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Communications to the Editor

Synthesis of Nanocrystalline Bismuth in Reverse Micelles

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Over the past decade, there has been a dramatic increase of interest in both the preparation and properties of nanocrystalline materials. This interest has been fueled by the unique properties that such materials possess when compared to bulk phases,[1] as well as the potential they hold for such varied applications as electronics,[2] catalysis,[3] and biological labeling.[4] The majority of the work in this field has focused on transition metal and semiconductor particles, with particular emphasis on gold[5] and II−VI compounds such as CdSe.[6] Although the formation of colloidal silicon[7] and germanium[8] nanoclusters has been studied, little work has been directed toward examining the preparation and fundamental properties of nanocrystalline main-group metals.

Recent theoretical studies suggest that bismuth materials of reduced dimensions may exhibit enhanced thermoelectric properties at room temperature.[9] Quantum confinement has already been exploited to increase the thermoelectric figure of merit, *ZT*, for PbTe[10] quantum well superlattices and an even larger thermoelectric effect might be achieved with bismuth under such dimensionally restricted conditions.[9a] The focus thus far has been on making these measurements on bismuth nanowires,[11] which possess diameters of 13−110 nm and lengths on the order of 10 μm.

Despite the enormous potential of this material for thermoelectric applications, little work has been directed toward the solution synthesis of nanocrystalline bismuth clusters. To the best of our knowledge, only one report exists of such material being prepared as a stable colloid,[12] and these clusters were prepared at very low concentrations in an aqueous polymer, making the isolation of significant quantities of such material difficult. In addition, the size of the nanocrystals was determined to be 8 or 12 nm, sizes which are large when compared to the smallest diameters of noble metal nanoclusters.[5] Very recently, the synthesis of nanocrystalline bismuth using an in situ polymerization process was reported;[13] however, the resulting particles were even larger (20 nm) and were also suspended in a polymer matrix. Although this polymer coating protects the particles from oxidation, it once again makes the further manipulation and characterization of the product difficult. The focus of our effort has been the isolation of macroscopic quantities of bismuth nanocrystals with diameters below 10 nm that could be obtained in a more easily manipulated form.

A variety of chemical methods have been reported in the literature for the preparation of noble metal nanoparticles, such as sonochemical reduction,[14] reduction in the presence of capping agents,[15] and reduction in inverse micelles.[16] We have recently examined a variety of reactions, in an attempt to prepare nanocrystalline bismuth clusters,[17] and have found difficulty in identifying a suitable capping agent. Traditional choices such as alkanethiols and TOPO have failed to provide proper control over both the nucleation and growth in our experiments with bismuth. Under proper conditions, however, the inverse micelle method has accomplished this.

The bismuth nanoclusters are prepared through reduction of an aqueous bismuth salt inside of AOT (dioctyl sulfosuccinate, sodium salt) reverse micelles. Briefly, AOT is dissolved in isooctane, and an appropriate amount of H_2O containing dissolved $BiOClO_4$ is added, forming the reverse micelles. A second micelle solution containing $NaBH_4$ dissolved in the aqueous phase is prepared at an identical *w* value (where $w = [H_2O]/[AOT]$), and the two solutions are combined under Ar. Within minutes, the clear and colorless solution darkens to a deep brown color. Prolonged stirring (on the order of hours) at room temperature results in the gradual precipitation of elemental bismuth. After several minutes, the solvent is removed in vacuo, and the resulting solid dried under vacuum and redispersed in toluene. The mixture is centrifuged to remove the insoluble solids, leaving a dark solution that contains the bismuth nanoclusters. The excess surfactant is removed by addition of MeOH, which causes precipitation of the AOT-capped bismuth particles and allows

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[†] Code 6371.

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(1) See for example the following: (a) Alivisatos, A. P. *Science* **1996**, *271*, 933. (b) Brust, M.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. *Adv. Mater.* **1995**, *7*, 795.

(2) (a) Narayan, K. S.; Manoj, A. G.; Nanda, J.; Sarma, D. D. *Appl. Phys. Lett.* **1999**, *74*, 871. (b) Schlamp, M. C.; Peng, X.; Alivisatos, A. P. *J. Appl. Phys.* **1997**, *82*, 5837. (c) Dabbousi, B. O.; Bawendi, M. G.; Onitsuka, O.; Rubner, M. F. *Appl. Phys. Lett.* **1995**, *66*, 1316. (d) Schön, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 101.

(3) (a) Aiken, J. D.; Finke, R. G.; *J. Am. Chem. Soc.* **1999**, *121*, 8803. (b) Klingelhöfer, S.; Heitz, W.; Greiner, A.; Oestreich, S.; Förster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10116.

(4) (a) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013. (b) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016.

(5) For examples of work with Au, see the following and the references therein: (a) Rao, C. N. R.; Kulkarni, G. U.; Thomas, P. J.; Edwards, P. P. *Chem. Soc. Rev.* **2000**, *29*, 27. (b) Loweth, C. J.; Caldwell, W. B.; Peng, X.; Alivisatos, A. P.; Schultz, P. G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1808. (c) Hostetler, M. J.; Murray, R. W. *Curr. Opin. Colloid Interface. Sci.* **1997**, *2*, 42.

(6) For examples of work with CdSe, see the following and the references therein: Green, M.; O'Brien, P. *J. Chem. Soc., Chem. Commun.* **1999**, 2235.

(7) (a) Yang, C. S.; Bley, R. A.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *J. Am. Chem. Soc.* **1999**, *121*, 5191. (b) Bley, R. A.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **1996**, *118*, 12461.

(8) (a) Taylor, B. R.; Kauzlarich, S. M.; Delgado, G. R.; Lee, H. W. H. *Chem. Mater.* **1999**, *11*, 2493. (b) Taylor, B. R.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *Chem. Mater.* **1998**, *10*, 22.

(9) (a) Dresselhaus, M. S.; Dresselhaus, G.; Sun, X.; Zhang, Z.; Cronin, S. B.; Koga, T. *Phys. Solid State* **1999**, *41*, 679. (b) Hicks, L. D.; Harman, T. C.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1993**, *63*, 3230. (c) Hicks, L. D.; Dresselhaus, M. S. *Phys. Rev. B* **1993**, *47*, 12727.

(10) Hicks, L. D.; Harman, T. C.; Sun, X.; Dresselhaus, M. S. *Phys. Rev. B* **1996**, *53*, R10493.

(11) Zhang, Z.; Gekhtman, D.; Dresselhaus, M. S.; Ying, J. Y. *Chem. Mater.* **1999**, *11*, 1659.

(12) Gutierrez, M.; Henglein, A. *J. Phys. Chem.* **1996**, *100*, 7656.

(13) Fang, J.; Stokes, K. L.; Wiemann, J.; Zhou, W. *Mater. Lett.* **2000**, *42*, 113.

(14) (a) Suslick, K. S.; Fang, M.; Hyeon, T. *J. Am. Chem. Soc.* **1996**, *118*, 11960. (b) Suslick, K. S.; Fang, M.; Hyeon, R.; Cichowlas, A. A. *Mater. Res. Soc. Symp. Proc.* **1994**, *351*, 443.

(15) (a) Yee, C.; Scotti, M.; Ulman, A.; White, H.; Rafailovich, M.; Sokolov, J. *Langmuir* **1999**, *15*, 4314. (b) Sun, S.; Murray, C. B. *J. Appl. Phys.* **1999**, *85*, 4325. (c) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.

(16) (a) Carpenter, E. E.; Seip, C. T.; O'Connor, C. J. *J. Appl. Phys.* **1999**, *85*, 5184. (b) Pileni, M. P. *Cryst. Res. Technol.* **1998**, *33*, 1155. (c) Pileni, M. P. *Langmuir*, **1997**, *13*, 3266.

(17) (a) Foos, E. E.; Berry, A. D.; Snow, A. W.; Armistead, J. P. *Mater. Res. Soc. Symp. Proc.* **1999**, *581*, 53. (b) Foos, E. E.; Berry, A. D.; Snow, A. W.; Armistead, J. P. *MRS Fall Meeting Abstracts*, **1999**, F8.22.

(18) Creighton, J. A.; Eadon, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3881.

10.1021/ja001118i CCC: $19.00

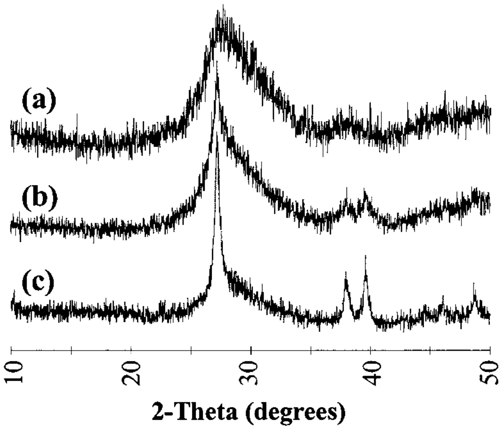

Figure 1. XRD patterns of (a) soluble nanocrystalline Bi ($w = 2$ reaction); (b) insoluble nanocrystalline Bi; (c) insoluble nanocrystalline Bi after annealing (200−260 °C).

them to be isolated as a waxy solid that can be dissolved in a variety of nonpolar solvents, forming dark brown solutions. These solutions are stable for several months at ambient conditions, with no special precautions necessary to protect them from oxygen or light. Using this procedure, it is possible to isolate up to 50 mg of nanocrystalline bismuth powder from a single 2.00 mmol scale reaction.

As the soluble material is washed with MeOH, the capping AOT groups are gradually removed and an insoluble black powder is isolated, a process which has been observed by FTIR. The initial (soluble) material shows several strong absorbances that correspond well with pure AOT. As this material is gradually washed from the surface, the peaks diminish in intensity. After approximately 10 washings, it appears that a small amount of AOT is still left on the surface and is responsible for protecting the particles from rapid oxidation. Results of elemental analyses (EA) on these samples are consistent with the infrared spectra. The soluble material contained 52.96% Bi and a significant amount of C (23.15%) and H (3.60%), along with several other elements (Na, 2.87%; Cl, 0.95%). The insoluble material washed 10 times with MeOH contained 95.35% Bi and considerably reduced quantities of C (4.00%) and H (0.59%). Thermogravimetric analysis (TGA) of the soluble material indicates a significant weight drop beginning about 300 °C, which is attributed to loss of the AOT. Powder X-ray diffraction (XRD) analysis of the black powder left on the pan after cooling to room temperature under nitrogen confirms the presence of elemental bismuth.

Powder XRD analysis of both the soluble and insoluble material shows a single, well-defined and extremely broad peak corresponding to the (012) reflection of rhombohedral bismuth, as seen in Figure 1a and b. Estimation of the approximate average particle size using the Scherrer equation leads to a calculated value of 2 nm, slightly smaller than observed by TEM (vide infra). Annealing the insoluble powder under Ar (at 200−260 °C) results in a sharpening of this main peak, as well as the appearance of peaks assigned to the (104) and (110) reflections, consistent with the presence of elemental bismuth as shown in Figure 1c.

To further characterize the size and crystal structure of the particles, the soluble products have also been examined using TEM. Bright-field images of the particles are shown in Figure 2a−c. The average particle size for each sample (mean ± 1 standard deviation, approximately 50 particles counted) is: $w = 1$, 3.2 ± 0.35 nm; $w = 2$, 6.9 ± 2.2 nm; $w = 3$, 8.0 ± 2.7 nm. High-resolution lattice images of each of the samples exhibit fringes ($d = 0.395$, 0.328 nm) that index to the (003) and (102) spacings of rhombohedral bismuth, respectively. Figure 2d shows a particle from the $w = 3$ sample imaged along a [241] zone. The composition of the particles was verified by energy-dispersive X-ray analysis, which showed only the presence of C and Cu (from the sample grid) and Bi; no oxygen peak was observed.

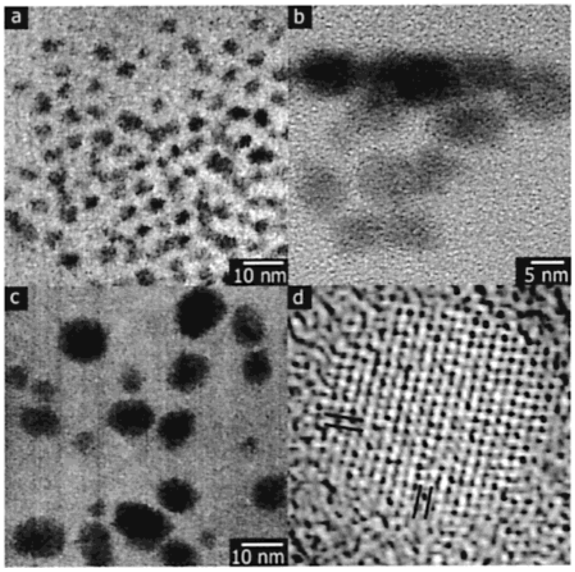

Figure 2. TEM of soluble Bi particles. (a) $w = 1$; (b) $w = 2$; (c) $w = 3$; (d) lattice image of a particle from the $w = 3$ sample, imaged along a [241] zone. The parallel lines indicate 0.328 nm, (102)-type spacings.

A maximum is seen in the UV/vis spectra of these clusters at approximately 196 nm, with no apparent change in the spectra between the $w = 1$, 2, and 3 samples. Gutierrez and Henglein have reported the only UV/vis data in the 200−700 nm region for colloidal bismuth,[12] as well as a calculated spectrum in the same region based on Mie theory. They report a maximum at 253 nm, and while our results do not show this absorbance, they are in good agreement with the theoretical spectrum above 200 nm and with a similarly calculated spectrum for colloidal bismuth reported elswhere.[18]

In summary, using the inverse micelle technique we have prepared nanocrystalline bismuth clusters exhibiting domain sizes of less than 10 nm, which fall well below the size range that has been obtained using other synthesis methods reported to date. The clusters can be isolated as stable colloidal material or, through repeated washing, as an air-stable powder. Further experiments into the potentially interesting properties of this material are currently underway.

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Supporting Information Available: Full details of the synthesis as well as FTIR, TGA, and UV/vis data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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