A Green Process for Preparing Silver Nanoparticles Using Spinning Disk Reactor

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The main theme of this research was to synthesize nanoparticles using green materials in a spinning disk reactor (SDR), which is a type of Higee equipment. The reducing agent and protecting agent were glucose and starch, respectively, either of which is an inexpensive and nontoxic material. Silver particles were prepared by continuously pumping two solutions, which were a mixture of $AgNO_3$ aqueous solution containing protecting agent and another mixture of NaOH aqueous solution containing the reducing agent, into the chamber of the SDR, where a liquid–liquid reaction took place. The reaction time was less than 10 min, which was much shorter than the traditional methods. After washing and redispersing, silver particles of 10 nm or smaller were obtained, and the redispersed aqueous suspensions were stable for more than 40 days with or without the addition of a dispersing agent. A high-gravity process that combines economic benefit with environmental benignancy was successfully developed to produce silver nanoparticles. © 2007 American Institute of Chemical Engineers *AIChE J,* 54: 445–452, 2008

Keywords: spinning disk reactor, silver nanoparticle, green process, stability of suspension

Introduction

Ultrafine silver powders have attracted much attention in the past decade due to their excellent electrical, thermal, biological, catalytic, and optical properties.[1–8] The particle size plays a decisive role in the application of silver colloids. When the silver particles are employed as pigments in ink-jet ink formulations, the image quality and print reliability can be improved when using particle sizes of less than 50 nm.[5] It is also widely known that silver particles in nanoscale exhibit high-antibacterial activity and have no intolerable cytotoxic effects for human beings.[6–8] Many methods for preparing silver nanoparticles, including the precipitation method,[9–14] irradiation method,[15] and microemulsion technique[4] have been developed. Each method has its own disadvantages. For example, the irradiation method is expensive and dangerous for human beings, and the microemulsion technique is too complicated to apply in industry.

The precipitation method is probably the most popular among the above-mentioned methods for its simplicity, low cost, and ease of manipulation. In general, the precipitation method involves the reaction of metal salts with a reducing agent. The common reducing agents used in the synthesis are dimethyl formamide, hydrazine, and formaldehyde.[9,10,12–14] For example, Chou and colleagues[12,13] synthesized nanosized silver particles using formaldehyde in alkaline solution. They proposed that the intermediate Ag_2O formed initially in the presence of hydroxyl ions then instantly converted to silver colloids. In addition, polyvinylpyrrolidone (PVP) was added as protecting agent to prevent the agglomeration of silver colloids. Although reducing agents of high activity can promote reaction rate, they also pose the potential of biological toxicity and environmental hazards. Development of a green chemical process is urgent, even in the field of nanotechnology. The green chemical process requires mild, nontoxic, and environmentally benign materials. Huang et al.[16] used

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heparin as both the reducing and protecting agents to synthesis silver nanoparticles. Heparin is derived from mucosal tissues of animals and is widely used as an anticoagulant in medicine. In their experiments, an aqueous solution of silver nitrate was mixed with heparin solution then heated at 70°C for 8 h. The silver nanoparticles so obtained were in the size range of 10–28 nm. Yang et al.[17] synthesized silver nanoparticles in polyethylene glycol by bubbling H_2 gas, which was used as reducing agent, at room temperature for 10 h. The produced silver particles were around 20 nm.

From literature survey, the best candidate for a protecting agent to be used in a green process is probably potato starch, which is allowed to dissolve a certain amount in aqueous media. Starch in aqueous solution is known to have a helical core, whose inner surface would act as the template for the formation of Zn particles of different shapes.[18] Vigneshwaran et al.[19] used starch as both the reducing and protecting agents to synthesize silver nanoparticles. Starch and silver nitrate were dissolved in water and the mixture solution was heated at 120°C and 15 psi for 5 min to produce silver nanoparticles, which were in the range of 10–34 nm. Raveendran et al.[20] developed a green chemical method to synthesize silver nanoparticles using glucose and starch as the reducing agent and the protecting agent, respectively. Glucose is mild, cheap, and not harmful to the environment. The mixture of aqueous solution, containing silver nitrate, starch, and glucose was heated at 40°C for 20 h in a stirred tank reactor to produce silver particles in the range of 1–8 nm. These starch-protected silver nanoparticles have a higher degree of stability and are potentially applicable in the pharmaceutical and biological fields. However, the green precipitation processes reported so far need a long reaction time or a high temperature to achieve a high conversion. In addition, the control of nanoparticle size has hardly been studied.

A precipitation process consists of three main steps: chemical reaction, nucleation, and crystal growth.[21] To prepare nanoparticles of small size and narrow distribution, a uniform and high level of supersaturation is necessary. To overcome these problems in a conventional precipitation method, i.e., large size and wide distribution of product particles, an efficient and cost effective method, high-gravity (Higee) technology, has been developed. The device, in the form of a rotating disk, is called a spinning disk reactor (SDR), in which a centrifugal force is used to produce an extremely thin film on the surface of a rotating disk. The waves generated on the disk surface enhance the mixing intensity and mass-transfer rate, thus shortening the reaction time. In addition, the reactor provides a high surface area to volume ratio, which could reduce the frequency of particle collision to avoid agglomeration. Cafiero et al.[22] synthesized barium sulfate with a SDR. When the rotation speed was increased from 200 to 1000 rpm, the average size decreased from 3.0 to 0.7 μm and the size distribution became narrower. They concluded that intense mixing in the SDR enhanced homogeneous nucleation; therefore, uniform distribution of particle size was obtained.

In our laboratory, rod-shaped submicron $BaCO_3$ particles were synthesized by dissolving CO_2 into $Ba(OH)_2$ slurry spread on the surface of a spinning disk.[23] Several factors, including the CO_2 flow rate, the rotation speed, and the solid-content of the feed slurry, were found to affect the particle size distribution of $BaCO_3$. A high rotation speed and low feeding rate of slurry yielded small particles and the effect of the rotation speed was very significant at a high CO_2 flow rate. Nanoparticles of magnesium hydroxide were also synthesized by continuously pumping two aqueous solutions of $MgCl_2$ and NaOH, respectively, into a SDR.[24] As the rotation speed increased, the number mean size decreased. Also, the reactant concentration ratio and the reactant flow rate had some effect on the $Mg(OH)_2$ particle size. The FEG-SEM micrograph showed the disk-like $Mg(OH)_2$ with a length of 50–80 nm and a thickness of 10 nm.

Attempts have been made in our laboratory to develop a green chemical process to produce silver nanoparticles in a SDR. We followed the same green chemistry proposed by Raveendran et al.,[20] who synthesized silver colloids using a stirred tank reactor for a long reaction time of 20 h, but we intended to shorten the reaction time. A reduction reaction was carried out in a SDR by introducing two streams of aqueous solution, one of which contained $AgNO_3$ and starch and the other one contained NaOH and glucose, onto the center of the spinning disk. Silver particles were produced when the two streams of reactant were mixed on the disk surface. Glucose and starch were tested as a reducing and a protecting reagent, respectively. The effects of various operating variables, including the concentration of $AgNO_3$ and glucose, weight ratio of starch to $AgNO_3$, flow rates of reactant streams, and rotation speed of disk, on the particle size and yield of silver nanoparticles were investigated. The silver particles were then characterized using a scanning electron microscope (SEM), an X-ray diffractometer (XRD), a dynamic light scattering analyzer, and a transmission electron microscope (TEM).

Experimental Section

The Higee system consists of a liquid feeding system, a SDR, and a slurry collection vessel. A schematic diagram of the experimental set-up is shown in Figure 1. It should be noted that the desk is placed vertically, instead of horizontally as in a gas–liquid contacting system, so that the produced particles can easily drop out of the reactor chamber. The liquid feeding system contains two tanks (A and B) from which liquid reactants are pumped separately into the reactor chamber through a flowmeter (D) and a liquid distributor (E). The two liquid distributors (E), which are straight tubes with a 3 mm-hole in the end, are set up parallel to and 5 mm apart from each other, and perpendicular to the spinning disk (F) at a distance of 5 mm from the disk. The main part of the SDR is a stainless-steel disk, 19.5 cm in diameter, driven by a variable-speed motor. The spinning disk is enclosed in a cylindrical acrylic-chamber of 23 cm in diameter and 10 cm in width.

The experiment was conducted in a recycle mode. In the beginning, tank A contained an aqueous solution of $AgNO_3$ and starch, and tank B contained an aqueous solution of NaOH and glucose. The volume of both solutions was 1 L, and the solutions were pumped at a specific flow ratio onto the center of the spinning disk with a rotation speed ranging from 1000 to 4000 rpm. The liquid was accelerated due to centrifugal force, causing it to spread over the disk surface and forming a thin film where the reducing reaction took

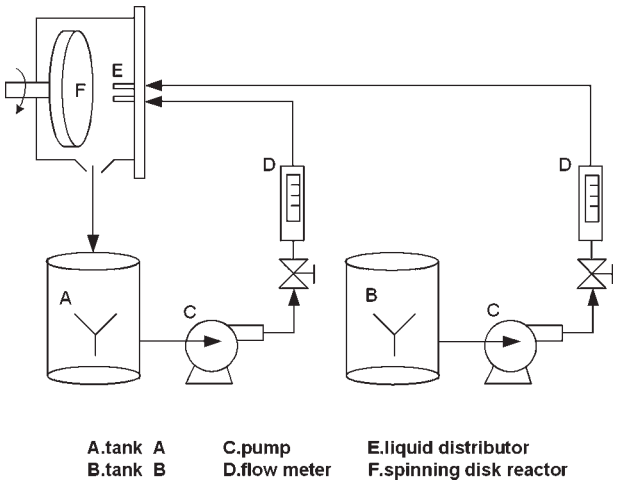

Figure 1. Experimental setup of high-gravity process for producing silver nanoparticles.

place. Then, the slurry flowed into tank A to mix with the $AgNO_3$ solution. After the solution in tank B was exhausted, the solution in tank A was continuously pumped around the system for 5 min. The recycle operation was adopted to give a high yield because the retention time on the spinning disk was short. To prevent reducing reaction taking place in the mixing tank for the recycle operation, the flow of $AgNO_3$ solution (L_A) was set at a rate that was much faster than that of reducing agent solution (L_B), i.e., $L_A/L_B = 4$. It was intended to exhaust all the reducing agent before the mixed reactant streams flowed back to tank A, where the $AgNO_3$ solution was stored at the beginning of an experimental run. After an experimental run, the yield and particle size of the silver colloids were checked by continuous stirring of the slurry in tank A for 1 h. The yield and particle size did not change much, indicating that the reducing reaction did not proceed further in tank A. This meant that the recycle time of 5 min was long enough.

The produced slurry was then centrifuged to separate the silver particles before being washed twice with a mixture of deionized water and acetone, in a volume ratio of 1–3, to remove starch and other impurities adsorbed on the silver particles. Finally, the product was reslurried to measure the particle size and to test the stability of the suspension. To determine the particle size distribution and mean size, several dispersing agents, including sodium dodecyl sulfate (SDS), PVP, and hydroxypropyl methyl cellulose (HPMC), were tested to disperse silver particles in water. For particle characterization, samples were subject to the following analyses: a TEM (JEOL, JEM1010) to observe the particle shape; a dynamic light scattering analyzer (Malvern, 3000HSA) to determine the particle size distribution and zeta potential; SEM (JEOL, J-5600) equipped with energy dispersive X-ray (EDX) to identify the composition of product; an XRD (Mac Science, MXP-3TXJ-7266) to analyze the morphology of product; a thermogravimetric analyzer (TGA) (Ulvac/Riko, TGD-7000HD) to estimate the residual quantity of protecting agent on the particle surface. In addition, to discuss the mixing efficiency, several aqueous starch solutions of different concentrations were measured by a Couette rheometer (BrookField, DV-III) to give the viscosity. The yield of this experiment was calculated by dividing the amount of centrifuged and dried particles with the theoretical amount produced from a complete reaction.

Results and Discussion

As the retention time of reactant streams in a SDR is very short, any process for producing fine particles must involve a fast reaction. In a preliminary test conducted in a stirred beaker to search for suitable conditions for instantaneous reaction of Ag^+ reduction, it was found that the sodium hydroxide concentration should be increased to 0.07 M, which was much higher than 0.01 M used by Chou and Ren.[12] They conducted the reduction experiment in a stirred tank and reported that the silver colloids were agglomerated when more NaOH was added to the reaction system, using PVP as protecting agent. Nevertheless, we decided to conduct the experiment under high alkaline conditions in the SDR, which had the advantages of intensive mixing and uniform supersaturation. Silver nanoparticles were obtained after several test runs by using a SDR. The product was analyzed by an EDX spectroscope with a thin polymer window and Si/Li detector and the spectrum was shown in Figure 2a. It clearly indicated that silver was the major product and that no carbon or oxygen element could be detected in the par-

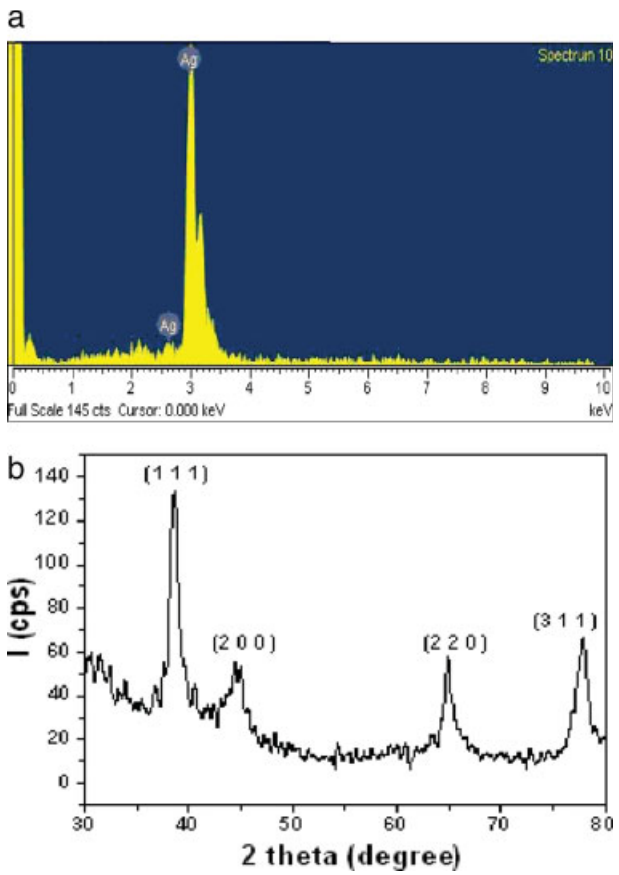

Figure 2. (a) EDX spectrum and (b) XRD pattern of synthesized silver particles of run 0807-A.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 1. Effect of Starch/$AgNO_3$ Weight Ratio on the Particle Size and Yield of Silver Colloids

Run No.	Weight Ratio (starch/$AgNO_3$)	Yield (%)	Particle Size of Silver Product: Number Mean (nm)	Particle Size of Silver Product: Volume Mean (nm)
1226-A*	0.5	65.8	15.9 (93.6%) 37.6 (6.4%)	16.3 (48.9%) 36.6 (51.1%)
0913	1	60.0	16.0	16.4
0928	1.5	50.0	16.3	19.9

Other operating variables kept constant are as follows: L_A = 0.8 L/min, L_B = 0.2 L/min, [NaOH] = 0.07 M, [$AgNO_3$] = 0.01 M, (glucose) = 0.01 M, N = 4000 rpm, and the total reaction time = 10 min.
*The particle size distribution had two modes.

ticles when glucose was used as the reducing agent. Besides this, the XRD analysis of 20 nm silver colloids from run 0807-A (in Table 3) presented in Figure 2b showed the characteristic peaks of crystalline silver. The XRD was equipped with Cu Kα radiation source and operated at 40 kV and 30 mA. Then, a mechanism of nanoparticle formation was proposed and the effects of several operating variables, including weight ratio of starch to $AgNO_3$, glucose concentration, reactants flow rates and rotation speed of disk on the yield and particle size of silver colloids, were investigated. Finally, the behavior of the redispersed suspension was reported.

Mechanism of silver nanoparticle formation in SDR

The reaction mechanism of silver ion (Ag^+) reduction to silver colloid in alkaline aqueous solution has been discussed by Chou and Ren.[12] They proposed that the silver ion would first react with the hydroxyl ion to form an intermediate, Ag_2O, which was hardly detected except at a very low temperature, i.e., -45°C.[25] Then, Ag_2O was reduced to silver colloids. No matter what the reducing reaction mechanism was, the reducing reaction took place in the thin film spreading over the spinning disk surface. Since the mixing was intensive in the thin film, i.e., good micromixing existing in a SDR,[22] uniform concentration of reactants and protecting agent was achieved immediately after the mixing of the two streams of reactants. Since the induction time was longer than the mixing time,[21] the nucleation occurred after the complete mix of reactant streams. A high efficiency of micromixing for the SDR was confirmed experimentally by Chen et al.[26] using the parallel-competing test reactions. Once the silver particles formed, starch acted as the protecting agent for preventing them from growing further. Besides, there is little backmixing when the slurry travels across the surface of the rotating disk. This offers less chance of particle collision and retarded agglomeration. As a result, small, uniform, and dispersed particles were obtained.

Effect of starch/$AgNO_3$ weight ratio

To prepare nanoparticles, the dosage of the protecting agent is crucial in the determination of particle size.[12] In this study, the effect of starch/$AgNO_3$ ratio was investigated by keeping other variables constant: the concentration of NaOH was 0.07 M acquired from the preliminary test using a stirred beaker; the concentration of glucose (reducing agent) 0.01 M was used by keeping the stoichiometric ratio of $AgNO_3$; the disk was rotating as high as possible at 4000 rpm to obtain good micromixing; the flow rates of L_A and L_B were 0.8 and 0.2 L/min, respectively, to prevent the reducing reaction from taking place in the stirred tank; and the recycle time was chosen as 5 min to achieve high yield.

Adjusting the weight ratio of starch/$AgNO_3$ from 0.5 to 1.5 while keeping other operating variables constant, the yield of silver colloids decreased from 65.8 to 50.0% as shown in Table 1. It was conjectured that the high concentration of starch reduced the mixing efficiency and the frequency of collision between reacting molecules, thus decreasing the product yield. It was evident that the increase in yield was only a few percent after the slurry had been stirred for 1 h in the storage tank. On the other hand, the change in particle size of primary particles for different dosage of starch was less significant, although a small portion, i.e., 6.4%; of particles agglomerated to form larger particles for the weight ratio of 0.5. This meant that at the weight ratio of 0.5, the amount of starch added to the solution was not high enough to disperse all the primary particles. As a result, two modes, 15.9 and 37.6 nm, appeared in the size distribution. When the weight ratio was higher than one, the particles were well dispersed. Thus, in the study of other operating variables done after this, the starch/$AgNO_3$ weight ratio was kept at 1/1. Similar trend were reported by Chou and Ren,[12] who synthesized silver nanoparticles using PVP as protecting agent in a stirred tank reactor and found that the particle size decreased with an increase in PVP/$AgNO_3$ weight ratio. When the weight ratio was 9.27, the mean particle size decreased to 10 nm. From our experience PVP was a better dispersing agent for suspended particles as compared with starch. It was obvious that a suitable weight ratio of dispersing agent to $AgNO_3$ for well dispersion was much lower for a SDR as compared with a stirred tank reactor.

Effect of glucose concentration

When adjusting the concentration of glucose from 0.01 to 0.05 M while keeping the other operating variables constant, the yield of silver increased from 60.0 to 70.9% as shown in

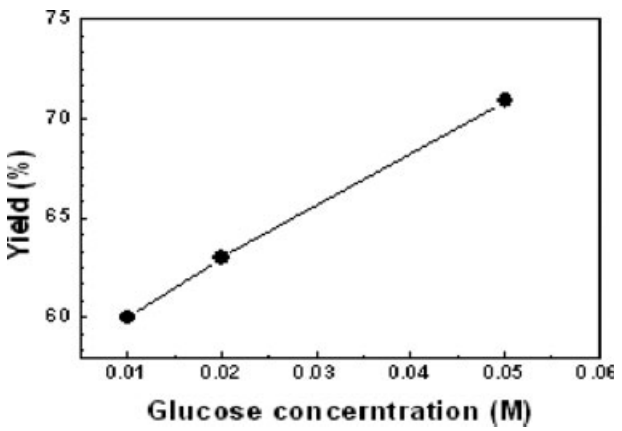

Figure 3. Effect of glucose concentration on the yield of silver colloids.

Other operating variables kept constant are: L_A = 0.8 L/min, L_B = 0.2 L/min, [NaOH] = 0.07 M, [$AgNO_3$] = 0.01 M, N = 4000 rpm, weight ratio (starch/$AgNO_3$) = 1, and the total reaction time = 10 min.

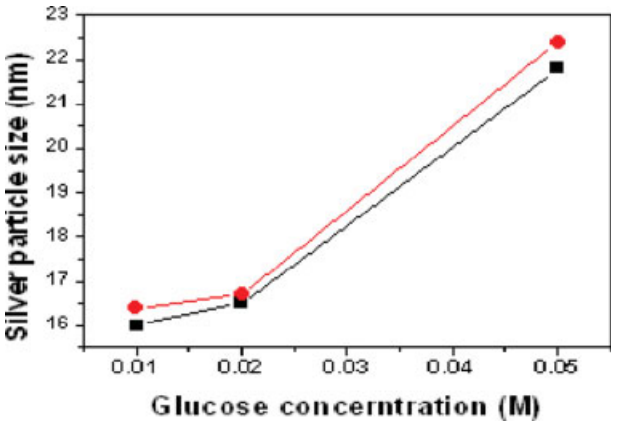

Figure 4. Effect of glucose concentration on the particle size of silver colloids.

Other operating variables kept constant are L_A = 0.8 L/min, L_B = 0.2 L/min, [NaOH] = 0.07 M, [$AgNO_3$] = 0.01 M, weight ratio (starch/$AgNO_3$) = 1, N = 4000 rpm, and the total reaction time = 10 min. ■, number mean size of silver particles; ●, volume mean size of silver particles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

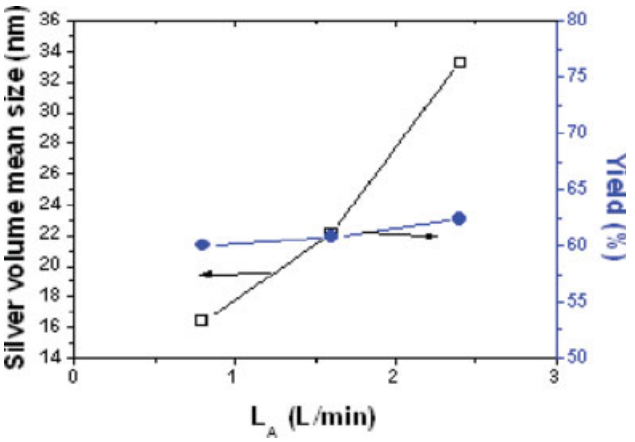

Figure 5. Effect of flow rate on the particle size and yield of silver colloids.

Other operating variables kept constant are L_A/L_B = 4, [NaOH] = 0.07 M, [$AgNO_3$] = 0.01 M, [glucose] = 0.01 M, weight ratio (starch/$AgNO_3$) = 1, N = 4000 rpm and the recycle time = 5 min. □, volume mean size of silver particles; ●, yield. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3. As far as the particle size was concerned, the number mean size increased from 16.0 to 21.8 nm, and the volume mean size increased from 16.4 to 22.4 nm as shown in Figure 4. A higher concentration of glucose resulted in a high reaction rate that increased the supersaturation, and the yield improved for the same reaction time i.e., the same retention time on the rotating disk. In general, higher supersaturation resulted in smaller primary particles, but increased the extent of agglomeration. In this case, the mean size of silver particles increased a little bit as the glucose concentration increased from 0.01 to 0.05 M.

Effect of flow rate

The effect of flow rate was studied under the constraint of L_A/L_B = 4. The reason for using this ratio of feed streams has been explained in the experimental section. As shown in Figure 5, the volume mean size of silver particles increased with an increase in flow rate and the yield was rather independent of flow rate. When the flow rate increased threefold, i.e., L_A varied from 0.8 to 2.4 L/min, the particle size increased by a factor of two and the yield increased by only 2.3%, which was insignificant. The result on particle size can be explained by the micromixing efficiency. Chen et al.[26] measured the segregation index, which represents the efficiency of micromixing, by changing the flow rates of reactant streams fed into the SDR. They concluded that the micromixing efficiency was higher at lower flow rates. Judging from nucleation theory, the success in preparing nanoparticles using the SDR was attributed to its high micromixing efficiency.[21,25] Thus, the particle size of silver colloids increased with increasing flow rate; however, they were in the nanoscale range, i.e., from 16.0 to 32.5 nm. This means that the size of nanoparticles can be controlled by adjusting the flow rate of feeding streams.

Effect of rotation speed

In this section, the effects of rotation speed between 1000 and 4000 rpm are discussed as the other operating variables remained constant. The mean particle size and yield of produced silver colloids are presented in Table 2. The rotation speed had little effect on the yield, ranging from 56.8 to 60.0%, and the number mean size, scattering between 13.3 and 16.0 nm. However, lower rotation speeds in the range between 1000 and 2000 rpm caused agglomeration of silver particles, as judged from the two modes of the size distribution. Usually, the influence of rotation speed on particle size is not observed when it exceeds 1000 rpm as reported by Cafiero et al.[21] It should be noted that in their experiment, no protecting agent, which is usually a polymer, was added to the system; however, starch was added in our experiment. The viscosities of starch solutions were measured at room temperature by a Couette rheometer (Brookfield, DV-III). The selection of spindle No. 0 and rotation speed between 60 and 90 rpm gave reproducible viscosity data. The results, presented in Figure 6, show that the viscosity increased from 1.08 to 2.33 mPa s when the starch concentration increased from 2 to 14 g/L. Chen et al.[27] reported that the segregation

Table 2. Effect of Rotation Speed on the Particle Size and Yield of Silver Colloids

Run No.	Rotation Speed (rpm)	Yield (%)	Particle Size of Silver in Product: Number Mean (nm)	Particle Size of Silver in Product: Volume Mean (nm)
0913	4000	60.0	16.0	16.4
0731-A*	2000	56.6	13.5	13.9 (92.2%) 50.4 (7.8%)
0808*	1500	56.8	13.3	13.3 (91.1%) 49.8 (8.9%)
0731-B*	1000	58.0	15.9	17.0 (91.9%) 51.2 (8.1%)

Other operating variables kept constant are as follows: L_A = 0.8 L/min, L_B = 0.2 L/min, [NaOH] = 0.07 M, [$AgNO_3$] = 0.01 M, (glucose) = 0.01 M, weight ratio (starch/$AgNO_3$) = 1, and the total reaction time = 10 min.
*The particle size distribution had two modes.

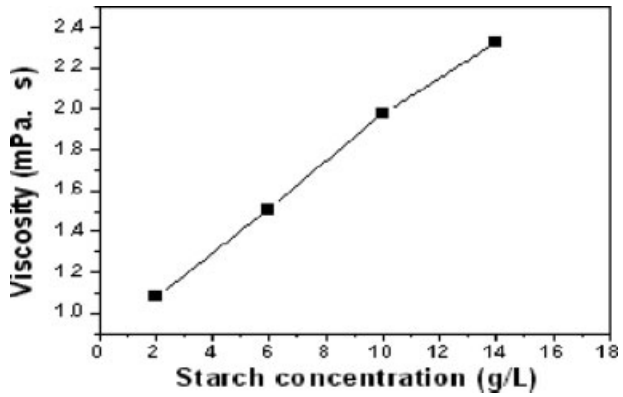

Figure 6. Viscosity of starch aqueous solution as a function of concentration.

index, which is a criterion for micromixing efficiency, increased as the viscosity increased from 1 to 3 mPa s. It is obvious that the solution with high starch concentration needed a high rpm of SDR to achieve good mixing. It is concluded that, at the rotation speed of 4000 rpm, an efficient mixing on the disk was achieved to enhance the agitation within the film, resulting in a uniform and high supersaturation. Thus, silver colloids with less agglomeration were produced.

Allowable $AgNO_3$ concentration for producing silver colloids

In this series of experiments, the $AgNO_3$ concentration was varied by a factor of 7, from 0.01 to 0.07 M, to increase the production rate. Other fixed operation variables were indicated in Table 3, in which the experimental results were presented. It should be noted that the weight ratio of starch to $AgNO_3$ was kept at one for producing dispersed silver nanoparticles. When the concentration of $AgNO_3$ increased from 0.01 to 0.05 M, the yield of silver decreased from 60.0 to 48.7%, and the mean size increased from 16.0 to 40.9 nm for number mean and from 16.4 to 41.3 nm for volume mean. When the concentration of $AgNO_3$ was increased further to 0.07 M, the silver colloids agglomerated and became larger particles. The highly agglomerated particles were difficult to dry, thus the yield was not analyzed. It was understandable that the produced particles were easily agglomerated at high concentration of $AgNO_3$ and starch due to higher reaction rate and poorer mixing.

TGA analysis of washed silver nanoparticles

If the protecting agent was retained on the surface of silver particles, some of the physical properties of particles would change. For example, a higher sintering temperature (from 150 to 400°C) was required when the protecting agent retained on the surface of silver particles was more than 0.087 g/g.[12,13] To determine the amount of protecting agent adsorbed on particle surface, TGA analysis was performed on the purified silver particles. The TGA analysis was carried out under the air atmosphere at a heating rate of 10°C/min. A typical thermogravimetric curve is shown in Figure 7. The first weight change of 0.2% at temperatures below 145°C was due to the vaporization of water and other volatile materials. The second weight loss of 2.5% in the temperature range between 145 and 310°C was due to pyrolysis and decomposition of the adsorbed starch as reported by Morita.[28] The total residual quantity of the protecting agent on the silver particles was roughly estimated to be about 2.7%. If the protecting agent adsorbed on the silver particles needs to be removed completely for biological or medical application, we need to find a better way to purify the nanoparticles.

Mean particle size and stability of redispersed suspension

If the produced silver particles were kept wet after washing and centrifugation, they were easily redispersed in pure water or aqueous solutions containing dispersing agent. The mean size of redispersed particles is listed in Table 4. The sample was from run 0913 in Table 1. The redispersed suspensions had a solid content (Ag colloids) of 0.1 wt %, and the dosage of dispersing agent expressed as weight ratio of dispersing agent to Ag colloids was presented in Table 4. For Run A, the sample was dispersed in pure water. The TEM micrograph of this redispersed sample is shown in Figure 8a, in which the largest particle size was about 10 nm. The particle size distribution measured by the dynamic light scattering analyzer was in the range between 4.3 and 11.2 nm with a volume mean size of 6.9 nm as shown in Figure 8b, in which the dashed line represents the unreliable region of the instrument. Runs B to D were designed to see the effect of dispersing agent, including SDS

Table 3. Allowable $AgNO_3$. Concentration for Producing Silver Nanoparticles Under the Constraint of Weight Ratio (starch/$AgNO_3$) = 1

				Particle Size of Silver Product	
Run No.	Concentration of $AgNO_3$ (M)	Concentration of Starch (g/L)	Yield (%)	Number Mean (nm)	Volume Mean (nm)
0913	0.01	2	60.0	16.0	16.4
0807-A	0.03	6	50.0	19.4	20.5
1108	0.05	10	48.7	40.9	41.3
0809-A*	0.07	14	†	199.1 (95.2%)	208.6 (32.2%)
				696.4 (4.8%)	713.1 (67.8%)

Other operating variables kept constant are as follows: L_A= 0.8 L/min, L_B = 0.2 L/min, [NaOH] = 0.07 M, concentration ratio (glucose/$AgNO_3$) = 1, N = 4000 rpm, and the total reaction time = 10 min.
*The particle size distribution had two modes.
†The yield was not analyzed because the silver colloids were highly agglomerated and difficult to dry.

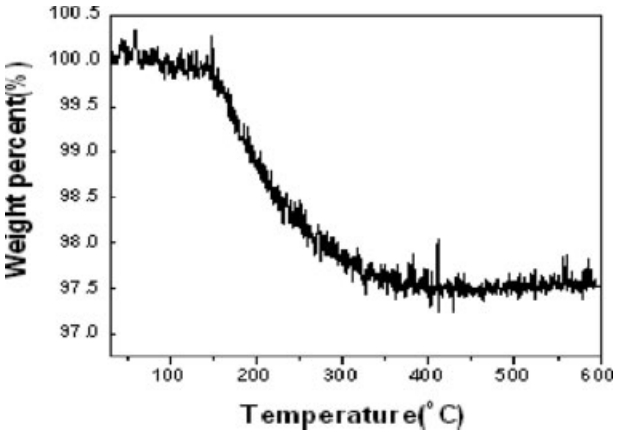

Figure 7. TGA analysis of silver colloids from run 0928.

(sodium dodecyl sulfate), PVP, and HPMC. Except Run C, which had a number mean size of 40.6 nm using PVP as dispersing agent, all other runs had a mean size around 5 nm. This result was unexpected because He et al.[29] prepared 10 nm silver colloids using PVP as protecting agent. The particle size is usually influenced by zeta potential which varies with solution pH. Generally speaking, a zeta potential of ± 30 mV is sufficient to disperse nanoparticles. Thus, particle size and zeta potential of the PVP-containing sample were measured at various pHs.

The silver particles covered with PVP were negatively charged in the whole pH range from 6.5 to 11.5 as shown in Figure 9, and the number mean size of silver particle was also plotted in this figure. The slurry pH of Run C was 6.5 and the pH was varied by adding NaOH solution. When the pH was higher than 8, the zeta potential became lower than -30 mV and the mean size decreased to around 5 nm. The mean particle size remained the same as the zeta potential further decreased to -60 mV. Therefore, the PVP was as effective as other dispersing agents used in this experiment. It should be noted that the particle size was similar for the cases with or without addition of dispersing agent. It was possible that the small amount of starch retained on the particle surface was enough for dispersing the silver nanoparticles.

The stability of the silver particle suspension was evaluated by measuring the change in particle size over time at room temperature. To find a good dispersing solution for stabilization, we chose Run A, Run B, and Run D in Table 4 to perform the stability test for a duration of 43 days. As seen from Figure 10, a slight change in the volume mean size with time for Run A and B was observed, and the mean size was below 10 nm even after 43 days. At the 38th day the volume mean size of Run D, which used HPMC as dispersing agent, increased to 40 nm. After 38 days, measurement of the volume mean size of Run D was stopped because the particles of the suspension agglomerated and settled.

Table 4. Effect of Redispersion Conditions on the Size of Silver Particles From Run 0913

Run No.	Type of Dispersing Agent	Weight Ratio (Dispersing Agent/Ag)	Particle Size of Silver Product	
			Number Mean (nm)	Volume Mean (nm)
A	–	0:1	5.1	6.9
B	SDS	1:1	4.1	5.0
C	PVP	1:1	40.6	47.0
D	HPMC	1:1	5.1	8.2

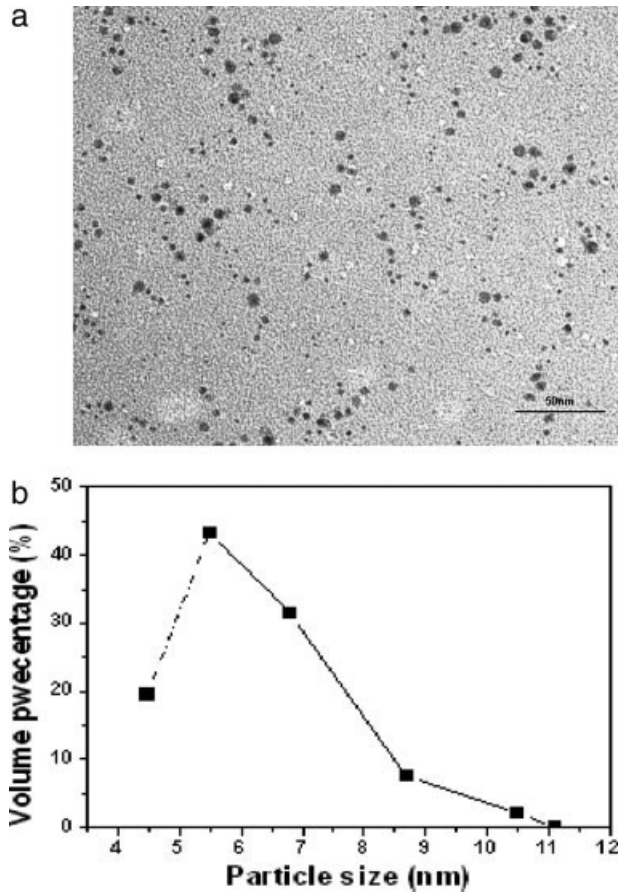

Figure 8. (a) TEM micrograph and (b) particle size distribution of redispersed silver particles of run 0913 in water.

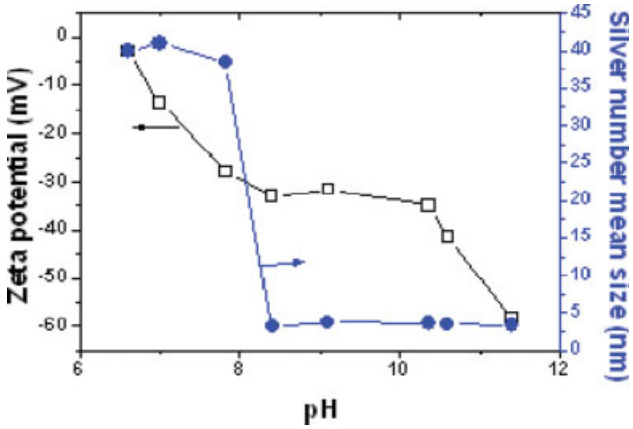

Figure 9. Zeta potential and number mean size of silver nanoparticles as a function of pH.

□, zeta potential; ●, number mean size of silver particles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

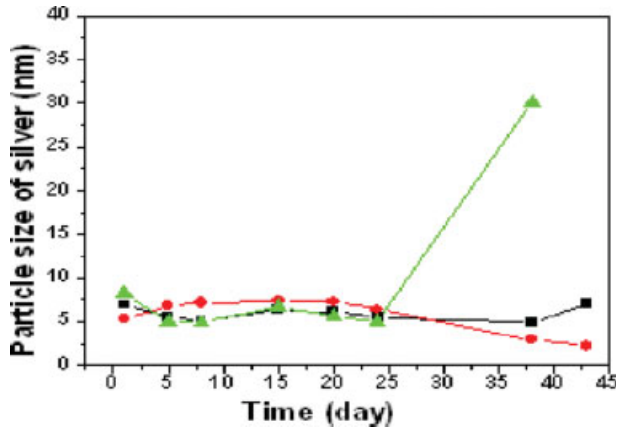

Figure 10. Stability test of redispersed silver particles on the basis of volume mean.

■, Run A-without dispersing agent; ●, Run B-SDS as dispersing agent; ▲, Run D-HPMC as dispersing agent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Conclusions

Silver nanoparticles were successfully synthesized using a green chemical process using a SDR. The inexpensive and environmentally-benign materials of starch and glucose were used as the protecting agent and reducing agent, respectively. The reaction was carried out at room temperature and the reaction time was around 10 min, which was considerably shorter than the conventional method. After the silver particles were separated from the slurry, the mean size of the redispersed sample was smaller than 10 nm, and the suspension was stable for more than 40 days when stored at ambient temperature. Several operating variables that affected the particle size and yield were investigated. A low weight ratio of starch to $AgNO_3$ or a high concentration of glucose led to high yield, which was as high as 70% in a total reaction time of 10 min. In the size measurement, it was found that a suitable dispersing agent should be carefully chosen. In addition, the pH value of the dispersing solution also affected the particle size. The zeta-potential of nanoparticles as a function of pH value should be measured to select appropriate conditions for size measurement.

Acknowledgments

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