

Journal of Materials Chemistry

www.rsc.org/materials

Volume 18 | Number 19 | 21 May 2008 | Pages 2161–2284



ISSN 0959-9428

HIGHLIGHT

Catherine J. Murphy
Sustainability as an emerging design
criterion in nanoparticle synthesis
and applications

COMMUNICATION

A. Sundaresan, C. N. R. Rao *et al.*
Crucial role of oxygen stoichiometry
in determining the structure and
properties of BiMnO_3

RSC Publishing



0959-9428(2008)18:19;1-U

Sustainability as an emerging design criterion in nanoparticle synthesis and applications

Catherine J. Murphy

DOI: 10.1039/b717456j

The precepts of green chemistry have been spreading since the mid-1990s, concomitant with advances in nanomaterial synthesis. Recently these two communities have begun to significantly converge. Nanomaterial synthesis groups are developing greener, more sustainable production methods, while nanoparticle application groups are exploring sustainable energy sources and environmental remediation as end goals.

Sustainability is a concept that, in a materials chemistry context, coincides with many of the principles of green chemistry.¹ For materials synthesis, these principles include the use of less toxic precursors to prepare nanomaterials; the use of water as a solvent where possible; using the least number of reagents and as few synthetic steps as possible; reducing the amount of byproducts and waste; and using a reaction temperature close to room temperature.^{1,2} A good starting point for recent advances in the environmentally responsible synthesis and use of nanomaterials is the Spring 2006 National

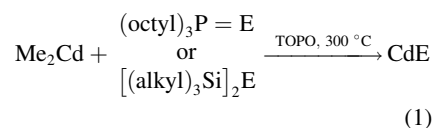
Meeting of the American Chemical Society (ACS), held in Atlanta, Georgia, USA.³ A special symposium at this meeting, entitled “Nanotechnology and the Environment,” was the fourth in a series at national ACS meetings on this topic, but the 2006 symposium was the first to highlight “green nanoscience.”

Less toxic quantum dots

Quantum dots are semiconductor nanoparticles that have a diameter in the 1–10 nm range, coincident with their respective excitonic Bohr radii.⁴ These materials are highly photoluminescent (when properly surface-passivated), resistant to photobleaching compared to organic fluorophores, and their bandgap energies are exquisitely tunable with

particle diameter, based on quantum confinement effects.^{4,5} The most popular quantum dots are the II–VI materials such as CdS, CdSe, and CdTe, which now can be made in an astonishing variety of shapes and sizes for a wide array of applications.^{6–11} All these materials possess bulk bandgap energies in the visible and near-infrared (NIR) portions of the electromagnetic spectrum; and the particle size in the 1–10 nm regime tunes the bandgap energies, and thus light emission energies, to shorter wavelengths compared to the bulk.

The first significant synthetic method to prepare CdSe quantum dots is that of Murray, Norris and Bawendi in 1993; the reactions they developed are (where E = S, Se, or Te):¹²



In this reaction, the trioctylphosphine oxide (TOPO) is both solvent and capping agent, and coordinates to the nanoparticle surface so that the particles do not grow too large; but it cannot bind so tightly that the particles cannot grow at all. Nanoparticle growth is kinetically controlled in many situations, where multiple interacting parameters simultaneously determine final nanoparticle size and shape.¹³ Therefore, simply swapping out one solvent for another, or one capping agent for another, is no guarantee of similar products. That the Murray, Norris and Bawendi paper¹² has been cited nearly 2300 times in fourteen years is a testament to the intense interest quantum dots arouse in the scientific community.

From the green chemistry point of view, there are abundant problems with

Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter St., Columbia, SC, 29208, USA. E-mail: Murphy@mail.chem.sc.edu; Fax: +1-803-777-9521; Tel: +1-803-777-3628



Catherine J. Murphy

Catherine J. Murphy is the Guy F. Lipscomb Professor of Chemistry at the University of South Carolina. She received two B.S. degrees, one in chemistry and one in biochemistry, from the University of Illinois – Urbana-Champaign, in 1986. In 1990 she received her Ph.D. in inorganic chemistry from the University of Wisconsin-Madison, under the direction of Arthur B. Ellis. From 1990–1993 she was an NSF and NIH postdoctoral fellow at the California Institute of Technology, with Jacqueline K. Barton. Since 1993 she has been a faculty member in the Department of Chemistry and Biochemistry at the University of South Carolina, winning numerous awards for both teaching and research. She and her research group have published over 120 papers in the areas of nanomaterials and biophysical chemistry. Her group has specialized in the synthesis, optical properties, chemical sensing and biological imaging applications of metallic nanomaterials; shape control of nanocrystals; optical probes of DNA structure and dynamics; nanocomposite materials; and inorganic coordination complexes for optical sensing. She is a Senior Editor for J. Phys. Chem., a member of numerous Editorial Advisory Boards (including Chem. Commun.), and is the Nanoscience Chair of the American Chemical Society's Division of Inorganic Chemistry for 2008.

eqn (1): the precursors, especially dimethylcadmium, are incredibly toxic, the solvent is nasty, the temperature is high and therefore costs energy. Should ions leach out of the final CdE (E = S, Se, Te) nanomaterial, toxic biological effects are likely¹⁴—and as a main application of quantum dots is biological targeting and imaging,¹⁵ toxicity is a serious concern. X. Peng, one of the speakers at the aforementioned ACS meeting, has developed greener synthetic methods to make CdSe quantum dots. In early work, his group found that the nonvolatile CdO is equally as good as, if not better than, the dimethylcadmium precursor used by Bawendi.¹⁶ Later, his group showed that cadmium acetate, amines and fatty acids as precursor, solvents and capping agents also give high quality CdSe nanocrystals.¹⁷ In 2007, Peng managed to dispense with cadmium altogether, and has made Mn(II)-doped ZnSe quantum dots.^{18,19} In these “d dots,” the emission in the visible comes from the d levels in the dopant Mn(II) ion, which does have some tunability in emission wavelength, albeit not as large as the bandgap tunability of the CdSe quantum dots based on size alone.

“Green gold”

Gold nanoparticles are of great interest for their optical properties, ultimately with (bio)chemical sensing, biological imaging, and biological therapeutics as major applications.^{20–24} In the ~4–200 nm size regime, gold nanoparticles are still large enough to have a conduction band like bulk metal, but their optical properties are dominated by resonant Mie absorption and scattering in the visible and NIR that depends on size, shape, local dielectric constant and degree of aggregation.^{25–30} Smaller gold nanoparticles are of great interest for unusual catalytic properties.^{31–33}

J. Hutchison, another speaker at that 2006 ACS meeting, has developed a greener method to make ultrasmall (1.5 nm) gold nanoparticles.^{2,3} The original preparation used benzene as a solvent and gaseous diborane as a reducing agent; Hutchison has managed to replace diborane by sodium borohydride, a solid; and benzene with toluene. The final purification nanoparticle step, involving liters of organic solvent, can be done with a

specially engineered filtration membrane.³⁴ Overall, the cost of the gold nanoparticles has decreased from \$300 000 per gram of product to \$500.³

Gold nanorods of various aspect ratios (aspect ratio = length/width) absorb and scatter light throughout the visible and NIR.^{25,30,35} We and other groups, notably those of El-Sayed, Mulvaney, and Liz-Marzan (several of whom were also present at that 2006 ACS meeting), have developed methods to make gold nanorods in water, at room temperature, with mild reducing agents in at least one step, using cheap cationic surfactants to direct the crystal growth into rods.^{25,30,35} Our synthesis consists of two steps: reduction of HAuCl₄ in water by sodium borohydride, in the presence of sodium citrate or hexadecyltrimethylammonium bromide (also called cetyltrimethylammonium bromide or CTAB) as a capping agent to make ~3.5 nm seed nanoparticles. Then, an aliquot of this seed solution is used to grow more metal on, from the same metal salt with a weak reducing agent (vitamin C) in the presence of more CTAB.^{30,36} Relatively small changes in growth conditions can lead to a whole host of different particle shapes and sizes, each of different color.³⁷ The particles end up with a bilayer, at least, of CTAB on their surfaces, which puts a ~3 nm thick hydrophobic layer adjacent to the metal surface.^{38,39} Could this synthetic method be any greener? Certainly more efforts could be made. HAuCl₄ is itself rather toxic, based on its materials safety data sheet; but other gold salts have not been examined. CTAB is a biocidal agent like any detergent, but of the ~40 other structure-directing agents we, at least, have explored, CTAB works by far the best to make gold nanorods. We have found that only about 15% of the metal ions we put into our reaction end up in the gold nanorods;⁴⁰ clearly, we need to recycle the reservoirs of unreduced metal ions that remain in solution for future reactions.

Interestingly, cytotoxicity studies, albeit in only one cell line for a relatively short time of exposure, show that ~4–20 nm gold nanospheres capped with either citrate, biotin (vitamin B7), or CTAB on their surfaces are not acutely cytotoxic, whereas HAuCl₄ alone and CTAB alone are cytotoxic, at low concentrations.⁴¹ One interesting implication is

that toxic substances might show less toxicity if they are bound tightly enough to a nanoparticle. However, there has been relatively little work in this area, and the more alarming possibility of nanoparticle-mediated transport of toxic agents, with subsequent environmental release, also needs to be thoroughly examined in many different systems.

Biomass extracts as precursors to metal nanoparticles

For the synthesis of metallic nanoparticles, an obvious approach is to take a metal salt in water and reduce it to the elemental metal. While one may not have many choices of different salts, there is an abundance of reducing agents that are available in biology—reducing sugars, glutathione, *etc.* More and more groups, then, are beginning to use plant and algal extracts to reduce metal ions to metal nanoparticles in water. Recent examples of biomass-derived reducing agents include starch,⁴² extracts from lemongrass,^{43,44} seaweed,⁴⁵ algae,⁴⁶ and mushrooms.⁴⁷ Gold, silver, cobalt, nickel, and cobalt–nickel alloy nanoparticles have been prepared with biomass-derived extracts, with reasonably good control over particle size, and, in some cases, shape. The advantages of these reactions are obvious from the sustainability point of view (*e.g.*, recycling food waste for chemical production). The principle disadvantage of this approach is that the chemical nature of the resulting nanoparticle products is ill-defined; but overcoating nanoparticles with known reagents might be a means to obtain workable materials.

Covering up surfaces for biocompatibility

In the event that a nanomaterial will be exposed to the open environment or to a living organism, the chemical nature of its inner core is likely not as important as the chemical nature of its surface.^{48–50} This important point was a key one from V. Colvin, another speaker at the 2006 ACS meeting. In the context of sustainability and safety, covering up potentially toxic surface groups with more innocuous ones appears to be a good strategy; and, this has the added bonus of improving the biocompatibility

of nanomaterials that might be intended ultimately for an *in vivo* application.

There are several common strategies one might employ to cover up nanomaterial surfaces. Depending on the nature of the nanomaterial, direct chemical covalent derivatization might be performed (e.g., carboxylating carbon nanotubes or exchanging thiols on a gold nanoparticle).² Intermediate layers might also be necessary. For cadmium-based quantum dots, which are typically already passivated with a thin ZnS or ZnSe shell, reaction with a bifunctional molecule such as mercaptopropyltrimethoxysilane (MPTMS, HS(CH₂)₃Si(OCH₃)₃) puts the thiol end on the quantum dot, displays the trimethoxysilane group to the solvent for subsequent reaction to produce a biocompatible silica shell.^{51,52} The use of MPTMS for overcoating gold and silver nanoparticles with silica also works.^{53,54} More recently, “soft shells” of polymers have been used to overcoat nanomaterials that retain the desired optical properties of the inner cores.^{55,56} An especially interesting example of a differing biological response to a nanomaterial that depends on surface chemistry has recently appeared.⁵⁷ In that paper, CTAB-coated gold nanorods were taken up by cells nonspecifically with no major ill effects; but replacement/overcoating of the CTAB by poly(ethylene) glycol chains, which are well known to reduce nonspecific protein adsorption to surfaces, greatly reduced cellular uptake of the nanorods.⁵⁷

What are nanoparticles good for? Two applications that emphasize sustainability

Let us assume that in the future, materials chemists develop an extensive toolkit to make their nanomaterials in sustainable ways. What, then, can we do with these materials that continues this promise? How can we use these materials to promote a sustainable future? *Science* published a special issue on sustainability on 9 February 2007, and its major theme was energy: how can we power the planet in a responsible, efficient, and clean way? In that issue of *Science*, Lewis described the abundance of joules from the sun, and advances in solar energy conversion that are needed to capture this energy, including design principles for nanomaterial-based

solar cells.⁵⁸ At the 2006 ACS meeting, V. Colvin described another type of sustainable application: environmental remediation. Specifically, she and her group have developed a method that uses magnetic iron oxide nanomaterials to remove arsenic from drinking water.⁵⁹

Providing clean, green energy and safe drinking water for human use are excellent examples of sustainable science in action. The United Nations declared the years 2005–2014 as the “Decade of Education for Sustainable Development,” and many schools and universities are responding to the challenge by implementation of curricula and institutional practices that emphasize sustainability.⁶⁰ The next generation of scientists, then, is growing up with the concepts of reducing waste, recycling, improving energy efficiency, using biodegradable packaging, and the use of renewable energy sources as standard practices.

Prospects for the future

The timeliness of “being green and nano” for nanomaterials synthesis is evident from two major reviews that have appeared in 2007.^{2,61} Clearly, nanomaterials syntheses that reduce and recycle their waste, and that use room-temperature aqueous solutions to achieve their products, are the best ones from the sustainability point of view. These design parameters also improve manufacturer safety and lower the cost of production. A parallel movement in synthetic organic chemistry is emerging, and, surprisingly, organic reactions “on water” (not “in water” because most organics are not water-soluble) can be superior to conventional reactions in organic solvents.⁶² It has been recognized for some time that the environmental impact of nanomaterials must be assessed,^{48,63} from many different points of view (fate, transport, waste, toxicity, biomagnification in the food chain). Overall, we can expect the ideas of sustainability to become part of the design criteria for nanomaterial production and application—especially if the next generation of scientists is already being trained with these ideas in mind.

References

- 1 P. T. Anastas and M. M. Kirchhoff, *Acc. Chem. Res.*, 2002, **35**, 686.

- 2 J. A. Dahl, B. L. S. Maddux and J. E. Hutchison, *Chem. Rev.*, 2007, **107**, 2228.
- 3 S. K. Ritter, *Chem. Eng. News*, 2006, **84**, 37.
- 4 M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.*, 1990, **23**, 183.
- 5 J. M. Klostianec and W. C. W. Chan, *Adv. Mater.*, 2006, **18**, 1953.
- 6 I. Robel, V. Subramanian, M. Kuno and P. V. Kamat, *J. Am. Chem. Soc.*, 2006, **128**, 2385.
- 7 Y. Zheng, S. Gao and J. Y. Ying, *Adv. Mater.*, 2007, **19**, 376.
- 8 D. V. Talapin, J. H. Nelson, E. V. Shevchenko, S. Aloni, B. Sadler and A. P. Alivisatos, *Nano Lett.*, 2007, **7**, 2951.
- 9 A. Dong, R. Tang and W. E. Buhro, *J. Am. Chem. Soc.*, 2007, **129**, 12254.
- 10 K.-J. Wu, K.-C. Chu, C.-Y. Chao, Y.-F. Chen, C.-W. Lai, C.-C. Kang, C.-Y. Chen and P.-T. Chou, *Nano Lett.*, 2007, **7**, 1908.
- 11 J. Lee, P. Hernandez, J. Lee, A. O. Govorov and N. A. Kotov, *Nat. Mater.*, 2007, **6**, 291.
- 12 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
- 13 Y. Yin and A. P. Alivisatos, *Nature*, 2005, **437**, 664.
- 14 A. M. Derfus, W. C. W. Chan and S. Bhatia, *Nano Lett.*, 2004, **4**, 11.
- 15 X. Michalet, F. F. Pinaud, L. A. Bentolilla, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir and S. Weiss, *Science*, 2005, **307**, 538.
- 16 Z. Peng and X. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 183.
- 17 L. Qu, Z. Peng and X. Peng, *Nano Lett.*, 2001, **1**, 333.
- 18 N. Pradhan, D. M. Battaglia, Y. Liu and X. Peng, *Nano Lett.*, 2007, **7**, 312.
- 19 N. Pradhan and X. Peng, *J. Am. Chem. Soc.*, 2007, **129**, 3339.
- 20 M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293.
- 21 N. Rosi and C. A. Mirkin, *Chem. Rev.*, 2005, **105**, 1547.
- 22 C. Loo, A. Lowery, N. Halas, J. West and R. Drezek, *Nano Lett.*, 2005, **5**, 709.
- 23 X. Huang, E. H. El-Sayed, W. Zian and M. A. El-Sayed, *J. Am. Chem. Soc.*, 2006, **128**, 2115.
- 24 J. Chen, D. Wang, J. Xi, L. Au, A. Siekkinen, A. Warsen, Z.-Y. Li, H. Zhang, Y. Xia and X. Li, *Nano Lett.*, 2007, **7**, 1318.
- 25 M. A. El-Sayed, *Acc. Chem. Res.*, 2001, **34**, 257.
- 26 *Metal Nanoparticles: Synthesis, Characterization and Applications*, ed. D. L. Feldheim and C. A. Foss Jr., Marcel Dekker, New York, 2002.
- 27 K. L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 668.
- 28 J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz and S. Schultz, *J. Chem. Phys.*, 2003, **116**, 6755.
- 29 I. O. Sosa, C. Nogues and R. G. Barrera, *J. Phys. Chem. B*, 2003, **107**, 6269.
- 30 C. J. Murphy, T. K. Sau, A. Gole, C. J. Orendorff, J. Gao, L. Gou, S. Hunyadi and T. Li, *J. Phys. Chem. B*, 2005, **109**, 13857.

- 31 M. S. Chen and D. W. Goodman, *Science*, 2004, **306**, 252.
- 32 M. D. Hughes, Y. Xu, P. Jenkins, P. McMorn, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnson, K. Griffin and C. J. Kiely, *Nature*, 2005, **437**, 1132.
- 33 S. Kanaoka, N. Yagi, Y. Fukuyama, S. Aoshima, H. Tsunoyama, T. Tsukudu and H. Sakurai, *J. Am. Chem. Soc.*, 2007, **129**, 12060.
- 34 S. F. Sweeney, G. H. Woehrlé and J. E. Hutchison, *J. Am. Chem. Soc.*, 2006, **128**, 3190.
- 35 J. Perez-Juste, I. Pastoria-Santos, L. M. Liz-Marzan and P. Mulvaney, *Coord. Chem. Rev.*, 2005, **249**, 1870.
- 36 C. J. Murphy, A. M. Gole, S. Hunyadi and C. J. Orendorff, *Inorg. Chem.*, 2006, **45**, 7544.
- 37 T. K. Sau and C. J. Murphy, *Philos. Mag.*, 2007, **87**, 2143.
- 38 B. Nikoobakht and M. A. El-Sayed, *Langmuir*, 2001, **17**, 6368.
- 39 T. K. Sau and C. J. Murphy, *Langmuir*, 2005, **21**, 2923.
- 40 C. J. Orendorff and C. J. Murphy, *J. Phys. Chem. B*, 2006, **110**, 3990.
- 41 E. E. Connor, J. Mwamuka, A. Gole, C. J. Murphy and M. D. Wyatt, *Small*, 2005, **1**, 325.
- 42 P. Raveendran, J. Fu and S. L. Wallen, *J. Am. Chem. Soc.*, 2003, **125**, 13940.
- 43 S. S. Shankar, A. Rai, B. Ankamwar, A. Singh, A. Ahmad and M. Sastry, *Nat. Mater.*, 2004, **3**, 482.
- 44 S. S. Shankar, A. Rai, A. Ahmad and M. Sastry, *Chem. Mater.*, 2005, **17**, 566.
- 45 B. Liu, J. Xie, J. Lee, Y. Ting and J. P. Chen, *J. Phys. Chem. B*, 2005, **109**, 15256.
- 46 R. Brayner, M.-J. Vaulay, F. Fievet and T. Coradin, *Chem. Mater.*, 2007, **19**, 1190.
- 47 N. Vigneshwaran, A. A. Kathe, P. V. Varadarajan, R. P. Nachane and R. H. Balasubramanya, *Langmuir*, 2007, **23**, 7113.
- 48 V. L. Colvin, *Nat. Biotechnol.*, 2003, **21**, 1166.
- 49 A. Hoshino, K. Fujioka, T. Oku, M. Suga, Y. F. Sasaki, T. Ohta, M. Yasuhara, K. Suzuki and K. Yamamoto, *Nano Lett.*, 2004, **4**, 2163.
- 50 A. M. Smith, H. Duan, M. N. Rhyner, G. Ruan and S. Nie, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3895.
- 51 P. Mulvaney, L. M. Liz-Marzan, M. Giersig and T. Ung, *J. Mater. Chem.*, 2000, **10**, 1259.
- 52 D. Gerion, F. Pinaud, S. C. Williams, W. J. Parak, D. Zanchet, S. Weiss and A. P. Alivisatos, *J. Phys. Chem. B*, 2001, **105**, 8861.
- 53 S. O. Obare, N. R. Jana and C. J. Murphy, *Nano Lett.*, 2001, **1**, 601.
- 54 S. E. Hunyadi and C. J. Murphy, *J. Phys. Chem. B*, 2006, **110**, 7226.
- 55 A. Gole and C. J. Murphy, *Chem. Mater.*, 2005, **17**, 1325.
- 56 W. W. Yu, E. Chang, J. C. Faulkner, J. Zhang, A. M. Al-Somali, C. M. Sayes, J. Johns, R. Drezek and V. L. Colvin, *J. Am. Chem. Soc.*, 2007, **129**, 2871.
- 57 T. B. Huff, M. N. Hansen, Y. Zhao, J.-X. Cheng and A. Wei, *Langmuir*, 2007, **23**, 1596.
- 58 N. S. Lewis, *Science*, 2007, **315**, 798.
- 59 C. T. Yavuz, J. T. Mayo, W. W. Yu, A. Prakash, J. C. Faulkner, S. Yean, L. Cong, H. J. Shipley, A. Kan, M. Tomson, D. Natelson and V. L. Colvin, *Science*, 2006, **314**, 964.
- 60 D. Rowe, *Science*, 2007, **317**, 323.
- 61 Y. Mai, T.-J. Park, F. Zhang, H. Zhou and S. S. Wong, *Small*, 2007, **7**, 1122.
- 62 S. Narayan, J. Muldoon, M. G. Finn, W. Fokin, H. C. Kolb and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2005, **44**, 3275.
- 63 M. A. Albrecht, C. W. Evans and C. L. Ralston, *Green Chem.*, 2006, **8**, 417.