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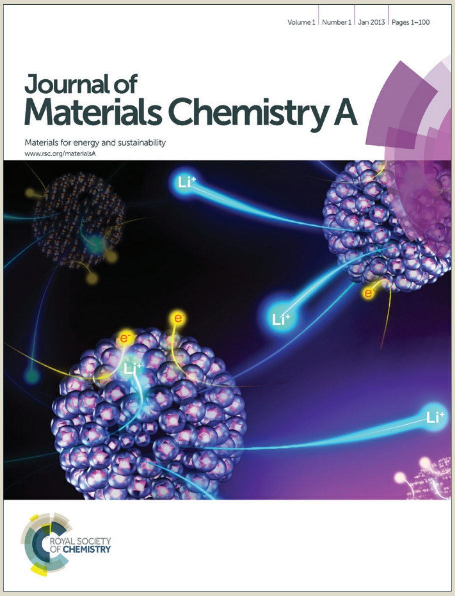

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COMMUNICATION

Continuous synthesis of size-tunable silver nanoparticles by green electrolysis method and multi-electrode design for high yield

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Although having developed some methods, high-yield controllable synthesis of silver nanoparticles in aqueous solution is still challenging. Here, we reported the green electrolytic synthesis in a continuous flow system. Nanoparticle-sizes could be tuned facilely by adjusting the flow velocity. Further, an improved multi-electrode electrolytic reactor was designed for increasing yield.

Introduction

In the last decade, the synthesis of silver nanoparticles (AgNPs) in aqueous solution has received increasing attentions due to its potential biomedical applications[1-5]. For biomedical applications, green synthesis and materials are desirable. However, liquid phase reduction is still the most commonly method and many harmful reagents are often used. Although AgNPs have already been controlled well in organic solutions[6-9], the synthesis of AgNPs in aqueous solution is still challenging due to the hard-to-control nucleation process arising from the high reactivity of silver precursors in water[10]. Particularly, when amplifying the liquid phase reaction for large-scale synthesis of monodisperse AgNPs, the process is hard to control well because the synthesis conditions such as temperature and matter are apt to differ in micro-regions of a bigger reaction system owing to the limitation of heat and mass transfer.

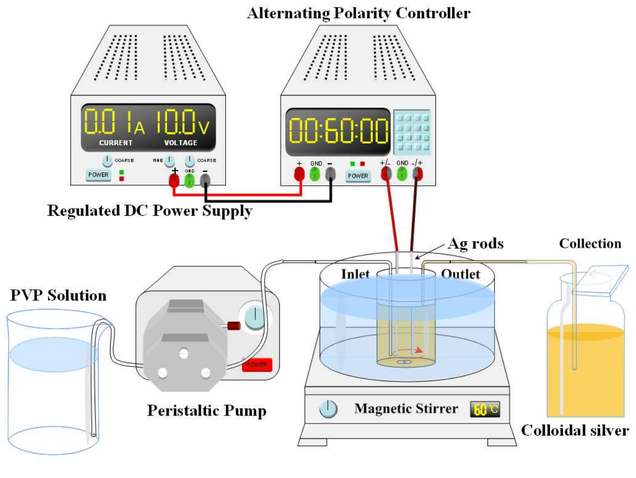
Electrochemical synthesis is a facile, rapid and green method. It's mainly used to precipitate AgNPs on the surface of the substrate through the redox taking place on/near the surface/interface of electrode[11-15]. If deposited AgNPs can be transferred efficiently from the surface of the substrate to the bulk solution, colloidal AgNPs can be obtained. Some groups synthesized AgNPs by the electrochemical reduction of silver salt[16-18], though the synthesis need be further controlled. Also, the few reported that AgNPs were directly synthesized by the electrolysis of pure silver, without adding any reducing agents and silver salts[19, 20]. So the synthetic products may have higher purity than those synthesized by general chemical reduction method, and are more suitbe for biomedical applications. In addition, some assisted method, for example, sonochemical technology was also used to enhance the transfer of AgNPs from the substrate to the bulk solution[21, 22].

Recently, the research has attempted to synthesize large-scale AgNPs by electrochemical discharge in a continuous flow system, but the morphology and size are uncontrollable due to the violent discharge reaction condition[23]. For all that, we had been enlightened from the research. Traditionally, electrochemical synthesis is seldom applied in a continuous flow system. We considered it is meaningful to achieve control of electrochemical synthesis in a continuous flow system. It maybe combines the advantages of electrochemical method and the continuous flow method. But there are some problems need to solve, for example, how to control the synthesis of AgNPs facilely and precisely, how to maintain the reaction going on and prevent the passivation of silver electrode, how to increase the yield of AgNPs in unit time.

In this work, we developed the silver electrolytic reactor in a continuous flow system, and researched the size control of AgNPs by faciely adjusting flow velocity. To increase synthesis yield of AgNPs in unit time, a pre-unreported multi-electrode electrolytic reactor was designed.

Results and discussion

For the purpose of controllable synthesis, we designed the silver electrolytic reactor in a continuous flow system as shown as Scheme 1. The reactor is an airtight cylinder container (Fig.S1). Considering the homogenization of reaction and the yield of AgNPs in unit time, the electrolytic cell is designed to a smaller volume (about 9.4mL) that with an inner diameter of 20mm and height of 30mm.



Scheme 1 Schematic of electrolytic synthesis in a continuous flow system

Two pure silver rods with the diameter of 2mm and the length of 20mm are fixed on the cover of the reactor as anode and cathode, respectively. The center distance of the two electrodes is 8mm. Regulated DC power supply is applied to the two electrodes through a homemade device that called "Alternating Polarity Controller". The input part, electrolytic reactor and output part are connected with two PTFE tubules, one extends close to the bottom of the reactor as the inlet for the reaction solution, and the other is embedded in the cover as the outlet for colloidal AgNPs solution. The reaction solution is pumped into the reactor with a peristaltic pump and the synthetic products flow out of the outlet tube.

When synthesizing AgNPs with the reactor, the silver rod as the sacrificial anode will lose electrons and dissolve to Ag^+. Near the anode oxygen gas is released due to the electrolysis of water, simultaneously, Ag_2O film is deposited on the surface of the anode. The migrated Ag^+ in the solution will be reduced to zero-valent Ag atoms on the cathode and hydrogen gas is released near the cathode. Under the attraction of Van der Waals forces, Ag atoms nucleate and grow to AgNPs. The synthesized AgNPs are further transferred to the bulk solution from the cathode by vigorous stirring.

As shown in Fig.1, it should avoid forming thick oxidation deposition coating on the surface of the anode. It's the key to keeping continuous electrolytic synthesis. The deposited Ag_2O film will lead to the passivation of the silver electrode and hinder electrolysis reaction. In addition, it easily breaks off many big impurity particles into the solution. Therefore, we designed the "Alternating Polarity Controller" to alternately change the polarities of anode and cathode every some time. The Ag_2O film may be reduced to Ag by H_2 when the anode change to the cathode. By the means, the oxide coating alternately deposited and dissolved on the surfaces of electrodes. So the two silver electrodes can be consumed synchronously rather than sacrificed only one, and the continuous synthesis can be kept going. We can set the proper alternating time with the device, and the optimal alternating time will be determined in the future research.

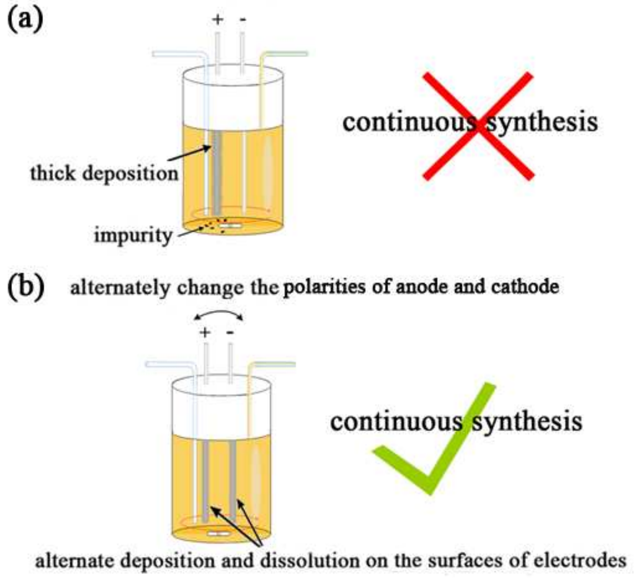


Fig. 1 The key factor for continuous electrolytic synthesis

The phase of the product can be determined by XRD. In Fig.2 (a), red lines show the standard XRD pattern of simple substance "Ag" (JCPDS NO. 04-0783)[24, 25]. It can be seen that the diffraction peaks of the product are corresponding with those of pure silver, and no peaks of impurities appear. Combining with XPS data analysis (Fig. S2), we can confirm the product is Ag rather than Ag_2O. The XRD pattern reveals the product has good crystallinity and high purity. It is worth noting that the intensity rate of $I_{(111)}/I_{(200)}$ is higher than the standard value. It indicates that (111) planes tend to be preferentially oriented[9, 26](HRTEM in Fig. S3). In Fig.2 (b), UV-Vis spectra of the products show absorption peaks are all near 420nm, which assigned to surface plasmon resonance of AgNPs[24, 27]. We found the red shift of absorption peaks and the increase of absorbances with the decrease of flow velocity. It implies the size and concentration of AgNPs increase when the flow velocity decreases, because the reaction solution may stay in the electrolytic cell for a longer time.

The sizes of AgNPs can be tuned facilely by adjusting the velocity of continuous flow solution. Fig.3 (a) - (c) show TEM images and size distributions of AgNPs synthesized with different flow velocity. As we have excepted, the flow velocity is faster, the synthesized AgNPs are smaller because of shorter reaction and growth time. When the flow velocity is 60mL/h, 80mL/h and 100mL/h, the average size (mean ± SD) of AgNPs is 18.5 ± 4.1nm, 9.4 ± 1.5nm and 3.0 ± 0.6nm, respectively, and the AgNPs are all well-monodisperse. TEM results are consistent with previous UV-Vis spectra of AgNPs.

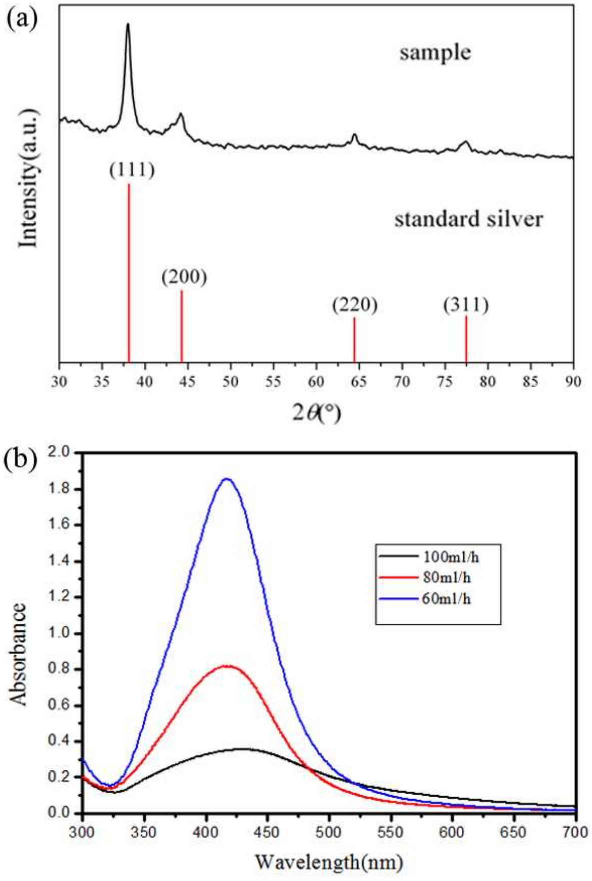


Fig. 2 (a) XRD pattern and (b) UV-Vis spectra of synthetic products

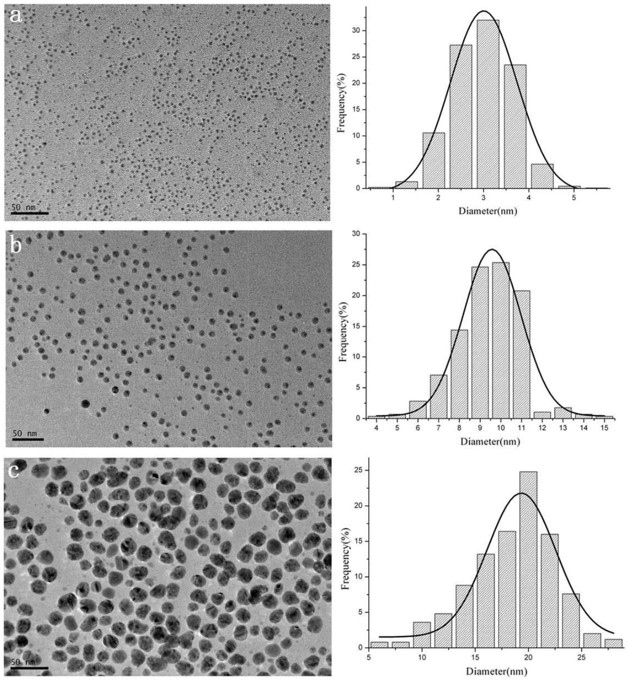


Fig. 3 TEM images and size distributions of AgNPs that synthesized with different flow velocity: (a) 100mL/h, (b) 80mL/h, (c) 60mL/h

To enhance the yield of AgNPs in unit time, the improved multi-electrode electrolytic reactor was designed (Fig.S4). The inner diameter and height of the electrolytic cell were increased to 40mm and 50mm, respectively. Eight silver rods with the diameter of 3mm and the length of 40mm were as anode and cathode, respectively. They are evenly arranged in the circle with a diameter of 20mm at the cover of the reactor. Each four interval silver rods are connected as a group of parallel electrodes with the same polarity. The tubule at the bottom of the reactor is the inlet for reactive solution, and the other tubule at the cover center is the outlet for the product.

According to our measurement, the electrical conductivity of 5mg/mL PVP aqueous solution is about 0.007S/m. So, based on the solution's property and applied electrolytic voltage, the voltage distribution and electric field distribution in the multi-electrode electrolytic reactor were simulated and shown in Fig.4. We can see that the parallel anodes and parallel cathodes have the highest and lowest voltage distribution, respectively. According to the distribution simulation of electric field, the two adjacent electrodes' facing surfaces were the locations having the highest electric field intensity. The redox of silver atoms and silver ions just happen there. In the electric field distribution diagram, the blue area that close to the inside wall and the center of the reactor but away from the electrodes have no or the weaker electric field intensity, and a relatively uniform ring electric field (the green area) forms along the arrangement of eight electrodes. The ring electric field distribution is approximately consistent with the whirly flow moving of the solution under the agitating condition. Therefore, silver ions are apt to transfer between the surface of adjacent electrodes along the arrangement ring of electrodes under the action of electric field and agitation. Although the volume of the electrolytic cell is increased several times, the all amount and length of silver electrodes are also increased in the synthesis system. It has the equivalent of the simultaneous electrolysis of eight pairs of electrodes. In the local reaction range that between the two adjacent electrodes, the synthesis is still in a smaller space and has a relatively uniform reaction conditions (the lower right part in Fig.4). Therefore, the designed multi-electrode structure of the reactor can provide the relatively uniform reactive condition for the synthesis of the monodisperse and uniform AgNPs. In addition, we can prepare more Ag^+ and reduce them to AgNPs through electrolyzing multiple parallel electrodes simultaneously, the yield of AgNPs in unit time can be increased significantly. The synthesized colloidal solution may show transparent brilliant yellow or brown yellow owing to different sizes and concentrations (Fig.S5). Similarly, the different sized well-monodisperse AgNPs can be synthesized by adjusting the flow velocity. For example, AgNPs with the size of 24.8 ± 4.7nm, 11.4 ± 2.3nm and 1.8 ± 0.6nm, were shown in Fig.S6.

Conclusions

In summary, we proposed a green method that combined electrochemical process and continuous synthesis strategy for the controllable synthesis of AgNPs in aqueous solution. We obtained a series of different sized AgNPs (about from 1nm to 30nm) successfully by adjusting the velocity of the continuous flow. The AgNPs synthesized by the method have higher purity than that by common liquid phase reduction due to the absence of silver salt and harmful reducing agent during synthesis. The monodispersity of AgNPs is also good because the reaction is located in a smaller electrolytic cell instead of bigger reaction volume all the time, and the output of AgNPs depends on total continuous synthesis time. In addition, with improved multi-electrode electrolytic synthesis system, the yield of AgNPs in unit time is significantly increased, whereas the morphology of AgNPs is still kept well.

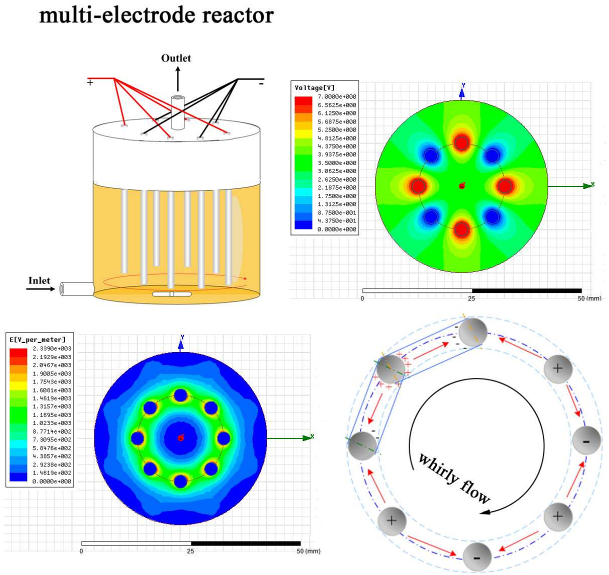


Fig. 4 Simulated diagrams of the voltage and electric field distribution in multi-electrode electrolytic reactor

Experimental

In the experiments, a good biocompatible polymer, polyvinyl pyrrolidone (PVP, K30), was used as stabilizing agent, and it is of analytical grade and used without further purification. Two silver rods with the diameter of 2mm were used as electrolytic electrodes, and the purity of silver rods is 99.9%. A classical synthesis process is as followed: firstly, the silver electrodes were polished, washed, and fitted on the cover of electrolytic reactor. Secondly, 5mg/mL PVP aqueous solution was prepared as the electrolyte and stabilizer. Finally, the PVP solution was pumped into the electrolytic reactor continuously by the peristaltic pump under a magnetic stirring condition at 60℃, and a voltage of 10V was applied to the silver electrodes simultaneously. The time for exchanging polarities of anode and cathode was set to 1min through the "Alternating Polarity Controller". For synthesizing different sized colloidal silver nanoparticles, the flow velocity of 100mL/h, 80mL/h and 60mL/h was used, respectively. The process of multi-electrode electrolytic synthesis is similar to this, and the detail is given in ESI. The phase composition of the product was analyzed with X'TRA Powder X-ray Diffraction Instrument (ARL, Switzerland) with CuKα radiation. The spectrum of the product was examined from 800nm to 300nm by UV-3600 UV-Vis spectrophotometer (SHIMADZU, Japan). The morphology of the synthesized nanoparticles was characterized by JEM-2000EX Transmission Electron Microscope (JEOL, Japan) and the size distribution was determined by counting all of nanoparticles in TEM photographs. The chemical state of silver nanoparticles was investigated using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, UIVAC) with an Al Kα radiation as the X-ray soure.

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Notes and references

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We report the green electrochemical synthesis of size-controlled AgNPs by tuning flow velocity in a continuous flow system, and an improved multi-electrode design is for increasing synthesis yield in unit time.