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ABSTRACT: Bismuth pseudocubes were prepared by thermal decomposition of the novel subvalent metal organic precursor tetraethylbismuthine Bi$_2$Et$_4$ under kinetic control at low temperatures. The pseudocubes were characterized by XRD, SEM, HRTEM, EDX and SAED and the influence of the thermolysis temperature and of the capping agents NaN(SiMe$_3$)$_2$ and PVP* on the size- and shape-selective growth of these nanoparticles was investigated.

Introduction

Low-dimensional nanocrystals with at least one dimension between 1 and 100 nm have received growing interest over the last decade due to their potential technical applications in nano- and optoelectronic devices. The morphology of a nanosized single crystal was found to strongly influence its electrical, optical, and chemical properties. Therefore, size- and form-selective approaches for the synthesis of nanocrystals with desired morphologies such as nanowires, nanotubes or nano-helices have been intensely studied. These nanomaterials are usually synthesized by the so-called "bottom-up" approach, starting either with a defined molecular, often metal organic, precursor which is thermally decomposed at elevated temperature, by reduction of a specific inorganic precursor or by use of well-established polyol process. Anisotropic growth is often achieved by addition of a specific surfactant, that preferentially binds to suitable crystal faces of the growing particles. The inherent anisotropy of the crystal structure or crystal surface reactivity forces the low-dimensional growth.

Spherical bismuth nanoparticles have been studied in detail due to their capability to serve as catalyst for the solution-liquid-solid (SLS) growth of a variety of semiconductor quantum wires as was shown by Buhro and others. Moreover, bismuth is a semimetal with singular electronic transport properties that are related to the remarkably small carrier effective mass, the long carrier mean free path, and the very big Fermi wavelength. In particular the small electron effective mass makes bismuth an ideal material for quantum confinement effects. Nanoscale bismuth has been predicted to have enhanced thermoelectric properties. Unfortunately, metals with low melting points such as bismuth (mp = 273.15 °C) are typically obtained as spherical nanocrystals in solution-based processes since the thermal decomposition of the precursors mostly requires high temperatures, often close to their melting points. Therefore, non-spherical bismuth nanocrystals can only be synthesized at reaction temperatures significantly below its melting point. Anisotropically grown nanowires and nanotubes were obtained by hydrothermal reduction, polyl processes and by template assisted methods such as electrodeposition, pressure injection, or vapor phase deposition of bismuth into porous alumina templates. Moreover, almost monodisperse triangular nanoparticles were prepared by a simple thermal process. Buhro et al. demonstrated the crucial role of the capping agents NaN(SiMe$_3$)$_2$ and polyvinylpyrrolidone (PVP) on the size- and shapeselective synthesis of such nanoparticles. In addition, nanodisks were prepared by a solvent-free procedure. In contrast, the synthesis of isotropically grown bismuth nanocubes is almost unknown. This is in remarkable contrast to the well-established synthesis of nanocubes of typical fcc metals such as Ag, Au, Pd and Pt. Only Wang et al. reported on the synthesis of bismuth nanocubes with an edge-length of 60 to 80 nm using a specific polyl process. Careful adjustment of the molar ratio of PVP and Bi was found to be crucial.

We became only recently interested in the synthesis of non-spherical bismuth particles and investigated the thermal decomposition of low-valent organometallic bismuth complexes, which typically show significantly lower decomposition temperatures than bismuth trialkyls or bismuth trimides. We report herein on the shape-selective low-temperature synthesis of almost monodisperse (25 nm) bismuth pseudocubes using the novel subvalent organobismuth precursor Bi$_2$Et$_4$. No further
reductant is necessary. Moreover, the role of the reaction temperature as well as the presence of Na[N(SiMe$_3$)$_3$]$\_2$ and poly(1-vinylpyrrolidone)-graft-(1-triacontene) (PVP*) on the shape-selective growth of bismuth pseudocubes was investigated.

Experimental Section

**Materials.** Bi$_2$Et$_4$ was prepared according to a literature method.$^{3}$ Na[N(SiMe$_3$)$_3$]$\_2$ (Fluka) and PVP* (CAS 136445-69-7; Aldrich) were used as received. 1,3-dissopropylbenzene (DIPB) was purchased from Aldrich, carefully dried over Na/K alloy and degassed prior to use. All synthetic steps were performed in a glovebox under Ar atmosphere.

**Synthesis of Bi cubes.** Freshly prepared solutions of 0.184 g Na[N(SiMe$_3$)$_3$]$\_2$ in 1 mL of THF and 0.125 g PVP* in 10 mL of DIPB were combined. 85 µL Bi$_2$Et$_4$ was added at ambient temperature, spontaneously yielding an orange solution. After stirring for 4 h at 50 °C, a black (precipitate-free) solution was obtained. This solution was then heated to 170 °C for 12 h, resulting in the formation of a black-colored suspension, from which a small amount of an insoluble black precipitate was isolated by centrifugation. The remaining black solution, which is stable for weeks under Ar atmosphere, contained colloidal-dissolved Bi particles, which were isolated after addition of methanol and centrifugation. PVP* was removed by repeated (2-3 times) redispersion (CHCl$_3$), precipitation (MeOH) and centrifugation under Ar atmosphere in the glovebox.

**SEM Analysis.** Scanning electron microscope studies (SEM) were carried out either on a Jeol JSM6400F equipped with an energy dispersive X-ray spectroscopy (EDX) device (Noran Voyager, HPGc), a Zeiss Leo Supra55 (Bruker Si(Li)), an ESEM Quanta 400 FEG or a Jeol JSM 6510 (Bruker Quantax 400).

**TEM Analysis.** Transmission electron microscopy studies (TEM) were performed on a Philips CM30T (LaB$_6$-cathode) operated at 300 keV and equipped with an EDS-detector (ThermoScientific NSS) for EDS-analysis. The samples were prepared on perforated carbon foils without further grinding.

**X-ray Powder Diffraction (XRD).** XRD patterns were obtained using a Bruker D8 Advance powder diffractometer with Cu K$_\lambda$ radiation ($\lambda$: 1.5418 Å) and a digitized Philips PW1050 with secondary monochromator with Co K$_\lambda$ radiation ($\lambda$: 1.7903 Å), respectively.

Results and Discussion

Bismuth trialkyls BiR$_3$ are thermally robust, typically showing decomposition temperatures higher than 200 °C, which limit their capability to serve as molecular precursor for the synthesis of isotropically (e.g. cubes, spheres) and anisotropically (e.g. wires, tubes) grown nanostructured Bi nanoparticles. As a consequence, alternate precursors had to be developed. Buhro et al. demonstrated that Bi[N(SiMe$_3$)$_3$]$\_2$ containing less strong bismuth-nitrogen bonds, can be used for the synthesis of mono-dispersed, spherical Bi nanoparticles of different (controllable) sizes, which have been found to effectively catalyze the SLS growth of several semiconductor quantum wires and rods, whose diameter is controlled by the size of the initiating Bi nanoparticle. In addition, Bi nanolopates and nanoribbons have been prepared by careful adjustment of the specific reaction conditions. We became interested in alternate, thermally less stable, metal organic precursors and focused on the use of low-valent dibismuthines of the general type Bi$_2$R$_4$. These are known to undergo disproportionation reactions with subsequent formation of elemental Bi and BiR$_4$, due to the weak bismuth-bismuth bond, hence allowing the synthesis of elementary bismuth at low temperatures without the use of any additional reductant. Bi$_2$Et$_4$ for instance was described to start to decompose in solution above 0 °C.$^{10}$

![Figure 1](image)

**Figure 1.** DSC of Bi$_2$Et$_4$ (red curve) proving the decomposition to start at about 60 °C with formation of Bi and BiEt$_3$, which shows a decomposition onset temperature of about 170 °C (Figure 1).

![Figure 2](image)

**Figure 2.** EDX spectrum of insoluble black precipitate formed at 170 °C.

Since the decomposition of Bi$_2$Et$_4$ in solution occurs at even lower temperature, the initial thermal decomposition of Bi$_2$Et$_4$ was performed at 50 °C within 4 h, hence resulting in the formation of a black solution. It should be noted that bismuth...
nanoparticles were previously synthesized at low-temperature (80 °C), but no size- and shape-control was achieved.\textsuperscript{31} The resulting black solution was then heated for additional 12 h at 170 °C, at which BiEt\textsubscript{3} also decomposes. A small amount of insoluble black solid was formed, which was isolated by centrifugation at 2000 RPM and washed with CHCl\textsubscript{3}.

According to EDX (Figure 2) and XRD (Figure 3) studies, these particles are pure, crystalline bismuth. All the reflection peaks in the XRD diffractogram can be indexed to rhombohedral bismuth.

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SEM analysis of this precipitate clearly showed the formation of a mixture of large (truncated) Bi cubes and Bi octahedrons, whose size ranges from 200 to 300 nm (Figure 4). These results were confirmed in the TEM studies, according to which these particles, which mostly show a cubic, truncated cubic or octahedral shape, are 200 to 300 nm in size (Figure 5). Unfortunately, these particles are too large to obtain any HRTEM picture. However, selected area electron diffraction (SAED) (Figure 6) and EDX studies clearly revealed the formation of crystalline Bi particles.

The black solution remaining after centrifugation of the insoluble large Bi nanoparticles contained colloidal-dissolved Bi nanocubes. These were isolated after repeated (3x) addition of methanol, centrifugation and redispersion in CHCl\textsubscript{3}. TEM analysis clearly proved that these particles are slightly truncated, almost monodisperse Bi nanocubes of about 25 nm in size (Figure 7).

Bismuth is a non-fcc metal which typically crystallizes in the rhombohedral (trigonal) space group R-3m (JCPDS 05-0519). However, in order to rule out the formation of cubic bismuth, which is a high-pressure phase,\textsuperscript{32,33} we carefully investigated the crystallography of the cubic-shaped nanocrystals. The SAED of a large number of these nanocubes has a similar pattern and the same d-values as the pattern shown in Figure 6. Thus, the bis-
muth nanocubes have a rhombohedral crystal system. HRTEM studies (Figure 8) clearly showed that the cube-like shape of the crystalline Bi nanoparticles is in no terms related to a cubic-phase structure. The d-spacings of a power spectrum (FFT) of the HRTEM micrograph (Figure 8) correspond very well with values as-reported for crystalline rhombohedral bismuth and confirmed the single crystal nature of the cube-shaped particles. Indexing of the FFT reveals the [241] zone axis orientation of rhombohedral bismuth. The angle between the {012} and {112} type of lattice planes is measured to 87.5° and thus deviates slightly from a 90° angle.

**Figure 8.** HRTEM micrograph of a bismuth nanocube obtained at 170 °C in [241] zone axis orientation. The indexed FFT of the crystal is shown on the right hand side (top) and a Bragg filtered image of the boxed area with pseudocubic symmetry is shown below. The 330 pm d-spacing stems from {012} lattice planes of rhombohedral bismuth.

**Figure 9.** Relation between lattices in rhombohedral bismuth. (blue: pseudo cubic F, yellow: rhombohedral, red: hexagonal R. The miller indices correspond to the pseudo cubic F cell.

The bismuth crystals are bound by {012} facets, whose planes are nearly perpendicular (interplanar angles 87.6°, calculated from ICSD-64703), which explains the - at the first glance cubic - morphology. The rhombohedral lattice of bismuth is remarkably close to cubic symmetry since the angles of its unit cell are 57.23° (ICSD-616526) compared to 60° of a cubic cell in rhombohedral representation. Alternatively the c/a ratio of the hexagonal R representation may be compared to a cubic system (see also Gurlo et al. [62]), for the relation between cubic F, rhombohedral and hexagonal R lattices see Figure 9). The c/a ratio of a hexagonal R representation of a cubic F lattice is approx. 2.449 (square root of 6: length of the body diagonal of a cube divided by half its face diagonal as shown in Figure 9). For bismuth the ratio is 2.6.

The preferred formation of {012} facets possibly indicates that the capping agents PVP and/or NaN(SiMe3)2 most strongly bind to these facets (see also section: Possible growth mechanism). Our experimental diffraction data do not give any evidence for the initial formation of cubic-phase bismuth nanoparticles, which might be the thermodynamically most stable phase. Starting from such cubic bismuth seeds, the formation of rhombohedral bismuth would also be possible by a surface-pressure-driven process.

The final shape of a crystal is determined either by the ratio of the growth rates or by the ratio of the lattice energy of the individual planes. Planes with a high translational velocity during the growth will vanish, thus crystals are bound by facets of a slow growth velocity. The {014} facets of the bismuth pseudocubes are smaller than the {012} facets, so the growth direction is {014}. One can assume the {001} direction of rhombohedral as the growing direction with the highest velocity as well, but unfortunately they are not present in the observed crystal orientations. The {001} planes are hexagonal closed packed and should have the lowest surface energy. A binding of capping agents to the {012} facets would enhance the formation of pseudocubes.

**Role of reaction temperature.** The reaction temperature of 170 °C as applied in these studies also resulted in the decomposition of initially formed BiEt3. In order to prove if pseudocubic bismuth nanoparticles are also formed at lower temperatures and to verify the role of BiEt3 on their formation, BiEt3 was injected into a preheated solution (100 °C) of PVP and NaN(SiMe3)2 in DIPB and stirred for 4 h. At this temperature, BiEt3 will not decompose. A black precipitate was formed, which was isolated by centrifugation. The remaining yellow solution did not contain any colloidal-dissolved bismuth particles. The black precipitate was shown to consist of large crystalline bismuth particles of about 200 nm in size (Figure 10).

**Figure 10.** SEM photographs of precipitated Bi pseudocubes formed at 100 °C in the presence of PVP and NaN(SiMe3)2 after 4 h.

In contrast, when BiEt3 was injected into a preheated solution (170 °C) of in PVP, NaN(SiMe3)2 and DIPB and stirred
for 12 h, large bismuth pseudocubes as well as large spherical particles were formed and isolated by centrifugation (Figure 11). The almost colorless residual solution did not contain any colloidal-dissolved Bi particles. According to these initial studies, the formation of small Bi pseudocubes with edges of about 25 nm in length requires the controlled thermolysis of Bi₂Et₄ at rather low temperatures, followed by an additional heating step at 170 °C. However, further experiments are necessary in order to fully understand the role of the reaction temperature in detail.

Figure 11. SEM photographs of Bi particles obtained after thermal decomposition of Bi₂Et₄ in a preheated (170 °C) solution of PVP*, NaNT(SiMe₃)₂, and DIPB.

Role of capping agents. In order to elucidate the role of the capping agents Na[N(SiMe₃)₂] and PVP* on the size and shape of the resulting bismuth nanoparticles, the thermal decomposition of Bi₂Et₄ both in the absence of any capping agents and in the presence of either Na[N(SiMe₃)₂] or PVP* was investigated.

Decomposition of Bi₂Et₄ in DIPB for only 4 h at 50 °C yielded a black solution, which contained trace amounts of a black precipitate that was removed by centrifugation. Figure 12 shows SEM photographs of the black precipitate, clearly proving the formation of largely aggregated Bi nanoparticles.

Figure 12. SEM photographs of precipitated Bi particles formed at 50 °C in the absence of Na[N(SiMe₃)₂] and PVP*.

The remaining solution was heated to 70 °C for 12 h, resulting in the formation of a black precipitate that was isolated as described before and repeatedly washed with CHCl₃ and methanol (2x). The SEM pictures clearly reveal the formation of Bi particles of different size and shape, which are also aggregated to larger agglomerates (Figure 13).

Figure 13. SEM photographs of precipitated Bi nanoparticles obtained at 70 °C.

In the absence of any suitable capping agent only large particles, most likely formed due to Ostwald-ripening process, were formed, which further show a strong tendency toward agglomeration. According to these studies, it is quite clear that the formation of small bismuth pseudocubes requires the presence of both size- and shape-controlling agent. We therefore performed the thermolysis of Bi₂Et₄ in the presence of Na[N(SiMe₃)₂] dissolved in 1 mL of THF. After the mixture was heated for 4 h at 50 °C, a large amount of a black precipitate was formed, that was isolated by centrifugation. Figure 14 shows the formation of largely agglomerated Bi particles covered with additional capping agent that could not be removed completely even after washing four times with CHCl₃.

Figure 14. SEM photographs of precipitated Bi particles, which were formed at 50 °C in the presence of Na[N(SiMe₃)₂].

Finally, the thermolysis of Bi₂Et₄ in the presence of PVP* was investigated. Small amount of a black precipitate was isolated after Bi₂Et₄ was heated for 4 h at 50 °C. The remaining solution was heated for 70 °C, yielding a black precipitate that was isolated by centrifugation and twice-washed with CHCl₃ and methanol.

Figure 15. SEM photographs showing Bi particles, which precipitated at 70 °C in the presence of PVP*.
SEM studies show that this precipitate consists of large Bi crystallites of different shape and size, which are agglomerated to a large extent (Figure 15).

According to the decomposition studies, the formation of 20 nm-sized bismuth nanocubes requires both Na[N(SiMe$_3$)$_2$] and PVP$^*$ as size- and shape-selective agents, whereas in the absence of any of these agents only large agglomerates were formed.

**Postulated growth mechanism.** It is generally accepted, that nanoparticles obtained from molecular precursors are formed by classical nucleation and growth processes (LaMer-type growth). For the size- and shape-selective growth of nanocrystals, the crystalline shape of the seeds at the nucleating stage is known to be critical. Single-crystal seeds of a fcc structure are expected to exist as truncated octahedrons (Wulff polyhedrons) bound by (111) and (100) facets, hence resulting in almost spherical profiles containing the smallest surface area, which minimizes the total interfacial free energy. Under thermodynamic control, these single crystal seeds will grow into octahedrons, cuboctahedrons, or cubes depending on the relative energies of the (111) and (100) directions. As a result, nanoparticle will form whose facets exhibit the lowest surface energy. Because the angles of rhombohedral bismuth (57.23 °) and a cubic F crystal in a rhombohedral setting (60 °) are almost equal, we can transfer our results to the growth behavior of cubic crystals. So the (100), (110) and (111) directions in a fcc system correspond to the rhombohedral (012), (014) and (001) directions. The rectangular shape of bulk bismuth crystals, grown from melts supports this comparison.

Further shape control can be achieved in kinetically controlled growth processes through the preferential growth of particular crystallographic surfaces of the nanocrystals. Coordinating (capping) agents kinetically control the growth of different crystal facets of a metal due to their chemical interaction with the metal surface. Since the strength of the interaction of the capping agent with different crystallographic planes at the surface of a single crystalline metal seed is different, the capping agent can change the order of free energies for different crystallographic planes, resulting in different relative growth rates or simply block the planes. PVP for instance was found to bind most strongly to the (100) facets of fcc metals such as Ag and Pd, hence forcing the addition of metal atoms to the other crystal facets. As a consequence, single-crystal seeds of fcc metals, which only show (111) and (100) facets, preferentially grow in the poorly passivated (111) direction. These adatoms then migrate to the face edges, resulting in a preferred growth of the (100) facets and the formation of nanocubes with sizes $>$25 nm. While this growth mechanism has been intensely studied over the last few years for fcc metals such as Au and Pt, the growth mechanism of non-fcc metals such as bismuth, which adopts the rhombohedral crystal structure, is still rather unknown.

We assume that under the specific low-temperature conditions (50 °C) used in our experiments, the precursor Bi$_3$Et$_4$ slowly decomposes with subsequent formation of small Bi seeds. The different surfaces of these crystalline seeds obviously show a different affinity (bond strength) to the capping agents (PVP$^*$ and Na[N(SiMe$_3$)$_2$]) used in these experiments. Wang and Poudel previously reported on the synthesis of Bi pseudocubes with an average edge length of 70 nm by adjusting a definite amount of PVP. According to their studies, PVP not only serves as stabilizing agent that protects particles from aggregation, but was also assumed to act as shape controlling agent. PVP influences the crystal growth kinetics via adsorption onto the surfaces of Bi crystals through O-Bi bond formation, since the crystalline Bi pseudocubes formed showed d-spacings of 0.32 nm, indicating that PVP stabilizes the (012) facet of rhombohedral Bi. Unfortunately, the specific adsorption bond strengths to different surfaces of a rhombohedral bismuth crystal, which might result in shape-selective crystal growth, have not been determined, to date. While only a very few reports on the growth of pseudocubic particles of non-fcc metals exist, the growth of nanosized metal oxides with a pseudocubic shape were investigated in more detail. Wang and Gao reported on the formation of pseudocubic Fe$_3$O$_4$ nanoparticles bound by (012) facets, which were formed as a result of the different surface energies of the preferential (012), (104), and (110) growth planes of hematite. Moreover, almost monodisperse rhombohedral V$_2$O$_5$ pseudocubes with an average edge length of 10 nm bound by (012) facets were recently synthesized by Xie et al. Based on crystallographic considerations, they argued that the formation of V$_2$O$_5$ pseudocubes relies on the high reticular density of (012) facets compared to (104) and (110) facets, for which these facets are more easily accessibility during growth process. In addition, Garito et al. explained the growth of pseudocubes due to structural analogies of the (012) facets in the rhombohedral structure and the (100) facets in the cubic structure. Since the growth of a cubic structure with exposed (100) facets typically yields a cubic morphology, the thermodynamically controlled growth of a rhombohedral structure with exposed (012) facets should result in the formation of a pseudocubic morphology.

However, the growth of the bismuth pseudocubes as observed in our experiments can also be rationalized on the basis of a kinetically controlled pathway. Keeping in mind, that PVP was found to bind stronger to (100) facets of fcc metals, hence forcing the formation of nanocubes with exposed (100) facets as described earlier, and the crystallographic analogy between the (100) facets in the cubic and the (012) facets in the rhombohedral structure, PVP$^*$ most likely binds stronger to the (012) facets in the rhombohedral structure as was proposed previously by Wang and Poudel for PVP. As a consequence, bismuth pseudocubes with exposed (012) facets should preferably be formed. Since we obtained as-described bismuth pseudocubes only in the presence of both capping agents, we assume that they are formed rather under kinetic than thermodynamic-control.

In order to evaluate the role of the initially formed crystal seeds, we investigated the black solution formed at 50 °C within 4 h in more detail. A very small amount of insoluble black precipitate was first isolated by centrifugation. The resulting black solution contained colloidal-dissolved Bi nanoparticles, which were isolated after repeated (3x) addition of methanol, centrifugation and redispersion in CHCl$_3$. TEM analysis clearly proved that these particles are star-shaped Bi nanoparticles of about 25 nm in size (Figure 16).
Figure 16. TEM photographs of colloidal-dissolved, star-shaped Bi particles formed at 50 °C.

Powder diffraction pattern of these particles correspond to rhombohedral Bi. A d-spacing of 323 pm stems from (012) lattice planes of rhombohedral bismuth as was observed for the Bi nanocubes. However, no cube-like morphology was observed for any seeds formed at 50 °C.

In order to rule out the formation of the bismuth pseudo-cubes by thermolysis of BiEt₃, which is formed in the disproportionation reaction of Bi₂Et₄, BiEt₃ was thermolyzed at 170 °C for 12 h. The resulting particles were isolated and investigated by TEM. No sign for the formation of Bi pseudocubes was found. Instead, only spherical Bi particles were isolated (Figure 17).

Figure 17. TEM photographs of Bi particles formed by thermolysis reaction of BiEt₃ at 170 °C.

The specific role of Na[N(SiMe₃)₂] on the growth of bismuth pseudocubes is unclear. Buhro et al. speculated that Na[N(SiMe₃)₂] serves as nucleation-controlling agent for the size-selective synthesis of small Bi spheres. Moreover, Na[N(SiMe₃)₂] was found to influence the agglomerative-nucleation process, in which the assembly of a critical-sized aggregate of small, primary nanoparticles is critical. These particles then coalesce to either single-crystalline or polycrystalline nanoparticles, which are viable for further agglomerative growth. Bis(trimethylsilyl)amide ligands were speculated to selectively bind to Bi [001] facets, forcing the anisotropic crystal growth and formation of Bi nanowires. In our studies, we didn’t observe anisotropic growth and formation of nanowires. However, the presence of Na[N(SiMe₃)₂] was found to be essential since in its absence, only larger agglomerates were formed. We therefore speculate that Na[N(SiMe₃)₂] mainly serves as stabilizing agent to protect particles from aggregating to form bigger particles. However, further studies are necessary since the same shape-controlling role for the formation of Bi nanocubes was also assigned to PVP molecules.

Conclusion. Highly crystalline, nearly monodisperse 25 nm sized bismuth pseudocubes were obtained from a controlled low temperature thermolysis reaction of the novel low-valent precursor Bi₂Et₄ in the presence of Na[N(SiMe₃)₂] and PVP*. This is the first time that a low-valent organobismuth complex was used for this purpose. Both Na[N(SiMe₃)₂] and PVP*, which were found to act as size- and shape-controlling agents, are essential for the stabilization of colloidal-dissolved Bi pseudocubes. The formation of larger Bi nanoparticles, which precipitate after 12 h at 170 °C, most likely occurred through an ongoing deposition of Bi atoms on the facets of the Bi pseudocubes as was reported for growth of Ag nanoparticles.

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ABBREVIATIONS
SLS, solution-liquid-solid; XRD, X-ray diffraction; SAED, selected area electron diffraction; SEM, scanning electron microscopy; HRTEM, high-resolution transmission electron microscopy; EDX, energy-dispersive X-ray; PVP*, poly(1-vinylpyrolidone)-graft-(1-triacontene).

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