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Fabrication of silver nanoparticles through reduction by ε-caprolactam without using protecting agent

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Abstract: ε-caprolactam (CL) was used as a multifunctional medium to synthesize silver nanoparticles (Ag NPs). In this method, CL played three key roles including reducing agent, protecting agent and solvent. The identity of the solid substance generated in molten CL, silver nanoparticles (Ag NPs), was verified by X-ray diffraction (XRD). The particle size of the as-synthesized Ag NPs was uniform and less than 15 nm. Coordination of CL with silver ions/atoms and moderate reduction contributed together to the resultant nanosize silver particles.

Applications of the significant features of silver are of continuing interest since ancient times. Because of the controllable size distributions and shapes, as well as a large surface area,[1] silver nanoparticles (Ag NPs) have potential applications such as novel electrical, optical, magnetic, catalytic, and sensing technologies.[2]

Since Faraday first presented the preparation of metal nanoparticles in aqueous medium,[3] a large number of methods have been developed for the synthesis of Ag NPs. Besides the irradiation of the solution containing silver ions with ultraviolet, visible light or microwave,[4] the most important strategy for Ag NPs fabrication is the chemical reduction of precursors by reducing agent such as sodium borohydride,[5] citrate,[6] polyalols,[7] N,N-dimethylformamide,[8] as well as polysaccharide.[9] In order to fabricate Ag NPs with ideal size and shape in aqueous medium, the reducing agent, protecting agent and solvent are the most important factors and should be carefully chosen.

ε-caprolactam (CL) has high polarity, high boiling point, good coordinating capacity, and is relatively stable at moderate temperature. We have demonstrated previously that it can act as an effective medium for NPs dispersion and guarantee uniform distribution of NPs in the resultant *in situ* polymerized product of polyamide 6 matrix.[10] When we precipitated metallic oxide NPs from molten CL for the first time,[11] it seemed that CL was likely to be a good medium for many metal salts,[12] which would facilitate the fabrication of NPs in molten CL.

In this paper, a brand new route for Ag NPs fabrication is presented in which neither extra solvent nor extra protecting agent were needed.[13] The CL itself played all three key roles: solvent, protecting agent and reducing agent, a process that has rarely been reported previously.

In a typical synthesis, different dosages of $AgNO_3$ (0.085~0.255 g) were added to 20 g CL melt at 140 °C. The mixture was stirred for 16 h under the protection of argon (Ar). The precipitate was collected by alternately wash with ethanol and centrifugation for three rounds. The suspension containing Ag NPs was characterized by TEM, and the results are illustrated in Figure 1. The size of

Ag NPs was less than 15 nm for all three samples. It can be seen that the weight ratio between CL and $AgNO_3$ strongly influenced the size of the resultant particles. All of the particles were less than 7.5 nm when the dosage of $AgNO_3$ was 0.085 g. About 85 % particles were spread between 2.5 and 6 nm. When the dosage of $AgNO_3$ was increased to 0.17 g, the size distribution became narrower and the size of most particles was in the range of 8~13 nm. The percentage of size between 8~12.5 nm was over 85 %. The size distribution was relatively narrow with a standard deviation of 9 %. With a further increase of dosage of $AgNO_3$, some particles with size less than 7.5 nm were generated. Compared with the former sample, although the particle size spanned the same range, the distribution was altered, and the standard deviation was 28 %.

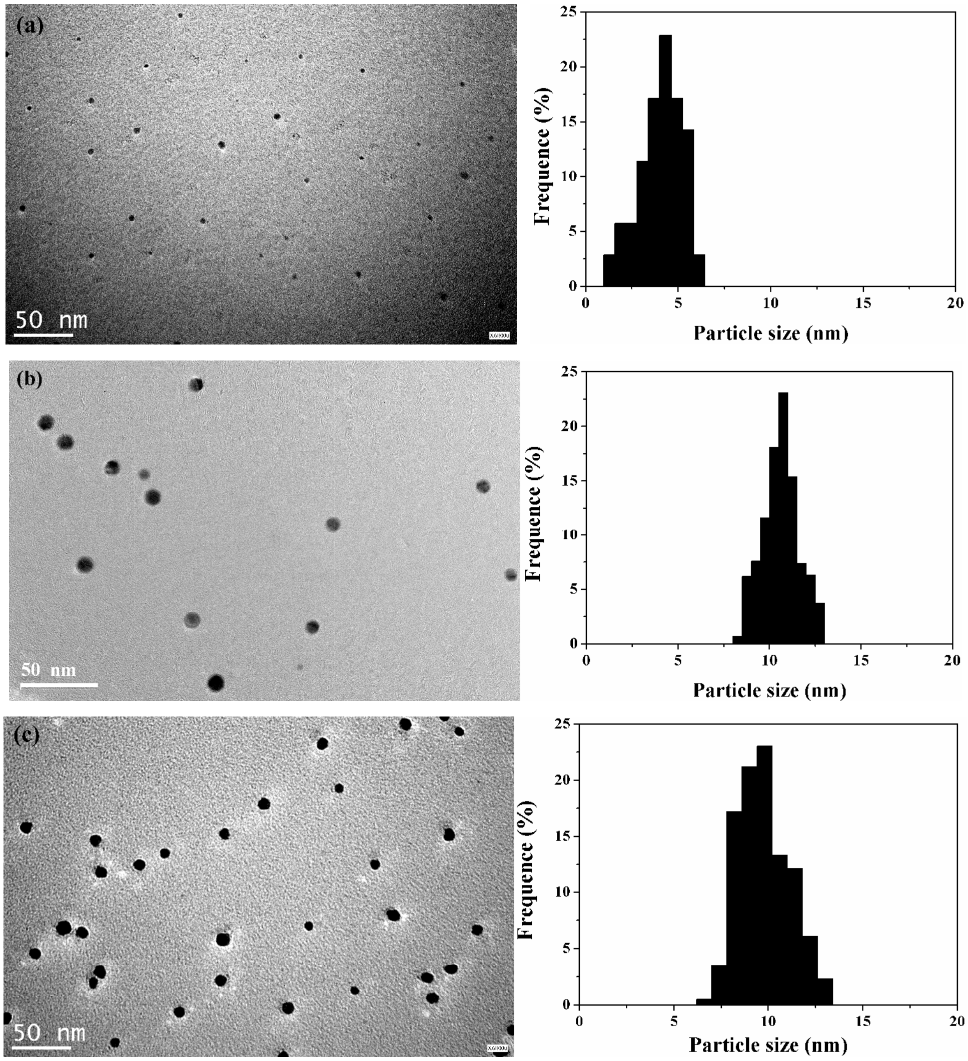

Figure. 1 TEM micrographs and particle size distribution of resultant Ag NPs. TEM graph From (a) to (c) correspond to Ag NPs prepared with different dosage of $AgNO_3$: (a) 0.085 g, (b) 0.17 g and (c) 0.255 g.

Precious metals are known for the possibility of sintering at relatively lower temperature when synthesized in organic or inorganic media.[14] As we performed at relatively high temperatures (140°C), the formation of the particles could be a result of particle-particle sintering during reaction. Close observation of the TEM in Figure 1 showed no sintered particles. The X-ray diffraction pattern of Ag NPs prepared at the dosage of $AgNO_3$ 0.17 g is shown in Fig. 2. The peaks centered at 2-theta corresponded to 38°, 44°, 64°, 77° and 81° corresponding to (111), (200), (220), (311), and (222) planes respectively[15]. The powder exhibits good crystallinity. According to the mathematical deconvolution of the peaks, the particle size can be calculated according to Scherrer formula.[14] Width at half maximum intensity of (111) plane indicated a crystallite size of 8 nm. This approximate value was close to the mean particle sizes calculated by image analyses of our colloids (ca. 11 nm). Since Scherrer formula always tends to underestimate the real crystallite size,[14] this result seems to favor the hypothesis of the monocrystallinity of the particles.

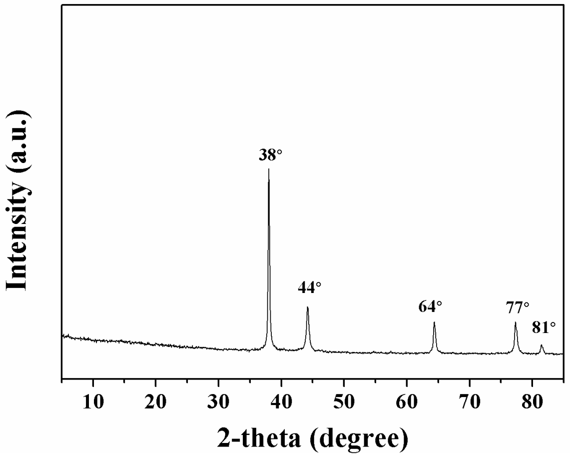

Figure. 2 XRD pattern of the synthesized Ag NPs

When the temperature was elevated to 140°C, the appearance of the mixture of $AgNO_3$ and CL changed gradually from clear and transparent at beginning, to yellow, and then to opaque black at the end, suggesting thermal reduction of $AgNO_3$ in molten CL. Previous reports of the change of graphene oxide to graphene by decomposition of labile oxygen-contained moieties in the molten CL after the treatment at 250°C for 8 hours was the indirect evidence for the reducibility of CL.[18] The shiny silver mirror on the inner surface of flask at the end of the reaction also indicated the formation of metallic silver.

The upper transparent solution was characterized by UV-vis spectra as shown in Figure 3. For comparison, UV-vis spectra of pure CL treated at different conditions were also recorded. Pure CL treated at 140°C for 16 hours under the protection of argon (Ar) showed no absorption at range of 220~500 nm (curve 1). However, when pure CL was treated by oxygen (O_2, 30 ml/min) at 140°C for 16 hours without addition of $AgNO_3$, an intensive absorption at 240 nm appeared (curve 3). This means that at 140 °C, O_2 could oxidize CL, and the new absorption peak at 240 nm corresponds to the oxidation product of CL. The same absorption peak at 240 nm was also observed when $AgNO_3$ was added to molten CL after the reaction sustained at 140°C for 16 h under protection of Ar (curve 2). The absence of absorption at 240 nm in the case of pure CL protected by Ar indicates that CL experienced no chemical conversion (curve 1). Similar absorption at 240 nm for CL treated by different oxidizing agents (O_2 and $AgNO_3$, curve 3 and curve 2) illustrates that the same oxidation product was generated, and as a result, we can conclude that reduction of $AgNO_3$ can be initiated by CL at 140 °C. Furthermore, the intensity of the absorption peak of oxidized CL was 0.75 when treated by $AgNO_3$ and 0.87 when treated by O_2, the sum of which was almost equal to the absorption intensity of 1.54 of the oxidized CL treated by $AgNO_3$ and O_2 together (curve 4). Thus, it can be deduced that in the preparation of Ag NPs, CL played the role of reducing agent and initiated the reduction of $AgNO_3$ at 140°C.

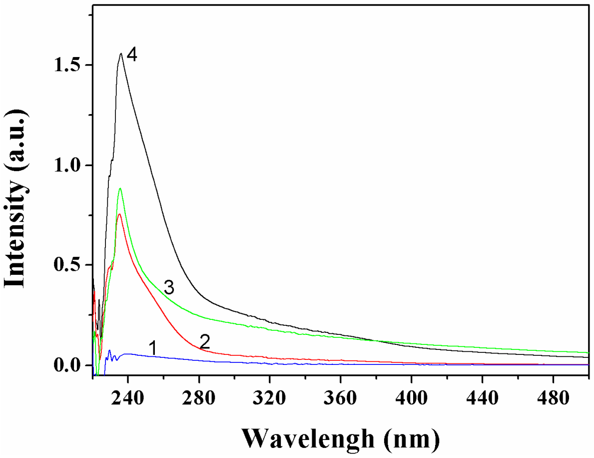

Figure. 3 UV-vis spectra of CL treated at different conditions. Curve 1 represents the pure CL treated under the protection of Ar. Curve 2 and curve 3 illustrate the CL treated by $AgNO_3$ and by O_2, respectively. Curve 4 corresponds to the CL treated by $AgNO_3$ and O_2 together.

In previous studies of the thermal oxidation of CL initiated by O_2, it was found that products of this reaction were caprolactam hydroperoxide, adipimide and adipic acid monoamide.[19] The kinetics analysis of thermally initiated oxidation of CL indicated that caprolactam hydroperoxide was the primary product, and adipimide and adipic acid arose from consecutive decomposition reactions of caprolactam hydroperoxide.[19] The UV-spectra in Figure 3 indicate that CL may be oxidized by $AgNO_3$ in a mechanism similar to that of the oxidation of CL initiated by O_2. Because the carboxylic group of adipic acid monoamide was the inhibitor of the oxidation of caprolactam,[19] only low yields of oxidation products of CL were reported.[20] Although there are several published works analyzing the impurities and oxidation products of CL,[21] the results are confusing. ^{13}C NMR spectra of pure CL, CL oxidized by $AgNO_3$ and O_2 showed no difference in the chemical shift in Figure 1S. Maybe this explains why the studies of oxidation of CL provided little statistical information about oxidation products of CL.[19, 20]

CL is the precursor monomer of polyamide 6, which is a well-known condensation-type polymer with extensive applications in the field of fibers and engineering materials.[16] In the *in situ* preparation of NP-filled polyamide composites, CL was always used as dispersant of NPs without using other solvents. As a result, potential particle aggregation of NPs caused by solvent evaporation was effectively avoided. Many metal salts could be completely dissolved in molten CL, and metallic oxide NPs could be generated when a precipitator (sodium hydroxide) was added.[11] The nanoscale size of the as-prepared particles could be attributed to the coordination of the metal ion/atom by CL.[11] The typical coordinating effect between CL and silver ions has been illustrated in Figure 2(S). The retardation in weight loss for CL could be explained by the coordination between CL and silver ions. The surface property of resultant Ag NPs was characterized by FTIR which is shown in Figure 3S. It is apparent that the silver particles collected from CL shared the typical signal of CL at bonds of amide I and amide II, as well as the stretch vibration of C-H. It means that the surface-bound CL may be responsible for the nanosize of the resultant Ag NPs.

In addition, the test of conductivity showed that the mixture of $AgNO_3$ and molten CL was ~100 $\mu S{\bullet}cm^{-1}$ (Figure.4S), while the conductivity of silver nitrate aqueous solution was greater than $10^5 \mu S{\bullet}cm^{-1}$ at the same concentration. This indicated that $AgNO_3$ was partly ionized in molten CL, but the concentration of silver ions from $AgNO_3$ in molten CL was very low. Unionized $AgNO_3$ was the stock of silver ions, which continuously replenished the silver ions after they were consumed through the reduction by CL. The little variation in conductivity of the mixture after 120 min indicated that the concentration of silver ions did not vary much. As a consequence, the low and stable concentration of silver ions kept the reaction of $AgNO_3$ with CL at a moderate rate. Combining the coordination between silver ions/atoms and CL and the moderated rate of reduction of $AgNO_3$, leads to production of nanosize silver particles.

Conclusions

In summary, we have presented a novel method employing CL as not only solvent, but also reducing agent and stabilizer for synthesis of Ag NPs. What's more, Ag NPs with homogeneous size were guaranteed (as is shown by TEM) because of the coordination effect of CL with silver ion/atom and moderate rate of reduction of Ag NO_3.

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Notes and references

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Support figures

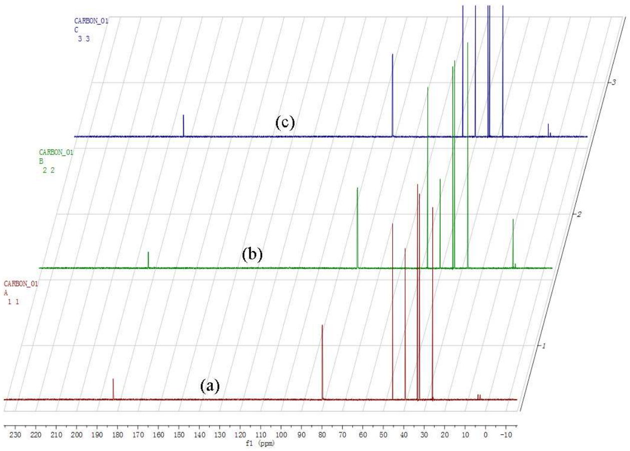

Figure. 1S NMR spectra of pure CL (a) and CL after oxidation by silver nitrate (b) and oxygen (c). (NMR samples were prepared by dissolving the purified CL and oxidizing CL by silver nitrate and oxygen to give a sample with concentration of 10mg/ml in $CDCl_3$. Solution ^{13}C NMR spectra were collected on a VNMRS 600 MHz NMR. A 5-mm NMR probe was used with an average of 2,000 scans to give sufficient signal-to-noise signals. The chemical shift was recorded in relation to TMS.)

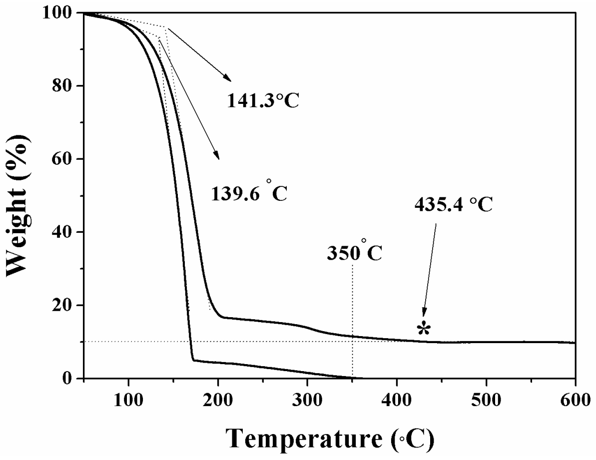

Figure. 2S TG curves for the CL and mixture of CL and silver nitrate. The mixture consisted of 10 wt% silver nitrate (It was performed over a temperature range of 50-600° C using TA instrument SDT Q600 under nitrogen atmosphere with heating rate of 10 ° C/min. After addition of silver nitrate, the maximum weight loss in TGA curve was shifted to 141.3° C from 139.6° C for the pure CL. Pure CL lost all its weight beyond its boiling point (350 ° C) via volatilization under nitrogen flux. Contrasted to pure CL, the weight of the AgNO3-CL was 11.6 wt% at 350°C. This value was higher than the initial ratio of silver nitrate in the mixture (10 wt%), which indicates 1.6 wt% CL existed at 350° C, and eventually the mixture lost all CL at 435.4° C. The retarded effect in weight loss of CL endowed by silver nitrate could be attributed to the coordinative effect between CL and silver nitrate.)

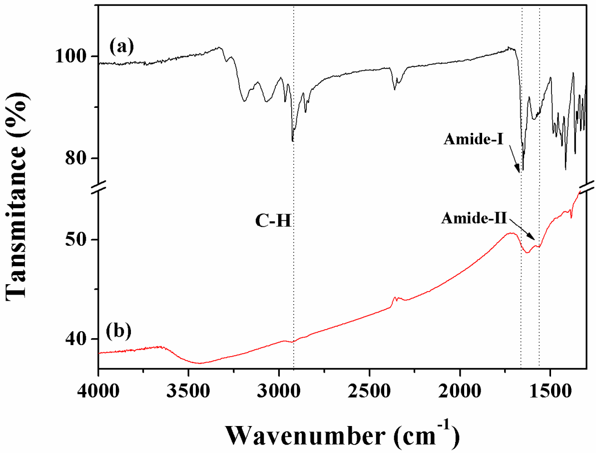

Figure. 3S FTIR spectra of pure CL (a) and Ag NPs (b). (Measurements were made at a resolution of 4 cm^{-1} with the use of 32 scans on a Bruker Vector 22 FTIR spectrometer. For pure CL, the characteristic vibration of C-H, amide-I and amide-II is clearly disclosed. The spectra of resultant Ag NPs possess the similar vibration of C-H, amide-I and amide-II. The most important feature distinguishing the surface binding CL onto Ag NPs was the red shift of amide-I and amide-II.)

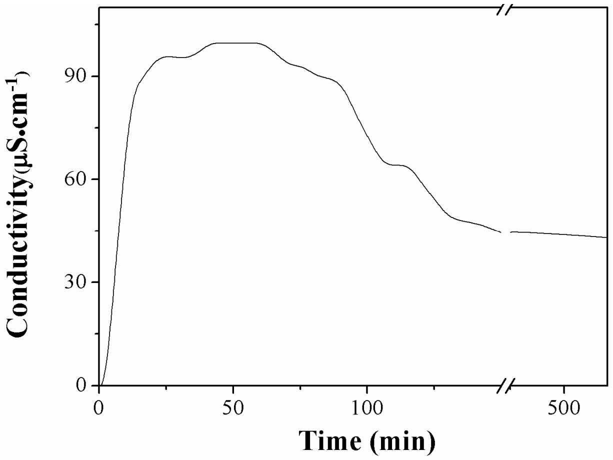

Figure. 4S Conductivity of mixture consisted of 0.17 g $AgNO_3$ and 20 g CL molten.

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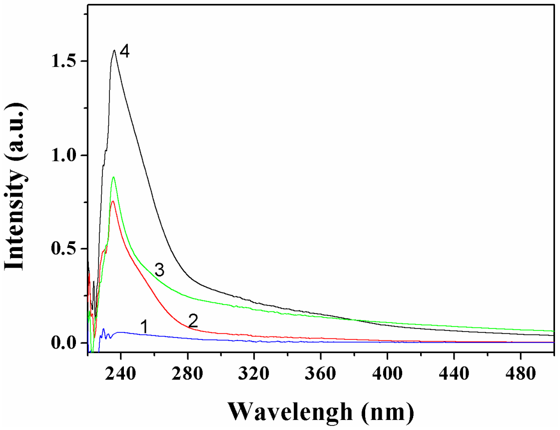
Contents

1 Colour graphic



2 Highlight

ε-caprolactam was used as a multifunctional medium to synthesize silver nanoparticles, in which ε-caprolactam played three key roles including reducing agent, protecting agent and solvent.