ACS APPLIED MATERIALS & INTERFACES

Letter

www.acsami.org

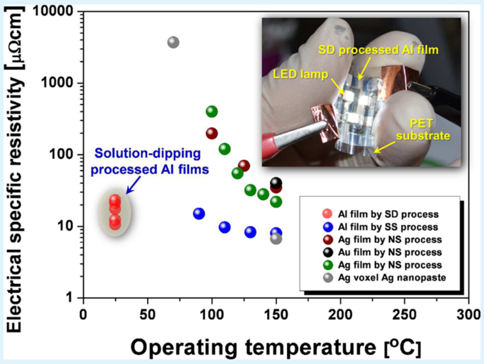
Direct Deposition of Highly Conductive Aluminum Thin Film on Substrate by Solution-Dipping Process

Hye Moon Lee,[*,†] Si-Young Choi,[‡] and Areum Jung[†]

][†]Powder & Ceramics Division and [‡]Advanced Metallic Materials Division, Korea Institute of Materials Science (KIMS), Changwondaero 797, Changwon Korea

Ⓢ *Supporting Information*

ABSTRACT: A solution-dipping process consisting of 2 steps, including (i) a catalytic treatment of the substrate and (ii) an immersion of the catalytically treated substrate into an aluminum precursor solution of $AlH_3\{O(C_4H_9)_2\}$, is suggested for the low-cost and simple preparation of aluminum thin film. This process can be applied to electric devices in the way of not only various film geometry including large area ($\square$ 100 mm (W) × 100 mm (L)) or patterned structure but also the diverse substrate selectivity including rigid or flexible substrate. More interestingly, preparations of aluminum film in this study can be unprecedentedly accomplished at room temperature with the help of chemical catalyst to decompose $AlH_3\{O(C_4H_9)_2\}$ into Al, $1.5H_2$, and $O(C_4H_9)_2$. Beyond the previously reported processes, the prepared Al films via solution-dipping process are comparable or even superior to Ag, Au, and Al films prepared by other solution processes and furthermore are found to be excellent in mechanical durability against external deformation.



KEYWORDS: *aluminum, thin film, solution process, patterned electrode, flexible electronics*

1. INTRODUCTION

Aluminum (Al) is the most excellent metal for the value of high electrical conductivity at low cost and very low in work function, indicating that Al is likely the best material for highly electrical conductive features as well as for ohmic contact electrodes.[1−3] The deposition of a highly conductive Al film on a specific substrate is generally performed by a vacuum deposition process due to the extremely active reaction of Al with oxygen and moisture. Its application is mostly limited to electrodes for ohmic contact, such as cathodes of OLEDs and organic solar cells as well as metal electrode of thin film transistors (TFTs). Although this vacuum deposition process has been regarded to be a useful tool for the deposition of metallic thin film, it incurs a large cost because of the expensive equipment, including vacuum chambers and devices, the consumption of a large amount of energy for the vacuum chamber at a low pressure, and the great loss of source materials (more than 70% of the source materials are typically deposited in undesirable areas). Moreover, even when a vacuum chamber is modified for the preparation of large-area metallic film, it results in an enormous increase in the cost of the vacuum process.

In this sense, a solution process has become attractive as an alternative tool for the cost-effective preparation of electronic devices with large-area thin films on both rigid and flexible substrates.[2−12] Thus, intense interest and many research attempts have been focused on the development of a solution-based process involving the highly conductive and inexpensive material Al. However, attempts to complete the solution-based deposition of Al have failed because of the sensitive activity of Al with oxygen and moisture, until an electroless aluminum plating method and a catalyst-assisted solution processes were recently introduced.[2,3,13−15]

The solution-stamping process[2,3] was demonstrated for highly conductive Al thin films on both rigid and flexible substrates. However, a few limitations still remained; (i) uniform and large-area thin film is difficult to obtain because of unavoidable temperature deviation in stamping method and (ii) large amounts of H_2 generated during decomposition of Al precursor deteriorates the film homogeneity.

Shen et al.[13] suggested a solution process for the selected deposition of high-quality aluminum film, which is optimized for the preparation of a locally patterned Al film. Furthermore, its process is complicated and expensive because it consists of the three steps using Pt as a catalyst.

Electroless plating method, where the reduction agent, i.e., LiH or $LiAlH_4$, and the catalyst such as Pd were required, was also utilized for preparation of Al films on rigid substrates;[14,15] however, this process is complicated and expensive since quire a long time is consumed for preparation of water-free Al ionic solution at inert and dry atmosphere. Furthermore, the electroless plated Al film consists of large sized Al grains, so that the prepared Al film exhibit the significant surface roughness. Therefore, the aforementioned processes are not

Received: March 5, 2013
Accepted: May 28, 2013
Published: May 28, 2013

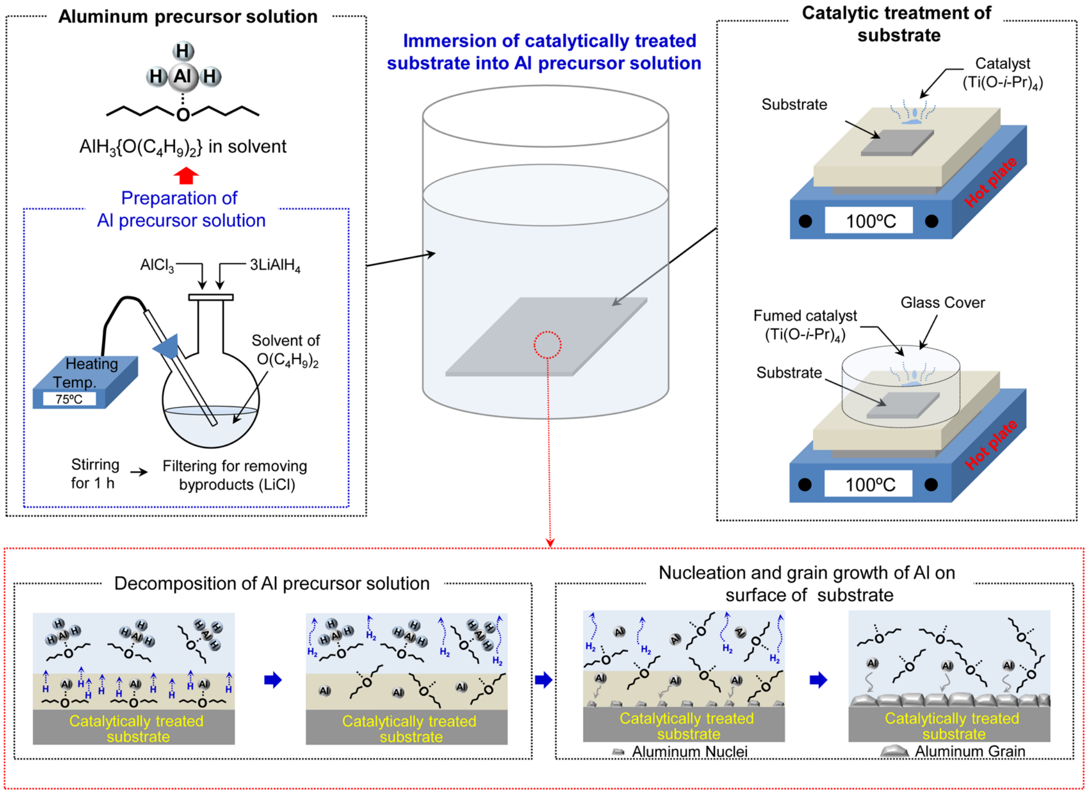


Figure 1. Scheme of the solution-dipping process for preparation of large area and patterned Al thin film with a highly electrical conductivity on substrates.

proper for the cost-effective fabrication of large area, homogeneous Al thin films with high density and excellent surface smoothness on both rigid and flexible substrates.

In this study, therefore, we propose an astonishingly simple and novel solution-dipping (SD) process for the low-cost preparation of large and patterned Al films without any deteriorating electrical and mechanical properties. This approach was demonstrated to be very effective for the preparation of large-area and specifically patterned Al films on both rigid and flexible substrates at room temperature.

2. EXPERIMENTAL SECTION

Figure 1 shows a schematic diagram of the SD process for fabricating a large-area or patterned Al film on a substrate. A chemical preparation of Al is achieved by the decomposition of $AlH_3\{O(C_4H_9)_2\}$ into $Al\{O(C_4H_9)_2\}$ and $1.5H_2$ and the subsequent decomposition of $Al\{O(C_4H_9)_2\}$ into Al and $O(C_4H_9)_2$.[2,3,16−19] This decomposition reaction commonly occurs at ~165 °C; therefore, the chemical preparation of Al cannot be performed at room temperature without using a catalyst to accelerate the decomposition rate. Thus, the catalytic treatment of the substrate is a crucial step for fabrication of an Al film on a substrate at room temperature. To develop the new solution-based method, therefore, we undertook a simple catalytic treatment that involve exposing the substrate to a catalytic atmosphere of Ti(O-*i*-Pr)$_4$ and subsequently immersing the catalytically treated substrate into the Al precursor solution of $AlH_3\{O(C_4H_9)_2\}$. Herein, the Al precursor solution of $AlH_3\{O(C_4H_9)_2\}$ was prepared by an ethereal reaction of $AlCl_3$ with $LiAlH_4$. A further explanation of the SD process is described in the Supporting Information, section S1.

3. RESULTS AND DISCUSSION

Figure 2 shows Al films formed on soda lime glass (SLG) by the SD process. As expected, we successfully demonstrated that a highly conductive Al film was formed on the surface of the substrate with the assistance of a catalytic treatment.

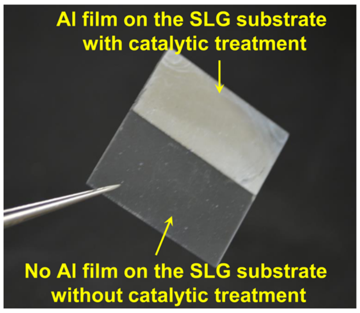


Figure 2. Al films formed SLG substrates by the solution-dipping process performed at room temperature.

Herein, to obtain Al film with uniform thickness, we attempted to optimize the optimum dipping time of catalytic treated substrate into Al precursor solution by experimentally assessing the effect of the dipping time on the thickness and electrical resistance of the SD-processed Al film thickness. The results are summarized in Figure 3. The SEM micrographs (Figure 3a) of the Al films with dipping times of 10−480 min show the mechanism of Al film growth on substrate via the SD process. Al film starts to form in ~2 min (not shown here) and covers the entire surface of the substrate within ~10 min. The thickness of Al film at dipping time of 10 min (Figure 3a-i) is ~15 nm with a small STD (standard deviation); and Al islands in an irregular shape start to appear from dipping time of 40 min (Figure 3a-iii), they continue to grow up with a dipping time. Further the micrograph of dipping time of 480 min (Figure 3a-vi) shows the Al surface is fully covered with

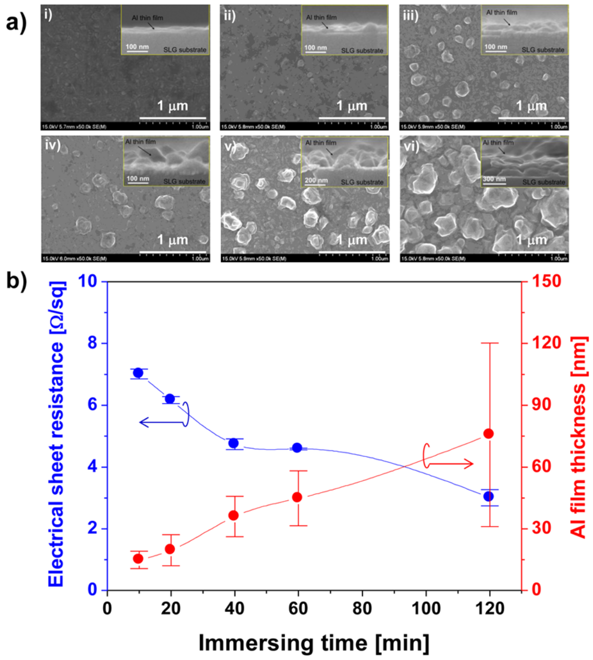


Figure 3. (a) Surface and cross-section SEM images and (b) thickness and electrical sheet resistance of the solution-dipping processed Al films on SLG substrates with dipping time of the catalytically treated substrate into Al precursor solution. Microstructures of SD processed Al films with dipping time of (i) 10, (ii) 20, (iii) 40, (iv) 60, (v) 120, and (vi) 480 min.

submicrometer-sized Al grains. As the dipping time increases, the increases of STDs are shown both in thickness and electrical resistance (Figure 3b), indicative of the Al film inhomogeneity by increasing a dipping time. Aside from the issue of the film inhomogeneity, the strong crystallinity in Al film is found to worsen the mechanical durability especially for the film on flexible substrate. Therefore, it is reasonable to immerse the catalytic-treated substrate into Al precursor solution for less than ~40 min to obtain a highly conductive Al film with a uniform thickness.

We fabricated a large-area Al film as wide as 100 mm (*W*) × 100 mm (*L*) to check the applicability of this method to such a large-area Al film; a large-area SLG substrate that had undergone the catalytic treatment was immersed into the Al precursor solution for 20 min (the optimized dipping time of the catalytically treated substrate into Al precursor solution). The Al film shown in Figure 4a was found to be ~20 nm thick when formed on a SLG substrate by the SD process at room temperature. Moreover, the fabricated Al film was found to be uniform without any bubble-type defects. Figure 4b demonstrates that such a patterned Al film on a substrate can be achieved by the SD process when the surface of the substrate is selectively exposed to a catalytic atmosphere. For this patterned Al film, we masked the SLG with a PET film with a specific pattern and then exposed the masked SLG to the fumed catalyst. We then dipped the SLG into the Al precursor ink for 20 min. Al film forms only in the unmasked area, which is exposed to the catalytic fume. Therefore, in this case, the letters "KIMS" and simple electric circuits consisting of Al films were formed on the SLG substrate by the decomposition of the Al precursor ink with the help of the catalytic treatment.

Sound electrical properties of Al film are necessary for the applicability of a film to electrodes of electronic devices. Thus, we measured the electrical specific resistivity of the fabricated Al films and compared them with those of Ag, Au, and Al films prepared by different solution methods, as shown in Figure 4c. As no metal electrodes were manufactured by a solution process performed at room temperature, the SD-processed Al films were compared with Ag,[4,20,21] Au,[22] and Al[2] films prepared by solution processes with at firing temperature ranging from 70 to 150 °C. Although Ag is known to be a metal with the lowest electrical specific resistivity of 1.59 $\mu\Omega$ cm, all of the Ag films fabricated by the printing and subsequently firing of the Ag nanoink had electrical specific resistivity values that exceeded 20 $\mu\Omega$ cm. In the case of the Au films prepared at firing temperatures that were lower than 150 °C, they were found to be electrically nonconductive, even beyond the description in Figure 4c. On the other hand, all of the Al films fabricated by the SD process at room temperature, showing superior electrical conductivity compared to Ag and Au films, were nearly identical to the solution-stamping processed Al films; however, as mentioned above, the SD process has more powerful advantages than the solution-stamping process in

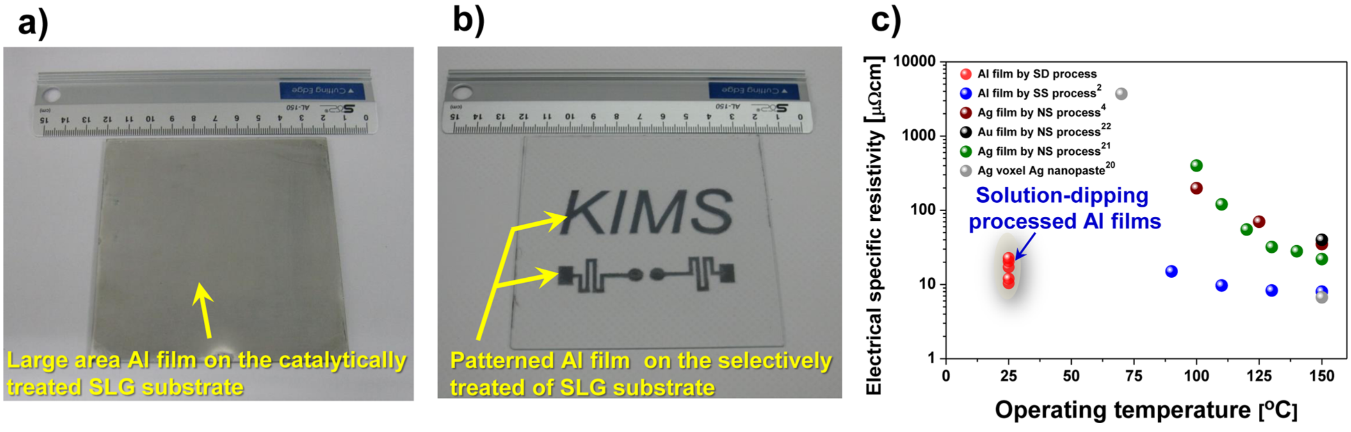


Figure 4. Large area and patterned Al films prepared on SLG substrate by SD process and their electrical specific resistivity. (a) Large area (100 mm (*W*) × 100 mm (*L*)) and (b) patterned Al films ("KIMS" and simple electric circuits shown as blackish color) prepared on SLG substrate by the solution-dipping process; and (c) comparison of electrical specific resistivity of Al films prepared by the solution-dipping process with those of Al, Au, and Ag films prepared by different solution processes performed at a temperature range of 70−150 °C (SS process, solution stamping process; NS process, normal solution process).

terms of its ability to fabricate large-area films. Although a temperature range of 100−150 °C is too low to remove the organic surfactant surrounding the Ag and Au colloidal nanoparticles and to enhance the contact area among them by melting the surface of the nanoparticles, the Al film created by the SD process is formed by the direct decomposition of the Al precursor and the growth of nanocrystalline Al on SLG. Therefore, this proposed simple SD process can be applied not only to large-area films but also to patterned Al thin films to offer excellent electrical conductivity.

Along with the good electrical properties, the various levels of mechanical durability should be guaranteed to apply the SD-processed Al thin films to electronic devices. Thus, a 3 M Scotch tape test[2,3] and a cyclic bending test[3,23] were performed to investigate film adhesion to the substrate and durability against damage such as scratching and bending deformation, and the methods of Scotch tape and cyclic bending test are well-described in the Supporting Information, section S2. Al films on SLG and PET substrates were used for the Scotch tape and the cyclic bending tests, respectively. During the Scotch tape test, the Al films did not peel off from any of the substrates, and the SD-processed Al film did not show the significant difference in electrical sheet resistances before (4.695 ± 0.171 Ω/□) and after (4.710 ± 0.190 Ω/□) the tape test, indicating that the SD-processed Al film exhibits strong adhesion to the substrate and durability against scratching and peeling. Figure 5 shows the normalized electrical resistance evolution of the Al film on a PET substrate during a cyclic bending test of 10 000 bending trials. The electrical resistance of the Al film formed on the PET substrate was found to increase by a factor of ~1.23 (from 2.6 to 3.2 Ω/□) after 10 000 cycles of bending deformation; however, the increased resistance of 3.2 Ω/□ after the durability test in the harsh environment is still feasible for application when compared to other pristine conductive films (Figure 4c). These findings indicate that the SD-processed Al films on the substrate possess excellent electrical and mechanical properties that are readily applicable to high-performance rigid and flexible electronics.

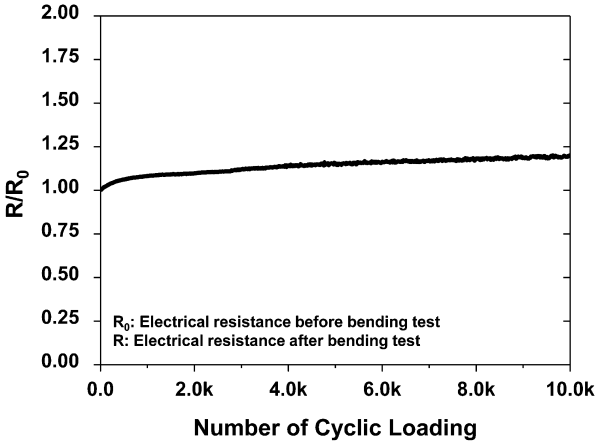


Figure 5. Normalized electrical resistance evolution of the SD-processed Al film on PET substrate during the 10000 times cyclic bending test.

Figure 6 depicts the performance of the SD-processed Al thin films in simple electronic devices to demonstrate the applicability of the current approach for actual high-performance electronic devices. Figure 6a and b show LED lamps mounted onto patterned Al films formed on rigid SLG and flexible PET substrates, respectively. The LED lamps in both cases flashed under DC bias, even working on bent Al films on a flexible PET substrate. Therefore, the SD-processed Al films are sufficiently feasible for rigid and flexible electronic devices.

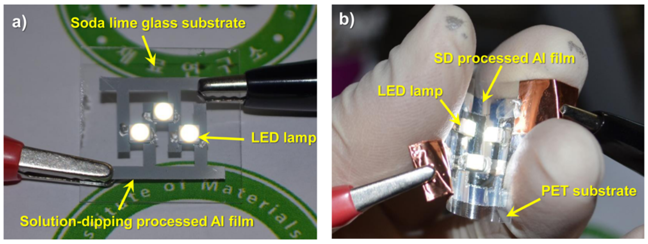


Figure 6. Digital pictures of the LED lamps on the solution-dipping processed Al line patterns on SLG and PET substrates. Flashed on LED lamps connected to (a) the flat line patterned Al films formed on SLG and (b) bent line patterned Al films on PET substrates.

4. CONCLUSION

We proposed a simple and novel solution-dipping process with only two steps, (i) catalytic treatment of the substrate and (ii) immersion of the catalytically treated substrate into an Al precursor solution of $AlH_3\{O(C_4H_9)_2\}$. This process allows the direct deposition of highly conductive Al thin films on rigid and flexible substrates at room temperature. The SD process was experimentally demonstrated to be very applicable not only for the preparation of large-area Al films but also to the patterned deposition of Al films on substrates. Furthermore, the SD-processed Al films on both rigid and flexible substrates were excellent in terms of electrical conductivity and mechanical durability against external deformation. Therefore, we expect that the SD process will be easily applicable to the production of large-area and patterned Al films for low-cost rigid/flexible electronics such as electric circuit boards, radio frequency identification (RFID) tags, electromagnetic interference (EMI) shields, and electrodes for energy-conversion and -storage devices.

■ ASSOCIATED CONTENT

Supporting Information

Detailed solution dipping process, such as preparation of Al precursor solution ($AlH_3\{O(C_4H_9)_2\}$), catalytic treatment of substrate, and immersion of the catalytically treated substrate into Al precursor solution, and Scotch tape and cyclic bending tests for investigating mechanical endurances of SD-processed Al film. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hyelee@kims.re.kr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a grant (M2009010025) from the Fundamental R&D program for Core Technology of Materials funded by the ministry of Knowledge Economy (MKE) of Republic of Korea and a grant from Korea Institute of Materials Science.

■ REFERENCES

(1) Siegel, A. C.; Philips, S. T.; Dicky, M. D.; Lu, N.; Suo, Z.; Whitesides, G. M. *Adv. Funct. Mater.* **2010**, *20*, 28−35.

(2) Lee, H. M.; Choi, S.-Y.; Kim, K. T.; Yun, J.-Y.; Jung, D. S.; Park, S. B.; Park, J. *Adv. Mater.* **2011**, *23*, 5524−5528.

(3) Lee, H. M.; Lee, H. B.; Jung, D. S.; Yun, J.-Y.; Ko, S. W.; Park, S. B. *Langmuir* **2012**, *28*, 13127−13135.

(4) Kim, D.; Jeong, S.; Shin, H.; Xia, Y.; Moon, J. *Adv. Mater.* **2008**, *20*, 3084−3089.

(5) Talapin, D. V.; Murray, C. B. *Science* **2005**, *310*, 86−89.

(6) Konstantatos, G.; Howard, I.; Fisher, A.; Hoogland, S.; Clifford, J.; Klem, E.; Levina, L.; Sargent, E. H. *Nature* **2006**, *442*, 180−183.

(7) Ahn, J. H.; Kim, H. S.; Lee, K. J.; Jeon, S.; Kang, S. J.; Sun, Y.; Nuzzo, R. G.; Rogers, J. A. *Science* **2006**, *314*, 1754−1757.

(8) Duan, X.; Niu, C.; Sahi, V.; Chen, J.; Parce, J. W.; Empedocles, S.; Glodman, J. L. *Nature* **2003**, *425*, 274−278.

(9) Kim, Y. J.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T.-Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222−225.

(10) Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissörtel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583−585.

(11) An, K. H.; Kim, W. S.; Park, Y. S.; Choi, Y. C.; Lee, S. M.; Chung, D. C.; Bae, D. J.; Lim, S. C.; Lee, Y. H. *Adv. Mater.* **2001**, *13*, 497−590.

(12) Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J. M. *Nature* **2000**, *407*, 496−499.

(13) Shen, Z.; Matsuki, Y.; Shimoda, T. *J. Am. Chem. Soc.* **2012**, *134*, 8034−8037.

(14) Koura, N.; Nagase, H.; Sato, A.; Kumakura, S.; Takeuchi, K.; Ui, K.; Tsuda, T.; Loong, C. K. *J. Electrochem. Soc.* **2008**, *155*, D155−D157.

(15) Shitanda, I.; Sato, A.; Itagaki, M.; Watanabe, K.; Koura, N. *Electrochim. Acta* **2009**, *54*, 5889−5893.

(16) Brower, F. M.; Reigler, P. F.; Rinn, H. W.; Roberts, C. B.; Schmidt, D. L.; Snover, J. A.; Terada, K. *J. Am. Chem. Soc.* **1976**, *98*, 2450−2453.

(17) Haber, J. A.; Buhro, W. E. *J. Am. Chem. Soc.* **1998**, *120*, 10847−10855.

(18) Jouet, R. J.; Warren, A. D.; Rosenberg, D. M.; Bellitto, V. J.; Park, K.; Zachariah, M. R. *Chem. Mater.* **2005**, *17*, 2987−2996.

(19) Frigo, D. M.; van Eijden, G. J. M. *Chem. Mater.* **1994**, *6*, 190−195.

(20) Wang, J.; Auyeung, R. C. Y.; Kim, H.; Charipar, N. A.; Pique, A. *Adv. Mater.* **2010**, *22*, 4462−4466.

(21) Greer, J. R.; Street, R. A. *Acta Mater.* **2007**, *55*, 6345−6349.

(22) Ko, S. H.; Park, I.; Pan, H.; Grigoropoulous, C. P.; Pisano, A. P.; Luscombe, C. K.; Frechet, J. M. L. *Nano Lett.* **2007**, *7*, 1869−1877.

(23) Park, I.; Ko, S. H.; Pan, H.; Grigoropoulous, C. P.; Pissano, A. P.; Frechet, J. M. J.; Lee, E. −S.; Jung, J. −H. *Adv. Mater.* **2008**, *20*, 489−496.