

Highly Monodisperse Bismuth Nanoparticles and Their Three-Dimensional Superlattices

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Abstract: A simple and reproducible synthesis of highly monodisperse and ligand-protected bismuth nanoparticles (Bi NPs) is reported. The size of the single-crystalline and spherically shaped NPs is controlled between 11 and 22 nm mainly by the reaction temperature. The high uniformity of the NPs allows their self-assembly into long-range-ordered two- and three-dimensional superstructures.

Bulk Bi is a semimetal with a set of unique properties such as large Fermi wavelengths,¹ strong diamagnetism, and very high magnetoresistance.^{2a} Bi has been extensively studied for quantum-transport and finite-size effects.² Because of small effective carrier masses, a semimetal-to-semiconductor transition is expected in nanosized Bi. This transition is still a subject of controversy in many experimental and theoretical studies.³ In materials chemistry, Bi NPs are widely used for nanowire growth via the solution–liquid–solid (SLS) strategy.⁴ Bi NPs can also be utilized as intermediates in the synthesis of other nanostructured compounds of Bi, such as thermoelectric Bi₂Te₃.⁵

To date, the works of Buhro and co-workers⁶ represent the most successful preparations of Bi NPs in the size range 3–100 nm. The synthesis was tailored to provide the best catalyst for growing Cd chalcogenide and other nanowires, but the use of long-chain polymers as stabilizers hampers the utility of Bi NPs for other purposes. Alternative approaches either use Au seeds^{4a} or suffer from poor control of the size and morphology of the NPs.⁷ With the aim of developing a polymer-free yet well-controlled preparation of colloidally stable Bi NPs, we propose here a novel organometallic synthesis of ligand-protected Bi NPs with controlled sizes and high size uniformity (Figure 1). The NPs are single crystals and show a strong tendency to self-assemble into long-range-ordered superlattice structures.

In a typical synthesis of 17 nm Bi NPs,⁸ hexadecylamine (HDA, 20 g) was loaded into a three-neck flask and heated under vacuum at 100 °C for 30 min to dry the solution. In a glovebox, a precursor solution was prepared by combining bismuth(III) tris[bis(trimethylsilyl)amide],⁹ Bi[N(SiMe₃)₂]₃ (0.2 mmol, 0.14 g), and Li[N(SiMe₃)₂] (1 mmol, 0.17 g) in 2 mL of toluene. The Bi precursor solution was injected into the HDA at 130 °C, resulting in the instant nucleation of Bi NPs. After ~15 s, the solution was rapidly cooled to room temperature. Anhydrous toluene (20 mL) was added to the mixture during cooling at ~50 °C to prevent solidification of HDA. The Bi NPs were isolated by adding ethanol and centrifuging at 6000g. The

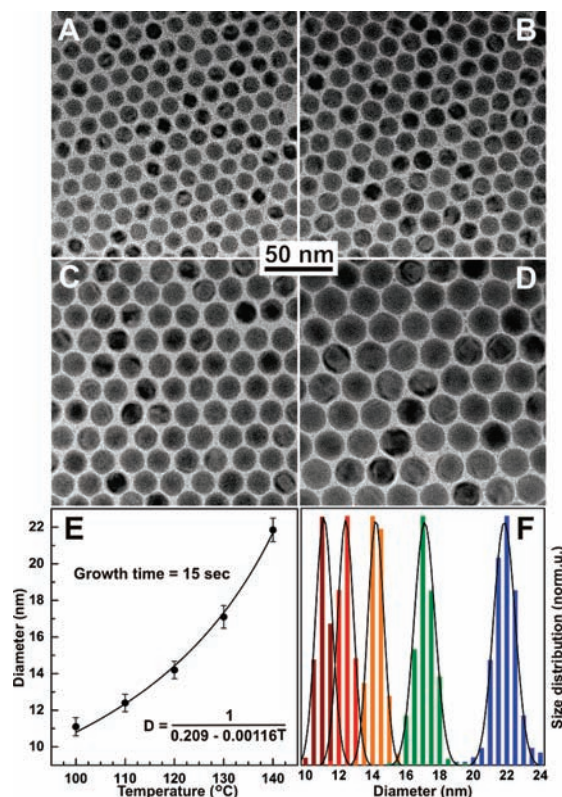


Figure 1. (A–D) TEM images of Bi nanoparticles of various sizes in the range 11–22 nm. (E) Experimentally derived dependence of the NP mean diameter on the injection temperature. (F) Examples of size histograms fitted by Gaussians to extract the size-distributions. It should be noted that all of the samples were prepared without size-selection procedures.

Bi NPs were redispersed in tetrachloroethylene (TCE) along with 0.1–0.2 mL of oleic acid (OA) and precipitated using ethanol. Finally, the Bi NPs were redispersed in common nonpolar solvents.

The Bi[N(SiMe₃)₂]₃ precursor was chosen on the basis of the prior success of the polymer-assisted synthesis by Buhro and co-workers.⁶ Thermolysis of Bi[N(SiMe₃)₂]₃ occurs presumably through homolytic cleavage of Bi–N bonds at ≥100 °C, resulting in the formation of elemental Bi. Optionally, Li(Et₃BH) can be added as a reducing agent to increase the reaction yield from 10–20 to 30–60%.⁸ HDA was chosen as both the solvent and a weakly binding surfactant. Notably, the use of strongly binding OA resulted in the formation of bismuth(III) oleate instead of elemental Bi. However, OA was used for postsynthetic surface modification to form long-term-stable colloidal solutions. Addition of Li[N(SiMe₃)₂] was found to be the most essential factor for growing monodisperse and nearly perfectly spherical Bi NPs

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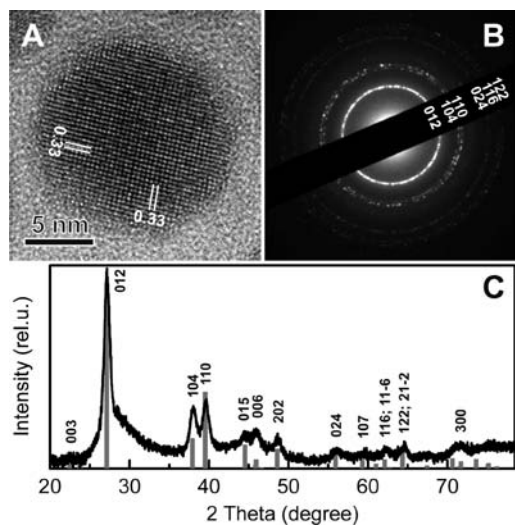


Figure 2. (A) HRTEM image of a single Bi nanoparticle viewed along the (221) direction. (B) SAED pattern taken from an ensemble of Bi NPs. (C) PXRD pattern for 14 nm Bi NPs.

[Figure S1 in the Supporting Information (SI)], which can be associated with the ability of $N(\text{SiMe}_3)_2$ groups to coordinate the surface Bi atoms. The reaction temperature was used as a main parameter for controlling the size of the Bi NPs (Figure 1E and Figure S2 and Table S1 in the SI). A detailed discussion of the synthetic conditions can be found in the SI. High-resolution transmission electron microscopy (HRTEM) images (Figure 2A) showed that each Bi NP is a single crystal. Selected-area electron diffraction (SAED) patterns (Figure 2B) and powder X-ray diffraction (PXRD) patterns (Figure 2C) were indexed to a rhombohedral crystal structure identical to that of bulk Bi (space group $R\bar{3}m$, $a = 0.4557$ nm, $c = 1.1862$ nm). The chemical purity of the Bi NPs was confirmed by energy-dispersive X-ray spectrometry (Figure S7).

Self-assembled two-dimensional (2D) and three-dimensional (3D) superstructures (superlattices) made from colloidal NPs have attracted broad interest within the last 10 years.¹⁰ In addition to their aesthetic beauty, these long-range ordered structures are expected to be useful for novel electronic and optoelectronic devices.^{10e} Recent studies of nanoparticle superlattices revealed various crystallographic aspects (defect formation, quasicrystalline ordering, binary and ternary structures, etc.)^{10a,c,11} similar to those found in atomic and ionic crystals. We found that Bi NPs exhibit a high tendency to form long-range-ordered 2D (Figure 1 and Figure S8) and 3D (Figure 3 and Figure S9) structures, which is a strong manifestation of their high uniformity and monodispersity. 3D colloidal crystals with a typical size of 10 to 50 μm were grown using a slow destabilization approach.¹² In this approach, the solution of Bi NPs was slowly destabilized by diffusion of a nonsolvent, leading to the evolution of interparticle interactions from strongly repulsive to attractive due to the change in solvent–ligand interactions.¹³ In a typical experiment, a TCE solution of NPs was placed in a vertically positioned glass tube and layered with toluene and butanol buffers and ethanol as a nonsolvent (top layer). The 3D crystals were collected from the tube walls after 2 weeks, suspended in ethanol, and deposited on Si substrates. Figure 3A presents a scanning electron microscopy (SEM) image of typical colloidal crystals, which mainly have hexagonal-prism, octahedral, or truncated-octahedron shapes. A single hexagonal plate and high-resolution image of its surface are shown in Figure 3B,C.

In summary, highly monodisperse Bi NP colloidal solutions have been developed. These materials can be used in the solution-based

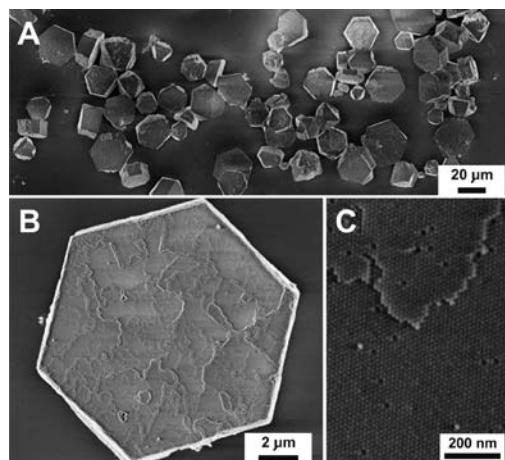


Figure 3. (A, B) SEM images of various colloidal crystals grown by slow destabilization of dispersions of Bi nanoparticles. (C) High-resolution SEM image of the superlattice surface shown in B.

catalytic growth of nanowires and as precursors for other Bi-based nanostructures. Highly ordered superlattice structures have been obtained from Bi NPs, which can be of interest for thermoelectric and magnetoresistance studies.

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Supporting Information Available: Detailed synthesis and characterization of materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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