.
(9) Chun, K. Y.; Oh, Y.; Rho, J.; Ahn, J. H.; Kim, Y. J.; Choi, H. R.; Baik, S. *Nat. Nanotechnol.* **2010**, *5*, 853−857.
(10) Hu, L.; Pasta, M.; Mantia, F. L.; Cui, L.; Jeong, S.; Deshazer, H. D.; Choi, J. W.; Han, S. M.; Cui, Y. *Nano Lett.* **2010**, *10*, 708−714.
(11) Prabhakar, P. K.; Raj, S.; Anuradha, P. R.; Sawant, S. N.; Doble, M. *Colloids Surf., B* **2011**, *86*, 146−153.
(12) Park, M.; Im, J.; Shin, M.; Min, Y.; Park, J.; Cho, H.; Park, S.; Shim, M. B.; Jeon, S.; Chung, D. Y.; Bae, J.; Park, J.; Jeong, U.; Kim, K. *Nat. Nanotechnol.* **2012**, *7*, 803−809.
(13) Chen, M.; Tao, T.; Zhang, L.; Gao, W.; Li, C. *Chem. Commun.* **2013**, *49*, 1612−1614.
(14) Avouris, P. *Chem. Phys.* **2002**, *281*, 429−445.
(15) Kim, T. A.; Kim, H. S.; Lee, S. S.; Park, M. *Carbon* **2012**, *50*, 444−449.
(16) Shang, S.; Zeng, W.; Tao, X. *J. Mater. Chem.* **2011**, *21*, 7274−7280.
(17) Kamyshny, A.; Ben-Moshe, M.; Aviezer, S.; Magdassi, S. *Macromol. Rapid Commun.* **2005**, *26*, 281−288.
(18) Grunlan, J. C.; Liu, L.; Regev, O. J. *J. Colloid Interface Sci.* **2008**, *317*, 346−349.
(19) Saint-Aubin, K.; Poulin, P.; Saadaoui, H.; Maugey, M.; Zakri, C. *Langmuir* **2009**, *25*, 13206−13211.
(20) Jeong, S.; Song, H. C.; Lee, W. W.; Choi, Y.; Ryu, B. H. *J. Appl. Phys.* **2010**, *108*, 102805.
(21) Jeong, S.; Song, H. C.; Lee, W. W.; Choi, Y.; Lee, S. S.; Ryu, B. H. *J. Phys. Chem. C* **2010**, *114*, 22277−22283.
(22) Jeong, S.; Song, H. C.; Lee, W. W.; Suk, H. J.; Lee, S. S.; Ahn, T.; Ka, J. W.; Choi, Y.; Yi, M. H.; Ryu, B. H. *J. Mater. Chem.* **2011**, *21*, 10619−10622.
(23) Jeong, S.; Lee, S. H.; Jo, Y.; Lee, S. S.; Seo, Y. H.; Ahn; Byeong, W.; Kim, G.; Jang, G. E.; Park, J. U.; Ryu, B. H.; Choi, Y. *J. Mater. Chem. C* **2013**, *1*, 2704−2710.
(24) Sekitani, T.; Nakajima, H.; Maeda, H.; Fukushima, T.; Aida, T.; Hata, K.; Someya, T. *Nat. Mater.* **2009**, *8*, 494−499.
(25) Shin, M. K.; Oh, J.; Lima, M.; Kozlov, M. E.; Kim, S. J.; Baughman, R. H. *Adv. Mater.* **2010**, *22*, 2663−266.

DOI: 10.1021/acsmacrolett.5b00374
ACS Macro Lett. 2015, 4, 769−773