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Ultrasonic synthesis of nano-size silver particles colloidal sol and its characterizations

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ABSTRACT

Using starch as the stabilizing agent, glucose as reducing agent, nano-size silver particles colloidal sols have been synthesized via ultrasonic irritation in aqueous solution. The synthesis process is completely green and the colloidal sols are safe to environment and human, and can be used as antibacterial agent in biology, medicine, food packaging and hauseware fields. The synthesis technology parameters for the silver particles with diameter of 15 to 45 nm, such as the ultrasonic power, reaction time, reaction temperature, concentrations of silver nitrate and capping agent were determined and discussed. The typical colloidal was characterized by ultraviolet-visible spectroscopy (UV-Vis), transmission electron microscope (TEM), X-ray powder diffractometer (XRD) and Zeta Sizer Nano Series.

KEYWORDS

Nano-size silver particles sol;
Green synthesis;
UV-Vis spectra;
Antibacterial.

INTRODUCTION

Silver nanoparticles colloidal is useful in areas such as ink-jet printing[1], photography, catalysis[2], conductivity[3,4], sensors[5], antibacterial or antimicrobial packaging[6-10], and so on. Recent years, there has been increased emphasis on the topic of "green" chemical synthesis of silver nanoparticles[11]. There are three main steps in the preparation of nanoparticles that should be evaluated from a green chemistry perspective: the choice of the solvent medium used for the synthesis, the choice of an environmentally benign reducing agent, and the choice of a nontoxic material for the stabilization of the nanoparticles[12]. The majority used chemicals in the reported methods to prepare silver particles are toxic chemicals, such as hydrazine, sodium borohydride ($NaBH_4$), dimethylformamide(DMF), polyvinyl pyrrolidone (PVP)[13], and these chemicals all have some potential risks to the environmental and human health.

It is well known that silver nanoparticle is a promising antibacterial material. While being relatively nontoxic to human cell, the large surface area of silver particles can improve their antibacterial effectiveness against a broad spectrum of bacterial strains. The silver nanoparticles may be used in form of colloidal sols or doping agents for a lot of composite materials with polymers or papers matrix, as an additive for antibacterial packaging used in pharmacy or food packaging elements. Starch is a renewable polymer, and it has extensive number of hydroxyl groups in aqueous solution, which can facilitate the complexation of metal ions to the molecular matrix. In fact, starch is found to be not

only an effective reducing agent but also a new morphology directing agent. In the present investigation, a clean, non-toxic, environmentally acceptable green chemistry synthesis procedure has been adopted. H_2O is utilized as the environmentally benign solvent throughout the preparation. Glucose is used as the reducing agent, and starch is selected as the stabilizing agent.

MATERIALS AND METHODS

Materials

All chemical regents used in this investigation were of analytical grade and they were used without further purification. Silver nitrate ($AgNO_3$) was purchased from Beijing Chemical Factory (Beijing, China). Glucose and starch were supplied by Sinopharm Chemical Reagent Co., Ltd (Beijing, China). De-ionized water was used to prepare aqueous solutions.

Preparations of nanosized silver colloids

The preparation of nanosized silver colloids is very straight-forward. Firstly, starch was added to the deionized water under magnetic heating and agitation. Then, $AgNO_3$ aqueous solution was added into above solution after starch completely dissolute. Finally, glucose aqueous solution was added. The reaction was processed in a KQ500DB Ultrasonic Cleaner (Kunshan Instruments Co., Ltd. China) at the temperature of 70°C. Several minutes after reaction, the solution became a little light yellow, illustrating that silver nanoparticles were already generated gradually.

Characterizations

The UV-Vis absorption specula were obtained in the range between 300nm and 600nm using an ultraviolet-visible spectrophotometer (UV-2501PC, Shimadzu, Japan). Distilled water was used as the blank and all samples were diluted five times before the measurements. Particle size was measured using a Zeta Sizer Nano Series (Malvern, England). The TEM images were obtained using a transmission electron microscope (H-700, Hitachi, Japan) and its sample was prepared by drying a drop of the silver colloidal solution on a TEM copper grid. The XRD pattern of Ag NPs is recorded by an X-ray power diffractometer (D8, Bruker, Germany).

RESULTS AND DISCUSSION

$AgNO_3$ concentration

The concentration of the starch aqueous is determined as 0.005Wt% to get a suitable viscosity. In order to get a proper size of the silver particles, the reaction temperature is determined as 70°C and reaction time is 180 minutes by experimental results. To study the effect of $AgNO_3$ concentration on the formation of the silver nanoparticles, silver nanoparticles colliods were prepared with different various concentrations of $AgNO_3$ in a 300W ultrasonic oscillation at 70°C for 180 minutes. It is well reported that the size and the shape of metal nanoparticles determine the spectral position of the plasmon band as well as its width[14]. As the particles grow bigger, the plasmon band broadened and shift to longer wavelength. Figure 1 gives UV-Vis spectra of the prepared colloids. The spectrum has an absorption band in the 400-420nm region, which suggested that the size of the silver particles in the colloids is 5-120 nm[15]. Figure 2 is the photographs of silver colloids prepared by different $AgNO_3$ concentration. The colloid prepared from lowest $AgNO_3$ concentration (0.05mol/L) appears light yellow, showing a maximum plasmon peak at 413.0nm. As the $AgNO_3$ concentration increased, the color of the colloids gradually changes to golden brown. As the firstly display a slightly blue shift from 413.0nm (0.05mol/L $AgNO_3$) to 402.4nm (0.15 mol/L $AgNO_3$), then a slightly red shift from 402.4nm (0.15mol/L $AgNO_3$) to 404.8nm (0.3mol/L $AgNO_3$), with continuing increases in its in-

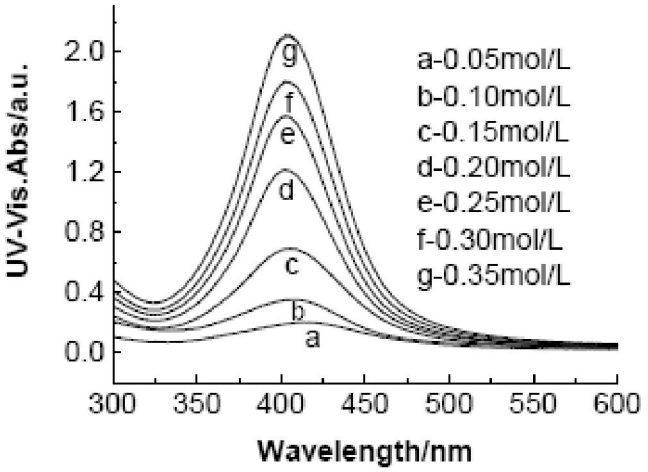

Figure 1 : UV-Vis absorption spectra of silver colloidal sols prepared by different $AgNO_3$ concentration

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(a) 0.05 mol/L (b) 0.1 mol/L (c) 0.15 mol/L (d) 0.2 mol/L (e) 0.25 mol/L

Figure 2 : Photographs of silver colloidal sols prepared by different $AgNO_3$ concentration

tensity, as shown in Figure 1. These suggest that the higher the initial $AgNO_3$ concentration, the smaller size and higher yields of silver nanoparticles. However, while the $AgNO_3$ concentration is more than 0.15mol/L, the silver nanoparticles aggregated to form larger particles, leading to a red shift of the absorption peak. Hence, the proper concentration of $AgNO_3$ is determined from 0.1 to 0.15mol/L.

The weight ratio of starch aqueous to $AgNO_3$ aqueous

The concentration of the starch aqueous is 0.005Wt%, and the concentration of the $AgNO_3$ aqueous is 0.1mol/L. Samples were prepared with different weight ratio of starch aqueous to $AgNO_3$ aqueous in a 300 W ultrasonic oscillation at 70°C for 180 minutes. Figure 3 shows UV-Vis absorption spectra of colloids with different weight ratio of starch aqueous to $AgNO_3$ aqueous. When there is no starch, there are only a few silver nanoparticles produced. As the weight ratio of starch aqueous to $AgNO_3$ aqueous is varied from 0.5:1 to 1.5:1, the position of plasmon absorption peak blue shifts from 415.8nm to 402.2nm. However, they do not change significantly as the ratio of starch aqueous to $AgNO_3$ aqueous varied from 1.5:1 to 2.5:1.The extensive number of hydrogen bonds in the starch provides surface passivation or protection against nanoparticles aggregation. With the increasing of the starch amount, the intensity is increased remarkably, rendering higher yields of silver nanoparticles. When the weight ratio of starch aqueous to $AgNO_3$ aqueous is more than 2.5:1, the viscosity of the colloid is too big to disperse the silver nanoparticles uniformly. To get the size of silver particles within 15 to 45 nm, the proper ratio of starch to $AgNO_3$ is determined as 2:1.

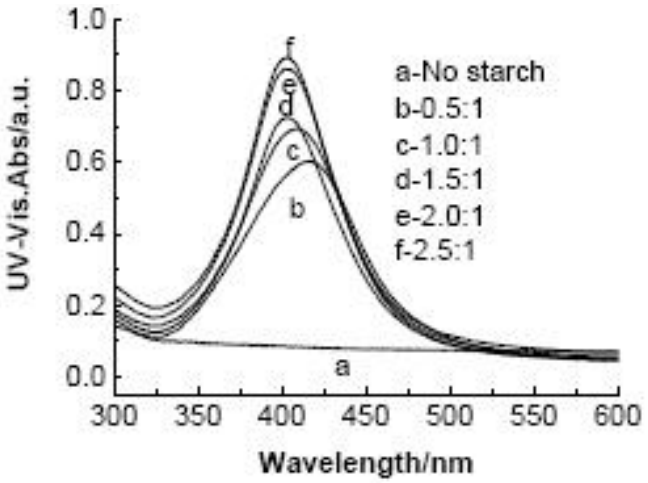

Figure 3 : UV-Vis absorption spectra of silver colloidal sols prepared with different weight ratio of starch aqueous to $AgNO_3$ aqueous

The concentration of glucose

Silver nanoparticles colloid samples were prepared with different various concentrations of glucose in a 300W ultrasonic oscillation at 70°C for 180 minutes. In Figure 4, the effect of the concentration of glucose on the Ag^+ conversion is exhibited. When the glucose content is relative lower, nanosilver generated is less, and the UV-Vis absorption intensity is lower. With the increasing of glucose concentration, The UV-Vis absorption intensity increases. The curve "e" and "f" is overlapped in Figure 4. The UV-Vis absorption intensity did not increase obviously after the concentration of glucose achieves to 0.4mol/L. As shown in Figure 4, the

curve "e (0.4mol/L)" and "f (0.5mol/L)" is overlapped. Thus, the proper concentration of glucose is 0.4mol/L.

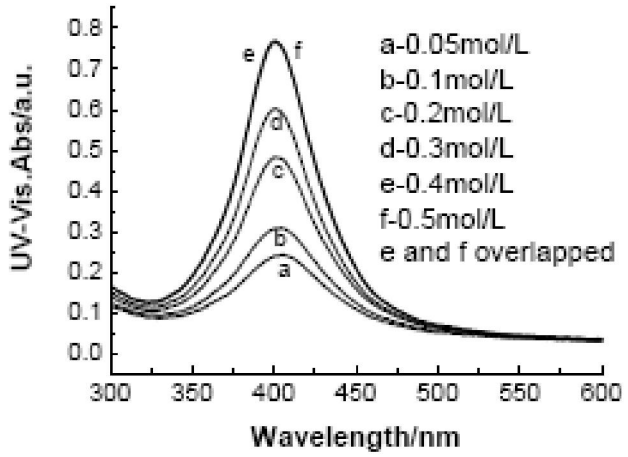

Figure 4 : UV-Vis absorption spectra of Ag colloids prepared by different concentration of glucose

Ultrasonic power

Figure 5 gives the UV-Vis absorption spectra of silver nanoparticles colloids prepared at different ultrasonic power. As the increasing of the ultrasonic power from 0 to 300 W, the absorbance intensity of silver colloids increases and the width at half- height of the absorbance peak decreases. It implies that the particle size distribution of the silver nanoparticles is narrower as the increase of the ultrasonic power. The ultrasonic power is determined as 300 W.

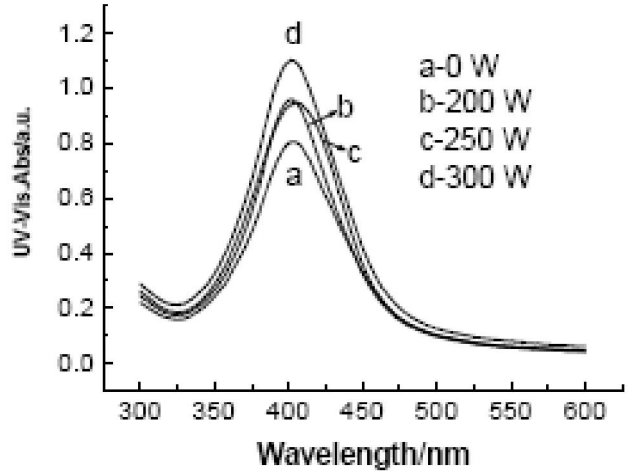

Figure 5 : The UV-Vis absorption spectra of silver nanoparticles colloids prepared at different ultrasonic power.

The typical nano silver particles sol and its characterizations

The concentration of the starch aqueous is 0.005Wt%, and the $AgNO_3$ aqueous is 0.10mol/L. The typical nano-sized silver particles sol was prepared with the weight ratio of starch to $AgNO_3$ at 2.0:1 at 70°C for 180 minutes, and the ultrasonic power is 300W. The sol was charactered by Zeta Sizer Nano Series, XRD and TEM. Figure 6 is the particle size distribution of the typical sol. Figure 7 is the TEM images of silver nano- particle sol. The size of the silver nanoparticles is from 15 to 45nm. The nanoparticles are mostly spherical in shape. Figure 8 is the XRD pattern of typical sol after dried. The diffraction pattern was in agreement with the values of standard, pure, crystalline silver structure (JCPDS 4-0783). The XRD pattern confirms that the structure of resultant silver nanoparticles is the face-centered cubic (FCC) crystal structure. However, only the diffraction peak at $2\theta = 38.1°$, marked by the indices (111) is presented. The low intensity of other silver peaks can be attributed to their embedding in soluble

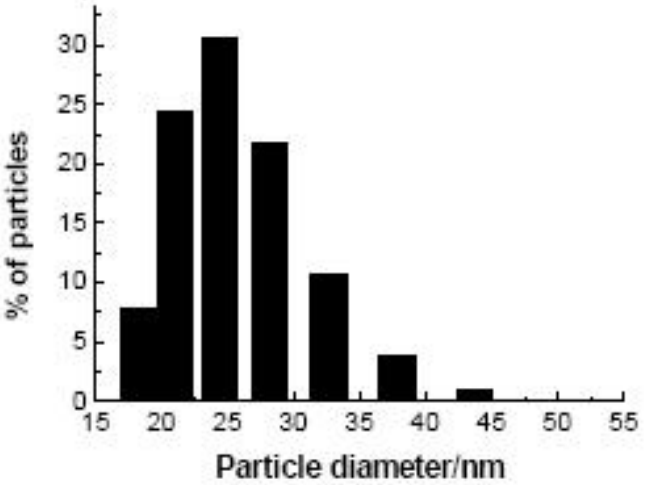

Figure 6 : Diameter distribution of the typical nano-sized silver particles sol

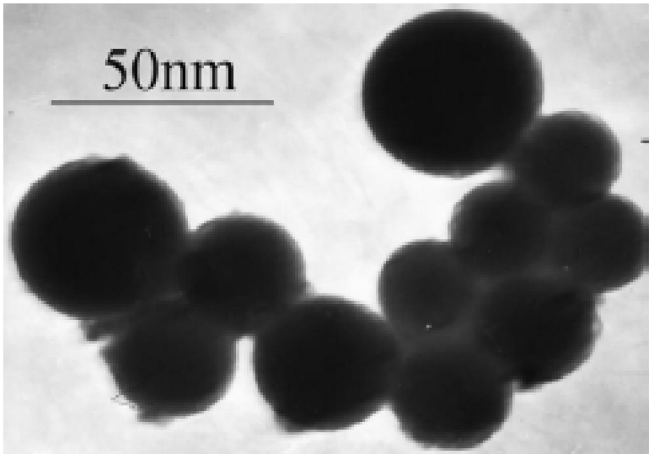

Figure 7 : TEM images of the typical nano silver particles sol

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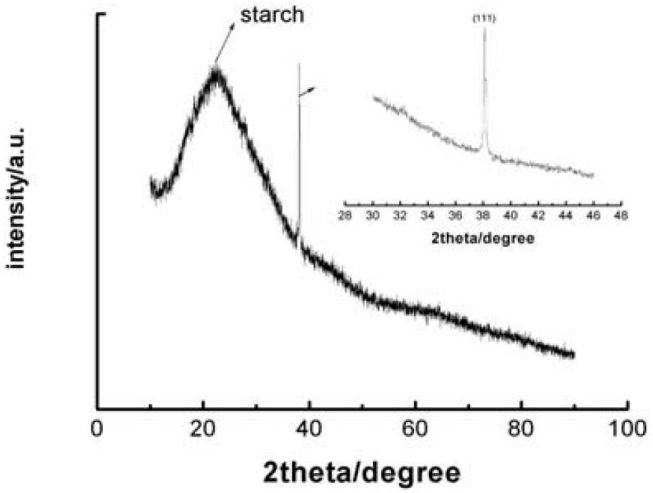

Figure 8 : XRD of the typical nano silver particle sol after dried.

starch. There is a broad reflection at about 20°, which is due to the low crystalline soluble starch.

CONCLUSION

A completely green and cost-effective method to synthesize nanosized silver colloids with a mean diameter of 25nm was developed by using starch and glucose as stabilizing and reducing agent. It is safe to environment and human, and can be used in the fields such as packaging materials for biology, medicine, food, etc. The concentration of the starch aqueous is 0.005Wt%, and the $AgNO_3$ aqueous is 0.10mol/L, and the glucose aqueous is 0.4mol/L. The typical nano-sized silver particle sol was prepared with the weight ratio of starch to $AgNO_3$ at 2.0:1 at 70°C for 180 minutes, and the ultrasonic power is 300 W.

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