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Electrochemical Template Deposition of Aluminum Nanorods Using Ionic Liquids

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There is interest in developing new techniques for producing nanomaterials that provide a high degree of control over their composition and structure. Metal nanoparticles have potential for applications in sensing,[1−3] photonics,[4,5] and catalysis.[6,7] Aluminum (Al) nanoparticles have the additional attraction of providing high energy density as a fuel or propellant.[8,9] Techniques for producing Al nanoparticles, such as ball milling, solution synthesis, or pyrolytic methods, do not provide much control of particle size or shape.[10] Less common are methods for making anisotropic Al nanoparticles, such as nanorods and nanodisks, including thermolytic methods, vapor depostion, metal-exchange chemistry, electromigration, and colloidal lithography.[11−15] A motivation for producing aluminum nanorods with well controlled diameters and lengths is their unique optical properties, such as the short wavelength ($<$160 nm) for their surface plasmon resonance (SPR) band. As such, Al nanorods may prove useful for testing theories concerning surface plasmon phenomena.

Template electrodeposition of metals from aqueous solutions has been developed and widely used for nanorod synthesis for numerous applications, often using either anodized aluminum oxide (AAO) or polycarbonate templates.[16,17] Previous work has been published on the production and study of Au, Ni, Pd nanorods.[18,19] These and other metals are typically deposited using aqueous metal cyanide or metal sulfate solutions that were either purchased (Technic Inc.) or made in house.[18−21] Unlike ions of other common metals, Al ions are difficult to reduce. This presents additional challenges, especially for template electrodeposition. Developing an analogous system for aluminum requires the combination of the templated electrochemical deposition technique with a nonaqueous aluminum plating solution and an air-free atmosphere.[9,20,22−25]

Electrodeposition involves electrochemical reduction of Al complexes. Approaches can be distinguished by the types of nonaqueous solutions used. There are two prominent methods of electrodeposition of aluminum from nonaqueous solutions. The earlier method, developed in the 1950s, involves dissolving $AlCl_3$ and either $LiAlH_4$ or LiH in either diethyl ether (Et_2O) or tetrahydrofuran (THF).[26] More recently, room temperature ionic liquids (ILs), such as 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl), have been developed as solvents for $AlCl_3$ in both electrochemical and electroless systems.[10,25,27−29] Both types of solutions have proven effective in the deposition of macroscopic aluminum structures, such as films. However, only limited, nonelectrochemical deposition of well-defined nanostructures has been reported. Langhammer et al. have reported using hole-mask colloidal lithography to fabricate Al nanodisks.[12] The disks range in diameter from ∼60 to ∼450 nm and are only ∼20 nm thick. To date, there has been no report of Al nanorod template electrodeposition.

The method discussed herein combines two existing technologies into a convenient and practical technique to produce nanorods composed of Al metal. Electrodeposition of metals in templates, previously restricted to metals conducive to electrodeposition with aqueous plating solutions,[20,21] is partnered with the use of nonaqueous, ionic liquid solutions that provide a wide enough electrochemical window to permit

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(1) Qiu, Z.; Luo, Y.; Song, S. *Mater. Corros.* **2007**, *58*, 109.
(2) Navale, S. C.; Ravi, V.; Mulla, I. S.; Gosavi, S. W.; Kulkarni, S. K. *Sens. Actuators, B* **2007**, *126*, 382.
(3) Takmakov, P.; Vlassiouk, I.; Smirnov, S. *Analyst* **2006**, *131*, 1248.
(4) Li, J. Z.; Kamata, K.; Iyoda, T. *Thin Solid Films* **2008**, *516*, 2577.
(5) van Hulst, N. F. *Nature* **2007**, *448*, 141.
(6) Braun, P. V.; Wiltzius, P. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 116.
(7) Fan, Z. Y.; Lin, J. Y.; Jiang, H. X. *Quantum Sensing and Nanophotonic Devices IV*, Proceedings of the SPIE Conference, San Jose, CA, Jan 22−25, 2007; SPIE: Bellingham, WA, 2007; Vol. 6479, p, I4791
(8) Dlott, D. D. *Mater. Sci. Technol.* **2006**, *22*, 463.
(9) Zamkov, M. A.; Conner, R. W.; Dlott, D. D. *J. Phys. Chem. C* **2007**, *111*, 10278.
(10) Koura, N.; Nagase, H.; Sato, A.; Kumakura, S.; Takeuchi, K.; Ui, K.; Tsuda, T.; Loong, C. K. *J. Electrochem. Soc.* **2008**, *155*, D155.
(11) Li, C. S.; Ji, W. Q.; Chen, J.; Tao, Z. L. *Chem. Mater.* **2007**, *19*, 5812.
(12) Langhammer, C.; Schwind, M.; Kasemo, B.; Zoric, I. *Nano Lett.* **2008**, *8*, 1461.
(13) Cheng, Q.; Raghunathan, S. *Method of Preparing Aluminum Nanorods*; Patent *WO/2006/085930*.
(14) Pang, Y. T.; Meng, G. W.; Zhang, L. D.; Shan, W. J.; Zhang, C.; Gao, X. Y.; Zhao, A. W. *Solid State Sci.* **2003**, *5*, 1063.
(15) Saka, M.; Nakanishi, R. *Mater. Lett.* **2006**, *60*, 2129.
(16) Martin, C. R. *Science* **1994**, *266*, 1961.
(17) Kazeminezhad, I.; Barnes, A. C.; Holbrey, J. D.; Seddon, K. R.; Schwarzacher, W. *Appl. Phys. A: Mater. Sci. Process.* **2007**, *86*, 373.
(18) Sando, G. M.; Berry, A. D.; Owrutsky, J. C. *J. Chem. Phys.* **2007**, *127*, 11.
(19) Sando, G. M.; Berry, A. D.; Campbell, P. M.; Baronavski, A. P.; Owrutsky, J. C. *Plasmonics* **2007**, *2*, 23.
(20) Cao, G. Z.; Liu, D. W. *Adv. Colloid Interface Sci.* **2008**, *136*, 45.
(21) Kline, T. R.; Tian, M. L.; Wang, J. G.; Sen, A.; Chan, M. W. H.; Mallouk, T. E. *Inorg. Chem.* **2006**, *45*, 7555.
(22) Gromov, A.; Ilyin, A.; Forter-Barth, U.; Teipel, U. *Propellants, Explos., Pyrotech.* **2006**, *31*, 401.
(23) Yang, Y. Q.; Wang, S. F.; Sun, Z. Y.; Dlott, D. D. *Propellants, Explos., Pyrotech.* **2005**, *30*, 171.
(24) Hurst, S. J.; Payne, E. K.; Qin, L. D.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 2672.
(25) Zhu, J. M.; Shen, Y. H.; Xie, A. J.; Qiu, L. G.; Zhang, Q.; Zhang, S. Y. *J. Phys. Chem. C* **2007**, *111*, 7629.
(26) Couch, D. E.; Brenner, A. *J. Electrochem. Soc.* **1952**, *99*, 234.
(27) Jiang, T.; Chollier Brym, M. J.; Dube, G.; Lasia, A.; Brisard, G. M. *Surf. Coat. Technol.* **2006**, *201*, 10.
(28) Chang, J. K.; Chen, S. Y.; Tsai, W. T.; Deng, M. J.; Sun, I. W. *Electrochem. Commun.* **2007**, *9*, 1602.
(29) Zein El Abedin, S.; Moustafa, E. M.; Hempelmann, R.; Natter, H.; Endres, F. *ChemPhysChem* **2006**, *7*, 1535.

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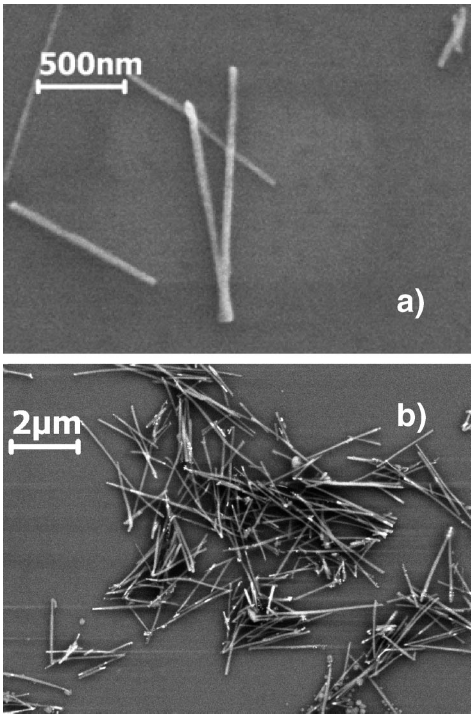

Figure 1. SEM of Al nanorods produced in nominally (a) 10 and (b) 30 nm diameter templates by electrodeposition in ionic liquid solution.

Al reduction. Specifically, the technique described uses commercially available polycarbonate templates with two different nanometer pore sizes. Polycarbonate templates require the use of IL-based methods for deposition, because organic/metal hydride solutions are detrimental to them. The consistency of the electrodeposition and the quality of the nanorods produced depend on the solution wetting the pores and conducting current. A recognized limitation of ILs is their high viscosity, which may hinder both wetting and conduction. Although some success was achieved with neat IL solutions, deposition was improved by adding xylene to the plating solution to decrease the viscosity and increase the electrical conductivity. The nanorods were fabricated using the procedure and apparatus previously reported for the production of Au, Ni, and Pd nanorods[14,15] except for the use of the ionic-liquid plating solution. The polycarbonate templates had a conductive layer attached to one side. Aluminum was electrodeposited at $\sim$2 V, 0.25 mA DC for 300−450 min depending on template pore size. The resulting Al nanorods are analyzed by UV−visible transmission spectroscopy, ultrafast transient absorption spectroscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) spectroscopy. Optical measurements were performed on the nanorods in the templates after removing the backing layer. SEMs were obtained after the nanorods were released by dissolving the template in methylene chloride. See the Supporting Information for experimental details.

SEM images (Figure 1) show that nanorods of conducting material (i.e., metal) are indeed produced and provide an indication of their dimensions. The clarity of the images is indicative of only limited surface oxidation. A survey of various images of the nanorods confirms their diameters to be $\sim$40 nm when fabricated with templates with a nominal pore diameter of 10 nm and $\sim$60 nm for the templates with nominally 30 nm diameter pores. These diameters are similar to those previously determined for nanorods of other metals (e.g., Au, Ni, Pd)[18,19,30,31] produced by electrodeposition with aqueous plating solutions using the same type of templates. The lengths are found to be 2−4 μm, which is somewhat less than the template thickness of about 6 μm. It is unclear whether the pores are incompletely filled or the rods break during SEM sample preparation.

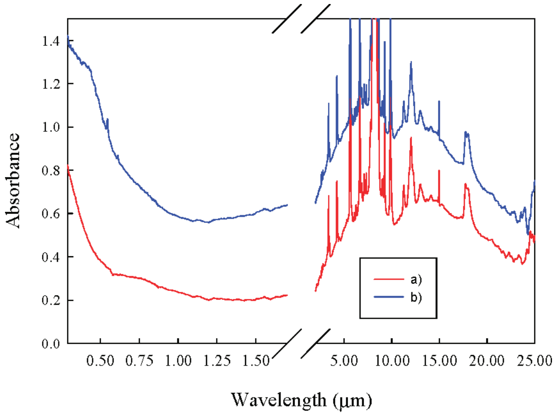

Figure 2. FTIR (right) and UV−visible (left) transmission spectra of (a) $\sim$40 and (b) $\sim$60 nm Al nanorods in the polycarbonate templates. The narrow bands in the IR spectra are due to the polycarbonate template. The small narrow lines in the UV−visible spectra are due to the lamp.

Concurrent with the SEM measurements, EDX was performed as a qualitative verification of the presence of Al metal on one of the samples and results are shown in Table S1 in the Supporting Information. The results indicate a high ($>$4 to 1) aluminum to oxygen atomic ratio suggesting a low degree of oxidation on the surface of the rods and a wide metallic aluminum core. Even if all of the oxygen seen in the EDX is from Al_2O_3, the ratio is consistent with the formation of a $\sim$5 nm thick oxide layer commonly expected for Al materials in ambient conditions.[12] Much of the oxygen is likely to come from the Si wafer, so the oxidation on the nanorods is probably thinner. If the oxide layer is similar on our nanorods after being dissolved from the template, then the core should remain metallic. Initial indications are that the nanorods are protected from oxidation while they remain in the templates.

The UV−visible transmission spectra (Figure 2) have characteristics expected for Al nanorods. The spectra show a broad absorption that is stronger at shorter wavelengths. This result is consistent with the presence of a strong band in the vacuum UV, which is expected to occur for the transverse surface plasmon band of Al nanorods near 7 eV (about 175 nm).[32] The longitudinal band (LSPR) is similar to those previously observed for metal nanorods with similar aspect ratios composed of other metals; there is a broad band that has a maximum around 1200 cm^{-1} or $\sim$8.3 μm in the

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(30) Schonenberger, C.; vanderZande, B. M. I.; Fokkink, L. G. J.; Henny, M.; Schmid, C.; Kruger, M.; Bachtold, A.; Huber, R.; Birk, H.; Staufer, U. *J. Phys. Chem. B* **1997**, *101*, 5497.

(31) van der Zande, B. M. I.; Bohmer, M. R.; Fokkink, L. G. J.; Schonenberger, C. *Langmuir* **2000**, *16*, 451.

(32) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag: Berlin, 1995; Vol. 25.

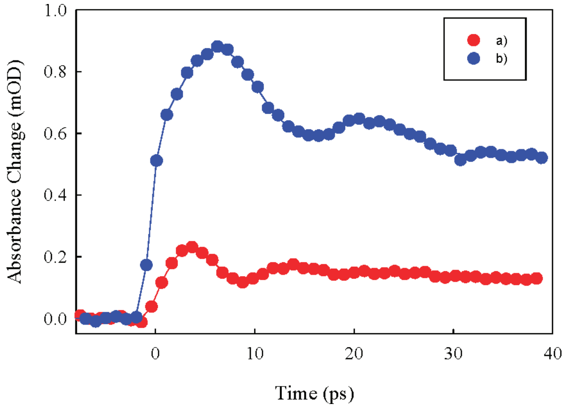

Figure 3. Transient absorption of (a) ~40 and (b) ~60 nm Al nanorods in the templates using 400 nm (~250 fs, 1 μJ with ~250 μm beam diameter) excitation pulses and 800 nm probe pulses as a function of delay time. The coherent acoustic mode oscillation periods are (a) 10.5 and (b) 16.6 ps, which are consistent with the periods calculated for ~40 and ~60 nm diameter Al nanorods, respectively. The points are the data and the line is a fit to a function that includes the oscillation.

FTIR spectra (Figure 2). The longitudinal band can be observed in the spectra for the nanorods in the polycarbonate templates oriented normal to the beam direction because the template pores have a broad angular distribution.[30] The maximum extinction is above 1 OD, which indicates relatively effective filling, especially considering that the band is broader on the high frequency side than for samples produced with other metals.[18,19] The band appears blue-shifted from that observed with Au nanorods. This is consistent with the fact the tuning rate (i.e., the shift of the LSPR with the nanorod aspect ratio) for Al is slower and indicates that the band is sensitive to the material. The material dependence of the SPR band is consistent with the Al nanorods being considered in the plasmonic regime.

One way to provide supporting evidence that Al nanorods have been produced in the templates is by measuring coherent acoustic breathing mode oscillations in transient pump–probe signals using ultrafast (femtosecond) spectroscopy. When the 400 nm pulse excites the nanorods, electrons are heated, thermalize in less than a picosecond, and then dissipate the energy within a few picoseconds to the lattice and into phonons. Since the acoustic breathing mode periods for these rods are long compared to the electron–phonon coupling time, they are impulsively or coherently excited. The oscillation period can be measured in real time using ultrafast absorption spectroscopy,[33–35] and it depends on the metal and the nanorod diameter. These types of measurements have been studied and reviewed in the literature for various shapes, dimensions, and compositions of nanoparticles.[33,34] We have characterized Au, Ni, and Pd nanorods with similar dimensions using this approach.[18,19] The breathing mode oscillations are observed for our nanorods because the periods are not only longer than the electron–phonon coupling time but also shorter than the acoustic dephasing time. The extensional modes of these long nanorods have periods that are much longer and are likely to be overdamped. The breathing mode oscillation period (T_{br}) depends on the metal and nanorod diameter: $T_{\mathrm{br}} = \pi R/2\varphi c_{\mathrm{l}}$, where R is the radius, φ is the eigenvalue for the solution of the classical breathing mode problem and depends on the Poisson ratio (υ) of the material (for Al, $\upsilon = 0.35$ and $\varphi = 2.187$), and c_{l} is the longitudinal speed of sound. For our Al nanorods, the time-resolved absorption signals have oscillation periods of 16.6 ± 2.5 ps and 10.5 ± 1.6 ps for the ~60 and ~40 nm diameter Al nanorods, respectively, as shown in Figure 3. These periods are consistent with the calculated periods based on the longitudinal speed of sound (6420 m/s) for Al. Observing the oscillations and the periods determined confirm that the synthesis has produced Al nanorods with dimensions that are indicated by the SEMs and that are similar to those of nanorods composed of other metals produced with these templates.

This is the first successful electrochemical deposition of aluminum in polycarbonate templates resulting in a nanorod morphology. Creating specific nanostructures of aluminum, as opposed to films, may lead to assorted novel uses. These include, but are not limited to, catalysis, catalyst supports, optoelectronics, sensing, and self-insulating wires. While in the templates, the rods are protected from ambient oxidizers, but the templates can be easily removed with methylene chloride when necessary to allow the metal to be functionalized. The rod diameter can be controlled by altering the size of the pores in the templates and the length can be controlled by varying the electrical current and/or the deposition time. Similar depositions may be conducted in other templates, including polymer templates with more uniform pore structures, and AAO templates. The use of AAO templates may also allow for the use of ether-based metal hydride solutions in lieu of ionic liquids. Nanorods of other metals that require nonaqueous solution for electrodeposition template synthesis, such as titanium, may also be fabricated in this way.

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Supporting Information Available: Further experimental details, UV–visible spectra, and EDX results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Hartland, G. V. *Annu. Rev. Phys. Chem.* **2006**, *57*, 403.
(34) Perez-Juste, J.; Pastoriza-Santos, I.; Liz-Marzan, L. M.; Mulvaney, P. *Coord. Chem. Rev.* **2005**, *249*, 1870.
(35) Burgin, J.; Langot, P.; Arbouet, A.; Margueritat, J.; Gonzalo, J.; Afonso, C. N.; Vallee, F.; Mlayah, A.; Rossell, M. D.; Van Tendeloo, G. *Nano Lett.* **2008**, *8*, 1296.