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Metal Nanoparticles via the Atom-Economy Green Approach

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Metal nanoparticles (NPs) of Cu (air-stable), Ag, and Au have been prepared using an atom-economy green approach. Simple mechanical stirring of solid mixtures (no solvent) of a metal salt and ammonia borane at 60 °C resulted in the formation of metal NPs. In this reaction, ammonia borane is transformed into a BNH_x polymer, which protects the NPs formed and halts their growth. This results in the formation of the BNH_x polymer protected monodisperse NPs. Thus, ammonia borane used in these reactions plays a dual role (reducing agent and precursor for the stabilizing agent).

The development of sustainable technology for the synthesis of metal nanoparticles (NPs) continues to be one of the most important challenges in modern materials science. Traditional methods of synthesis of metal NPs are the "top-down" approach, which utilizes physical methods, and the "bottom-up" approach, which employs solution-phase colloidal chemistry.[1] Whereas NPs on large scales could be obtained, size control is very difficult to achieve using the physical methods. Albeit the colloidal approach offers great control over the particle size and shape, only subgram quantities have been realized. In addition, the realization of monodisperse NPs on large scales essential for practical applications is not feasible by both of these methods.

A sustainable solution to this problem can be obtained via atom-economy and solventless approaches. Atom economy could be achieved by choosing reagents that are capable of playing multiple roles. Also, the use of fewer numbers of reagents simplifies or eliminates purification procedures. Even though it has been recognized that "the best solvent is no solvent", very few attempts have been made in this direction.[2] Jeszka and co-workers reported the synthesis of Ru, Co, and Rh NPs by solid-state decomposition of organometallic precursors dispersed in polymer films under H_2.[3] Recently, Geckeler and co-workers used high-speed vibration milling for the synthesis of Au NPs via a solid-state route.[4] They used $NaBH_4$ as the reducing agent and poly(vinylpyrrolidone) as the protecting agent.

Ammonia borane (AB; $H_3N \cdot BH_3$), a classical Lewis acid−base adduct, is a white stable solid at ambient conditions. Neat AB (solid state) undergoes decomposition above 100 °C, resulting in the formation of products like $(BH_2NH_2)_x$ or $(HBNH)_x$ (BNH_x polymers) along with H_2 evolution.[5] AB was found to reduce various metal salts in aqueous and nonaqueous solvents. Stucky and co-workers used amine boranes as reducing agents for the synthesis of highly monodisperse dodecanethiol-capped Au and Pd NPs in a one-phase (toluene) method.[6] Some of us have earlier reported that hydrolysis/methanolysis of AB for the release of H_2 in the presence of first-row transition-metal salts resulted in the formation of metal/metal boride NPs, and the in situ generated metal clusters were the real catalysts in these reactions.[7] Motivated by these results, we attempted the synthesis of metal NPs through solid-state reactions, wherein AB plays a dual role (atom economy), i.e., reducing agent and stabilizing agent.

Anhydrous $CuCl_2$, $AgNO_3$, and $AuCl_3$ were used as the starting metal precursors for the synthesis of Cu, Ag, and Au NPs, respectively. In a typical synthesis procedure, a Schlenk tube equipped with a stirbar containing AB was inserted into an oil bath maintained at 60 °C. To this was added metal salt in a batchwise (~5 mg) manner under a N_2 atmosphere, and the reaction mixture was stirred vigorously for 3 h. No solvent was used in these reactions. The AB/metal salt ratio was maintained at 10 in all cases. The resulting powders were characterized using UV−visible spectroscopy, transmission electron microscopy (TEM), and powder X-ray diffraction (XRD) techniques.

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In each of these cases, the reactions proceeded by color (metal salt) changes: Ag, colorless to yellow; Cu, brown to reddish-brown; Au, yellow to dark red. The solid-state UV−visible spectra showed bands around 575, 400, and 510 nm respectively in the cases of Cu, Ag, and Au reactions (see the Supporting Information). It is well documented in the literature that Cu, Ag, and Au NPs possess a strong surface plasmon resonance (SPR) band in the visible region that can be tunable with the shape and size of the NPs.[8] Thus, it was apparent from the UV−visible spectral data that the products were comprised of the respective metal NPs. In order to ascertain this, further characterization was carried out using TEM and powder XRD techniques.

The nanopowders obtained were redispersed in tetrahydrofuran (THF) by sonication, and TEM samples were prepared by placing a 2 μL sample on a Cu grid. The TEM bright-field (BF) image (Figure 1a) of the Cu sample showed the presence of spherical NPs with a size distribution range of 3−10 nm (Figure 1b). The average particle size is 4.7 ± 2.1 nm. The corresponding selective area electron diffraction (SAED) pattern is shown in Figure 1c. All of the rings match with the lattice planes of the face-centered-cubic (fcc) Cu^0 phase. The TEM BF image (Figure 1d) of the Ag sample revealed the presence of 5−11-nm-sized particles (Figure 1e) with an average particle size of 4.5 ± 2.5 nm. The SAED pattern (Figure 1f) showed a ring pattern corresponding to the fcc Ag^0 phase. Similar to Cu and Ag, spherical NPs with a size distribution range of 2−10 nm and an average particle size of 8.2 ± 1.4 nm were obtained in the case of Au, as evidenced by the TEM BF image (Figure 1g,h). The SAED pattern further supports the presence of pure Au^0 NPs (Figure 1i). In all three cases, we noted that more than 90% of the grid consisted of monodisperse NPs; in addition, some regions had agglomerated particles (see the Supporting Information). This could be due to poor mixing of the reactants because the reactions were just carried out by simple mechanical stirring and the reaction mixtures were not uniform to the naked eye. High-resolution TEM (HRTEM) images (Figure 2) show that, in all three cases, the NPs obtained were crystalline in nature. The lattice fringes in the fast Fourier transform (FFT) patterns in Figure 2a−c show the (111) planes of the fcc phase of Cu, Ag, and Au NPs, respectively. The powder XRD patterns obtained from the respective products after washing with THF indicated the presence of metal(0) powders along with NH_4Cl. Further washing with water showed peaks corresponding to pure metal(0) nanopowders (Figure 3).

In a recent study, we found that $CuCl_2$ (in a catalytic amount) assists the thermolysis of AB and generates H_2 even at 60 °C.[9] Also, Chen and co-workers reported the partial reduction of Co^{2+} and Ni^{2+} by AB in the solid state.[10] It has been documented in the literature that dehydrogenation of amine boranes in a nonaqueous medium or in the solid state yields BNH_x polymers as the final boron-containing products.[11] Alongside metal NPs, we also noticed a polymeric material in the TEM images in the present work. Ammonia borane used here acts as a reducing agent as well as a precursor of the protecting agent of NPs, herein the BNH_x polymer. The addition of a metal salt to AB results in the reduction of metal ions and in situ generation of BNH_x polymers, almost simultaneously. Thus, the polymer formed stabilizes the NPs and prevents their agglomeration. The protective nature of the BNH_x polymers was evident when the Cu NPs obtained herein were exposed to air: even after 24 h, the SPR band remained unaltered.[12] The presence of

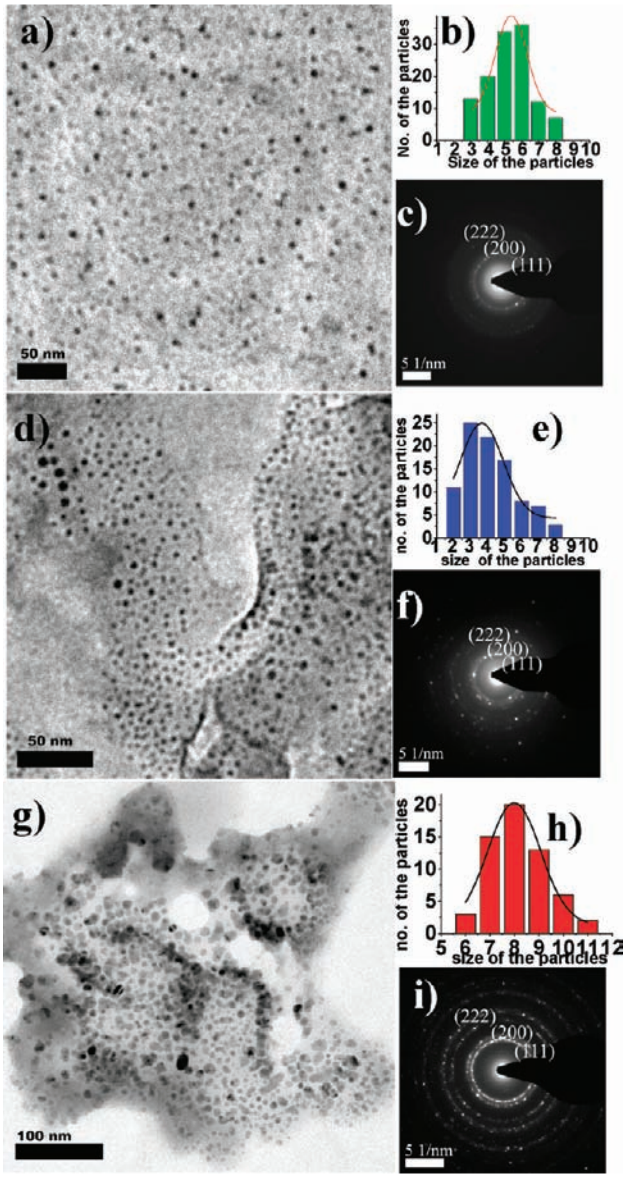

Figure 1. Cu NPs: (a) TEM BF image; (b) histogram showing the particle-size distribution; (c) SAED pattern. Ag NPs: (d) TEM BF image; (e) histogram showing the particle-size distribution; (f) SAED pattern. Au NPs: (g) TEM BF image; (h) histogram showing the particle-size distribution; (i) SAED pattern.

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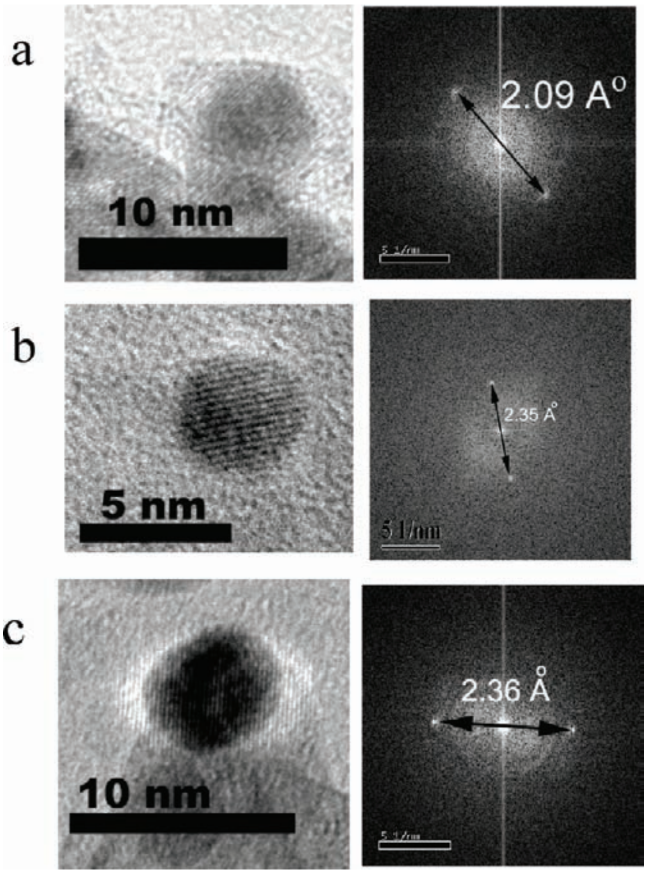

Figure 2. HRTEM images and corresponding FFT patterns of (a) Cu, (b) Ag, and (c) Au NPs.

BNH_x polymers was apparent from IR spectroscopy (see the Supporting Information).

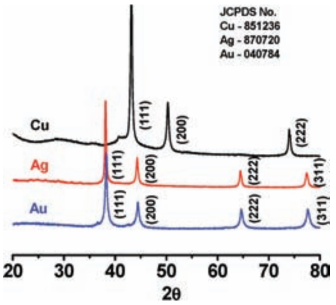

Figure 3. Powder XRD patterns of Cu, Ag, and Au nanopowders after washing with THF and water.

In conclusion, we have demonstrated a facile atom-economy green route for the synthesis of Cu (air stable), Ag, and Au NPs. The BNH_x polymers generated during the reduction of metal ions by AB stabilize the NPs. Preliminary results have shown that this method can be extended to other noble metals. The scope of scalability (thorough mixing of the reactants should be achieved using techniques like vibration milling) of this method make this process attractive for large scale synthesis of NPs. It should be possible to get further control over the size distribution by using much milder reducing amine boranes such as dimethyl- or trimethylamine borane; efforts toward this direction are underway in our laboratories.

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Supporting Information Available: Experimental details, UV−visible and IR spectra, TEM images, EDX data, and powder XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.