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Synthesis of chitosan-stabilized gold nanoparticles by atmospheric plasma

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ABSTRACT

We report a facile method to prepare gold nanoparticles by atmospheric plasma. Chitosan, was used as a stabilizing agent and gold precursor. In chitosan solution was reduced by atmospheric plasma at room temperature. We find the plasma treatment is effective for reducing the gold precursor and the process only takes minutes. The obtained gold nanoparticles were characterized with UV–vis spectroscopy and transmission electron microscopy. The results indicated that the morphology and size distribution of gold nanoparticles prepared varied with treatment time and the ratio of chitosan to precursor metal salts. Additionally, a preliminary study on air component analysis indicated that the moisture in air plays an important role in producing the active ingredient for the production of gold nanoparticles.

1. Introduction

Compared with bulk materials, nanoscale metals have many unique physical and chemical properties, such as catalytic activity, novel electronic, optical and magnetic properties, and have already been found applications in biotechnology, chemistry and material science (Daniel & Astruc, 2004; Shipway, Katz, & Willner, 2000). A general method for the preparation of metal nanoparticles particularly gold involves the treatment of metal salts with a chemical reducing agent and a stabilizing agent. These agents may not be environmentally friendly. Therefore, efforts have been dedicated to developing “green” and reagentless methods.

In recent years, biomolecules and bioorganisms have been used as stabilizing agents, sometimes both as reducing agents and stabilizing agents, in the preparation of metal nanoparticles because of their excellent biocompatibility and biodegradability (He & Kunitake, 2004; Qi et al., 2004; Sastry, Ahmad, Khan, & Kumar, 2003). An amino polysaccharide, chitosan, has been received much attention due to its outstanding intrinsic features, such as biocompatibility, biodegradability, pH-responsive and gel- and film-forming properties (Rinaudo, 2006). Chitosan is a linear polysaccharide obtained by partial deacetylation of chitin. Chitin is abundant in nature and chitosan is positively charged in solution. It is reported that chitosan can be used as both protecting and reducing agent in the synthesis of gold nanoparticles. Esumi has shown that chitosan can be used as a protecting agent in preparation of gold nanoparticles (Esumi, Takei, & Yoshimura, 2003). Yang et al. prepared gold nanoparticles by reducing gold salts with chitosan which was used as both reducing agents and stabilizing agents (Huang & Yang, 2004).

UV–light (Fukushima, Yanagi, Hayashi, Suganuma, & Taniguchi, 2003), fluorescence light (Kim, Lavin, Burnett, & Boote, 2011) and laser (Besner, Kabashin, Winnik, & Meunier, 2009) have been adopted as alternatives for traditional chemical reduction methods. In our present study, we provide a new method to synthesize gold nanoparticles in the presence of chitosan by atmospheric plasma. Plasma is a state of matter similar to gas in which a certain portion of the particles are ionized. It is described as an electrically neutral medium of positive and negative particles. Mainly, it contains electrons, positive ions, negative ions, excited atoms or molecules, ground state atoms or molecules and photons (Bogaerts, Neyts, Gijbels, & van der Mullen, 2002). Concerning air plasma, molecules (OH, NO, CN,O_3) and atomic (H, O, N) radicals, and other active species, such as N_2^+, were identified (Machala et al., 2007). Some of these particles are extremely reactive and have the potential of being used as reducing agents (Saito, Hieda, & Takai, 2009). The plasma we used was generated by surface discharge (Gibalov & Pietsch, 2000) of air under atmospheric pressure. Scheme 1 illustrates the plasma-generating process. When there is an applied voltage between the two electrodes, the air will discharge on the surface of nonconductor to produce atmospheric plasma. The plasma flow is guided to the surface of chitosan solution containing gold salts. In several minutes, the solution turns from yellow to red indicating the formation of nanoparticles. This new method allows a rapid fabrication of chitosan-stabilized gold nanoparticles without heating or adding other reducing agents.

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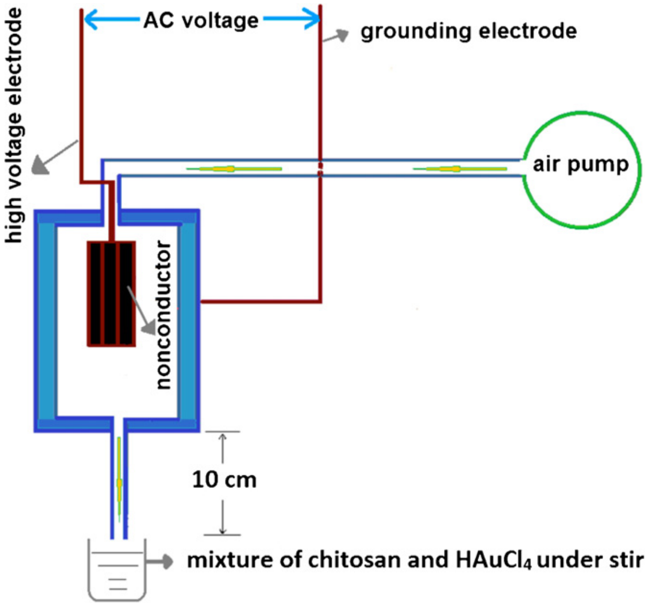

Scheme 1. Schematic diagram of plasma-generating process.

2. Experimental

2.1. Materials

$HAuCl_4$ was purchased from Aldrich and used without further purification. Chitosan with medium molecular weight and a degree of deacetylation of 75–85% was purchased from Sigma. PBN (N-tert-buthyl-α-phenylnitrone) with a purity of 98% was purchased from Alfa Aesar. Acetic acid (A.R.) was diluted to 3% (v/v) aqueous solution before use. All aqueous solutions were made with deionized water.

2.2. Preparation of gold nanoparticles

All glassware used was cleaned in freshly prepared aqua regia solution ($HCl:HNO_3$, 3:1) and then rinsed thoroughly with water. Chitosan solution (1%, w/v) was prepared by dissolving chitosan in dilute acetic acid (3%, v/v). Due to the poor solubility of chitosan, the mixture was filtered and kept for about 1 week until a clear solution was obtained. A stock aqueous solution of $HAuCl_4$ (80 mM) was prepared by dissolving $HAuCl_4$ in H_2O. A typical procedure for gold nanoparticles preparation is shown as follows: An aqueous solution of $HAuCl_4$ (100 μl) was mixed with a diluted solution of chitosan (3.9 ml). The mixture was stirred for 3 min and incubated for 3 h. Then the mixture was placed below the plasma generator, as shown in Scheme 1. The distance between the plasma outlet and the surface of chitosan solution is 1 cm. The mixture was processed by plasma for 15 min under magnetic stirring. The applied voltage of the generator is 5800 V and the flow rate of plasma is 6 l/min.

2.3. Measurement

The gold nanoparticles obtained were characterized by UV/vis absorption spectroscopy (UV–vis) and transmission electron microscope (TEM). The morphology of the nanoparticles on carbon-coated copper grids was observed by a JEM-2100 (HR) transmission electron microscope at accelerating voltage of 200 kV. UV–vis absorbance spectra of gold nanoparticles were collected using a UV-1601PC UV-visible spectrophotometer (Shimadzu, Japan).

3. Results and discussion

In our initial study, we examined the feasibility of $AuCl_4^-$ reduction by atmospheric plasma. $AuCl_4^-$ solution (10 mM) was treated by plasma for 15 min under stirring at room temperature. We observed a thin layer of black powder floating on the surface. Presumably, this black film was formed by aggregates of gold nanoparticles since there were no stabilizing agents in the solution. Next we included chitosan (0.5%, w/v) in $HAuCl_4$ solution and the mixture was kept for 3 h at room temperature. This procedure ensures well dispersion of $AuCl_4^-$ in chitosan and the formation of strong electrostatic interactions between cationic chitosan and $AuCl_4^-$. Then the solution was treated with plasma, it showed a red color after several minutes and there was no aggregates found. Further examination by TEM shows the existence of gold nanoparticles in solution. This initial experiment indicates that plasma is effective to reduce $AuCl_4^-$ at ambient conditions and chitosan serves as a stabilizing agent.

We further investigated the influence of chitosan concentration on the generation of gold nanoparticles. $HAuCl_4$ (10 mM) in various concentration of chitosan solution (0.125%; 0.25%; 0.5%; 0.75%; 1%) was treated by plasma for 15 min, respectively. The photograph of treated solution in Fig. 1(a) shows the color turns from light blue to wine red with the increase of chitosan concentration. Their UV–vis absorption spectra were collected from 400 nm to 800 nm. As shown in Fig. 1(b), samples with red color all exhibit the characteristic surface plasmon (SP) resonance band around 520 nm, suggesting the formation of gold nanoparticles (Daniel & Astruc, 2004; Ishizuki, Torigoe, Esumi, & Meguro, 1991). However, the sample prepared with a chitosan concentration of 0.125% showed an absorption band at 620 nm. The color change and UV–vis spectra suggest that the concentration of chitosan is vital for the stabilization of nanoparticles. At low concentration of chitosan (0.125%), chitosan does not stabilize the nanoparticles formed and the nanoparticles are prone to aggregation and precipitation. Fig. 1(c) shows the TEM images of gold nanoparticles prepared with 0.25% chitosan. The TEM images show that nanoparticles are generally spherical in shape and the average diameter, as shown in Fig. 1(d), is about 4 nm.

Note that the concentration of $HAuCl_4$ may affect the morphology of the gold nanoparticles; we fix the concentration of chitosan at 0.75% and change the concentration of $HAuCl_4$. With the increase of the concentration of $HAuCl_4$, the resulting solutions show a color change from red to purple, as shown in Fig. 2(a). The UV–vis absorption spectra are shown in Fig. 2(b). It is found that the plasmon absorption of gold nanoparticles increases with increasing $HAuCl_4$ concentration. There is also a slight red-shift of the absorption maximum with the increase of $HAuCl_4$ concentration. These results indicate that the size or shape of gold nanoparticles formed varies with the concentration of $HAuCl_4$. TEM images in Fig. 2(c) and (d) can further confirm this assumption. When the concentration of $HAuCl_4$ reaches 40 mM, we can see in Fig. 2(c) that there is formation of polygonal particles and nanorods and the size of nanoparticles is larger than that prepared with 10 mM $HAuCl_4$, which are relatively spherical with diameter about 20 nm, as shown in Fig. 2(d). The appearance of polygonal particles and nanorods was also observed in other study using medium molecular weight chitosan as stabilizing and reducing reagent for nanoparticles formation (Huang & Yang, 2004). Probably, the formation of polygonal particles was caused by decomposition and recombination of preformed spherical nanoparticles.

We also studied the time effect on the formation of gold nanoparticles. The mixture containing 10 mM of $HAuCl_4$ and 0.5% of chitosan was processed by plasma for various periods. The red color of the mixture becomes darker as the time increases from 10 min to 70 min. Fig. 3(a) shows the UV–vis absorption spectra

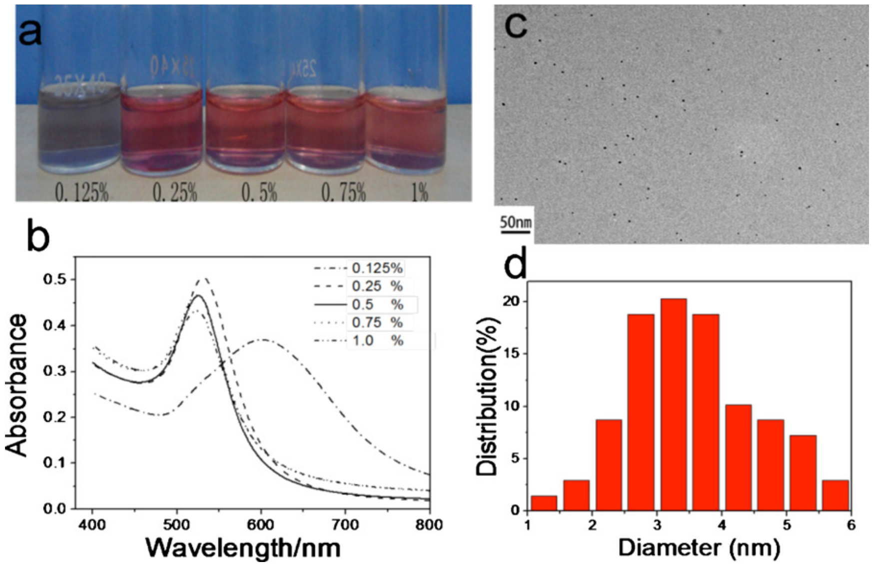

Fig. 1. The optical picture (a); UV–vis absorption spectra (b) of gold nanoparticles prepared with chitosan of different concentrations (0.125%; 0.25%; 0.5%; 0.75%; 1%); TEM images of gold nanoparticles prepared with 0.25% chitosan (c) and its histogram of particle size distribution (d).

of the mixture. The plasmon absorption increases with increasing processing time and there is a red-shift of the absorption maximum. The result indicates that size or shape probably changes with time. Fig. 3(b) and (c) shows the TEM images of nanoparticles processed by plasma for 20 min and 60 min, respectively. With longer plasma process time, the resulting gold nanoparticles show a slight increase of size (mean diameter increased from 20 nm to 25 nm) and become more anomalous.

As mentioned above, the plasma was generated by surface discharge of air under atmospheric pressure. We replaced air with

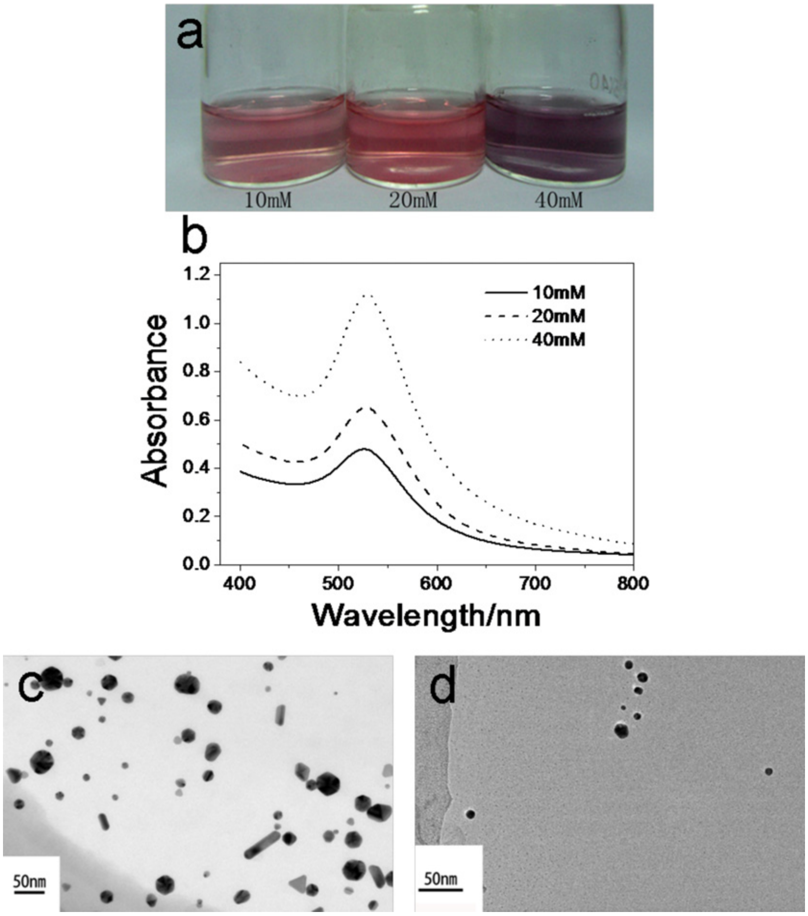

Fig. 2. Optical pictures (a) and UV–vis absorption spectra (b) of gold nanoparticles prepared with $HAuCl_4$ of different concentrations (10 mM; 20 mM; 40 mM); TEM images of gold nanoparticles prepared with different concentrations of $HAuCl_4$ at 40 mM (c) and 10 mM (d).

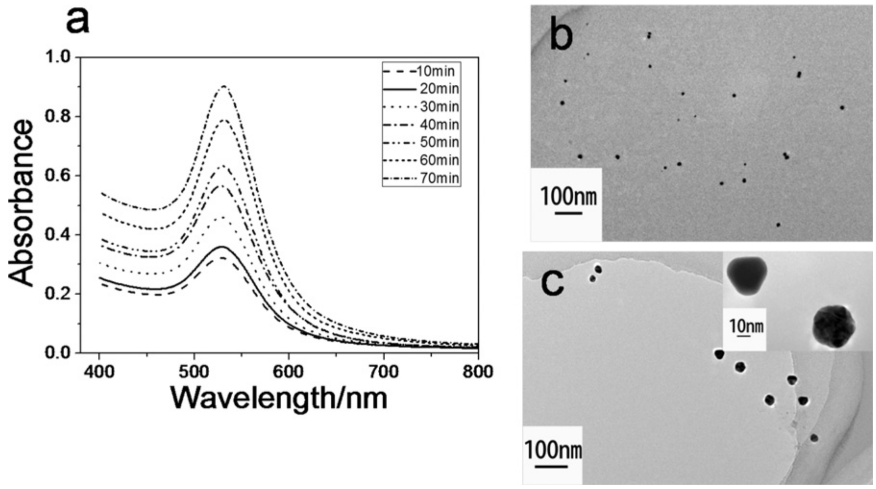

Fig. 3. UV–vis absorption spectra of $HAuCl_4$ and chitosan solution by plasma processing for different time (a) and TEM images of gold nanoparticles processed for 20 min (b) and 60 min (c).

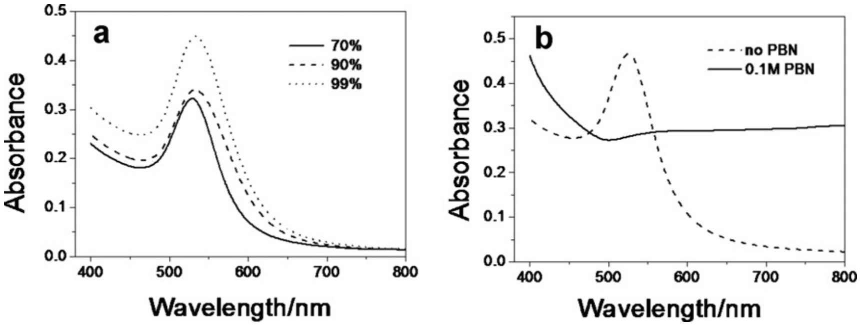

Fig. 4. UV–vis absorption spectra (a) of gold nanoparticles prepared with different relative humidity; UV–vis absorption spectra (b) of the obtained solutions with or without 0.1 M PBN.

pure oxygen, nitrogen and the mixture of pure oxygen and nitrogen to discharge under the same circumstance. The generated plasma was used to process the mixture of $HAuCl_4$ (10 mM) and chitosan (0.5%). There was no color change observed in the solutions. At the same time, no distinct absorption peak of gold nanoparticles occurred on the UV–vis spectra, which means no reduction of gold nanoparticles under these circumstances. We anticipate that moisture in air may play an important role. To get further insight of the role of moisture, we decided to alter the relative humidity of air. The mixture of $HAuCl_4$ (10 mM) and chitosan (0.5%) was reduced by plasma generated with air at different humidity. From the UV–vis spectra in Fig. 4(a), we can see that with the increase of air humidity, the intensity of absorption rises and there is a red-shift of absorption maximum. Additionally, we examine the existence of free radicals in solution by a spin trap agent, N-tert-buthyl-α-phenylnitrone (PBN). Fig. 4(b) shows that there is no formation of gold nanoparticles after addition of PBN, which means that free radicals generated are trapped by PBN and do not work as reducing agents any more. Considering the information in Fig. 4 and the fact that hydrogen radicals are active species for metal ion reduction (Bratescu, Cho, Takai, & Saito, 2011), we believe that it is moisture in air that discharges to produce hydrogen radicals which act as reducing agents. The possible reaction route might be

$$H_2O \rightarrow H^{\bullet} + OH^{\bullet} \qquad (1)$$

$$AuCl_4^{-} + 3H^{\bullet} \rightarrow Au^0 + 3HCl + Cl^{-} \qquad (2)$$

where the moisture in air discharges to produce $H^{\bullet}$, as shown in (1), and the H radicals are necessary to reduce the Au^{3+} to Au^0, as shown in (2).

4. Conclusion

We synthesized gold nanoparticles by plasma generated by surface discharge of air successfully. In general, nanoparticles prepared have a high stability and no signs of aggregation are found after 1 month storage. We can prepare nanoparticles with different size and shape by controlling the ratio of $HAuCl_4$ and chitosan or changing the reaction time. We believe that the moisture in air discharges and produces hydrogen radicals to act as reducing agents. This method proposed for the preparation of gold nanoparticles is considered to have its own advantage because of the use of a naturally derived polysaccharide, chitosan and atmospheric plasma which allows a rapid reaction rate.

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