Ammonia-free preparation of Ag@SiO₂ core/shell nanoparticles

Zhipeng Li, Lifeng Jia, Yueming Li, Tao He, Xue-Mei Li

1. Introduction

Ag@SiO₂ core/shell nanoparticles have garnered intense interest due to their optical, electrical and chemical properties that have enabled applications in diverse areas such as catalysis, surface-enhanced Raman scattering (SERS) imaging and sensing, and drug delivery. The silica shell is chemically inert and optically transparent, which further renders surface functionality, reactivity and stability to the nanocomposites. In addition, silica is porous allowing inner nanoparticles to interact with the outside environment.

Various methods have been used to prepare Ag@SiO₂ nanocomposites, including sol–gel formation of silica shell. Some coating processes involve the use of coupling agents. Surfactants have been used as well. Direct coating of silver nanoparticles with silica via the Stöber approach is most straightforward by using tetraethyl orthosilicate (TEOS) as the precursor which undergoes hydrolytic condensation in the presence of ammonia. Xia and coworkers published the direct coating of silver nanorod with silica by ammonia-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) and subsequent condensation of silica on the silver nanowires following the Stöber method without a primer, however, they observed the etching of silver core in the silver/silica nanocable during the reaction process. It was reported that the etching became significant for a reaction time of up to 45 min. The etching mechanism was ascribed to the reaction of silver with dioxygen followed by the formation of a complex and that the silica shell is porous. In order to avoid the use of ammonia, Mulvaney and coworkers have utilized sodium silicate as the silica source, which upon addition of ethanol at supersaturated concentration can yield silica coating layer on Ag nanoparticles. Unfortunately, this approach often yields core-free silica nanoparticles and of poor uniformity. Suzuki and coworkers reported the preparation of Ag@SiO₂ nanoparticles by microwave irradiation using dimethyl amine (DEA) as the alkaline catalyst, silver core etching could also be observed in their TEM images, which was not mentioned in the report. The etching of the silver core could be due to the high concentration of DEA, which was kept constant at 0.8 M throughout the reaction process. Karimipour et al. reported the use of octadecyl amine (ODA) capped Ag nanoparticles for microwave synthesis of Ag@SiO₂ nanocomposites, where no Ag core etching was observed. This process is ammonia free, although ODA was applied in the process, the silica layer formation was a result of microwave radiation. However, it should be noticed that the ODA concentration was very low and the solution pH was not monitored in their process. Overall, the Stöber approach is often the primary choice, but preparation of the core–shell system without the involvement of ammonia is highly desirable.

Herein, we report the preparation of Ag@SiO₂ nanocomposites by a sol–gel approach without the involvement of ammonia or...
ammonia. Several bases were tested and their effects in the preparation of silica coated silver nanoparticles were investigated in terms of solution pH and aggregation formation. The nanocomposites were characterized by UV–Vis spectroscopy, and transmission electron microscopy (TEM). The stability of the ammonia free Ag@SiO2 core/shell nanocomposites was compared with the typical Stöber approach in order to illustrate the advantages of ammonia free methodology.

2. Experimental

2.1. Materials and instruments

All reagents are used as received unless stated otherwise. Tetraethoxysilane (TEOS, ≥98.0%) was purchased from Fluka. Silver nitrate (AgNO3, ≥99.8%) was purchased from Shanghai Shenbo Chemical Company. Ammonia (25–28% NH3 in water) was from Shanghai Zhongshi Chemical Company. Sodium citrate (≥99.0%) was from Shanghai Laboratory Reagent Company. Reagent grade Na2CO3, NaHCO3, and NaOH were supplied by Sinopharm Group. Ethanol was of analytical grade. Doubly distilled water was used throughout the experiments. UV–Visible spectra were recorded with a Unico UV-2802 spectrophotometer. Transmission electron micrographs were taken at a JEOL JEM-2010 transmission electron microscope (TEM).

2.2. Preparation of silver nanoparticles

Silver nanoparticles were synthesized according to literature reports [23]. Briefly, 8.16 mL (38.8 mM) sodium citrate aqueous solution was added drop-wise into 400 mL boiling water containing 73 mg of AgNO3 under vigorous stirring. The colorless solution changed gradually greenish yellow. After citrate introduction, the mixture was kept boiling for 1 h and cooled down to room temperature. The reaction mixture was centrifuged (high speed centrifuge TGL-16C, Shanghai Anting) at 500 rpm for 1 h to remove larger nanoparticles. The supernatant was then centrifuged at 5000 rpm for 50 min to yield the seed silver nanoparticles. To determine the concentration of the nanoparticles (based on silver ion concentration), the nanoparticles were collected, washed thoroughly with ethanol, and dried (18.5 mg, yield: 34.2%). Re-dispersing the nanoparticles in 133 mL water yielded a seed solution (1.29 mM, based on silver ion concentration).

2.3. Stöber synthesis of core/shell nanoparticles

In a typical Stöber process, the silver nanoparticle seed solution (1.29 mM, 25 mL) was dispersed in a flask containing 100 mL of ethanol. Thereafter, the pH of solution was adjusted to 11 using ammonia solution (about 10 mL). Under vigorous stirring, a TEOS ethanolic solution (10 mM) was added within 8 h at half an hour time interval. The reaction mixture was stirred overnight. The products were collected by centrifugation at 5000 rpm for 50 min. The products were washed three times with ethanol and re-dispersed in ethanol by sonication yielding light brown dispersions of Ag@SiO2 nanocomposites.

2.4. Ammonia free approach

A silver seed solution (1.29 mM, 12.5 mL) was dispersed in ethanol (50 mL). The pH of the dispersion was first adjusted to desired pH using a base solution. The base solutions tested included 0.1 M NaOH, Na2CO3/NaHCO3 (9:1) mixture, and trisodium citrate solution. After initial pH adjustment, 1 mL of TEOS ethanol solution (10 mM) was added dropwise into the dispersion under vigorous stirring. The TEOS addition was repeated by 0.5 h time interval. After the first 1 h of reaction, a drop of NaOH solution (5 μL, 0.1 M) was added to the solution mixture right with each TEOS addition. The total TEOS solution volume was fixed to 12.5 mL. After completion of TEOS addition, the reaction mixture was stirred overnight. The products were collected by centrifugation.

3. Results and discussion

3.1. Stöber preparation

Ag@SiO2 core/shell nanocomposites was prepared following the method developed by Liu and coworkers [18] with slight modification via controlling the initial concentration of silver nanoparticle in the solution and the amount of TEOS added. The seed concentration used in this case was about three times as high as literature-reported concentration. By adjusting the volume of TEOS solution added, nanocomposites with different shell thickness were prepared denoted as 1, 2, and 3 as shown in Table 1. UV–Vis spectra of the Ag nanoparticle seeds and nanocomposites were shown in Fig. 1a. The localized surface plasmon resonance (LSPR) peak of the Ag nanoparticles appeared around 426 nm. The LSPR bands of Ag@SiO2 nanocomposites appeared at 440 nm. Compared to the bare Ag nanoparticles, the plasmon resonance bands of the Ag@SiO2 nanocomposites are red shifted, which agrees with literature reports [12,17,18]. TEM images analysis of the Ag@SiO2 nanocomposites revealed that the silica layer thickness for sample 1, 2, and 3 is 35, 50, and 85 nm, respectively (Fig. 1a–c). It was found that some of the nanocomposites showed silver cores that appeared to be etched away. It is not clear to us when the etching took place. More interestingly, sample 3 appeared to have more silver core etching as compared to sample 1. In addition, the LSPR bands of the nanocomposites showed blue-shifts with time, which might be related to the etching of the silver core upon prolonged preservation in the preparation solution as shown in Fig. 2. TEM images of the samples preserved in the preparation solution for 21 days clearly demonstrated core etching for Ag/SiO2 composites 1, 2, and 3 (Fig. 2d–f). The etching of silver core by the ammonia in the preparation solution has been reported before [19], which was ascribed to the oxidation of silver in the presence of ammonia forming soluble Ag(NH2)2+ complex. In order to avoid core etching, Ung et al. [21] developed an ammonia free Ag/SiO2 preparation method, which involved nanoparticle surface activation with amino-propylsilane (APS) and controlled precipitation of silica on the silver nanoparticles surface. They have shown that the etching of the silver core took place upon the addition of ammonia into their colloids system, which was ascribed to oxygen facilitating oxidation of the metallic silver. Xia and coworkers [19] have provided direct evidence of the etching of silver nanowires during preparation using the ammonia catalyzed polycondensation of TEOS in the preparation of silica coated silver nanocables. The etching was ascribed to the reaction of silver with oxygen and ammonia as well.

In our case, the etching of the silver core is apparent as witnessed by the blue shift of the LSPR with time in their UV–Vis spectra of the composites and the TEM imaging. The methodology developed

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>pH</th>
<th>TEOS solution (1 mM, mL)</th>
<th>Shell thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ammonia</td>
<td>10–11</td>
<td>12.5</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Ammonia</td>
<td>10–11</td>
<td>45</td>
<td>50</td>
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<tr>
<td>3</td>
<td>Ammonia</td>
<td>10–11</td>
<td>67.5</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>NaOH</td>
<td>9.5</td>
<td>12.5</td>
<td>16</td>
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</table>
by Ung et al. required the use of primer, which is tedious for the preparation process. Therefore, an ammonia free approach for the preparation of Ag@SiO₂ nanocomposites was attempted without the requirement of primer.

3.2. Ammonia free approach

Sodium citrate is weakly basic and was used as the stabilizing ligand for the silver seeds, which was tried as the base for the hydrolytic condensation of TEOS. However, the addition of TEOS has caused immediate turbidity of the reaction mixture and no LSPR peak was observed as shown in Fig. S1 (Supporting Information). It should be noted that the pH of the Ag colloids solution was adjusted to 10.1 before TEOS admission. As a matter of fact, Ag colloids were prepared by citrate reduction, and the surface should be negatively charged. Upon further addition of citrate, there was no immediate change of the colloidal solution. However, the addition of TEOS into the solution leading to immediate aggregation was not expected, which has nevertheless indicated that citrate is not a suitable base for TEOS polycondensation.
Furthermore, mixtures of Na₂CO₃ and NaHCO₃ were prepared by mixing Na₂CO₃ and NaHCO₃ at different ratios. When the solution pH was adjusted to 10.2 by Na₂CO₃:NaHCO₃ (9:1), no immediate aggregation was observed. After TEOS addition, however, significant aggregation was observed and the solution yielded very low UV absorbance. When the colloid solution pH was adjusted to 9.48 with Na₂CO₃:NaHCO₃ at ratios of 9:1 it appeared that some nanocomposites were yielded as confirmed by the red shift of the LSPR bands. But aggregation was still present as witnessed by the presence of the second peak around 680 nm (Fig. 3). The formation of aggregation was not clearly understood. However, it is well known that the TEOS sol–gel process is a result of interplay of hydrolysis, condensation and phase separation. The kinetics and thermochromistry of the these processes vary in a complicated fashion and presence of excess charged groups such as citrate and carbonate may influence the solubility of the evolving intermediates, which led to the precipitation. Also, the presence of silver nanoparticles may be another factor that affects the solubility of the evolving intermediates. In order to avoid the charging issues, we have further tried NaOH as the base source.

Sodium hydroxide is a strong base and is often used for pH adjustment. NaOH was used to adjust the pH of two silver colloid solutions to 9.88 and 10.23, respectively. One solution without pH adjustment was compared for the silica shell formation. Stepwise addition of TEOS was carried similar to literature procedures [18].

For the solution with pH adjusted to 9.88, two peaks were observed in the UV–Vis spectra (Fig. 4), where the first peak appeared at 440 nm and the second 637 nm. The first peak was about 14 nm red-shifted as compared to the bare silver colloids indicating the formation of silica coating layer. The second peak was ascribed to aggregates formation as witnessed by the appearance of black precipitates on the wall of the reaction flask. When the pH of Ag colloids solution was adjusted to 10.23, black precipitates were observed before TEOS addition. It is therefore not surprising that no peak was observed in the UV–Vis spectrum. In comparison, for control experiments, a 7 nm LSPR shift was observed for the samples without pH adjustment. It should be noted that without pH adjustment, the solution pH was 8.28, slightly basic. Because the solution showed a LSPR shift much lower than the Stöber approach, we believe that under this pH condition, the hydrolytic condensation was slow. Thereby, the silica coating effect was insignificant. More noticeably, when ammonia was used as the base, even at solution pH above 11, no aggregation of the silver colloids was observed. In contrast, when the solution pH was adjusted by NaOH, the aggregation of silver colloids occurred at pH >9.5.

Above results appeared to indicate that pH adjustment of the silver colloids solution using NaOH toward above 9.5 can lead to irreversible aggregation of the silver colloids. In contrast, the addition of ammonia does not cause colloidal aggregation even at much higher pH values (we have tested pH 11.37, with no aggregation). In order to avoid ammonia and aggregation of the nanoparticles and core etching, a multistep approach was attempted.

3.3. Multistep coating process

Based on the results of using different alkaline source, it appears that NaOH has caused the least aggregation of the nanocomposites. Therefore, NaOH was used as the only alkaline source for the silica layer formation. The multistep coating approach was carried out as: first initiate the silica formation with the least base necessary; after initial silica coating layer formation, adjust the solution pH with each TEOS addition in order to control the silica formation process.

The silver seed solution pH was adjusted to 9.5 before TEOS addition. It should be pointed out that the solution pH decreased with each addition of TEOS solution and the addition of NaOH was to ensure the reaction mixture stay alkaline enough for a sufficient reaction rate. After the initial polycondensation, subsequent addition of NaOH did not cause any aggregation of the colloids (Fig. 5a). The resulting nanocomposites product was denoted as sample 4. Its LSPR peak was red shifted to 431 nm, indicating a core shell system formation. Further evidence was obtained by TEM imaging after 3 days incubation in the solution (Fig. 5b). It can be seen that each silver core was encapsulated by a silica shell, no silver free silica particles were present. The average thickness of the silica shell was about 16 nm, which is rather uniform irrespective of the Ag particle morphology. It should be pointed out that the silica layer thickness was expected to be around 35 nm, when ammonia was used as the alkaline source. This layer thickness difference indicates nevertheless, the silica layer formation process was slower under lower pH conditions. In addition, by comparison of Fig. 1b with Fig. 5b, we can see clearly that the silica layer prepared using the modified approach appears not as smooth.

Further attempts were conducted in order to verify the solution pH effect on the nanocomposites formation. After initial silica layer formation, the solution pH was adjusted to a higher value up to 12 using NaOH, and then TEOS was added. Upon reaction completion, some black precipitates were observed. The UV–Vis spectra showed a broad peak at around 680 nm, which evidenced the aggregates formation. After repeated experiments with pH adjustment, it was found that a critical control of the solution pH to below 10 is
essential to ensure the nanocomposites formation without severe aggregation formation.

The stability of the sample 4 was monitored with UV–Vis spectroscopy. It can be seen that the freshly prepared Ag@SiO$_2$ nanocomposites had a LSPR peak of 431 nm, 10 nm red-shifted in comparison to the bare Ag colloids. After incubation in the solution for 2 weeks, no LSPR band shifts were observed (Fig. 5a), indicating that this preparation approach can indeed avoid the core etching problems in the typical Stöber approach.

4. Conclusions

An ammonia free approach was developed for the preparation Ag@SiO$_2$ core/shell nanocomposites in order to avoid the core etching of Ag by ammonia in a typical Stöber approach. TEOS was used as the silica source and silver nanoparticles prepared by citrate reduction as the core. Several bases were tested as the alkaline sources, it was found that the introduction of bases caused irreversible aggregation of Ag colloids at pH above 9.5. Thereby, the initial pH before TEOS addition should not be higher than 9.5. After initial silica layer formation, further pH was adjusted with each TEOS admission. Stability test of the Ag@SiO$_2$ nanoparticles prepared as such were stable without Ag core etching after 2 weeks indicating the applicability of the methodology.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2015.03.159.

References