Facile Aqueous-Phase Synthesis of an Ultrasmall Bismuth Nanocatalyst for the Reduction of 4-Nitrophenol

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ABSTRACT: Bismuth metallic nanoparticles have evoked considerable interest in catalysis owing to their small size, high surface area-to-volume ratio, and low toxicity. However, the need for toxic reductants and organic solvents in their synthesis often limits their desirability for application development. Here, we describe a green strategy to synthesize bismuth nanodots via the redox reactions between bismuth nitrate and D-glucose, in the presence of poly(vinylpyrrolidone) in the basic aqueous phase. Both reagents play a crucial role in the formation of monodisperse bismuth nanodots acting as mild reducing and capping agents, respectively. We further demonstrate that the catalytic activity of these dots via the successful reduction of the environmental contaminant 4-nitrophenol to its useful 4-aminophenol analogue requiring only 36 μg/mL nanocatalyst for 20 mM of the substrate. Moreover, they can be recovered and recycled in multiple reactions before the onset of an appreciable loss of catalytic activity. The proposed facile synthetic route and inexpensive matrix materials lead the way to access bismuth nanodots for both the fundamental study of reactions and their industrial catalysis applications.

INTRODUCTION

Nanosized metallic materials have been the subject of intense research during the past decades due to their remarkable properties including tunable size and shape, large surface area-to-volume ratio, and highly active surfaces with potential applications in catalysis, optics, sensing, detection, and biotechnology. Among these metallic nanostructures, bismuth has recently attracted particular interest because its transition from a semi-metal to a semiconductor could occur when the crystalline size of bismuth is small enough according to the quantum confinement effect. More importantly, based on its low toxicity profile, bismuth nanoparticles have recently been investigated for applications such as multifunctional theranostic agents and in X-ray computed tomography/photoacoustic imaging-guided photothermal therapy. This stems from the ability to strongly attenuate X-rays, and their strong near-infrared absorbance and high photothermal conversion efficiency. Additionally, bismuth-containing materials also have promising implications in many advanced applications ranging from photodetectors to thermoelectricity and photocatalysis. For example, in the last few years, bismuth nanomaterials have been integrated with typical photocatalysts (e.g., TiO2, g-C3N4, Bi2WO6), as plasmonic metal nanostructures, to effectively improve the photocatalytic performance for the degradation of environmental pollutants in water.

To date, several strategies have been developed for the synthesis of pure bismuth nanomaterials since it is a well-known “green element” that is inexpensive and relatively nontoxic among the heavy metals. These commonly employed methods are mainly divided into the following four categories: (i) thermal decomposition, (ii) mechanochemical processing, (iii) photochemical, and (iv) solution-phase chemical reduction methods. Generally, the thermal decomposition method could be used to obtain high-quality monodisperse elemental bismuth nanoparticles. Buhro and co-workers made significant contributions to the synthesis of near monodisperse, size- and shape-controlled Bi nanoparticles using thermal decomposition of organometallic precursors. However, this method requires harsh preparation conditions, expensive organometallic precursors, high temperatures, and long reaction times, which limit its broad application. The mechanochemical processing technique, including laser ablation and sonication exfoliation methods, usually employs inexpensive and nontoxic bulk bismuth pellets as precursors; however, the synthesis process is demanding with respect to energy-consumption along with the need for costly instrumentation (e.g., high-powered lasers). The photochemical reaction was used for the synthesis of bismuth nanoparticles by Wiesner and co-workers who reported the preparation of nanoparticles via a photochemical polythiol process under ambient light, requiring 24 h or even longer reaction times. Feldmann and co-workers reported the synthesis of bismuth particles via photochemical synthesis.

Supporting Information
but did not achieve high product yield. In recent years, the simple solution-phase chemical reduction method (e.g., solvothermal and microwave methods) has garnered significant attention as an alternative. This approach often involves the reduction of bismuth metal salts in the presence of a surfactant that acts as a stabilizer. However, the experimental process is not easy to control, and organic solvents are typically required, resulting in bismuth nanomaterials with poor morphological purity. Another attractive approach in developing nanocatalysts is through the fabrication of nanohybrids that aim to achieve high catalytic activity as shown by Li et al., who designed Bi nanoparticles supported by N-doped graphene. Although some of the current research studies have investigated the fabrication of nanoscale bismuth through simpler approaches, the use of toxic reductants and/or organic solvent is still inevitable during synthesis. Therefore, it remains desirable to develop a facile and green method for the synthesis of high-quality bismuth nanoparticles in aqueous solution. To the best of our knowledge, there are few reports concerned with the direct aqueous-phase synthesis of high-quality pure bismuth nanoparticles with dimensions on the order of and less than 5 nm.

In this work, we develop a direct aqueous-phase synthesis strategy to fabricate ultrasmall bismuth-containing nanodots in water by reducing Bi\(^{3+}\) ions with D-glucose in the presence of poly(vinylpyrrolidone) (PVP). The entire experimental process follows the concept of green chemistry using inexpensive raw materials, water as the solvent, and mild reaction conditions. The nanodots are extensively characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) to confirm the size, phase, and chemical states. In a proof concept, we evaluate the catalytic activity and stability of the obtained bismuth nanodots in the reduction of 4-nitrophenol (4-NP), which is usually catalyzed by noble metal nanoparticles such as gold, silver, and platinum. The recovery and reusability of the bismuth nanodot catalyst are also investigated in multiple reaction cycles.

RESULTS AND DISCUSSION

Following the synthesis and purification, powder XRD was used to characterize the crystal phase of the bismuth nanodots. Figure 1a depicts the XRD pattern of the bismuth nanodots prepared by direct aqueous-phase chemical synthesis. All of the diffraction peaks can be well indexed to the pure rhombohedral phase of Bi (JCPDS no. 44-1246), revealing that the obtained product, under the current synthetic conditions, is elemental bismuth. The reflections at 27.2, 37.9, 39.6, 48.7, and 64.5° 2θ can be indexed to the (012), (104), (110), (202), and (122) planes of rhombohedral bismuth, respectively. No trace of the Bi\(_2\)O\(_3\) phase was detected in the bismuth nanodot sample evidenced by the absence of prominent Bi\(_2\)O\(_3\) reflections (JCPDS no. 65-2366) typically noted at 27.4, 33.1, and 33.3° 2θ. It should be noted that D-glucose and PVP molecules play a crucial role in the formation of Bi nanodots in this aqueous-phase synthesis with D-glucose acting as a mild reducing agent for the reduction of metal salts, and PVP as a stabilizer to protect the nanoparticles from aggregation. In the absence of D-glucose, Bi\(^{3+}\) ions could not be reduced to elemental Bi and instead, a pure α-Bi\(_2\)O\(_3\) sample was obtained (Supporting Information (SI), Figure S1). Additionally, when PVP was excluded from the reaction, bulk bismuth pellets formed (SI, Figure S2).

Figure 1. (a) X-ray diffraction (XRD) pattern of bismuth nanodots. The standard pattern of bulk Bi is also provided for comparison (JCPDF 44-1246); TEM images of quasi-spherical Bi nanodots at (b) low magnification and (c) high magnification—insets: (b) digital image of the bismuth nanodot colloidal dispersion in water and (c) HR-TEM analysis of the Bi nanodots revealing lattice fringes with 0.33 nm spacing; (d) particle size distribution analysis of the Bi nanodots showing an average of 3.7 ± 0.6 nm; (e) EDS analysis of the Bi nanodots revealing the presence of Bi as the dominant element.

The isolated bismuth nanodots can be easily dispersed in water forming a black colloidal dispersion (Figure 1b inset), which was analyzed using transmission electron microscopy (TEM) as shown in Figure 1b,c. The nanodots show a quasi-spherical morphology with a Gaussian size distribution ranging from 2 to 5.5 nm and a mean particle size of 3.7 ± 0.6 nm (Figure 1d). It is interesting to note that when ammonium bismuth citrate was used as the bismuth source, ultrasmall bismuth nanoparticles can also be successfully prepared but the particle size distribution is polydisperse (SI, Figure S3). The high-resolution TEM image (Figure 1c inset) reveals the crystalline nature of the obtained nanodots and lattice fringes with a measured interplanar d spacing of 0.33 nm, which is in good agreement with the (012) plane of rhombohedral Bi. Energy-dispersive X-ray analysis shown in Figure 1e demonstrates that the bismuth nanodots contain bismuth (Bi), carbon (C), and oxygen (O) elements. The strong bismuth peaks indicate the successful synthesis of bismuth nanodots, while the weak O peak may arise from PVP molecules on the surface of particles and surface oxidation of bismuth nanodots (vide infra), which is responsible for its overall catalytic activity. We also investigated the hydrodynamic diameter for a freshly prepared colloidal dispersion of bismuth nanodots using dynamic light scattering (DLS) (SI, Figure S4). A significant difference between the crystallite size observed by TEM (3.7 nm) and the hydrodynamic size (68.8 nm) as measured by DLS may be attributed to the surrounding hydration layer and the PVP molecules attached to the surface of nanodots, which confer good colloidal stability to the dots and minimize instances of aggregation. The colloidal dispersion of the dots shows a broad absorbance profile ranging from the ultraviolet to the near-infrared spectral regions. The absorbance features located around 400 and 550 nm (Figure S5) may arise from surface plasmon resonance and light scattering phenomena, which are also observed in bismuth nanospheres prepared by high-temperature thermolysis of bismuth acetate in oleylamine.

To further confirm the nature of the chemical states at the surface of the nanodots, X-ray photoelectron spectroscopy was performed. Figure 2a presents the XPS survey spectrum of the Bi nanodot powder, and we note the binding energy positions (along with their respective % composition) assigned to Bi (18.25%), O (35.22%), and C (46.53%), confirming the...
Having demonstrated the successful formation of the Bi nanodots provided the impetus to investigate their catalytic performance in the reduction of nitroaromatic compounds. The reduction of nitroaromatic compounds to amines is an important reduction reaction in synthetic organic chemistry and the production of industrially relevant chemicals. The reduction of 4-nitrophenol (4-NP) over metal nanoparticles, especially noble metal nanoparticles in the presence of NaBH4, is an efficient strategy to produce 4-aminophenol (4-AP).21 Metal nanoparticles enable the catalytic reduction of 4-NP by relaying the electrons from BH4− to 4-NP when both reactants are adsorbed on the surface of the nanocatalyst.22 In contrast to noble metal nanoparticles, there are few reports on the catalytic reduction of 4-NP by inexpensive bismuth nanoparticles, especially ultrasmall bismuth nanodots. Herein, to investigate the catalytic performance of our non-noble Bi nanodots, the reduction of 4-NP to 4-AP by NaBH4 at room temperature was used as a model reaction, and the reduction progress was monitored by UV−vis absorption spectroscopy on the reaction mixture following the addition of bismuth nanodots. It should be noted that the color of the 4-NP aqueous solution changed from light to bright yellow immediately upon mixing with NaBH4 and an intense UV−vis absorption peak appeared at 400 nm rather than the original absorption peak at 317 nm (SI, Figure S6). This is ascribed to the formation of the 4-nitrophenolate compound under basic conditions following the addition of NaBH4. In the absence of the nanocatalyst, the solution color remains bright yellow and the absorption spectra shape and peak intensity remain essentially unchanged even after 12 h, indicating that the reduction of 4-NP is kinetically restricted (SI, Figure S7). On the other hand, with the addition of Bi nanodots, the catalytic reduction of 4-NP to 4-AP is greatly accelerated. Figure 3a shows the time-resolved UV−vis absorption spectra of 4-NP by NaBH4 in the presence of Bi nanodots. The characteristic absorption peak at 400 nm of 4-NP gradually

Figure 2. (a) XPS survey spectrum of Bi nanodots. (b) High-resolution XPS spectrum of Bi 4f7/2 and Bi 4f5/2 states. (c) High-resolution XPS spectrum of O 1s. (d) Fourier-transform infrared (FTIR) spectra of Bi nanodots and PVP molecules.

Additional characterization was carried out using FTIR spectra to further study the chemical composition of the obtained bismuth nanodots. The binding energies for the spin−orbit splitting of the two characteristic Bi 4f7/2 and Bi 4f5/2 peaks are observed at 164 and 159 eV, respectively. The binding energy corresponding to the characteristic Bi 5d peak of metallic bismuth is also observed at 26 eV, which coincides with the reported literature value.18 The binding energy recorded at 531 eV corresponds to the characteristic peak of O 1s, evidence of the existence of oxide species on the surface of Bi nanodots. The high-resolution XPS spectrum of the Bi 4f level is presented in Figure 2b. The binding energy values obtained at 159.1 and 164.5 eV are assigned to the core levels of Bi 4f7/2 and Bi 4f5/2, respectively, which can be ascribed to Bi=O in Bi2O3, indicating the formation of amorphous oxide species on the surface of bismuth nanodots. Two weak peaks of metallic bismuth appear at binding energies of 157.6 and 162.2 eV. As shown in Figure 2c, the O 1s peaks can be deconvoluted into three peaks at 532.7, 530.9, and 529.7 eV, which can be assigned to O−H, O−C, and O−Bi, respectively. The XPS results here reveal that the Bi nanodots are indeed surface oxidized, which could not be verified by powder X-ray analysis as this technique is not sufficiently sensitive to provide such information.

Additional characterization was carried out using FTIR spectra to further study the chemical composition of the bismuth nanodot surface. The spectrum in Figure 2d depicts the FTIR spectrum of the Bi nanodots, which show a vibration at 3220 cm−1 ascribed to O−H asymmetric stretching noting that this would be observed for pure PVP molecules at 3440 cm−1. This shift is attributed to the interaction of PVP with the nanodot surface, which has also been observed in other PVP-decorated nanoparticles.4 Moreover, the absorption bands assigned to the C=H asymmetric stretching at 2850 cm−1, C−O stretching at 1650 cm−1, and C−N vibrations at 1285 and 1035 cm−1 are identified and found to be consistent with the characteristic peaks of PVP molecules.20 These observations confirm that PVP molecules are indeed decorating the surface of the bismuth nanodots adsorbed on the nanodot surface conferring colloidal stability and dispersibility.

Figure 3. (a) Time-dependent UV−vis absorption spectra during the reduction of 4-nitrophenol (4-NP) by NaBH4 in the presence of Bi nanodots at room temperature over 150 min. The top inset shows a digital photograph of 4-NP before and after the reduction reaction catalyzed by Bi nanodots; (b) relationship between ln(C/C0) and the reaction time during the course of catalytic reduction of 4-NP over bismuth nanodots in the presence of NaBH4; (c) reusability of bismuth nanodots as nanocatalysts for the reduction of 4-NP during the three cycles of use. The nanodots were isolated and reused in 3 separate reactions over a 30 min time frame. The reduction of 4-nitrophenol (4-NP) over metal nanoparticles, especially noble metal nanoparticles in the presence of NaBH4, is an efficient strategy to produce 4-aminophenol (4-AP).21 Metal nanoparticles enable the catalytic reduction of 4-NP by relaying the electrons from BH4− to 4-NP when both reactants are adsorbed on the surface of the nanocatalyst.22 In contrast to noble metal nanoparticles, there are few reports on the catalytic reduction of 4-NP by inexpensive bismuth nanoparticles, especially ultrasmall bismuth nanodots. Herein, to investigate the catalytic performance of our non-noble Bi nanodots, the reduction of 4-NP to 4-AP by NaBH4 at room temperature was used as a model reaction, and the reduction progress was monitored by UV−vis absorption spectroscopy on the reaction mixture following the addition of bismuth nanodots. It should be noted that the color of the 4-NP aqueous solution changed from light to bright yellow immediately upon mixing with NaBH4 and an intense UV−vis absorption peak appeared at 400 nm rather than the original absorption peak at 317 nm (SI, Figure S6). This is ascribed to the formation of the 4-nitrophenolate compound under basic conditions following the addition of NaBH4. In the absence of the nanocatalyst, the solution color remains bright yellow and the absorption spectra shape and peak intensity remain essentially unchanged even after 12 h, indicating that the reduction of 4-NP is kinetically restricted (SI, Figure S7). On the other hand, with the addition of Bi nanodots, the catalytic reduction of 4-NP to 4-AP is greatly accelerated. Figure 3a shows the time-resolved UV−vis absorption spectra of 4-NP by NaBH4 in the presence of Bi nanodots. The characteristic absorption peak at 400 nm of 4-NP gradually

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decreases after the introduction of Bi nanocatalyst and is accompanied by the increase of new bands at ~230 and 300 nm ascribed to 4-AP. The presence of an isosbestic point at ~275 and 314 nm confirms that only 4-AP is obtained from catalytic reduction without the occurrence of any side reactions. In a control experiment, we also investigated bulk bismuth pellets obtained through nanodot synthesis, in the absence of PVP, and we noted that they do not show any catalytic activity for the reduction of 4-NP to 4-AP (SI, Figure S8). This can be attributed to the smaller percentage of the available Bi atom sites at the surface. This renders the bulk form less reactive than its nanoscale counterpart.

The time evolution of the reduction process can be conveniently assessed using time-resolved UV–vis spectroscopy of the reaction mixture. Under pseudo-first-order conditions ([4-NP] = 0.22 mM, [NaBH₄] = 22 mM, [Bi nanodots] = 36 μg/mL) a plot of ln(A/Åₒ) vs time displays an initial nonlinear behavior followed by a linear decay of absorbance band at 400 nm (Figure 3b). This behavior is in agreement with the previously proposed mechanism, where at the initial stages of the reaction, the nanoparticle undergoes surface modifications thereby activating the surface for catalytic reduction. This initial slow induction period is followed by linear decay as is expected from the pseudo-first-order reaction. The rate constant was determined to be 6.033 s⁻¹ g⁻¹, which is comparable—if more efficient—to other reported metal-based catalysts. It is also noted that some reported hybrid or noble metal-based systems are more efficient, but are not as cost-effective as our system. The reusability of the Bi nanocatalyst for the reduction of 4-NP by NaBH₄ was investigated. The Bi nanodots were recycled and used repeatedly up to three cycles, showing its practicality for 4-NP reduction. The catalytic performance decreases in part with the increase of cycles, but still exhibits good catalytic performance (Figure 3). TEM images of the nanodots show aggregation after cycling uses (SI, Figure S9a), and EDS analysis reveals a similar elemental composition profile to that prior to the reduction reactions (SI, Figure S9b). In addition, it is noted that the recycled nanodots possess a similar diffraction pattern when compared to the pattern prior to the cycling experiments suggesting that they are still primarily composed of Bi (SI, Figure S10). The decrease in the catalytic activity is ascribed to the loss of Bi nanocatalysts during centrifugation (SI, Figure S10). The decrease in the catalytic activity for the reduction of 4-NP to 4-AP is expected from the pseudo-first-order conditions with a step size of 0.02° and a 0.5 s count time. Analysis was carried out using MDI Jade software.

Transmission Electron Microscopy Analysis. The size and morphology of the bismuth nanodots were obtained using a Philips Tecnai G2 F20 transmission electron microscope (TEM) with a field emission gun operating at 200 kV. The TEM samples were prepared by depositing 20 μL droplets of nanodots in ethanol on 300 mesh Carbon Type-B Formvar film-coated Cu grids (Ted Pella) and drying for several hours. Nanoparticle size distribution was determined by manual measurement using ImageJ software. A minimum of 100 individual nanoparticles were used to calculate the mean and standard deviation.

X-ray Photoelectron Spectroscopy Analysis. X-ray photoelectron spectra (XPS) were measured on a Thermo Scientific K-Alpha spectrometer. The obtained binding energies were calibrated with that of the adventitious carbon (C 1s) core level peak at 284.8 eV. Each analysis was performed in triplicate with 10 runs for each scan. The average of the triplicates was plotted for both the survey and the high-resolution scans.

UV–Vis–NIR Absorbance Analysis. The UV–vis–NIR absorption spectra were performed on a Cary 5000 UV–vis–NIR spectrophotometer from 300 to 1200 nm. A 1 cm quartz cuvette was used for analysis. The instrument was set to a 2 nm bandwidth for analysis coupled with a wavelength changeover at 800 nm. The data was processed using Cary Eclipse software.

Hydrodynamic Diameter Measurements. The hydrodynamic diameters were measured using a Malvern Zetasizer Nano-S. All experiments were carried out using a disposable folded capillary cell (Malvern). For each experiment, 10 measurements comprising 20 runs were recorded. For each sample, experiments were repeated three times. The concentration of the samples was ~0.5 mg/mL in Millipore water. Measurements were carried out using 0.7 mL of the solution.

MATERIALS AND METHODS

Materials. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and poly(vinylpyrrolidone) (PVP, Mn = 40 000) were purchased from Alfa Aesar. D-Glucose and 4-nitrophenol were obtained from Sigma-Aldrich. Sodium borohydride (NaBH₄) was purchased from Fluka. All of the reagents were of analytical grade and were used directly without further purification.

Synthesis of Bismuth Nanodots. In a typical procedure, 1 mmol of Bi(NO₃)₃ was added to a solution of D-glucose and PVP in 50 mL Millipore water. The mixture was stirred in a water bath at 70 °C, and 10 mM of 5 M aqueous NaOH, preheated to 70 °C, was added dropwise, upon which black bismuth particles began to form. The mixture was kept stirring at 70 °C for 2.5 h and then left standing at 25 °C for 10 h. The resulting product, a black powder, was collected from the supernatant via centrifugation. Purification was achieved by washing with ethanol and water three times. The product was freeze-dried for 24 h and stored at 25 °C thereafter.

Powder X-ray Diffraction Analysis. X-ray diffraction patterns were measured on a Bruker D2 Phaser diffractometer using Cu Kα radiation (λ = 0.15405 nm). Analysis of the powder was carried out over the range of 2θ = 10–80° with a step size of 0.02° and a 0.5 s count time. Analysis was carried out using MDI Jade software.

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Fourier-Transform Infrared Spectroscopy (FTIR). FTIR spectra were collected using a Thermo Scientific Nicolet iS5 equipped with an iDS ATR accessory. Spectra were collected over the range of 525–4000 cm⁻¹ using 64 scans, with a resolution of 0.4 cm⁻¹, a gain of 1, an optical velocity of 0.4747, and an aperture setting of 100. The data were processed using the Omnic 9 software package.

**Catalytic Reduction of 4-Nitophenol.** A freshly prepared aqueous solution of NaBH₄ (30 mM, 1 mL) was added to 0.3 mL 4-NP aqueous solution (2 mM) and 1.4 mL of water. The color of the solution quickly changed from light to deep yellow following the addition of NaBH₄. The bismuth nanodot suspension in water (0.75 mg/mL) was then added to the mixture until the deep yellow solution gradually became colorless. During the course of the catalytic reduction reaction, UV–vis absorption spectra were recorded to monitor reaction progress over time, from 250 to 550 nm, at 25 °C. The bismuth nanodots were separated, freeze-dried, and reused for 3 successive repeated cycles to investigate the reusability of bismuth nanodot catalysts for the same reaction procedure.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01736.

PXRD, TEM, DLS, and image of bismuth nanoparticles prepared for control experiments; UV–vis spectra of control experiments (PDF)

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**ABBREVIATIONS**

PVP, poly(vinylpyrrolidone); 4-NP, 4-nitrophenol; 4-AP, 4-aminophenol; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; UV–vis–NIR, ultraviolet–visible–near-infrared; FTIR, Fourier-transform infrared; XRD, X-ray diffraction; JCPDS, Joint Committee on Powder Diffraction Standards; SAED, selected area diffraction; DLS, dynamic light scattering

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