Inorganic Chemistry

Photochemical Synthesis of Bismuth Selenide Nanocrystals in an Aqueous Micellar Solution

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The photolytic decomposition of triphenylbismuth and di-*tert*-butyl diselenide under aqueous micellar conditions yields 5-nm bismuth selenide nanocrystals of the BiSe stoichiometry. This is the first example of the bismuth-rich BiSe phase being prepared in a well-dispersed colloidal nanocrystal form.

Bismuth selenide Bi_2Se_3 is a small band gap semiconductor with a direct band gap, $E_g = 0.35$ eV,[1,2] that is of some interest for thermoelectric applications,[3] as a potential material for solar energy conversion[4] and as a 3D topological insulator with potential magnetoelectric, spintronic, and quantum-computing applications.[5,6] While the Bi_2Se_3 composition of bismuth selenide is the most studied, the Bi/Se ratio can actually vary over a wide range,[7] with bismuth-rich compositions closing the bandgap and producing a range of well-defined semimetals.[8] A series of hexagonal Bi_xSe_y phases are based on a structure layered along the crystallographic c axis, in which a selenium-faced, five-atom-thick layer of stoichiometry $(Bi^{3+})_2(Se^{2-})_3$ is regularly intercalated with two atomic layers of Bi^0.[7-9] The selenium-rich limit gives the well-known Bi_2Se_3 stoichiometry, which does not contain any Bi^0 layers. Periodic incorporation of Bi^0 layers into this structure results in materials with increasingly bismuth-rich stoichiometries, such as Bi_3Se_4 and BiSe. There are only a few references to BiSe in the literature, but it is known to have interesting properties. For example, BiSe is metallic within the atomic layers parallel to the crystallographic *ab* plane, but not in out-of-plane directions due to the interplanar van der Waals gaps.[9]

The direct combination of bismuth and selenium at high temperatures leads to bulk BiSe.[9,10] More recently, lower-temperature routes to BiSe have been found using single-source precursors. O'Brien et al. used $Bi[(SePPh_2)_2N]_3$ to produce nanocrystalline thin films,[11] while Kedarnath and co-workers employed bismuth tris(3-methylpyridine-2-selenoate) in the preparation of thin films and particulate BiSe architectures with overall micrometer dimensions.[12] While colloidal nanocrystals of Bi_2Se_3 have been produced in various forms using chemical reductants,[13-15] there is still much to be achieved in terms of developing solution-based routes to colloidal Bi_xSe_y nanocrystals with different stoichiometries and under mild reaction conditions.

In the past 10 years, there have been several reports of semiconductor nanocrystals being photochemically prepared at room temperature. These routes rely upon the photochemical decomposition of at least one precursor to initiate nucleation and growth of the nanocrystals. The most commonly used route involves the photochemical decomposition of chalcogen containing ionic precursors (e.g., $S_2O_3^{2-}$, $SeSO_3^{2-}$, SeO_3^{2-}) that then react with an appropriate metal cation.[16] There is one prior photochemical preparation of ~35 nm Bi_2Se_3 nanocrystals via the < 290 nm irradiation of aqueous Bi^{3+} and $SeSO_3^{2-}$ precursors.[17] Most recently, we have explored the utility of dialkyl dichalcogenides as precursors to semiconductor nanocrystals[18] and found that di-*tert*-butyl ditelluride was a convenient precursor to Te

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nanorods upon photolysis under aqueous micellar conditions.[19] Herein, we extend this work to allow for the photochemical synthesis of BiSe nanocrystals using di-*tert*-butyl diselenide in a related dispersion system.

Di-*tert*-butyl diselenide possesses a UV absorption band at 286 nm, with a molar extinction coefficient of 470 M^{-1} cm^{-1} at 254 nm (see Supporting Information, Figure S1a and Table S1) that makes it well suited for photolytic decomposition at that wavelength. Likewise, Ph_3Bi possesses strong UV absorption with broad shoulders at ca. 282 and 251 nm, and a molar extinction coefficient of 12 000 M^{-1} cm^{-1} at 254 nm (see Supporting Information, Figure S1b and Table S1). As such, the photochemical synthesis of BiSe nanocrystals was performed at 254 nm for 4 h with a deaerated solution containing Ph_3Bi (50.0 mg, 0.114 mmol), $^tBu_2Se_2$ (11.4 μL, 0.0570 mmol), 1-dodecylamine (100 mg, 0.540 mmol), Pluronic P-123 (5.0 mL; a triblock copolymer of approximate mean composition $EO_{20}PO_{70}EO_{20}$, where EO = oxyethylene and PO = oxypropylene), and deionized water (150 mL). The resulting colloidal suspension was dark brown due to broad adsorption throughout the visible region (see Supporting Information, Figure S1d). The colloidal suspension was stable for several months at room temperature under a nitrogen atmosphere.

The combination of Pluronic P-123 and 1-dodecylamine passivates the nanocrystal surface quite satisfactorily. This is evidenced by the small nanocrystal size (*vide infra*) and the long-term stability of the as-prepared nanocrystal suspension. These species likely bind to the semipolar surface of the BiSe nanocrystals through a double layer of the amphiphilic amine and/or triblock copolymer. The as-prepared nanocrystals were isolated by the addition of trioctylammonium bromide (TOAB) and 1-dodecanethiol in dichloromethane, followed by the addition of saturated aqueous Na_2SO_4 to lower the cloud-point of the Pluronic P-123 to below room temperature.[20] The surfactant and nanocrystals then readily pass into the organic phase. After washing and centrifugation, the isolated nanocrystals spontaneously redisperse in toluene or 1,2-dichloroethane upon gentle agitation. The recovered yield of the BiSe nanocrystals, based on isolation and calcination to 450 °C under N_2 to remove organics, was 45% of theoretical.

The powder X-ray diffraction (XRD) pattern (see Figure 1) of the BiSe nanocrystals was consistent with the hexagonal nevskite phase (JCPDF #00-029-0246). Energy dispersive X-ray spectroscopy was used to analyze the elemental composition of the BiSe nanocrystals (see Supporting Information, Figure S2). An analysis of eight randomly selected areas (each of several square micrometers) gave an average Bi/Se composition of 0.48:0.52. This experimentally determined $Bi_{0.48}Se_{0.52}$ elemental stoichiometry is consistent with the $Bi_{0.50}Se_{0.50}$ phase of bismuth selenide determined by XRD analysis.
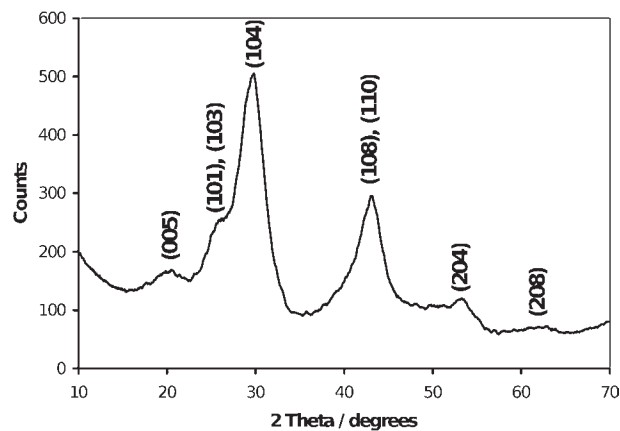

Figure 1. Powder XRD pattern of the hexagonal BiSe nanocrystals.

Transmission electron microscopy (TEM) revealed well-dispersed nanocrystals with semimajor axes of 4.7 ± 1.0 nm, but with evident differences in morphology (Figure 2a). High-resolution TEM (HR-TEM) images of apparent single-crystalline particles displayed (104) lattice planes (d = 0.30 nm, Figure 2c), and simultaneous (104) and (005) planes (d = 0.31 and 0.44 nm respectively; interplanar angle = 57.3°, Figure 2d). HR-TEM analyses on a large number of nanocrystals did not give any indication of the presence of more than one phase. Selected-area electron diffraction (SAED) gave two diffraction rings of observable intensity, with the most intense being indexed to (104) and the other to (110), analogous to the XRD data (Figure 2b).

As a consequence of the low enthalpy of the Bi−Ph bonds (ca. 194 kJ mol^{-1}),[21] Ph_3Bi is known to undergo photolytic bond homolysis to generate $Ph^\bullet$ and bismuth-centered radical species.[22] Under aqueous micellar conditions, photolysis of Ph_3Bi at 254 nm (photon energy = 471 kJ mol^{-1}) produces darkly colored suspensions that immediately bleach upon exposure to air. It is presumed that these are small, unprotected Bi nanocrystals that oxidize to form colorless bismuth oxide upon exposure to the air. Di-*tert*-butyl diselenide also possesses relatively weak Se−Se and Se−C bonds (ca. 170 and 240 kJ mol^{-1})[23] that can undergo bond homolysis to give Se and an organic byproduct.[24] Indeed, the photolytic decomposition of $^tBu_2Se_2$ at 254 nm under aqueous micellar conditions gives red amorphous Se that readily transforms to the crystalline gray allotrope after isolation and aging (see Supporting Information, Figure S3).

While it is clear that both Ph_3Bi and $^tBu_2Se_2$ absorb 254 nm photons, as demonstrated by the photolytic decomposition of each, the extinction coefficient for Ph_3Bi is 25.5 times higher than that of $^tBu_2Se_2$. Spectra taken of various combinations of surfactant, $^tBu_2Se_2$, and Ph_3Bi in aqueous micellar solution graphically illustrate this point (see Supporting Information, Figure S1c). The disparity in extinction coefficient suggests that in a 2:1 molar-ratio

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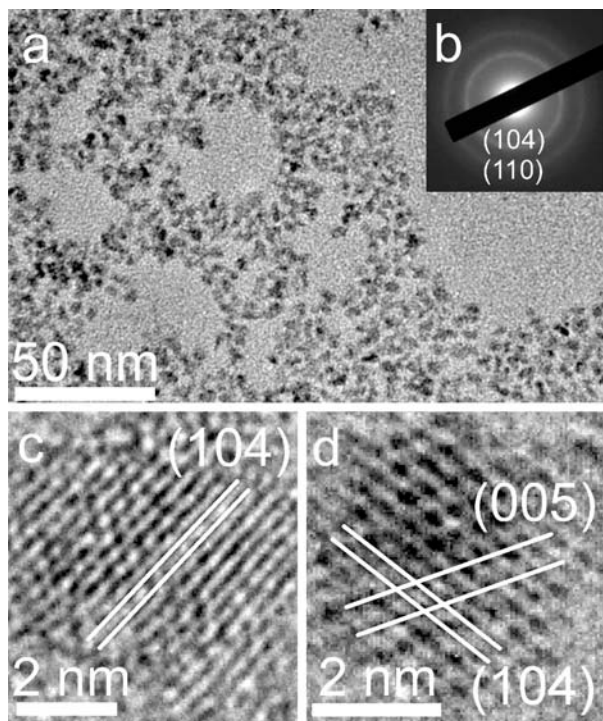(22) Hey, D. H.; Shingleton, D. A.; Williams, G. H. *J. Chem. Soc.* **1963**, 5612–5619.

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Figure 2. TEM analysis of the BiSe nanocrystals. (a) Low-resolution TEM image; (b) SAED pattern indexed to the hexagonal phase of BiSe; (c, d) HR-TEM images of single particles showing lattice fringes consistent with the hexagonal phase of BiSe.

mixture of the two, Ph_3Bi will absorb ~50 photons for each photon absorbed by $^tBu_2Se_2$, and thus the primary radical generation is likely dominated by Ph_3Bi photolysis. The photolytically generated reactive bismuth species (e.g., $Ph_2Bi^•$) will be rapidly intercepted by $^tBu_2Se_2$

concentrated in the micelle, to form Bi−Se complexes (e.g., $Ph_2Bi−Se^tBu$). Further photolysis of the intermediate complexes will homolytically split-off $R^•$ radicals, leading to further condensation and the ultimate formation of BiSe nanocrystals. A preferential photolytic decomposition of Ph_3Bi relative to $^tBu_2Se_2$ may explain why formation of the bismuth-rich BiSe phase occurs under these photolytic conditions. Moreover, to eliminate the possibility that Ph_3Bi and $^tBu_2Se_2$ react upon mixing to yield a single-source precursor, a control reaction (under ambient light, 25 °C) was performed whereby the two species were added to deuterochloroform. No reaction was observed by NMR spectroscopy (see Supporting Information, Table S2), which suggests no reaction occurs prior to photolysis and corroborates the UV−vis data.

In summary, we have presented a novel photochemical synthesis of well-dispersed 5-nm BiSe nanocrystals, a bismuth selenide stoichiometry not previously prepared in colloidal nanocrystal form. We employed lipophilic organo-element starting materials (i.e., Ph_3Bi and $^tBu_2Se_2$) that are known to undergo homolytic photolysis to produce BiSe nanocrystals without use of a chemical reductant. Future studies will focus on extending this photochemical synthesis utilizing dialkyl dichalcogenide precursors to the preparation of other semimetal and semiconductor nanocrystals.

Supporting Information Available: Experimental details; UV−vis data; EDX of BiSe; XRD of Se; control NMR reaction between Ph_3Bi and $^tBu_2Se_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.