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Facile route to silver submicron-sized particles and their catalytic activity towards 4-nitrophenol reduction

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ABSTRACT

A facile, efficient, and environmentally friendly synthetic route was developed to fabricate silver submicron-sized particles by reducing silver nitrate with EDTA in aqueous solution. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM) analysis revealed the formation of silver particles, with sizes ranging from 100 to 800 nm. By varying the amount of EDTA utilized in the reaction medium and/or hydrothermal reaction time, the size of prepared silver particles can be readily controlled. Compared with silver nanoparticles, the as-synthesized submicron-sized silver particles were found to show a comparable catalytic activity towards the reduction of 4-nitrophenol to 4-aminophenol in the presence of an excess amount of $NaBH_4$.

1. Introduction

Silver materials have attracted tremendous attention in recent years due to numerous applications including surface-enhanced Raman scattering (SERS), catalysis, optoelectronics, and biomedicine [1–3]. Generally, the intrinsic properties of silver materials can be effectively tailored by controlling their size, shape, composition, crystallinity, and structure. For example, a recent study by Liang et al. has shown that the nanometer-scale surface roughness of silver particles can provide several hot spots on a single particle, which could significantly increase SERS enhancement [4]. So far, there have been a variety of routes to synthesize silver particles of various morphologies for desirable properties, such as chemical reductions [5–10], photoinduced method [11], electrochemical method [12], ultrasonic-assistant method [13], solvothermal method [14], and templates method [15,16]. In particular, chemical reduction of silver precursor in the presence of both reducing agent (e.g., sodium borohydride or hydrazine) and capping agent (e.g., PVP) is the most commonly used method. However, the reducing agents used in some of these approaches are somewhat expensive, and have been suggested to be harmful to the environment [9]. Further, most of these studies are limited to silver nanoparticle system. There is only limited literature on the controllable synthesis of silver crystals at sub-micrometer scale, although large colloidal silver particles may find important applications in catalysis, sensing, SERS, and photonic crystals [17,18]. Therefore, it is desirable to develop a facile, low-cost, and environmentally friendly method for the fabrication of submicron-sized silver particles as well as to explore their property, such as catalytic activity.

As a well-known chelating agent, ethylenediaminetetraacetic acid (EDTA) has been widely adopted as a crystal-growth-regulator in the fabrication of micro-/nanostructured materials owing to its outstanding chelating ability [19–21]. We have recently developed a double-chelating-agent system for the morphology-controlled synthesis of fluorapatite microcrystals, where EDTA was utilized as a chelating agent [22–25]. In contrast, the report on the fabrication of micro-/nanostructured material by using EDTA as a reducing agent is scarce. In pioneering work reported by Lee et al., silver colloids were synthesized by using EDTA as a reducing agent [26]. Recently, Bright et al. have demonstrated a self-assembly onto organosilane-coated substrates of colloidal Ag nanoparticles derived from citrate reduction and from EDTA reduction [27]. To the best of our knowledge, there is no documentation about the synthesis of submicron-sized silver particles by the reduction of silver salt using EDTA as a reducing agent. Herein, we demonstrate the first example of preparation of silver submicron-sized particles via a simple hydrothermal process using EDTA as a reducing agent. The size of the prepared silver particles can be readily controlled by varying the amount of EDTA utilized in the reaction medium and/or hydrothermal reaction time. In addition, a potential application of the resulting silver particles toward catalyzing a redox reaction of 4-nitrophenol in the presence of an excess amount of $NaBH_4$ are discussed in detail.

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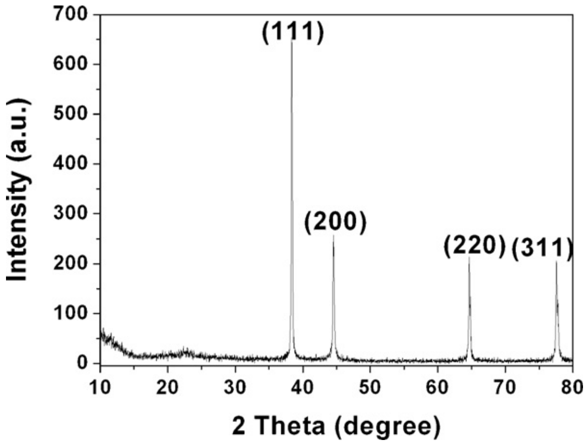

Fig. 1. Typical XRD pattern of sub-microsized silver particles prepared at 150 °C for 4 h in the presence of EDTA.

2. Experimental

Ethylenediaminetetraacetic disodium salt (Na_2EDTA), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), and 4-nitrophenol were purchased from Sinopharm Chemical Reagent Co., Ltd., China and used as-received without any further purification.

In a typical procedure, 0.9306 g of Na_2EDTA was first added to 20 mL of distilled water at room temperature. After Na_2EDTA was completely dissolved, 0.1673 g of $AgNO_3$ was added to the above solution, leading to the formation of white precipitant. After being stirred for 30 min, the mixture was transferred into a Teflon-lined stainless steel autoclave with a volume of 25 mL, and a thermal treatment was performed for the autoclave in an electric oven at 150 °C for 4 h. After the autoclave was cooled naturally to room temperature, the resulting powders were collected by centrifugation and washed for at least three cycles using deionized water and one cycle using pure ethanol. The as-synthesized samples were then dried in a vacuum oven at 40 °C overnight to remove the absorbed water or pure ethanol for the subsequent characterizations.

The phase purity and crystal structure of the obtained samples were examined by X-ray diffraction (XRD) using D8 Advance X-ray diffraction (Bruker axs company, Germany) equipped with Cu-Kα radiation (λ) 1.5406 (Å), employing a scanning rate of $0.02^\circ\,s^{-1}$ in the 2θ range from 10 to 80°. The morphology of the silver sub-microsized particles were examined by scanning electron micrograph (SEM) using a field emission SEM (FESEM) instrument (Hitachi S-4800 II, Japan). Transmission electron microscopy (TEM) was recorded on a JEOL-JEM-2010 (JEOL, Japan) operating at 200 kV.

The catalytic redox reaction process was set up in a standard cell with 1 cm path length and 3 mL volume. Firstly, 0.2 mL of 0.3 M freshly prepared $NaBH_4$ aqueous solution was added to a quartz cell containing 4-nitrophenol (2.8 mL of a 0.1 mM solution) with stirring at 295 K, and the solution color changed from light yellow to yellow-green rapidly. Immediately after the addition of as-prepared silver particles prepared with EDTA/$AgNO_3$ molar ratio of 1:1 (0.1 mL of a 0.5 mM dispersed solution), the absorption spectra were continually recorded by a Shimadzu UV2550 spectrophotometer over a scanning range of 200–600 nm at 295 K with a time interval of 240 s. The rate constant of the redox reaction was dependent on the change in absorbance at 400 nm as a function of time.

3. Results and discussion

The crystal structure and the phase purity of sub-microsized silver particles obtained via hydrothermal process at 150 °C for 4 h in the presence of EDTA (molar ratio of EDTA/$AgNO_3$ is 1:1) were determined by XRD. Fig. 1 shows a typical XRD pattern of the as-prepared silver sample, clearly confirming the presence of face-centered cubic (fcc) structure of bulk silver. No impurity phase could be found in the sample. The high and sharp peaks indicate that the as-prepared sub-microsized silver particles were well crystallized.

The morphology of the as-synthesized silver particles was investigated by FESEM first. Fig. 2a is a typical FESEM image of the as-synthesized silver product indicating that the sample consists of abundant spherical particulates with sizes ranging from 400

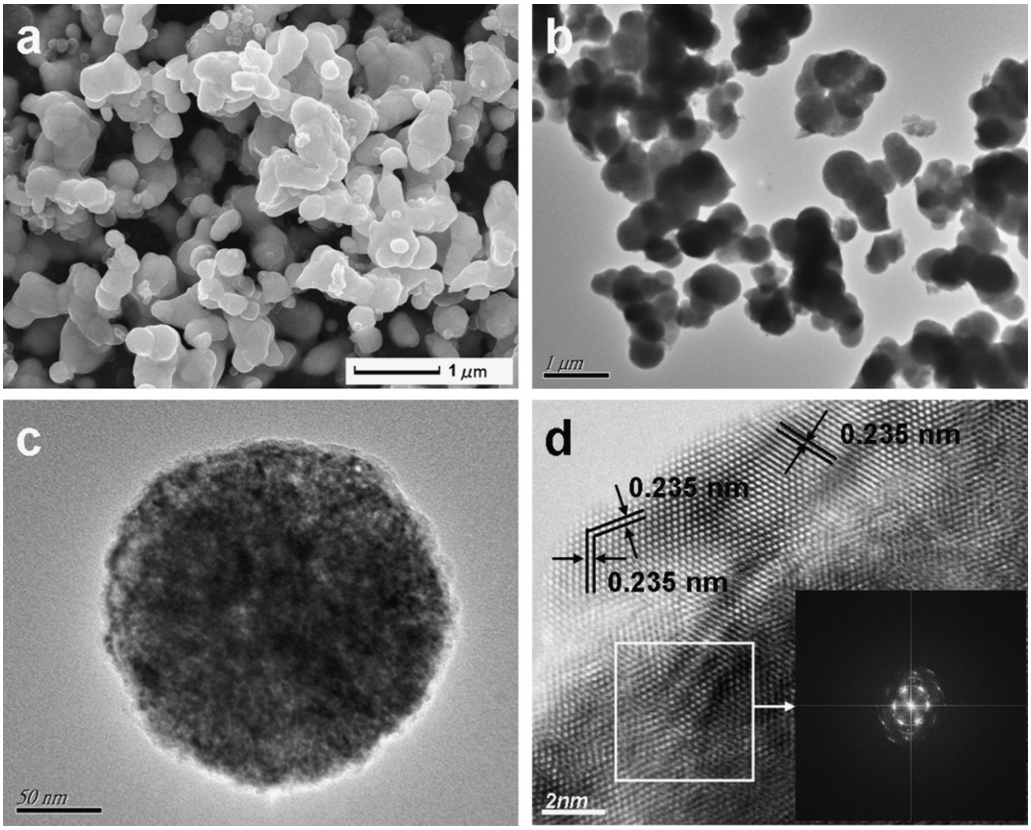

Fig. 2. (a) FESEM image, (b and c) TEM images with different magnifications, and (d) HRTEM image of the submicron-sized silver particles obtained by reducing silver nitrate with EDTA in aqueous solution. The inset in Fig. 2d is the corresponding fast Fourier transform (FFT) image of the selected area.

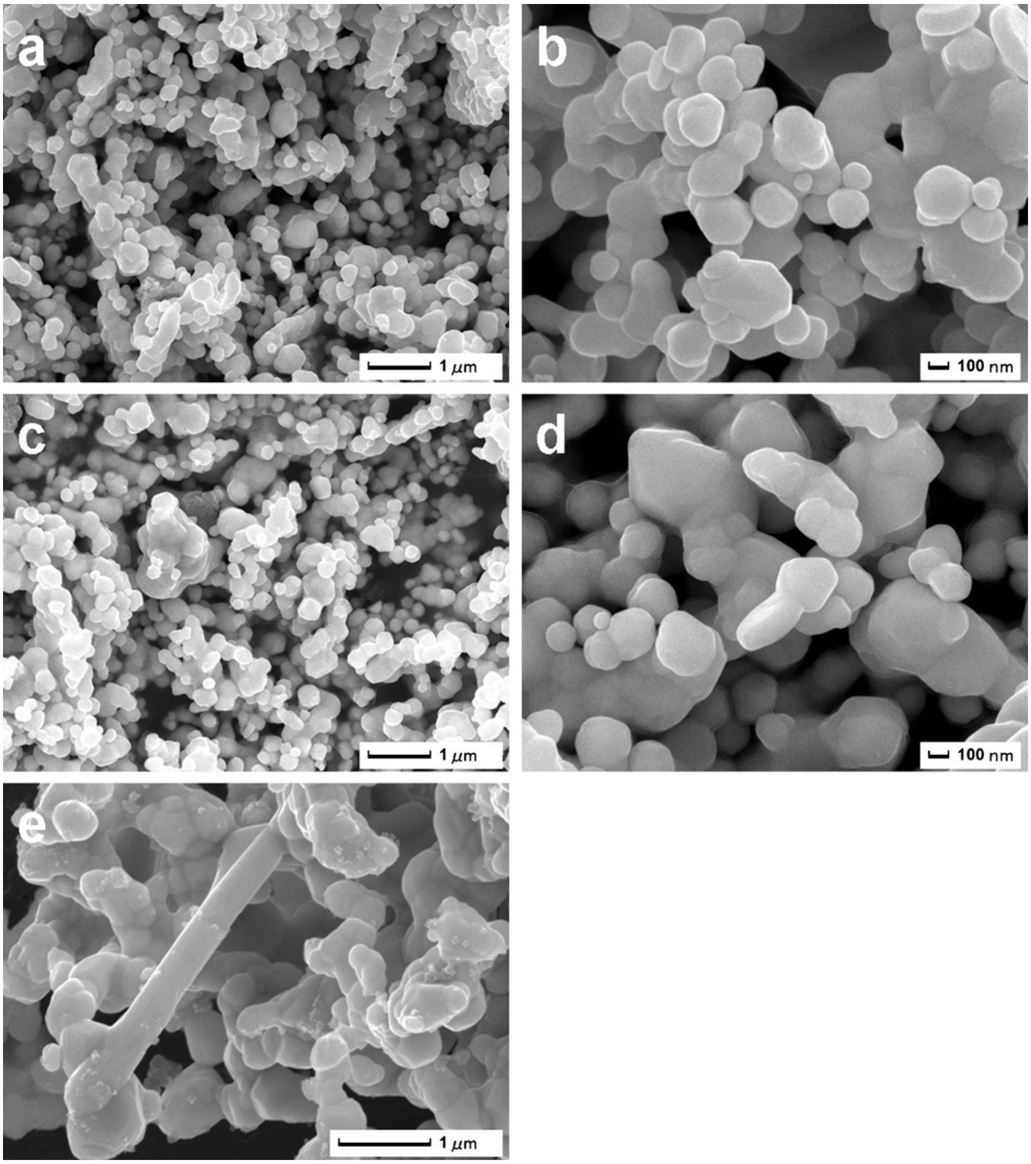

Fig. 3. FESEM images of submicron-sized silver particles prepared with varying initial molar ratios of EDTA to $AgNO_3$: (a and b)1:4; (c and d)1:2; (e)2:1.

to 600 nm. The crystalline structure of the silver submicron-sized particles was further characterized by TEM. Fig. 2b presents a low-magnification TEM image of the prepared silver submicron-sized particles. It further indicates that the majority of the silver particles were spherical in shape, with a slight aggregation. Close observation from a high-magnification TEM image in Fig. 2c of a single spherical silver particle reveals that the formed particle is polycrystalline, although the lattice fringes in the HRTEM image (Fig. 2d) were all determined to be 0.235 nm, which are well-indexed to the (1 1 1) lattice plane of face-centered cubic silver. The inset in Fig. 2d is the corresponding fast Fourier transform (FFT) image of the selected area, further suggesting the polycrystalline nature of the as-synthesized submicron-sized silver particles.

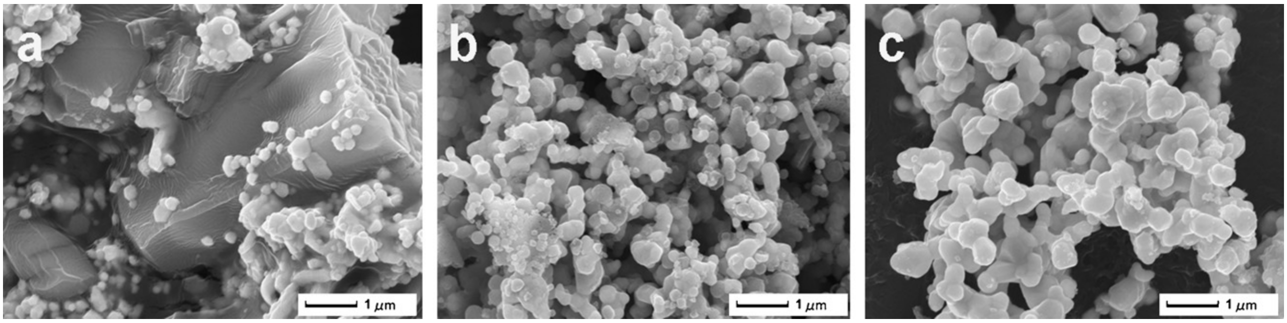

Fig. 4. Typical FESEM images of silver samples prepared in the presence of EDTA at 150 °C for (a) 0.5 h, (b) 1 h, and (c) 2 h.

In a control experiment, no silver particles formed after the hydrothermal process at 150 °C for 4 h in the absence of EDTA. This suggests that EDTA could play a crucial role in the formation of submicron-sized silver particles. To reveal the effect of EDTA on the formation of submicron-sized silver particles, we performed a series of experiments by varying the initial molar ratios of EDTA to AgNO$_3$, while keeping other parameters constant. In the absence of EDTA, no product was formed. As shown in Fig. 3a and,b, silver particles with sizes ranging from 100 to 300 nm were obtained when the initial molar ratio of EDTA to AgNO$_3$ was 1:4. By increasing the added amount of EDTA (EDTA/AgNO$_3$ = 1:2), the morphology and size of the resulting silver particles are almost unchanged (Fig. 3c and,d). In contrast, when the molar ratio of EDTA to AgNO$_3$ was continuously increased to 1:1, the size of the obtained silver particles increased (Fig. 2a). However, increasing the EDTA to AgNO$_3$ molar ratio to 2:1 led to the formation of silver particles with nonuniform morphology. It can be found that silver microrods and sub-microparticles coexisted in the sample (Fig. 3e). In comparison with the samples prepared at lower EDTA/AgNO$_3$ molar ratios (see Figs. 2aand 3b and d), the silver sample synthesized under this condition appears silver particle aggregations, with a larger size up to about 800 nm. The size change of Ag particles could be attributed to the fact that, as more EDTA was used, there may be more Ag nuclei are formed as a result of the reduction of AgNO$_3$ by EDTA, which then aggregate into larger Ag particles as the reaction going on. On the basis of these observations, it can be assumed that the size of the silver particles can be readily tuned by varying the amount of EDTA utilized in the synthesis.

To investigate the details of the formation of silver submicron-sized particles, time-dependent experiments were carried out. The molar ratio of EDTA/AgNO$_3$ was kept at 1:1. Fig. 4 shows the growth evolution of the silver particles. With hydrothermal reaction for 0.5 h, the resulting silver sample consists of large microsized particles, along with many small nanosized silver particles with an average size of around 100 nm (Fig. 4a). When the hydrothermal reaction time was 1 h, the as-prepared sample was dominant by submicron-sized silver particles, having an average size of ∼300 nm (Fig. 4b). With increasing the reaction time to 2 h, the resultant silver sample was still composed of submicron-sized particles, but with a rather larger size of ∼400 nm (Fig. 4c). As shown in Fig. 2a, when the hydrothermal time was 4 h, silver particles with sizes of ∼400–600 nm were obtained. From these observations, a growth process from small nanoparticles to final submicron-sized particles was clearly observed. It also reveals that the size of silver particles can be adjusted by varying the hydrothermal reaction time.

As a well-known chelating reagent, EDTA has been widely used as crystal-growth-regulator for obtaining micro-/nanoparticles with distinct shapes [19–21]. EDTA has also been used as derivatizing agent for obtaining stable nanoparticles [28]. Base on the fact that the two oxygen atoms of the carboxylate groups of EDTA can be coordinated symmetrically to the Ag atoms, Wang and co-workers have recently synthesized silver nanoparticles coated with EDTA by citrate reduction method [29]. Similarly, Bright et al. have demonstrated a self-assembly onto organosilane-coated substrates of colloidal Ag nanoparticles derived from citrate reduction and from EDTA reduction [27]. In the present work, EDTA was employed not only as the reductant for the reduction of Ag salts, but also probably as the chelating reagent for the formation of Ag-EDTA complexes, which enables the controlled release of Ag$^+$ ions into the reaction medium and subsequent size control of the final submicron-sized silver particles. Though the mechanism behind the fast reduction of silver salt in the presence of EDTA is still not clear at this time, the results obtained here do provide the prerequisite for the controlled synthesis of submicron-sized silver particles through the approach proposed here. The exact mechanism of the present reduction reaction is worth further investigation.

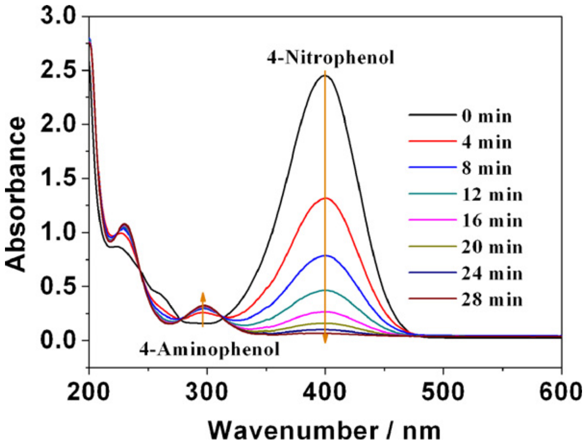

Fig. 5. UV/vis absorption spectrum for the reduction of 4-nitrophenol over silver submicron-sized particles (prepared with EDTA/AgNO$_3$ molar ratio of 1:1) with an excess amount of NaBH$_4$ in aqueous media at 295 K.

One of the important applications of the metal nanoparticles is to activate/catalyze some reactions that are otherwise unfeasible. To this end, the catalytic activity of submicron-sized silver particles on the reduction of 4-nitrophenol was investigated in the study. In the absence of silver particle catalyst, the absorption peak at 400 nm remained unaltered for a long period, which implies that 4-nitrophenolate anions cannot be reduced by aqueous NaBH$_4$. When silver submicron-sized particle dispersion, with particle sizes ranging from 400 to 600 nm (prepared with EDTA/AgNO$_3$ molar ratio of 1:1), was added to the reaction system, a fading and ultimate bleaching of yellow-green color of 4-nitrophenolate ion in aqueous solution was observed, revealing the occurrence of the reduction reaction. The UV/vis spectra in Fig. 5 unambiguously verify this conclusion as well, as the absorption band of 4-nitrophenolate ion at 400 nm decreases and disappears within 28 min, with the concomitant appearance of two new peaks at 300 nm and 230 nm, respectively, which were attributed to the generation of 4-aminophenol. Since the concentration of BH$_4^-$added in the system is much higher than that of 4-nitrophenol, it is reasonable to assume that the concentration of BH$_4^-$remains constant during the reaction. In this context, pseudo-first-order kinetics could be used to evaluate the kinetic reaction rate of the current catalytic reaction. Fig. 6 shows a linear correlation between ln(A)

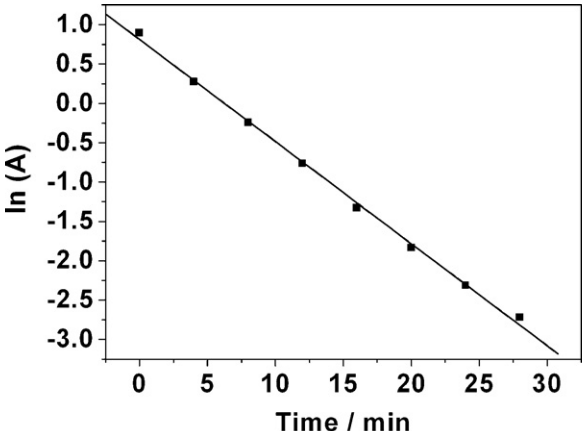

Fig. 6. Plot of ln(A) versus time for the silver submicron-sized particles (prepared with EDTA/AgNO$_3$ molar ratio of 1:1) catalytic reduction of 4-nitrophenol.

and reaction time at 295K, indicating that the reaction is a pseudo-first-order. The apparent rate constant (k) at 295K was calculated from the slope to be $2.15 \times 10^{-3}\,\mathrm{s}^{-1}$. This value obtained for 4-nitrophenol reduction is comparable to the previous findings in the literature for the nanosized silver particles. For example, Li et al. demonstrated that the largest kinetic reaction rate constant of catalytic reduction among those of the prepared Ag nanomaterials with varying morphologies and sizes is $1.27 \times 10^{-2}\,\mathrm{s}^{-1}$ [9]. Our values are close to the values reported by Lu et al. for such catalytic conversion using poly(N-isopropylacrylamide)-based Ag nanoparticles [30]; and these values also are close to the values by Rashid et al. for the same catalytic conversion using Ag nanostructures with different dendritic morphologies [31]. We thus believe that the submicron-sized Ag particle obtained by our reported method is another promising candidate for use as a catalyst in the redox reaction of 4-nitrophenol.

4. Conclusions

We have shown that submicron-sized silver particles can be synthesized by using EDTA as a reducing agent. No environmentally harmful reducing agent or surfactant is needed in the procedure, making the reported route attractive for the large-scale silver particle production. The as-synthesized silver particles have sizes ranging from 100 to 800 nm, which can be readily tuned by varying the amount of EDTA and/or hydrothermal reaction time. Moreover, in comparison with silver nanoparticles, the as-synthesized submicron-sized silver particles were found to exhibit a comparable catalytic activity towards the reduction of 4-nitrophenol to 4-aminophenol with an excess amount of $NaBH_4$ in aqueous media. It is important to note that this silver-particle synthesis approach may be reasonably extended to the preparation of other metal nanoparticles, which is part of our on going work.

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