A simple and controlled method of preparing uniform Ag midnanoparticles on Tollens-soaked silica spheres

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Abstract

Ag midnanoparticles (midnanoparticles are those particles whose diameters are in the range from 20 to 80 nm) with average size of 30–50 nm and tunable packing densities were formed on the surface of preformed Tollens-soaked silica spheres by a simple and controlled method. The process mainly involved two steps. In the first step the absorption of Ag(NH₃)₂⁺ ions occurred on the silica spheres and in the second step Ag(NH₃)₂⁺ ions on the silica spheres were reduced to Ag midnanoparticles in the presence of glucose solution. The amount of Ag midnanoparticles on the silica spheres could easily be tuned by varying the washing times in the process of preparing the Tollens-soaked silica spheres. The washing process also effectively avoided the reduction of Ag(NH₃)₂⁺ ions and the nucleation of Ag particles in solution and easily produced more uniform Ag midnanoparticles on the silica spheres. Attributing to the uniform Ag midnanoparticles, the Ag midnanoparticle-coated silica spheres show unique optical properties in the UV–vis absorption spectra. The resulting Ag midnanoparticle-coated silica spheres were characterized with transmission electron microscopy, UV–vis–IR recording spectrophotometry, and X-ray photoelectron spectroscopy.

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1. Introduction

Recently, the preparation and characterization of nano-sized metal particles have been an active area of investigation [1] because of their unique electronic and optical properties. Due to their properties being substantially distinct from those of both the bulk phase and individual molecules, these nanoparticles would be potentially applied in biological labeling [2], surface-enhanced Roman [3,4], solar cells [5], electrochromic devices [6], electroluminescent films [7,8], nonlinear optical switches [9], and high-density information storage systems [10]. As an important part, colloidal particles coated or deposited with functional metal nanoparticles have attracted more and more attention in modern materials science. A number of reports have been published on the preparation of submicrometer colloids coated with nanoparticles, such as magnetite [11], quantum dots [12], metals [13–15], metal compounds [16], ZnS [17], and silica [18]. Ag and Au nanoparticles are well known to produce optical responses (plasmons) by the excitation of free electrons at the metal surface [19]. At the same time, Ag or Au midnanoparticles have merited particular attention due to their intense plasmon responses and large scattering cross section [19,20]. Several investigators have previously reported on some techniques of preparing Ag or Au nanoparticle-coated silica or polymer spheres. For example, Liz-Marzán and co-workers prepared Ag nanoparticles on silica spheres by pretreatment steps in electroless plating [21]. Gedanken and co-workers first completely studied the silica spheres coated with silver nanoparticles [22], Wang and Asher fabricated nanocomposite monodisperse silica spheres containing homogeneously dispersed Ag quantum dots by a photochemical method [23]. Tang and co-workers synthesized compact Ag nanoshells on polystyrene
spheres through electrostatic attraction [24], and Xia and co-workers prepared aqueous dispersion of Ag particles through the Tollens process and deposited the Ag nanoparticles on silica microspheres [25]. However, as far as we know, the synthesis of uniform Ag midnanoparticle-coated silica or polymer spheres with tunable packing densities by a simple method has not been reported. Previously we have prepared polymer microspheres with Ag nanoparticles in them through an ion-exchange method [26]. Here, using Tollens-soaked silica spheres as scaffold, we develop a simple and versatile method for producing 30–50 nm Ag nanoparticles with tunable packing densities on submicrometersized silica spheres. The Tollens-soaked silica spheres qualify as hard spherical substrates for the following reasons: (a) the Tollens process has been successfully employed in Ag-plating on plane substrate to generate reflective mirrors (better known as the Ag mirror reaction); (b) the Stöber silica particles are low density and porosity comparing to the amorphous bulk silica and Ludox silica. They can swell at the particle surface in water solution, so the numerous nanometer-sized pores inside them can favor the absorption of Ag(NH$_3$)$_2^{+}$ ions and release [27–32]; (c) silanol groups on the silica spheres help to immobilize Ag(NH$_3$)$_2^{+}$ ions through electrostatic interaction [21]; and (d) silica colloids with narrow size distribution can be achieved over a wide range. Previous studies have indicated that such hybrid materials may have a range of applications in developing nonlinear optical devices, electrostatic shielding coating, and supported catalysts [21,33,34]. This method is relatively inexpensive, is environmentally benign, and can easily be extended to other systems.

2. Experimental

2.1. Materials

Ag nitrate (AgNO$_3$, 99.8%), ammonium hydroxide (NH$_4$OH, 25 wt% in water), tetraethyl orthosilicate (TEOS, 28%), and glucose were analytical grade and used as received. In all preparations, absolute ethanol and Milli-Q water were used.

2.2. Preparation of silica spheres

Silica spheres with a narrow size distribution were prepared by the well-known Stöber method [35], which comprises the base-catalyzed hydrolysis of TEOS in water–ethanol mixtures. More specifically, 40 ml of aqueous ammonia and 200 ml of ethanol were added into a 500-ml three-necked flask fitted with a reflux condenser and a mechanical stirrer. This system was placed in a water bath at 20°C. Then 20 ml of TEOS was added quickly under vigorous stirring. Gentle stirring was then continued for at least 24 h to ensure that the reaction completed. After washing three times by sonication to remove the impurities, the resulting silica spheres were about 470 nm in diameter.

The silica spheres were then dispersed in water by sonication before use. To ensure that Ag(NH$_3$)$_2^{+}$ ions were diffused into the silica spheres to the maximum extent, we added 4 ml of an aqueous solution of 0.3 M ammonical AgNO$_3$ to 2 ml of 2 wt% silica sphere dispersion and stirred the mixture with a magnetic stirrer for 6 h. The Tollens-soaked silica spheres were then washed for different times, centrifuging at 9000 rpm for 8 min, removing supernatant, and redispersing in 15 ml water. Finally, the Tollens-soaked silica spheres were dispersed into 5 ml of water and 5 ml of 0.5 M aqueous solution of glucose were added into the system. Then the uniform Ag midnanoparticles with different packing densities were formed on the silica spheres after the reaction mixture was stirred at ambient temperature for 3 h.

2.3. Characterization

The morphologies of Ag midnanoparticle-coated silica spheres were investigated by transmission electron microscopy (TEM) using a JEOL JEM 2010 at an accelerator voltage of 200 kV. UV–vis absorption spectra were obtained on a Shimadzu 3100 UV–vis–near-IR recording spectrophotometer. X-ray photoelectron spectroscopy (XPS) of Ag midnanoparticle-coated silica spheres on a silicon wafer was performed using a VG ESCALAB MKII spectrometer with an Al-Kα monochromatized X-ray source.

3. Results and discussion

Fig. 1 outlines the formation procedure of Ag midnanoparticles on the silica spheres. In step 1, the Tollens agent is first diffused into the silica spheres to form Tollens-soaked silica spheres through electrostatic interaction between the positive Ag(NH$_3$)$_2^{+}$ ions and the negative charges.
of the silica spheres [21]. In step 2, the Tollens-soaked silica spheres serve as oxidization agents in the succeeding redox reaction after consecutive centrifugation/redispersion procedures for different times in water. We found that the resulting dispersion remained milky white, indicating that the redox reaction had not begun. XPS of Fig. 2 (line A) confirms the presence of Ag(NH$_3$)$_2^+$ ions on the silica sphere after removing the excess Ag(NH$_3$)$_2^+$ ions in the solution. The Tollens-soaked silica spheres are still smooth as shown in TEM micrograph of Fig. 3a, implying that the reduction of Ag(NH$_3$)$_2^+$ ions did not occur and no Ag nanoparticles formed before step 2. With the addition of excess glucose aqueous solution in step 2, a redox reaction occurs involving the reduction of Ag(NH$_3$)$_2^+$ ions to Ag and oxidation of glucose to its corresponding acid. The fundamental redox reaction involved in step 2 can be simplified as the following:

\[
\text{Ag(NH}_3\text{)}_2^+(\text{on the spheres}) + \text{RCHO(aq)} \rightarrow \text{Ag(on the spheres)} + \text{RCOOH}.
\]

As a result, the dispersion turns from milky white to pale yellow or dark brown, which implies that Ag nanoparticles are formed on the silica spheres from the reduction of Ag(NH$_3$)$_2^+$ ions. The formation of Ag midnanoparticles also can be confirmed by XPS as shown in Fig. 2 (line B). The Ag(NH$_3$)$_2^+$ ions 3d$_{5/2}$ peaks (line A) appear at 366.6 and 372.6 eV, while the Ag nanoparticles peaks (line B) are centered at 368.3 and 374.3 eV [36]. By comparing Figs. 3a and 3b, we found that the surface roughness of the resulting silica spheres increased due to the formation of Ag nanoparticles. These Ag midnanoparticles uniformly distributed on the silica spheres and formed a similar structure like strawberry. The insert of Fig. 3b shows the size distribution of Ag midnanoparticles and the average diameter is 36.5 nm. The UV–vis absorption spectrum of Ag nanoparticle-coated silica spheres in Fig. 3d (line A) also proves that uniform Ag nanoparticles were formed on the silica spheres.

Although the Tollens-soaked silica spheres used in Fig. 3b had been washed two times by a centrifugation/redispersion procedure for removing the residual Ag(NH$_3$)$_2^+$ ions in the solution before reaction, we still observed a lot of Ag nanoparticles formed on the silica spheres. If the Ag(NH$_3$)$_2^+$ ions only come from the surface of the silica spheres, only a few Ag particles should be formed on each silica sphere. This result may depend on the fact that Ag(NH$_3$)$_2^+$ ions mainly come from inside the silica spheres, which are released slowly to the surface due to the microporous inside them and generated more uniform Ag particles on the silica spheres during the reaction.

To avoid the nucleation and conglomeration of Ag nanoparticles in the solution and simultaneously ensures that the reaction mainly takes place on the Tollens-soaked silica spheres, the procedure of centrifugation/redispersion was performed in our experiment. As a comparison, Fig. 3c shows the formation of Ag nanoparticles on the silica spheres without the washing procedure. We noted that there are a lot of nonuniform Ag nanoparticles in the solution and on the silica spheres in Fig. 3c, while the Ag midnanoparticles with a more uniform size distribution only present on the surface of silica spheres in Fig. 3b. In addition, Fig. 3d shows the UV–vis absorption spectra of these two cases corresponding to Figs. 3b and 3c. The absorption peak related to Fig. 3b is centered at 437 nm; a broad peak corresponding to Fig. 3c is observed at about 550 nm. It is clearly red-shifted with respect to the usual surface plasmon peak position of Ag nanoparticles. Such a red shift is partly attributed to the formation of larger particles, but mainly to the interaction between neighboring particles, which has been shown before to promote both red shift and broadening of plasmon bands for thin films on flat substrates [37,38] and also for Au nanoparticles deposited on silica spheres [13]. This result coincides well with the comparison of Figs. 3b and 3c. All above are based on the facts as following. On the one hand, except for the Ag(NH$_3$)$_2^+$ ions absorbed onto the silica spheres being deoxidized to Ag nanoparticles, a portion of Ag particles produced in the solution were also deposited onto the surface. It surely increased the packing densities of Ag nanoparticles. On the other hand, the nucleation and conglomeration of small Ag particles produced by the reduction of a large amount of Ag(NH$_3$)$_2^+$ ions in the solution formed numerous wide-size-distribution nanoparticles, some of them were absorbed on the silica spheres, most of others were dispersed into the solution. It resulted in a broader absorption peak in the UV–vis spectrum.

Fig. 4a to 4d shows TEM micrographs of Ag midnanoparticle-coated silica spheres soaked with 0.3 M aqueous solution of Ag(NH$_3$)$_2^+$ ions and then treated with centrifugation/redispersion procedure for 1, 2, 3, and 5 times, respectively. The effect of washing times on the system is presented in Fig. 4. Although the Ag nanoparticles formed on the sil-
Fig. 3. TEM micrographs and UV–vis absorption spectra of silica spheres. (a) Tollens-soaked silica spheres. (b) Ag midnanoparticle-coated silica spheres treated with centrifugation/redispersion procedure. The insert shows the size distribution of Ag midnanoparticles. (c) Ag midnanoparticle-coated silica spheres without centrifugation/redispersion procedure. (d) UV–vis absorption spectra of Ag nanoparticle-coated silica spheres corresponding to Figs. 3b (line A) and 3c (line B).

Silica spheres in Fig. 4a are more uniform than in Fig. 3c, some congregation of Ag particles on the surface of silica spheres was still observed. But it was not the same case in Fig. 4b, illustrating that after one cycle of centrifugation/redispersion, more Ag(NH$_3$)$_2^+$ ions not based on the electrostatic interaction were released fast to the surface of silica spheres during the reaction and formed the conglomeration. The packing densities decreased clearly with increasing the washing time from 1 to 4. This corresponds to the color change of silica dispersion from dark brown to brown to yellow. But this tendency gradually becomes nonobvious with further increasing cycle time. It is because that when the washing reaching a certain time, the Ag(NH$_3$)$_2^+$ ions absorbed to the silica spheres without electrostatic interaction have been consumed and the remaining based on electrostatic interaction release slowly. In this case, we could not observe obvious decrease of packing densities of Ag nanoparticles on the silica spheres although increasing the washing times. But if we did not add glucose to the Tollens-soaked silica spheres until several hours later, only a few Ag particles formed in the solution instead of on the silica spheres, indicating that almost all the Ag(NH$_3$)$_2^+$ ions in the silica spheres can be released if the silica spheres were immersed into the water for a longer time. Fig. 5 shows the UV–vis absorption spectra of Ag midnanoparticle-coated silica spheres in Fig. 4. It is well known that the absorption peak attributed to the surface plasmon resonance is generally observed at around 440 nm for Ag nanoparticles; the absorption intensity will therefore increase with the amount of Ag particles. As we expected, except for line A, which had a broad
peak attributed to the nonuniform Ag nanoparticles, the absorption intensities decreased with increasing the washing times when silica sphere concentration was kept invariant in our experiment, while the peak position was unchanged, as shown in Fig. 5. This tendency coincides well with the TEM micrographs in Fig. 4, illustrating that without changing the size of Ag nanoparticles, we can easily tune the packing densities by varying the washing times in the process of preparing the Tollens-soaked silica spheres. We also prepared some samples with Tollens concentration from 0.25 to 0.45 M and then washed the samples two times with water as described in the experiments. The results showed that the concentration of the Tollens almost did not affect the diameter of the Ag nanoparticles and the packing density. It provides more evidence to illustrate that the Ag(NH$_3$)$_2^{+}$ ions mainly come from the inside of the silica spheres. So in a certain Tollens concentration range, the absorbed Ag(NH$_3$)$_2^{+}$ ions amount of the silica spheres is almost identical after the two times washing, which leads to the same results described above.

4. Summary

We have demonstrated a simple and controlled method of preparing uniform Ag midnanoparticles with tunable packing densities on the surface of Tollens-soaked silica spheres. The process mainly involves the absorption of Ag(NH$_3$)$_2^{+}$ ions on the silica spheres, the centrifugation/redispersion washing procedure, and the reduction of Ag(NH$_3$)$_2^{+}$ ions in the presence of glucose solution. This showed that the reduction of Ag(NH$_3$)$_2^{+}$ ions mainly occurred on the silica spheres in a uniform manner and therefore produced Ag
midnanoparticles with a more uniform size distribution. The number of Ag midnanoparticles formed on the silica spheres could easily be tuned by varying the washing times in the process of preparing the Tollens-soaked silica spheres. The Ag midnanoparticle-coated silica spheres showed unique optical properties in the UV-vis absorption spectra. This method effectively avoided the reduction of Ag(NH$_3$)$_2^+$ ions and the nucleation of Ag particles in solution and easily produced more uniform Ag midnanoparticles on the silica spheres. Furthermore, this method will also provide a powerful platform for preparing other metal particles such as Au or platinum on plane or spherical surface due to its convenience and controllable.

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References