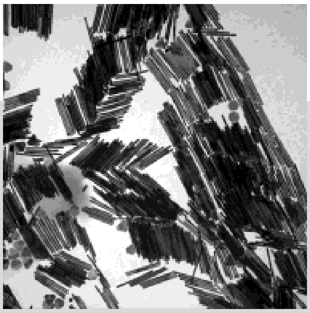
ADVANCED MATERIALS

Controlling the Aspect Ratio of Inorganic Nanorods and Nanowires

By *Catherine J. Murphy** and *Nikhil R. Jana*



Semiconductors and metals exhibit unusual optical, electronic, and magnetic properties on the nanometer scale. Chemists and materials scientists are developing methods to make non-spherical shapes of semiconductors and metals on the nanometer scale. We use a seed-mediated growth approach to make metallic nanorods and nanowires in homogeneous solution. Control of the ratio of metallic spherical seeds to metal salt in the reduction reaction controls the aspect ratio of the resulting rods and wires.

1. Introduction

Inorganic nanoparticles of generally spherical shape have been of interest to the broad scientific community for decades. For example, gold nanospheres with diameters of ~100 nm have been used as contrast agents for biological electron microscopy samples since the 1970s.[1] The photographic industry has relied on the photochemical reactivity of silver and silver halide nanoclusters.[2] Since the 1980s both experiment and theory have shown that the electronic properties of semiconductors on the ~1–10 nm scale are governed by quantum mechanical considerations, and thus 1–10 nm diameter spheres of semiconductors are known as quantum dots.[3,4] Fundamentally, the light that is absorbed and emitted by semiconductor nanoparticles are tunable by nanoparticle diameter because the photogenerated electron–hole pair has an exciton diameter that is on the 1–10 nm scale.[3,4] For metallic nanoparticles, interesting optical and electronic effects are expected on the ~10–100 nm scale because the mean free path of an electron in a metal is ~10–100 nm.[5] There is still great current interest in the making of inorganic nanoparticles that are spheres of defined size, decorated with particular surface groups, for optical and biological applications.[6,7]

The aspect ratio of a shape is defined as the length of the major axis divided by the width of the minor axis. Thus, spheres have an aspect ratio of 1. We define, for this article, nanorods as materials that have a width of ~1–100 nm and aspect ratios greater than 1 but less than 20; and we call “nanowires” analogous materials that have aspect ratios greater than 20.

Why is there such great current interest in nanorods and nanowires? The optical properties of metallic nanoparticles depend on shape (Fig. 1). This is due to the absorption of visible light both along the length of the nanorod (the longitudinal plasmon band) and along the width of the nanorod (the transverse plasmon band). The larger the aspect ratio, the more red-shifted the longitudinal plasmon band, as theory predicts[5] and experiment confirms.[8–12] Recent exciting work with semiconductor nanorods and nanowires has shown that polarized light emission and lasing are observable from these nanomaterials.[13,14] Other workers have predicted and in some cases shown that unique and improved surface-enhanced Raman scattering properties,[15] mechanical properties,[16] magnetic properties,[17] and electronic properties[18] are possible with anisotropic nanomaterials compared to spheres. The different atomic planes available on the surface of shapes other than spheres can also translate into materials that catalyze different reactions based on their shape.[5] Finally, visions of computer chips with elements on the near-molecular scale have driven the synthesis and rational assembly of metallic nanorods and nanowires.[19–21]

2. Syntheses of Inorganic Nanorods and Nanowires

We classify synthetic approaches for making inorganic nanorods and nanowires into the following groups:

Synthesis in Hard Templates: In this approach, a premade nanoporous template (e.g., an alumina membrane) is used as a reaction vessel for the electrochemical deposition of a metal.[8] The membrane must be attached to an electrode for the synthesis. Aspect ratio is controlled by the amount of metal

---

[*] Prof. C. J. Murphy
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208 (USA)
E-mail: murphy@mail.chem.sc.edu

Dr. N. R. Jana
R R R Mahavidyalaya
Hooghly-712406, WB (India)
E-mail: njana@lycos.com

© WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2002 0935-9648/02/0101-0080 $ 17.50+.50/0

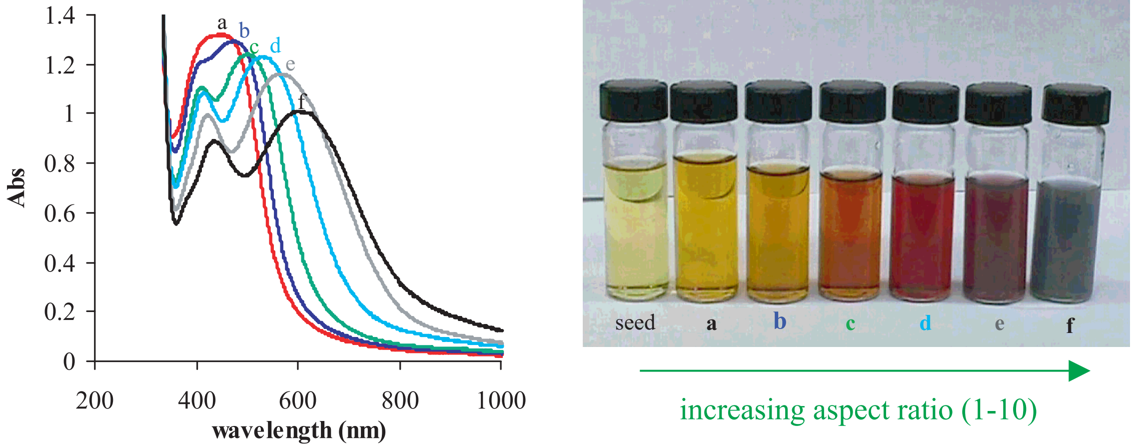


Fig. 1. Aqueous solutions of silver nanoparticles show a beautiful variation in visible color depending on the aspect ratio of the suspended nanoparticles: far left in the photograph, silver nanospheres 4 nm in diameter that are used as seeds in subsequent reactions; a–f) silver nanorods of aspect ratio 1–10. The corresponding visible absorption spectra for (a)–(f) are also shown.

present. To produce free nanorods, the template must be dissolved.

Synthesis with Soft Templates: Rodlike micelles, microemulsions, and surfactants in solution can also direct the growth of anisotropic nanomaterials.[9,10,22–25] For gold, reduction of a gold salt in an electrochemical cell has been a popular approach.[9,10] The shape of the rodlike micelle promotes the formation of rodlike nanomaterials from ionic precursors; in the case of surfactants, “medium-strength” binding of a surfactant to a growing crystal face helps direct nanorod growth. The aspect ratio of the resulting nanorods can be controlled by the shape and size of the micellar/microemulsion template, and by the relative concentrations of precursors, salts, and surfactants.

Nanowire Growth by Phase Separation: Lieber and his group have developed high-temperature (~800–1000 °C) methods for growing semiconductor nanowires out of 3–4 nm seed catalysts based on the temperature-dependent solubility of the nanowire material with the seed material.[26]

Seed-Mediated Growth in Solution: We have developed a seed-mediated growth approach to making metallic nanorods and nanowires in aqueous solution at or near room temperature.[11,12,27] Our procedure (Fig. 2) begins with the synthesis of metallic nanospheres by chemical reduction of a metal salt with a strong reducing agent such as sodium borohydride. Citrate is present as a capping agent to prevent particle growth. The gold or silver spheres thus generated are 3–5 nm in diameter and serve as seeds on which to grow more anisotropic nanostructures. These seeds are then added to a solution containing more metal salt, a weak reducing agent (e.g., ascorbic acid), and a rodlike micellar template (cetyltrimethylammonium bromide, CTAB). The seeds serve as nucleation sites for nanorod and nanowire growth; under our conditions, no metal salts are reduced to metal unless the seeds are present. Typical product dimensions are 10–20 nm diameter short axis, and aspect ratios up to 20 for nanorods, while 2–4 μm long nanowires are obtainable (Figs. 3 and 4). Aspect ratio is controlled by the ratio of metal seed to metal salt; a lower concentration of seeds produces longer rods.[12] Fine-tuning of solution conditions produces nanowires.[11] The presence of additives in the reaction media can fine-tune the morphology of the resulting nanorods; cylindrical gold nanorods and needle-like gold nanorods are both obtainable by the seed-mediated growth procedure,[12,27] with the presence of small amounts of organic solvent that allegedly “loosen” the CTAB micellar

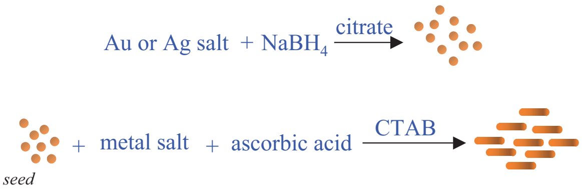


Fig. 2. Cartoon representation of seed-mediated growth for gold and silver nanorods and nanowires. See text for more details.

Fig. 3. Transmission electron micrograph of gold nanorods, aspect ratio 18, made by the seed-mediated growth approach.

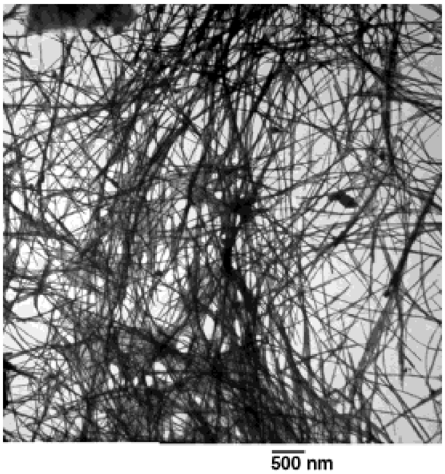


Fig. 4. Transmission electron micrograph of silver nanowires, aspect ratio ~100, made by the seed-mediated growth approach.

framework favoring the nano-needle shapes.[27] In all cases, some degree of centrifugation and extraction are necessary to separate rods from any spheres that have been formed.

Both the soft template approach and the seed-mediated growth approach to controllable aspect ratio nanomaterials share the advantage of easy solution preparation. However, the exact mechanisms by which the growth proceeds are still not rigorously worked out, even for the simpler case of nanospheres growing into larger spheres.[28] There is a need, then, for improved theoretical models of nanorod growth that can be tested.

3. Conclusions

The seed-mediated growth approach we are developing for controlling the aspect ratio of metallic nanorods and nanowires has many appealing features. The syntheses are performed in homogeneous solution, amenable to scaling up; reagents are relatively cheap; the dissolution of a hard template is not required; high temperatures are not required; and the aspect ratio of the resulting nanomaterial is not limited by the dimensions of a template. On the other hand, an incomplete understanding of the nanorod synthetic reaction mechanism in solution translates into many hours of laborious fine-tuning of reaction conditions to achieve reproducible syntheses. Liquid crystalline alignment of nanorods and nanowires from solution does occur spontaneously (Fig. 3), but the hard template methods are presently better-suited for more rigorous alignment and connection of nanorods and nanowires. We anticipate that the next five years will be an exciting time for the scientists who work at this interface of chemistry and materials science as syntheses improve and linkage chemistries become more developed.

---

[1] *Colloidal Gold: Principles, Methods, and Applications*, Vol. 1 (Ed: M. Hayat), Academic, San Diego, CA **1989**.
[2] B. Trosken, F. Willig, K. Schwarzburg, A. Ehret, M. Spitler, *Adv. Mater.* **1995**, *7*, 448.
[3] H. Weller, *Adv. Mater.* **1993**, *5*, 88.
[4] A. P. Alivisatos, *Science* **1996**, *271*, 933.
[5] M. A. El-Sayed, *Acc. Chem. Res.* **2001**, *34*, 257.
[6] V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H. J. Eisler, M. G. Bawendi, *Science* **2000**, *290*, 314.
[7] M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss, A. P. Alivisatos, *Science* **1998**, *281*, 2013.
[8] C. A. Foss, G. L. Hornyak, J. A. Stockert, C. R. Martin, *J. Phys. Chem.* **1994**, *98*, 2963.
[9] Y. Y. Yu, S. S. Chang, C. L. Lee, C. R. C. Wang, *J. Phys. Chem. B* **1997**, *101*, 6661.
[10] S. Link, M. B. Mohamed, M. A. El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 3073.
[11] N. R. Jana, L. Gearheart, C. J. Murphy, *Chem. Commun.* **2001**, 617.
[12] N. R. Jana, L. Gearheart, C. J. Murphy, *J. Phys. Chem. B* **2001**, *105*, 4065.
[13] J. T. Hu, L. S. Li, W. D. Yang, L. Manna, L. W. Wang, A. P. Alivisatos, *Science* **2001**, *292*, 2060.
[14] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, P. D. Yang, *Science* **2001**, *292*, 1897.
[15] J. P. Kottmann, O. J. F. Martin, D. R. Smith, S. Schultz, *Chem. Phys. Lett.* **2001**, *341*, 1.
[16] P. E. Marszalek, W. J. Greenleaf, H. Li, A. F. Oberhauser, J. M. Fernandez, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 6282.
[17] T. Thurn-Albrecht, J. Schotter, G. A. Kastle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, T. P. Russell, *Science* **2000**, *290*, 2126.
[18] L. Li, J. Hu, W. Yang, A. P. Alivisatos, *NanoLetters* **2001**, *1*, 349.
[19] J. K. N. Mbindyo, B. D. Reiss, B. R. Martin, C. D. Keating, M. J. Natan, T. E. Mallouk, *Adv. Mater.* **2001**, *13*, 249.
[20] E. Dujardin, L. B. Hsin, C. R. C. Wang, S. Mann, *Chem. Commun.* **2001**, 1264.
[21] J. R. Heath, *Pure Appl. Chem.* **2000**, *72*, 11.
[22] M. P. Pileni, B. W. Ninham, T. Gulik-Kryzwicki, J. Tanori, I. Lisiecki, A. Filankembo, *Adv. Mater.* **1999**, *11*, 1358.
[23] X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59.
[24] A. Filankembo, M. P. Pileni, *J. Phys. Chem. B* **2000**, *104*, 5865.
[25] M. Li, H. Schnablegger, S. Mann, *Nature* **1999**, *402*, 393.
[26] X. Duan, C. M. Lieber, *Adv. Mater.* **2000**, *12*, 298.
[27] N. R. Jana, L. Gearheart, C. J. Murphy, *Adv. Mater.* **2001**, *13*, 1389.
[28] N. R. Jana, L. Gearheart, C. J. Murphy, *Chem. Mater.* **2001**, *13*, 2313.

0935-9648/02/0101-0082 $ 17.50+.50/0