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Metathetical Conversion of Nd_2O_3 Nanoparticles into NdS_2 Polysulfide Nanoparticles at Low Temperatures Using Boron Sulfides

Li-Ming Wu,[†] Renu Sharma,[‡] and Dong-Kyun Seo*,[†]

Department of Chemistry and Biochemistry, Arizona State University,
Tempe, Arizona 85287-1604, and Center for Solid State Science, Arizona State University,
Tempe, Arizona 85287-1704

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A new simple metathetical sulfidation method using boron sulfides has been developed to prepare nanoparticles of NdS_2 via conversion of ca. 50-nm-sized nanoparticles of Nd_2O_3 at 450 °C, in which boron and sulfur powders form boron sulfides in situ and evaporate to sulfidize the oxide. The X-ray powder diffraction analysis revealed that the products were purely NdS_2, and the atomic absorption spectrometric analysis confirmed nonexistence of boron in the products after washing with water. The detailed TEM studies showed that the NdS_2 nanoparticles maintained the original size of the oxide particles without fusion during the low-temperature sulfidation process.

Metal sulfides are widely used in industrial applications, and various synthetic methods for the compounds have been reported in the literature for many decades.[1] Depending on the reaction conditions, the various synthetic methods utilize different sulfiding agents that include hydrogen sulfide (H_2S), carbon disulfide (CS_2), alkali-metal sulfides (A_2S; A = alkali metal), and sulfur-containing organic compounds. However, recent interest in nanostructured materials and their potential use has prompted further exploration of other synthetic routes that are particularly useful in tailoring the sizes and shapes of the solid state materials.[2]

Despite the variety of the existing sulfiding agents, we believe that it is worth exploring new agents that may lead to new synthetic methodologies, and our recent research has been focused on boron sulfides. To date, boron sulfides (B_2S_3, BS_2, and nonstoichiometric compounds with intermediate B/S ratios) have not been familiar in solid state syntheses other than for preparations of thioborates,[3] and their use for sulfidation has been reported only in organic or organometallic reactions, yet sporadically.[4] The sulfides do not have a well-defined melting point, but they begin to sublime at about 300 °C under vacuum from our experience as well as that of others.[5] Previous studies concluded that stoichiometric $B_2S_3(s)$ vaporizes congruently to give $B_2S_3(g)$ and its polymers, while sulfur-rich samples vaporize incongruently into $(BS_2)_n(g)$ and $(B_2S_3)_n(g)$.[6] The corrosive nature of the gaseous boron sulfides reported in the literature is probably the main reason for their scarce use in solid state reactions, and indeed, the silica reaction vessels need to be heavily carbon-coated for the synthesis of alkali thioborates which is carried out typically above 600 °C for several days.[3]

For sulfidation reactions, however, the corrosiveness of the gaseous boron sulfides could be advantageous, especially under low-temperature reaction conditions which are often required in preparation of nanostructured materials. Furthermore, the boron sulfides on the sulfur-rich end may allow us to access the polysulfide compounds that exist only at low temperatures and decompose at elevated temperatures.[7] To probe new opportunities for boron sulfide chemistry, we chose rare-earth disulfides for our first test examples, because

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* To whom correspondence should be addressed. E-mail: dseo@asu.edu.
[†] Department of Chemistry and Biochemistry.
[‡] Center for Solid State Science.

(1) See for example: (a) *Sulfur. Its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology*; Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, 1984. (b) *Transition Metal Sulfur Chemistry; Biological and Industrial Significance*; Stiefel, E. I., Matsumoto, K., Eds.; ACS Symposium Series 535; American Chemical Society: Washington, DC, 1996.

(2) See for example: (a) Alivisatos A. P. *Science* **1996**, *271*, 933. (b) Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. *Science* **1995**, *267*, 222. (c) Mdleleni, M. M.; Hyeon, T.; Suslick, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 6189. (d) Wilcoxon, J. P.; Samara, G. A. *Phys. Rev. B* **1995**, *51*, 7299. (e) Zelenski, C. M.; Dorhout, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 734. (f) Che, G.; Jirage, K. B.; Fisher, E. R.; Martin, C. R. *J. Electrochem. Soc.* **1997**, *144*, 4296.

(3) Conrad, O.; Jansen, C.; Krebs, B. *Angew. Chem., Int. Ed.* **1998**, *37*, 3209 and references therein.

(4) See for example: (a) Schumaker, R. R.; Engler, E. M. *J. Am. Chem. Soc.* **1977**, *99*, 5521. (b) Callahan, K. P.; Durand, P. J. *Inorg. Chem.* **1980**, *19*, 3211. (c) Eagle, A. A.; Tiekink, E. R. T.; George, G. N.; Young, C. G. *Inorg. Chem.* **2001**, *40*, 4563 and references therein.

(5) *Ullmann's Encyclopedia of Industrial Chemistry*; Gerhartz, W., Yamamoto, Y. S., Campbell, F. T., Pfefferkorn, R., Rounsaville, J. F., Eds.; VCH Publishers: Weinheim, 1985; Vol A4; p 315.

(6) Chen, H.-y.; Gilles, P. W. *J. Am. Chem. Soc.* **1970**, *92*, 2309.

(7) While most of known rare-earth and transition-metal sulfides are practically insoluble in water and/or alcohols, B_2O_3, the reaction byproduct, absorbs moisture in air to form H_3BO_3 which is soluble at room temperature in water (10−50 g/L), methanol (200 g/L), glycerol (280 g/L), and 95% ethanol (<1 g/L) and, hence, can be washed away in those solvents: *CRC Handbook of Chemistry and Physics*, 67th ed.; Weast, R. C., Astle, M. J., Beyer, W. H., Eds.; CRC Press: Boca Raton, FL, 1986.

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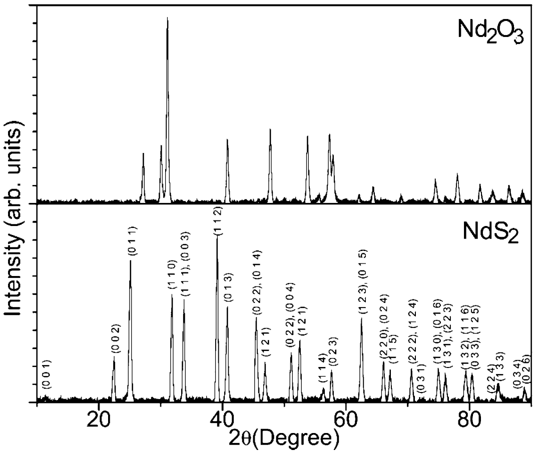

Figure 1. Powder XRD patterns of the Nd_2O_3 and NdS_2 nanoparticles.

(1) their previously reported syntheses require relatively high temperatures,[8] and (2) nanostructures of the compounds have not been reported in the literature, to our knowledge. The reaction of La and Nd oxides with H_2S begins at 700 °C,[9] and the reaction temperature could be lowered only to 500 °C under a high-pressure condition.[10] Crystals of the rare-earth disulfides formed when the corresponding sesquisulfides were treated with elemental sulfur over 600 °C.[11] In this Communication, we report a simple "one-step" low-temperature synthesis of NdS_2 nanoparticles via sulfidation of Nd_2O_3 nanoparticles by employing the boron sulfides.

First, 0.337 g (1 mmol) of Nd_2O_3 powder (99.9%, 49−64 nm, Nanostructured & Amorphous Materials Inc.) was placed in a short fused silica tube. Excess amounts of amorphous boron (99.99%, 325 mesh, Alfa Aesar) and sulfur powders (99.999%, Alfa Aesar) were mixed in the ratio of 1:4 and placed in a separate fused silica tube of the same size. The two tubes were subsequently situated inside a larger silica tube container, with the tube of Nd_2O_3 on top of the other. After the whole container was evacuated and flame-sealed, it was gradually heated to 450 °C, kept at the temperature for 1 day, and radiatively cooled to room temperature. The pale violet color of the original oxide powder turned into grayish yellow after the reaction. The silica reaction tubes were intact, and there was no visible indication of corrosion on the inner surface of the tubes. Figure 1 compares the powder X-ray diffraction (XRD) patterns of the original Nd_2O_3 particles and our reaction product NdS_2 and indicates that the Nd_2O_3 was completely converted into an X-ray pure NdS_2 product.

Later reactions with various boron−sulfur mixtures with higher or lower sulfur contents all provided the disulfide without any other sulfides, and we found unreacted boron powder in the lower silica tube after most of our reactions. These observations imply that the gaseous boron sulfides are polysulfidic in nature. It is known in the literature that complete reactions of boron and sulfur require much higher reaction temperatures and prolonged reaction time.[12] Using only elemental sulfur as a sulfiding agent under the same reaction conditions provided no sulfides, but a small amount of Nd_2O_2S and mostly unreacted oxide in the reaction products. This indicates that the initial formation of boron sulfides is essential for the sulfidation of Nd_2O_3. Overall reaction occurs as follows:

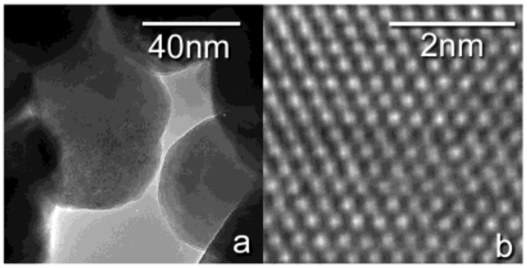

Figure 2. HRTEM micrographs of the Nd_2O_3 nanodisks (starting material). Part b is a zoomed image around the center of part a.

$$Nd_2O_3 + 2B + 4S \rightarrow 2NdS_2 + B_2O_3$$

Unreacted sulfur, boron sulfides, and the byproduct B_2O_3 were washed away from the product by using CS_2 and deionized water, and the filtered powder sample was found to be boron-free on the basis of our atomic absorption spectrometric analysis within the detection limit (5 ppm) of the instrument (Varian SpectrAA-400 Flame). Samples for high-resolution transmission electron microscopy (HRTEM) studies were prepared by dispersing a few drops of the suspensions of this powder and Nd_2O_3, respectively, in deionized water on holey carbon grids. A JEOL 4000 EX transmission electron microscope (TEM), operated at 400 kV (1.7 Å point resolution), was used to obtain HRTEM images. The crystals were oriented along various zone axes using a double-tilt stage, and HRTEM images were recorded on photographic films.

Comparison of the HRTEM images of both the Nd_2O_3 starting material and our NdS_2 product revealed that the original size and shape of the Nd_2O_3 were well maintained after the sulfidation process as shown in the representative images (Figures 2a and 3a). The disklike shape of both Nd_2O_3 and NdS_2 nanoparticles could be from the layerlike nature of the structures of the two compounds.[13,14] Indeed, a closer look perpendicular to the Nd_2O_3 nanodisks, i.e., along the $\langle 001 \rangle$ direction (Figure 2b), reveals a hexagonal symmetry that reflects the atomic arrangement in the *ab*-plane of the Nd_2O_3 structure.[13] The measured repeat distances (3.8 Å along the two in-plane axes) are in good agreement with the reported value of the bulk structure ($a = 3.83$ Å). Meanwhile, the corresponding HRTEM images of the NdS_2 nanodisks oriented along the $\langle 001 \rangle$ direction (Figure 3b) reveal atomic positions well arranged in a square lattice with a repeat

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(8) Vasilyeva, I. G. Polysulfides. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Lander, G. H., Eds.; Elsevier: Amsterdam, 2001; Vol. 32 and references therein.

(9) Aloman, A. *Rev. Chim. (Bucharest)* **1968**, *19*, 507.

(10) Le Rolland, B.; Molinié, P.; Colombet, P.; McMillan P. F. *J. Solid State Chem.* **1994**, *113*, 312.

(11) Flahaut, J.; Guittard, M. *C. R. Acad. Sci., Ser. C* **1957**, *245*, 2291.

(12) Martin, S. W.; Bloyer, D. R. *J. Am. Ceram. Soc.* **1990**, *73*, 3481.

(13) Boucherle, J. X.; Schweizer, J. *Acta Crystallogr., Sect. B* **1975**, *31*, 2745.

(14) Eliseev, A. A.; Uspenskaya, S. I.; Fedorov, A. A. *Zh. Neorg. Khim.* **1971**, *16*, 1485.

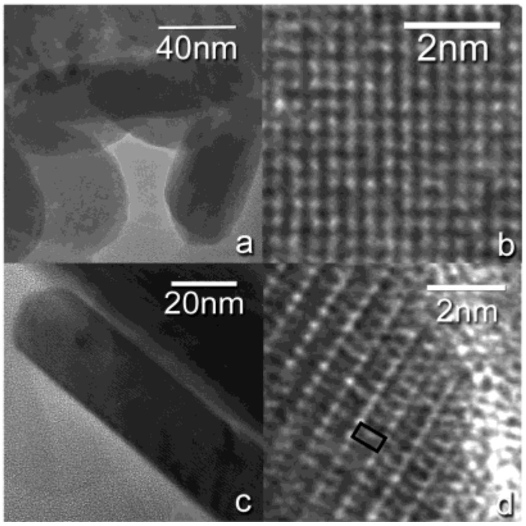

Figure 3. HRTEM micrograph of NdS_2 nanoparticles (product). Part b is a representative zoomed image from the top of the disks in part a. (c) Side view of an NdS_2 nanodisk. (d) Representative zoomed image of the side of NdS_2 nanodisk around a corner.

distance of 4.0 Å which is consistent with the *a*-spacing (4.022 Å) of the unit cell of the bulk NdS_2.[14] In Figure 3c, a nanocrystal with thickness of ca. 30 nm is oriented along the ⟨010⟩ direction, and the high magnification image is shown in Figure 3d. The measured repeat distances of the two-dimensional rectangular unit cell in Figure 3d, 4.0 and 8.0 Å, are consistent with *a* (or *b*) and *c* unit cell parameters of the bulk NdS_2 structure (4.022 and 8.031 Å, respectively).[15] It is probable that the same disklike shapes of the starting material and the final product are due to the similar type of the layered structures of Nd_2O_3 and NdS_2. We also made similar observations from our preliminary sulfidation reactions of nanoparticles of cubic-structured Eu_2O_3, Er_2O_3, and Sm_2O_3 compounds in which the isotropically shaped oxide particles transformed into disklike nanoparticles of the corresponding disulfides (isotypic with NdS_2).[16]

In conclusion, by employing boron sulfides as a sulfiding agent, we have successfully converted nanoparticles of Nd_2O_3 into nanoparticles of NdS_2 without any noticeable fusion of the particles at the unprecedented low temperatures. The new sulfidation reaction scheme does not require continuous flow or pressurization of sulfiding gases such as H_2S or elemental sulfur. This allows us to afford a much simpler experimental setup that is inherently safe from possible explosions or leakage of harmful gases. It may be possible that utilization of boron sulfides will provide an alternative route in preparing other nanosized metal sulfide materials that are not easy to prepare by other means.

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(15) Two polymorphs with slight distortions from the tetragonal structure have been reported for NdS_2, from single crystal X-ray crystallography studies. Our powder XRD and HRTEM studies did not distinguish the small distortions.

(16) Wu, L.-M.; Sharma, R.; Seo D.-K. In preparation.