Scalable Synthesis and Application of Mono-dispersed Hierarchical Silver Micro-particles

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***Abstract*—Hierarchical metals with abundant nanostructures are expected to provide excellent performance characteristics in electronic printing or packaging, catalysis, molecular detection, sensing, and microfluidic flow control, due to the inherent fascinating properties of metal framework (e.g. superior electrical conductivity, catalytic activities, optical properties, etc.) and the general characteristics of hierarchical materials. Yet it is still great challenging to synthesize hierarchical metals with controllable morphologies and nanostructures in large-scale via a facile synthetic method. Here we demonstrate a one-step method to fabricate mono-dispersed hierarchical silver micro-particles with tailored size and morphology in high yields. The silver micro-particles can be obtained merely by mixing the silver salts, reducing agents and surfactants simultaneously. Controllable morphologies and nanostructures can be realized simply by adjusting the reaction parameters, such as the concentration of reactants, mixing velocity, reaction temperature, and so forth. These silver micro-particles possess unique hierarchical structures with abundant nano-sized structures and uniformly distributed mesopores, which provide excellent low-temperature sintering ability and strong electromagnetic field enhancement effect. The facile and efficient synthetic method, along with such intriguing characteristics, renders the silver micro-particles with considerable interest in a wide variety of applications in future electronic devices.**

Keywords—silver micro-particles; hierarchical structures; low-temperature sintering; electronic devices

I. INTRODUCTION

Hierarchical micro/nanostructures have progressively attracted considerable attention in recent years [1, 2]. The physicochemical nature of their micro/nanostructures and the synergy between these structures endow them with higher functionality and performance, showing immense potential applications in surface-enhanced Raman scattering (SERS), electronic packaging, optoelectronic devices, microfluidic devices, biomedical science, field emission, etc. [1, 3-7]. Hence, synthesis of hierarchical micro/nanostructures with well-defined morphologies and sizes is highly desired. To date, great efforts have been devoted to the synthesis of hierarchical micro/nanostructures. Generally, hierarchical structures could be synthesized by the assembly of nanoparticles, nanorods, nanobelts as building blocks and complex hierarchical micro/nanostructures have been obtained through different ways, such as induced by an electric field, chemical vapor deposition, template technique, electron irradiation, electrochemical deposition, colloidal chemistry, etc. [2, 3, 6-10]. Nevertheless, these methods suffer from disadvantages such as requiring special equipment, involving multi-steps, low-yielding, or being difficult to tailor the size and morphology precisely, and thus limits its applications in wider fields.

Nanostructured noble metallic materials, in particular, silver, are widely studied because of their excellent combination of optical properties and electrical and thermal conductivities compared to other metals [11]. So far, nanostructured silver has find broad applications in many fields, such as printed electronics [12, 13], printed circuit boards [14], thermal interface materials [15], electrically conductive composites [16, 17], SERS active substrate [18], and so on. Hierarchical micro/nanostructured silver is conducive to higher functionality and performance in such applications. Thus, it is of great significance to develop a facile and scalable method to prepare hierarchical micro/nanostructured silver with precisely tailored size and morphology.

Here we report a facile and one-step method to fabricate mono-dispersed hierarchical silver micro-particles with tailored size and morphology. The synthesis involves a simple mixed reaction of the silver salts, reducing agents and surfactants, and thus can be scaled up easily. Merely by adjusting the reaction parameters, such as the concentration of hydrazine hydrate solution, reaction temperature and shaking speed, the size and morphology of the hierarchical micro/nanostructured silver particles can be tunable, as well as the surface nanostructures. The as-prepared silver micro-particles possess unique hierarchical structures with abundant nano-sized structures and uniformly distributed mesopores, which provide excellent low-temperature sintering ability and strong field enhancement effect. The facile and efficient synthetic method, along with such intriguing characteristics, renders the silver micro-particles with considerable interest in a wide variety of applications in future electronic devices.

II. EXPERIMENTAL

A. Materials

Silver nitrate ($AgNO_3$) powder (99%) and hydrazine hydrate ($N_2H_4 \cdot H_2O$) solutions (85 wt% aq.) were purchased from Sinopharm Chemical Reagent Co., Ltd., and the tween 80

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was obtained from Guangzhou Chemical Reagent Factory, China.

B. *Preparation of the Hierarchical Silver Micro-particles*

The reaction parameters (e.g. the concentration of reactants, reaction temperature, shaking speed) were accurately controlled, so as to critically tailor the size and morphology precisely. Typically, equal volumes of silver nitrite aqueous solution (0.06 M), hydrazine hydrate solution (0.12 M) and tween 80 aqueous surfactant solution (1 wt%) were continuously pumped at a velocity of 15 rpm and mixed together by a peristaltic pump. The droplets were mixed in an Erlenmeyer flask, which was shaken in an alcohol bath at 0 oC. After feeding has stopped, the shaking continued for another 5 min until the reaction completed. The precipitate was collected and washed by deionized (DI) water for several times, and then dried in a vacuum desiccator at room temperature.

C. *Characterizations*

The morphologies of the silver micro-particles were investigated by the field emission scanning electron microscope (ZEISS SUPRA® 55, Germany). The crystalline informationof the silver micro-particles was collected by powder X-ray diffraction at a scan rate of 10 °/min using a Rigaku diffractometer (D/MAX-2500, Japan) equipped with Cu-Kα radiation (λ = 1.5418 Å). Raman spectrum was recorded by a Jobin-Yvon Horbia 800 spectrometer at an excitation wavelength of 532 nm using argon laser source.

III. RESULTS AND DISCUSSIONS

A. *Characterization of the Hierarchical Silver Micro-particles*

The morphology and crystalline structure of the silver micro-particles are shown in Fig. 1. As shown in Fig. 1a and b, the as-prepared silver micro-particles were of pollen-like hierarchical structure, with a uniform particle size of about 5 μm. It is clearly observed in Fig. 1b that the pollen-like micro-particles are near-spherical hierarchical secondary particles, which derive from the assembly of smaller-sized irregular silver particles. As shown in Fig. 1c, the surface of the pollen-like micro-particles is covered with countless nanotips, with a uniform diameter less than 10 nm, which indicating excellent low-temperature sintering property and unique optical characteristics. The XRD pattern of the as-prepared pollen-like micro-particles shows a sharp and strong diffraction peak together with four weak diffraction peaks, which are indexed to the (111), (200) (220), (311) and (222) planes of the face-centered cubic crystalline structure, respectively. The intensity ratio of the (200) and (111) diffraction peaks is about 0.21, which is slower than the standard silver powder pattern (JCPDS card no. 04-0783, 0.45), indicating the preferred orientation along the (111) lattice pattern.

B. *Effects of Reaction Parameters on Silver Products*

Studying the functions of reaction parameters is critical to tailor the size and morphology of the reaction product precisely. In this reaction system, the concentration of hydrazine hydrate solution, reaction temperature and shaking speed, as the most critical reaction parameters, were investigated systematically.

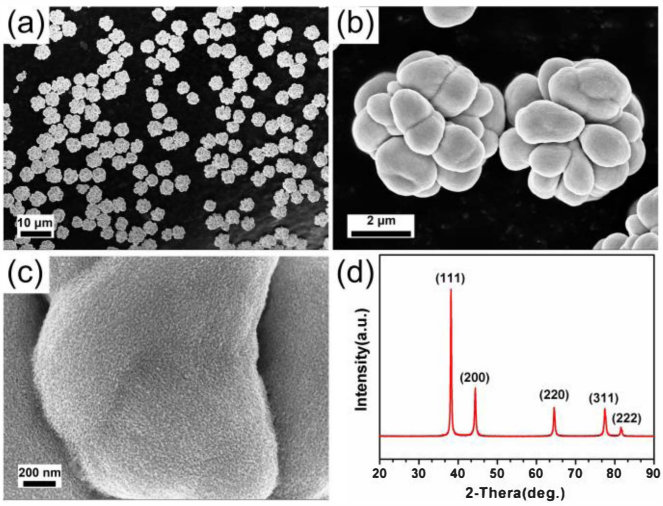

Fig. 1. (a) Low magnification SEM image of the pollen-like hierarchical silver micro-particles. (b) High magnification SEM image of the micro-particles. (c) SEM image of the surface morphology of the micro-particles. (d) XRD pattern of the pollen-like hierarchical silver micro-particles.

Herein the effect of the concentration of hydrazine hydrate solution was investigated, when the concentration of silver nitrite aqueous solution and tween 80 aqueous surfactant solution remained unchanged, and the droplets were still mixed at the same shaking speed at 0 ºC. As shown in Fig. 2a, the silver products became submicron silver sponges, with irregular interconnected ligaments ranged from 20nm to 50nm, when the concentration of hydrazine hydrate solution was decreased to 0.06 M. At a higher hydrazine hydrate concentration of 0.12 M, peony-like silver micron particles, with a uniform particle size of 10 μm, were obtained (Fig. 2b).

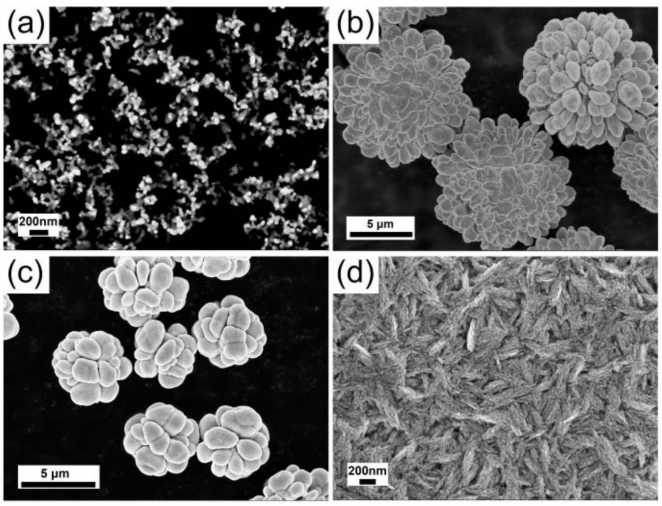

Fig. 2. (a) SEM image of the submicron silver sponges at the $N_2H_4 \cdot H_2O$ concentration of 0.06 M. (b) SEM image of the hierarchical peony-like micron silver particles at the $N_2H_4 \cdot H_2O$ concentration of 0.12 M. (c) SEM image of the hierarchical pollen-like micron silver particles at the $N_2H_4 \cdot H_2O$ concentration of 0.48 M. (d) SEM image of rice ears-like silver at the $N_2H_4 \cdot H_2O$ concentration of 0.60 M.

Compared to the typical pollen-like silver particles synthesized at the hydrazine hydrate concentration of 0.48 M (Fig. 2c), the peony-like silver particles were hierarchical secondary particles assembled from more irregular primary particles, which possessed larger aspect ratio, and thus resulted in larger secondary particle size. When the hydrazine hydrate concentration was increased to 0.60 M, no near-spherical silver micron particles were obtained. As shown in Fig. 2d, the silver products turned into rice ears-like silver, with a width of less than 200 nm and a length of more than 500 nm, deriving from the self-assembly of the rice-like silver nanoparticles, with a uniform diameter of about 10 nm. The high hydrazine hydrate concentration provides stronger reducibility, which leads to a fast nucleation and thus provides homogeneously sized silver seeds and nanoparticles. In addition, higher concentration of hydrazine hydrate solution also affect the self-assembly of nanoparticles significantly, thus, no micron silver particles were obtained in this condition.

Apart from the concentration of the reducing agent, reaction temperature can influence the silver products effectively as well. Based on the typical synthesis, the function of reaction temperature was studied. The experiments were carried out in an alcohol bath where the reaction temperatures of 0 ºC, 10 ºC and 20 ºC were investigated, and water bath for 30 ºC. It can be clearly observed in Fig. 3 that hierarchical micron silver particles were obtained at the temperature ranging from 0 ºC to 30 ºC. When the reaction temperature was

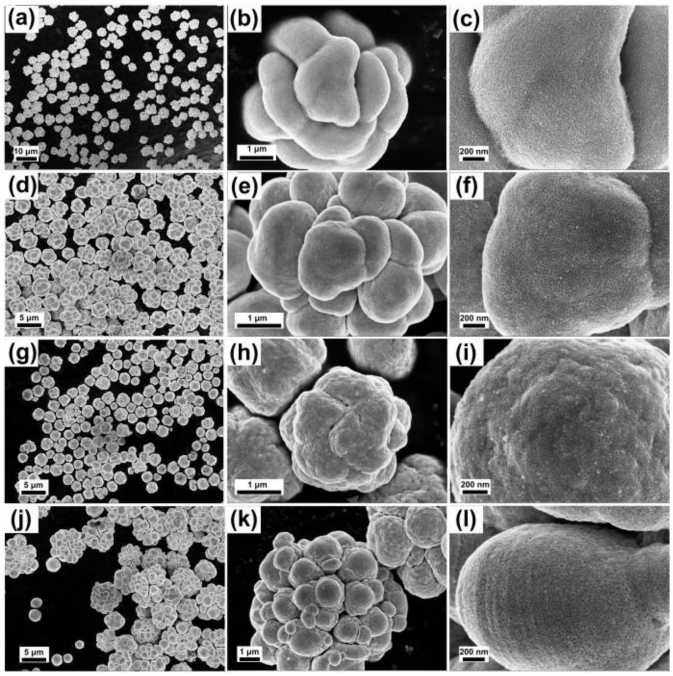

Fig. 3. (a) ~(c) SEM images of the silver micro-particles prepared at 0 ºC. (d) ~ (f) SEM images of the silver micro-particles prepared at 10 ºC. (g) ~ (i) SEM images of the silver micro-particles prepared at 20 ºC. (j) ~ (l) SEM images of the silver micro-particles prepared at 30 ºC.

lower than 20 ºC, the as-prepared micron silver particles are of uniform size and the silver particle size decrease with the increase of temperature. As the temperature is increased, the primary particles show a greater level of fusion with each other (Fig. 3b, e and h), and the surface morphology changes

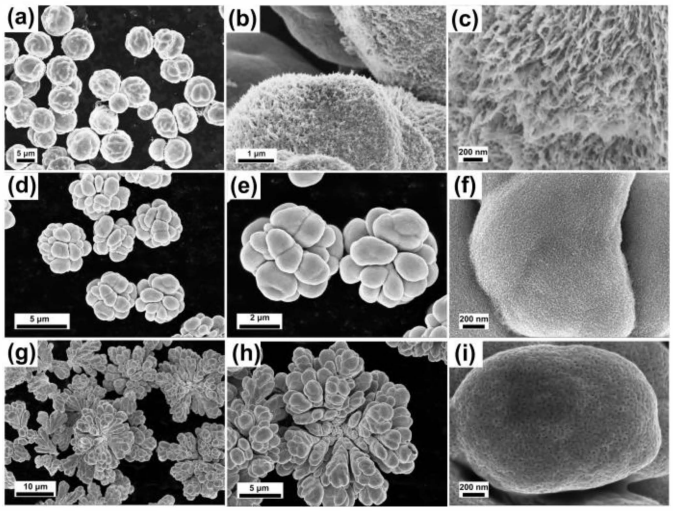

Fig. 4. (a) ~(c) SEM images of the silver micro-spheres prepared at high shaking speed. (d) ~ (f) SEM images of the silver micro-particles prepared at medium shaking speed. (g) ~ (i) SEM images of the silver micro-flowers prepared at low shaking speed.

significantly (Fig. 3c, f and i). Compared to the surface of pollen-like silver micron particles prepared at 0 ºC, there is no nanotip on the surface of silver particles prepared at 10 ºC, but widespread ordered mesopores and more gradual fusion interfaces, which may be attributed to the low-temperature sintering of the abundant superficial nanostructures. When the temperature rises to 20 ºC, as shown in Fig. h and i, the fusion among the primary particles are more remarkable, which renders the silver micro-particles a smaller size and higher degree of sphericity. Meanwhile, the surface of the silver particles becomes rougher with lower porosity, due to the further sintering and fusing of nanostructures. However, when the reaction temperature reaches 30 ºC, the silver particle size increases instead, and the secondary particles contain more irregular primary particles with uneven sizes (Fig. 3j and k). The particle surface abounds with close-packed nanoparticles, conducing a very low porosity (Fig. 3l). High temperature accelerates the nucleation and growth of silver and provides more thermal energy, which renders the assembly of the silver particles more complex with less control.

Mixing velocity always has significant effects on nanostructures, especially in the kinetics controlled process. Thus, the effects of shaking speed on silver products were explored. Changing the shaking speed in the typical synthesis, micron silver particles with different size and morphology can be obtained. As shown in Fig. 4, more branched structures remained in the micro-particles, with the decreasing of the shaking speed. Compared to the typical pollen-like - silver micro-particles synthesized at medium shaking speed (about 300 rpm), the silver micro-spheres were obtained at a higher shaking speed (about 500 rpm) with a hairy surface. Close observation of the surface shows that the hairs are of uniform diameters of about 10 nm, with the aspect ratio more than 20 (Fig. 4c). The fluffy nanostructures are not completely separated from each other, but sintered with adjacent silver hairs to a certain extent, which is attribute to the high surface energy of the fluffy nanostructures, indicating broad applications in low-temperature interconnection. While, lower

shaking speed (about 100 rpm) induces the formation of dendritic silver micro-particles, as shown in Fig. 4g~i. Low magnification SEM image (Fig. 4g) shows that the dendritic silver particles are in poor integrity and of uneven particle sizes. A zoom-in image of a silver particle (Fig. 4h) shows that the secondary particles were formed through a multi-level self-assembly process. Fig. 4i provides a close view of the surface morphology of the dendritic silver particles, which shows a porous smooth surface, similar to the surface morphology shown in Fig. 3f. Shaking speed has a significant influence on the morphologies and surface nanostructures of the silver micro-particles, which indicates the formation process of the silver micron particles is kinetically controlled.

According to the above results, the concentration of hydrazine hydrate solution, reaction temperature and shaking speed affect the size and morphology of the silver particles, as well as the surface nanostructures significantly. Thus, we can obtain the required silver product with desired size and morphology, even with specific surface nanostructures merely by adjusting the reaction parameters.

C. Study of the Stability and Application in SERS Detection

Stability is a vital index for the storage and application of silver micro-particles. Thus, the stability of the pollen-like silver micro-particles, as the typical product, was investigated. As shown in Fig. 5, there is no remarkable change in size and morphology of the silver particles, after storage in reaction solution for 18 days at room temperature. Close observation shows the disappearance of the nonotips and appearance of porous smooth surface, which further confirms the excellent low-temperature sintering property. The surface change can be impeded by drying the silver particles timely, and thus can be stored and applied stably.

The as-prepared pollen-like silver micro-particles were explored for surface enhanced Raman Scattering (SERS) detection. Rhodamine 6G (R6G) was used to evaluate the SERS enhancement ability of the pollen-like silver micro-particles. For this propose, 1 mL of the as-prepared silver products were dropped onto a glass slide. After drying in air, 1 mL of rhodamine 6G (R6G) with the concentration of 10^{-5} M was dropped cast onto the dried silver micro-particles, and allowed to air dry. Pollen-like silver micro-particles possess broad surface plasmon absorptions in both visible light and infrared (IR) regions; thus, their SERS enhancement ability is not restricted to only a few excitation wavelengths, as shown in Fig. 4. The SERS spectrum of R6G on the submicron spongy silver is dominated by the relatively strong peaks at 1647, 1566, 1509, 1364, 1204, 1129, 774, 615, 350 and 194 cm^{-1}. The high SERS sensitivity is due to the abundant hot spots in the sample, originating from plentiful nanostructures of the silver particles in 3D space, which promises broad applications in high-performance nano-devices for SERS detection [5, 18].

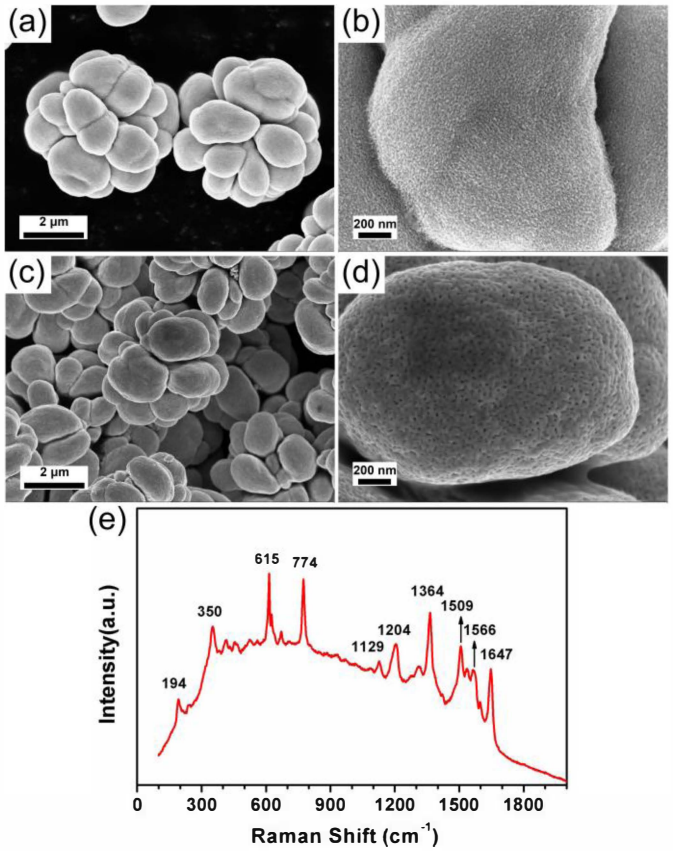

Fig. 5. (a) ~ (b) SEM images of the as-prepared silver micro-particles. (c) ~ (d) SEM images of the silver micro-particles, after storage in reaction solution for 18 days at room temperature. (e) Raman spectrum of 10^{-5} M R6G on the silver micro-particles.

IV. CONCLUSIONS

In summary, we for the first time demonstrate a facile and one-step method to fabricate mono-dispersed hierarchical silver micro-particles with tailored size and morphology. The process involves a simple mixed reaction of the silver salts, reducing agents and surfactants, and thus can be scaled up easily. The reaction parameters, such as the concentration of hydrazine hydrate solution, reaction temperature and shaking speed, can influence the size and morphology of the silver particles, as well as the surface nanostructures significantly. Thus, it shows great promise for designing the silver products with desirable size and morphology, even with specific surface nanostructures through a facile method. The as-prepared silver micro-particles possess unique hierarchical structures with abundant nano-sized structures and uniformly distributed mesopores, which provide excellent low-temperature sintering ability and strong field enhancement effect. The facile and efficient synthetic method, along with such intriguing characteristics, renders the silver micro-particles with considerable interest in a wide variety of applications in future electronic devices.

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