One-Step Preparation and Characterization of Poly(propyleneimine) Dendrimer-Protected Silver Nanoclusters

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ABSTRACT: Highly stable silver nanoclusters with narrow size distribution have been prepared by heating a third-generation poly(propyleneimine) dendrimer/$AgNO_3$ aqueous solution without the additional step of introducing other reducing agents and protect agents. UV−vis absorption, transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS), and X-ray diffraction (XRD) have been used to characterize the resulting products. The as-obtained sample was in coexistence of Ag and Ag_2O. It also suggested that increasing temperature resulted in both the decrease in number of small particles and the increase in size of large particles.

Introduction

In recent years, considerable attention from both fundamental and applied research has been paid to synthesizing and characterizing inorganic nanoclusters.[1] Metal nanoclusters, particularly gold, silver, and copper, have been the focus of great interest due to their unique optical properties.[2] Silver nanoclusters play important roles as substrates in studies of surface-enhanced Raman scattering and catalysis.[1d,3] Various methods for the preparation of metal nanoclusters including wet and dry atmospheres have been developed over the past years, and some excellent reviews can now be available;[4] however, the chemical reduction of metal ions in a solution is the most common preparative route. Unfortunately, unprotected metal colloids are susceptible to irreversible aggregation in solution due to small size. One of the effective strategies is to protect colloids with protective agents such as thiols, surfactants, polymers, and polyelectrolytes which can spontaneously adsorb on the particle surface to prevent agglomeration, resulting in stable particles.[5]

Dendrimers are a new class of monodisperse macromolecules with regular and highly branched three-dimensional architecture and surface functionality and widely used in the fields of medicinal chemistry, host−guest chemistry, and catalysis.[6] Dendrimers have recently attracted increasing attention in nanoscale science as a new type of potential template to host inorganic nanoclusters by forming intradendrimer complexes as reported by Balogh's group, Crooks' group,[7] and Esumi's group.[8] In their work, dendrimers served as a template within which metal ions were trapped due to complexation of the metal cations with amine groups in the dendrimer followed by reduction with a reducing reagent to form nanoclusters. Dendrimers have also been used to stabilize and control the growth of nanoclusters by forming interdendrimer complexes, resulting in larger metal nanoclusters protected by the exterior amine groups of dendrimers.[8] Other reports on the preparation of dendimer−inorganic particle nanocomposites have been documented.[9] Additionally, UV, laser,

and X-ray irradiation have also been proved to be effective methods for preparing gold or silver nanoclusters in the presence of dendrimer.[8a,10] As an extension of previous preparative method of dendrimer−inorganic particle nanocomposites, we develop herein a one-step, one-pot method for preparing highly stable dendrimer-protected silver nanoclusters with narrow size distribution whereby silver nanoclusters are directly yielded via heating a third-generation poly(propyleneimine) (**G3 PPI**) dendrimer/$AgNO_3$ aqueous solution, with the use of **G3 PPI** dendrimer to serve as a mild reducing agent and an excellent protective agent.

Experimental Section

G3 PPI dendrimer, fifth-generation poly(propyleneimine) (**G5 PPI**) dendrimer**,** and $AgNO_3$ were purchased from Aldrich and used as received without further purification. The water used throughout all experiments was purified through a Millipore system. The colloidal silver sample was prepared according to the following procedure: First, 200 μL of $AgNO_3$ aqueous solution (0.0168 M) and **G3 PPI** dendrimer aqueous solution (0.0463 M) were added together into a beaker with initial molar ratio 1:10 of **G3 PPI** dendrimer to Ag. The resulting solution was diluted to 20 mL with water and then heated at 100 °C for 70 min.[11]

UV−vis spectra were collected on a CARY 500 Scan UV−vis−near-infrared (UV−vis−NIR) spectrophotometer. TEM measurements were made on a JEOL 2000 transmission electron microscope operated at an accelerating voltage of 160 kV. The sample for TEM characterization was prepared by place a drop of colloidal solution on carbon-coated copper grid and dried at room temperature. Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLAB MKII using Mg as the exciting source. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 200 mA) radiation.

Results and Discussion

Figure 1 shows the UV−vis spectra of the as-prepared silver nanoclusters in water. The colloidal silver thus formed exhibits a strong absorption at 394 nm, corresponding to the dipole resonance of silver nanospheres.[12] Metallic silver is known to have an intense plasmon absorption band in the visible region, and it was confirmed that the Ag 4d to 5sp interband transition generally occurs around an energy corresponding to 320

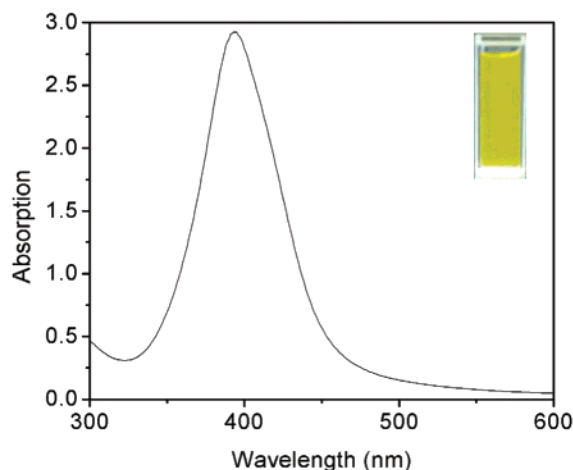* Corresponding authors. E-mail: ekwang@ciac.jl.cn. and dongsj@ciac.jl.cn.

Figure 1. UV–vis absorption spectra and photograph (inset) of colloidal silver sample prepared with initial molar ratio 1:10 of **G3 PPI** dendrimer to Ag at 100 °C.
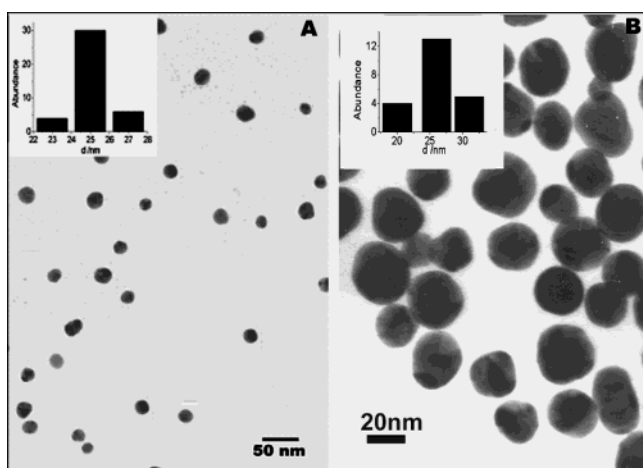

Figure 2. Typical TEM image and the corresponding particle size distribution histogram (inset) of colloidal silver sample prepared with initial molar ratio 1:10 of **G3 PPI** dendrimer to Ag at 100 °C.

nm.[13] The characteristic red shift of the plasmon absorption band confirms the formation of **G3 PPI** dendrimer-protected silver nanoclusters.[14] The yellow color of the colloidal sample (inset) is indicative of the spherical silver particles,[15] providing clear evidence for the formation of silver nanoclusters.

The formation of silver nanoclusters was further confirmed by TEM data. Figure 2A shows typical TEM image and the corresponding particle size distribution histogram (inset) of silver nanoclusters produced. The photograph shows that all of the particles are almost spherical. The size distribution histogram reveals that the average particle size of the resulting silver nanoclusters is 25 nm with a narrow size distribution. Also, it can be clearly seen that all these particles are well separated from each other. It was reported that lower generation dendrimers, due to their small size, stabilize nanoclusters by attaching multiple dendrimers to one particle, leading to the formation of dendrimer-protected nanoparticles.[8b] From the size of **G3 PPI** dendrimer (~2.4 nm),[8e] it is easily understood that the silver nanoclusters cannot be formed inside the **G3 PPI** dendrimer because the size of as-prepared silver particles is larger than **G3 PPI** dendrimer itself. Esumi et al. suggested that dendrimer molecules would be ad-
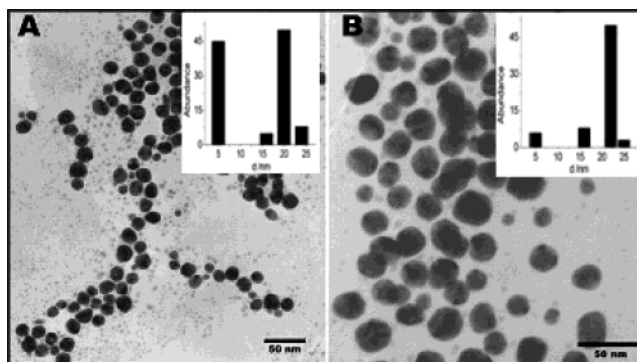

Figure 3. Typical TEM images and corresponding particle size distribution histograms (inset) of colloidal silver samples obtained with initial molar ratio 1:10 of **G3 PPI** dendrimer to Ag at 60 °C (A) and 80 °C (B).

sorbed on the silver nanoclusters to protect the silver nanoclusters.[8e] Therefore, we suggest that the **G3 PPI** dendrimer molecules stabilize silver nanoclusters by attaching multiple dendrimers to one particle. Note that silver nanoclusters thus formed were free from flocculation or aggregation for several months, suggesting **G3 PPI** dendrimer serves as a very effective protective agent for silver nanoclusters. We also investigated the influence of different generation of **PPI** dendrimer on the size of these silver nanoclusters whereby we heated a **G5 PPI** dendrimer/AgNO$_3$ aqueous solution with initial molar ratio 1:10 of **G5 PPI** dendrimer to Ag at 100 °C until the solution color changed to yellow and no further color change occurred. The TEM image indicates that the particles are almost spherical (Figure 2B), and the size distribution histogram (inset) reveals that the average particle size of the particles is 26 nm with a narrow size distribution. It suggests that the generation of **PPI** dendrimer has little effect on the particle size. Our observations are well consistent with another report.[8e]

To examine the influence of reaction temperature on the formation of silver nanoclusters, another two samples, under otherwise identical conditions, were prepared at 60 and 80 °C, respectively. Figure 3 shows the typical TEM images and corresponding particle size distribution histograms (inset) of the produced products. At 60 °C, the resulting silver nanoclsuters consisted of a large quantity of large particles (~20 nm) and a large amount of small particles, as shown in Figure 3A. However, the reaction temperature 80 °C resulted in the formation of a large quantity of large silver particles (~22 nm) and a small quantity of small of small particles (Figure 3B). When reaction occurred at 100 °C, only large particles (~25 nm) were produced, as shown in Figure 2. It is well-known that the formation of small particles is kinetically favored and that the formation of large particles is thermodynamically favored. From a standpoint of kinetics, small particles are easier to nucleate. But small particles have a larger surface area-to-volume ratio and represent a higher energy state than large particles. Hence, small particles are easily formed at lower temperature, but these small particles have a tendence to grow larger particles to attain a lower energy state when the reaction temperature is higher. Our observations also indicate that increasing temperature resulted in both the decrease in number of small particles and the increase in size of large particles, indicating that the growth of silver nanoclusters follows Ostwald ripening growth mechanism.[16] Also mentioned
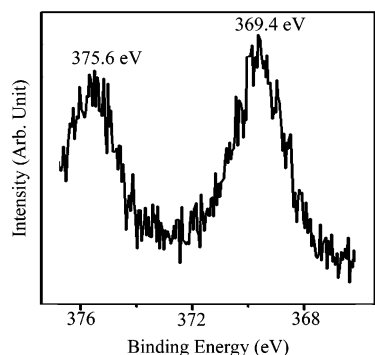
Figure 4. XPS spectrum of silver nanoclusters obtained with initial molar ratio 1:10 of **G3 PPI** dendrimer to Ag at 100 °C.

is that spherical shape of the large silver nanoparticle domains suggests that they may be agglomerates of individual nanocomposite particles.[17]

Because of the heating reaction condition, the surface of silver nanoclusters may be oxidative. We therefore collected the XPS spectrum of silver nanoclusters obtained at 100 °C to carry out the surface analysis. Figure 4 shows the XPS spectrum obtained. It was reported that metal silver 3d peaks are centered at 367.9 and 373.9 eV.[18] The silver 3d peaks in our present study appear unexpectedly at 369.4 and 375.6 eV. The shift of 3d peaks reveals the oxidation of metal silver to Ag_2O oxide,[19] confirming the surface of silver nanoclusters being oxidative. The XRD pattern (data not shown) of precipitates of colloidal sample shows four peaks at 38.1°, 44.2°, 64.5°, 77.3°, and 81.5° assigned to 111, 200, 220, 311, and 222 crystal planes, respectively, indicating the formation of metal Ag.[20] It is reasonable that XPS, as a surface analysis method,[21] can only detect the surface species Ag_2O. On the basis of these results, we can conclude that as-obtained sample is in coexistence of Ag and Ag_2O.

Amine-functionalized polymer can serve as reducing agent for the formation of metal nanoclusters. Dai et al. reported that heat-induced reduction could yield silver nanoclusters in $PEI^{22}-Ag^+$/PAA films.[23] We prepared sliver or gold nanoclusters by heating a PEI/$AgNO_3$ or PEI/$HAuCl_4$[24] solution without the addition of extra reducing agent. More recently, **G3 PPI** dendrimer molecules were used as reducing agent and protective agent for preparing dendrimer-protected gold nanoclusters in our previous study.[25] In that study, gold nanoclusters can slowly generate from **G3 PPI** dendrimer/$HAuCl_4$ solution at room temperature within several days; however, rapid formation of gold nanoclusters occurred within several minutes by heating a **G3 PPI** dendrimer/$HAuCl_4$ solution, indicating that raising the temperature can considerably accelerate chemical processes (roughly doubles the reaction rate by every 10 K). It is well-known that the reduction potential of Au(III) to Au(0) is higher than that of Ag(I) to Ag(0), meaning Ag^+ is harder to reduce than $AuCl_4^-$. As expected, no observable change occurred for **G3 PPI** dendrimer/$AgNO_3$ solution after it has been stored at room temperature for several weeks. We may suggest that the heat-induced spontaneous formation of dendrimer-protected silver nanoclusters in our present work can be assigned to the direct redox between $AgNO_3$ and **G3 PPI** dendrimer and that heat treatment can accelerate the electron-transfer rate from Ag^+ to dendrimer, resulting in the rapid formation of silver par-
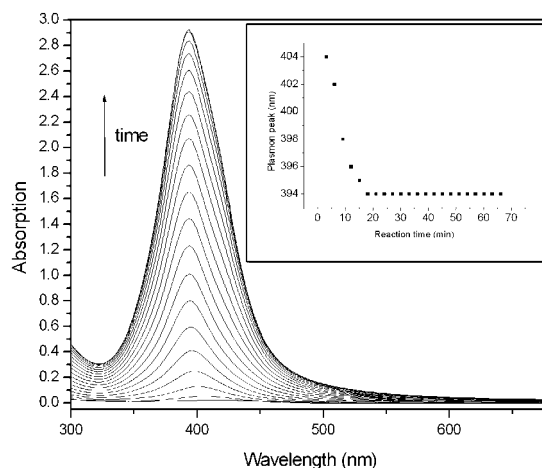

Figure 5. UV−vis absorption spectra indicative of silver nanoclusters growing as a function of time in **G3 PPI** dendrimer/$AgNO_3$ solution with initial molar ratio 1:8 of **G3 PPI** dendrimer to Ag at 100 °C with time interval 3 min. Inset: plot of plasmon peak position vs reaction time.

ticles. However, it is at the present time not clear what byproducts of the oxidized **G3 PPI** dendrimer molecules exist in this preparation. It is worthwhile mentioning that mixing $AgNO_3$ with **G3 PPI** dendrimer (strong base) may at least partially hydrolyze the metal ion salt to Ag(OH) large domains that are not UV-active and does not have a plasmon peak. Heating of the solution may accelerate the loss of water to Ag_2O, which is simultaneously reduced to Ag.[26]

The formation process of silver nanoclusters was further traced by the UV−vis absorption method. Figure 5 shows the time-dependent absorption spectra collected at 100 °C during the whole reaction process at time intervals of 3 min. At 0 min, a very broad UV−vis band appeared, showing that the particles were not formed at that time. When the reaction continued, a remarkable peak at 404 nm occurred, the peak position blue-shifted from 404 to 402 nm at 6 min to 394 nm at 18 min, and the position of the peak did not change and remained at 394 nm when the reaction continued, as is evidenced by the plot of SP peak position vs reaction time (inset). On the basis of the observations described above, we can roughly elucidate the possible growth process as follows. As the redox reaction occurred, silver ions were reduced by **G3 PPI** dendrimer to form silver atoms. With the elapsed time, new Ag atoms were generated in this system, and nucleation occurred as the concentration of silver atoms reaches a critical supersaturation, resulting in the formation of nuclei. The nuclei grew rapidly to small nanoparticles by further addition of silver atoms, and then the small nanoparticles thus formed soon aggregated to form large nanoparticles because of their high density. The large particles are not stable in this nonequilibrium process and will be broken into small nanoparticles.[27] The **G3 PPI** dendrimer molecules in the solution can attach to these small nanoparticles and make them separate from the large ones, resulting in the formation of **G3 PPI** dendrimer-protected silver nanoclusters. It was also found that the absorption gradually increased during the reaction, which can be attributed to a considerable increase of the amount of reduced silver. Also mentioned is that the peak shape changed from asymmetric to symmetric, and the peak became narrower during the reaction, indicating that the size distribution becomes

narrower. Seventy minutes later, the UV−vis spectra showed no observable change in intensity and peak position, indicating that the process of particle generation and growth has stopped.

Conclusion

Via heating a third-generation poly(propyleneimine) dendrimer/$AgNO_3$ aqueous solution, we obtained highly stable dendrimer-protected silver nanoclusters with narrow size distribution involving the use of dendrimer as both a reducing agent and a protective agent. Heat treatment is proved to an effective and simple way for the one-step preparation of dendrimer-protected silver nanoclusters. As-obtained sample was in coexistence of Ag and Ag_2O. It also suggests increasing temperature results in both the decrease in number of small particles and the increase in size of large particles.

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