

具有表面拉曼增强活性的银纳米材料的合成和表征

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摘要: 利用简易无模板湿化学法合成了由纳米片组装的具有三维分级结构的银纳米材料。场发射扫描电子显微镜表明柠檬酸氢二铵在这种结构形成过程中起到很重要的作用。X 射线衍射和透射电子显微镜表征进一步证明了这种结构的形成。此外本文还对这种分级结构进行了紫外和拉曼表征。这种新型的银纳米结构有望作为一种高灵敏度的表面拉曼增强基底。

关键词: 湿化学法; 银; 表面拉曼增强; 罗丹明

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Synthesis and Characterization of SERS-Active Silver Nanomaterial

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Abstract: Three-dimensional (3D) hierarchical silver nanomaterials (HSNs) were prepared by a simple surfactant-free wet-chemical method at room temperature. The as-prepared HSNs exhibit spherical morphologies and are constructed with many 2D nanoflakes as building blocks. Field emission scanning electron microscopy (FESEM) studies show that diammonium 2-(carboxymethyl)-2-hydroxysuccinate (diammonium hydrogen citrate) ($C_6H_{14}N_2O_7$) plays a key role in the formation of such HSNs. X-ray diffraction (XRD) and transmission electron microscopy (TEM) results confirm the formation of HSNs. The optical properties and surface-enhanced Raman scattering (SERS) effect were also investigated by UV-Vis and Raman spectra. The HSNs could be served as highly sensitive surface-enhanced Raman scattering (SERS) substrates for chemical detection.

Key words: wet-chemical method; silver; surface-enhanced Raman scattering (SERS); Rhodamine (R6G and RB)

0 Introduction

In recent years, much attention has been paid to three dimensional (3D) hierarchical nanostructures due to their promising complex functions and widespread potential applications in gas sensor, drug delivery, photo catalysis and other applications^[1-5]. Hierarchical nanostructures can be prepared by self-assembling of low-dimensional (0D, 1D and 2D)

primary crystals. These primary units may stack in an oriented fashion to produce a larger structure, in which the adjacent primary units are self-assembled by sharing a common crystallographic orientation. To date, a wide variety of inorganic materials, including metal, metal oxide, sulfide, hydrate and other minerals have been successfully prepared with hierarchical shapes by various self-assembly methods^[1-5]. However, it is still a challenge to develop a novel and simple

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synthetic approach for building hierarchically self-assembled architectures.

The nanostructures of noble metals, especially the relatively low-cost and highly conductive silver, have received intense research attention during the past few years because of their unique electrical, optical, and thermal properties, as well as their potential applications in catalysis, electronics, biosensing, and surface-enhanced Raman scattering (SERS), etc.^[6-9]. The intrinsic properties of the metal nanostructures can be tuned by controlling their shape, size, and crystallinity. Various silver nanostructures, including nanoparticles^[10-11], nanorods^[12], nanowires^[13], nanoplates^[14-16], nanocubes^[17-18], hierarchical structures (dendritic, flower-like and sphere-like)^[19-28] and so forth have been prepared by different methods. Among these structures, the complex HSNs constructed by low-dimensional primary units (nanoparticles, nanorods and nanoplates) have attracted particular interest. However, the routine methods normally involved the reduction of silver salts in the presence of potentiostat or organic surfactants, or at elevated temperature, or requiring the removal of template/substrate to get pure products. Therefore, it is interesting and important to introduce a convenient method to prepare three-dimensional (3D) hierarchical silver nanostructures (HSNs).

Herein, we report a simple, cost-effective and versatile strategy for the large scale synthesis of hierarchical silver nanostructures (HSNs), which are self-assembled from tiny silver nanoplates. The morphology evolution process was studied through adjusting the amount of diammonium hydrogen citrate ($C_6H_{14}N_2O_7$), the molar ratio of silver nitrate to ascorbic acid ($C_6H_8O_6$) and reaction time. Surface-enhanced Raman scattering (SERS) activities of as-prepared products were also studied.

1 Experimental

1.1 Sample preparation

All chemical reagents were of analytical reagent grade and were used as received without further purification. Firstly, 2.0 mmol of $AgNO_3$ was dissolved in 40 mL of distilled water with magnetic stirring for

10 min. Then, 0.05 g diammonium hydrogen citrate ($C_6H_{14}N_2O_7$) was added into the above solution with stirring and a white precipitates were obtained. Finally, 20 mL $0.1 \text{ mol} \cdot \text{L}^{-1}$ ascorbic acid aqueous solution was poured into the above suspension and stirred for 1 h. The powder was then isolated by centrifugation and washed several times with distilled water and absolute ethanol in sequence. Finally, the products were dried at 50°C for 3 h.

1.2 Characterization

The as-prepared silver nanostructures were characterized by X-ray diffraction (German Bruker AXSD8 Advance), using $Cu K\alpha$ radiation ($\lambda=0.154 \text{ nm}$), Hybrid monochromators, and X accelerator detector. Corresponding working voltage and current were 40 kV and 40 mA, respectively. Field emission scanning electron microscopy images were taken on a HITACHI S-4800 scanning electron microscope, operating at accelerating voltage of 15 kV. Transmission electron microscopy and high resolution transmission electron microscopy images were obtained on a FEI F-30 instrument (America), using accelerating voltage of 300 kV. FTIR spectra were taken by Varian FT-IR70 spectrophotometer (America). Raman spectra were recorded using a Britain Renishaw Invia Raman spectrometer with a solid-state laser (excitation at 532 nm, 35 mW) at room temperature in the range of $1\ 800\sim 800 \text{ cm}^{-1}$. Spectra were accumulated 1 scan (1 time), with an exposure time of 10 s. The beam diameter was approximately $1 \mu\text{m}$ on the sample surface.

1.3 SERS

Rhodamine 6G (R6G) and Rhodamine B dyes were used as Raman probes for the SERS measurements. The as-prepared HSNs were immersed in different concentrations of solutions of target molecules for 12 h, respectively. Then, the HSNs solutions were carefully dropped on specially cleaned glass slides and dried in air. Finally, the SERS of the samples were measured using a Britain Renishaw Invia Raman spectrometer with a solid-state laser (excitation at 532 nm, 35 mW) at room temperature in the range of $800\sim 1\ 800 \text{ cm}^{-1}$.

2 Results and discussion

2.1 Characterization of the as-prepared HSNs

Typical hierarchical silver nanostructures (HSNs) were synthesized by the reaction between silver AgNO_3 and $\text{C}_6\text{H}_8\text{O}_6$ in absence of 0.05 g diammonium hydrogen citrate ($\text{C}_6\text{H}_{14}\text{N}_2\text{O}_7$) at room temperature for 1 h. Fig.1 displays the typical diffraction pattern of hierarchical silver nanostructures (HSNs). Significant diffraction peaks are located at 37.9° , 44.2° , 64.4° , and 77.2° , which correspond respectively to the (111), (200), (220), and (311) plane diffraction peaks of the metallic silver cubic structure. It is in agreement with the reported data ($R=0.409$ nm, PDF No.4-783). No impurity peaks are found indicating a pure phase HSNs obtained by this method.

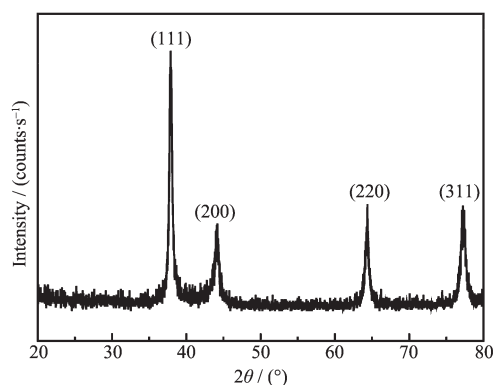


Fig.1 XRD patterns of the as-prepared three-dimensional (3D) hierarchical silver nanostructures (HSNs) prepared between silver nitrate and ascorbic acid in presence of diammonium hydrogen citrate (0.05 g) for 1 h at room temperature (the molar ratios for silver nitrate to ascorbic acid is 1:1)

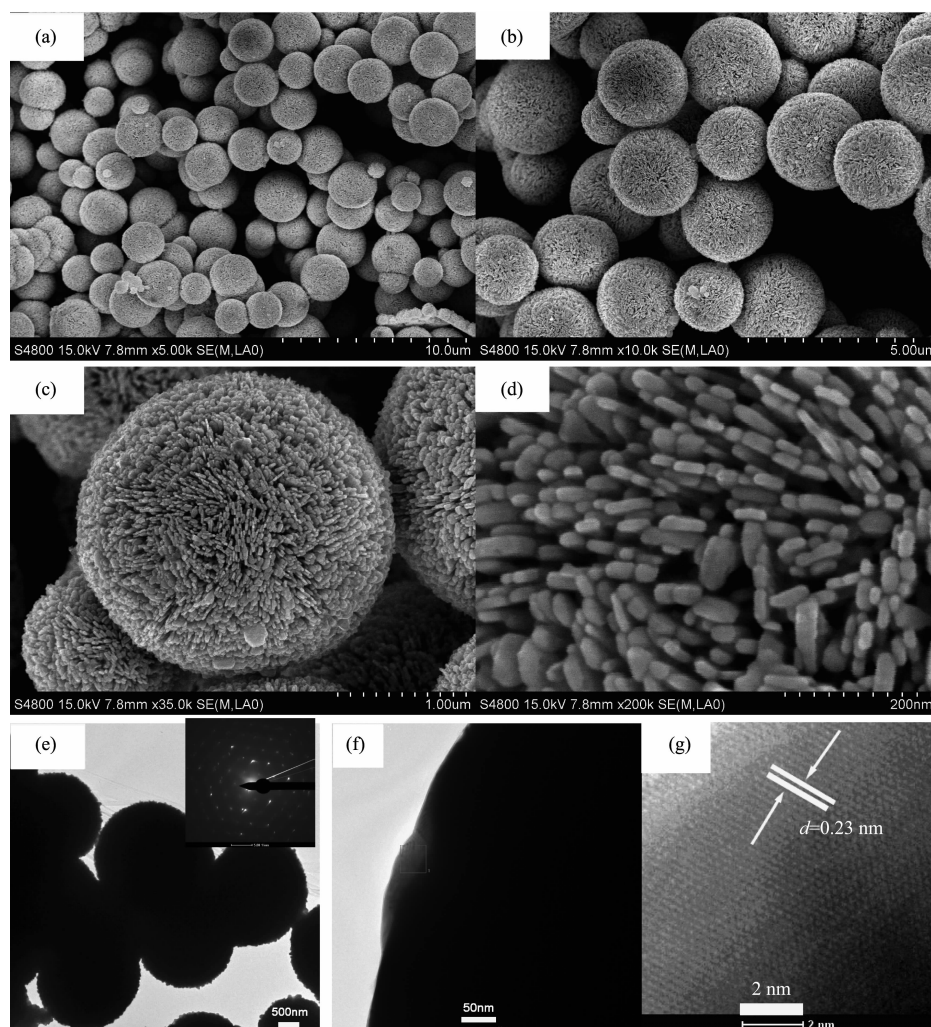


Fig.2 FESEM, TEM and HRTEM images of the as-prepared HSNs (a, b) low magnification (c) medium magnification (d) high magnification and (e) TEM (f, g) HRTEM (the molar ratio of silver nitrate to ascorbic acid is 1:1 and in presence of 0.05 g diammonium hydrogen citrate)

Fig.2 shows the FESEM images of HSNs at low, medium, and high magnification, respectively. The as-prepared HSNs contained numerous sphere-like aggregates and almost all of them show the same morphology (Fig.2a and b). The diameters of these microspheres range from 2 to 3 μm . Each sphere is made up of many thin nanoplates (Fig.2c). Careful examination reveals that the Ag nanoplates are several hundreds nanometer in size and about 15 nm in thickness (Fig.2d). The TEM image in Fig.2e further confirms their sphere-like hierarchical structures constructed with nanoplates. Fig.2f depicts the typical HRTEM image of an individual Ag nanoplate. The enlarged image (Fig.2g) of the area labeled in Fig.2f by a rectangle further reveals the single-crystal structure of Ag nanoplates. The clearly resolved lattice fringes are 0.23 nm, which correspond to the (111) plane of cubic phase silver. The selected area electron diffraction of single microspheres (SAED, the inset of Fig.2d) also could be indexed to a pure fcc phase, which agrees with the results from oriented

growth.

2.2 Effect of the reaction parameters on size and the morphology of hierarchical silver nanostructures (HSNs)

2.2.1 Effect of the amount of ammonium hydrogen citrate on the size and the morphology of the as-prepared HSNs

In the present preparation process, the formation of the hierarchical silver nanostructures (HSNs) is strongly depended on the amount of diammonium hydrogen citrate. When the amount of ammonium hydrogen citrate increases to 0.1 g, smaller microspheres with overall diameters of 0.8 μm (Fig.3a and b) are formed. Moreover, the surrounding nanoplates on the surface of the microspheres become smaller. A further increase in the amount of diammonium hydrogen citrate to 0.5 g produces microspheres of approximately 0.7 μm in size (Fig.3c and d). However, the surrounding nanoplates on the surface of the microspheres becomes tiny nanoparticles with about 10 nm in diameter. When

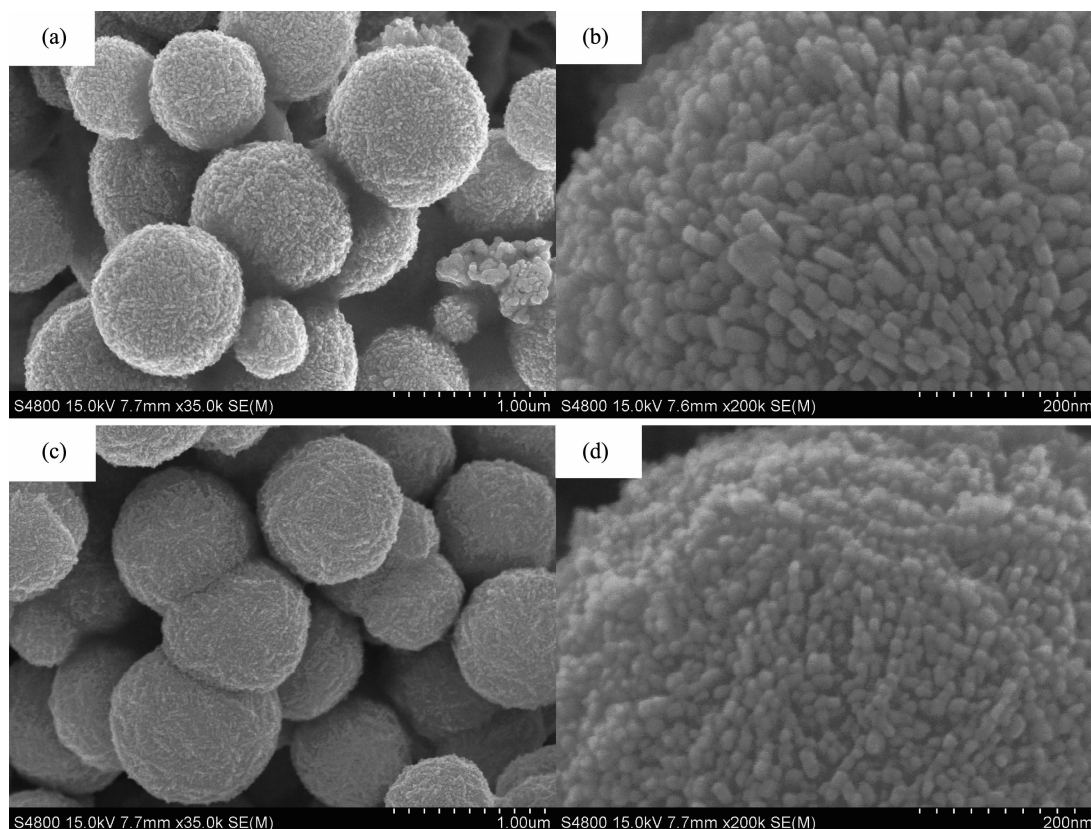


Fig.3 FESEM images of as-prepared Ag nanostructures with different amount of ammonium hydrogen citrate (a, b) 0.1 g (c, d) 0.5 g (keeping other parameter constant)

the reaction is carried out in the absence of ammonium hydrogen citrate, only irregular spherical particles with a larger particle size of about $5\text{ }\mu\text{m}$ are obtained in our early reports^[29]. This indicates that diammonium hydrogen citrate is a necessary condition for the growth of the HSNs.

2.2.2 Effect of the molar ratio of the reactants on the size and the morphology of the as-prepared HSNs

When the molar ratio of AgNO_3 to ascorbic acid is 0.25, microspheres with diameter about $200\sim 400$

nm are obtained (Fig.4a and b). Careful examination reveals that the surface of these sphere-like structures is covered with irregular particles of 40 nm in size. When the molar ratio is 0.5, microspheres with diameter about $1\text{ }\mu\text{m}$ are the dominant products, and the surface of these sphere-like structures is covered with regular nanoplates of 40 nm in thickness (Fig.4c and d). Further increasing the molar ratio to 2, a large quantity of hollow Ag microspheres with a mean particle size of about $2\text{ }\mu\text{m}$ is found. Interestingly, the particles of the surface of these micro-spheres further

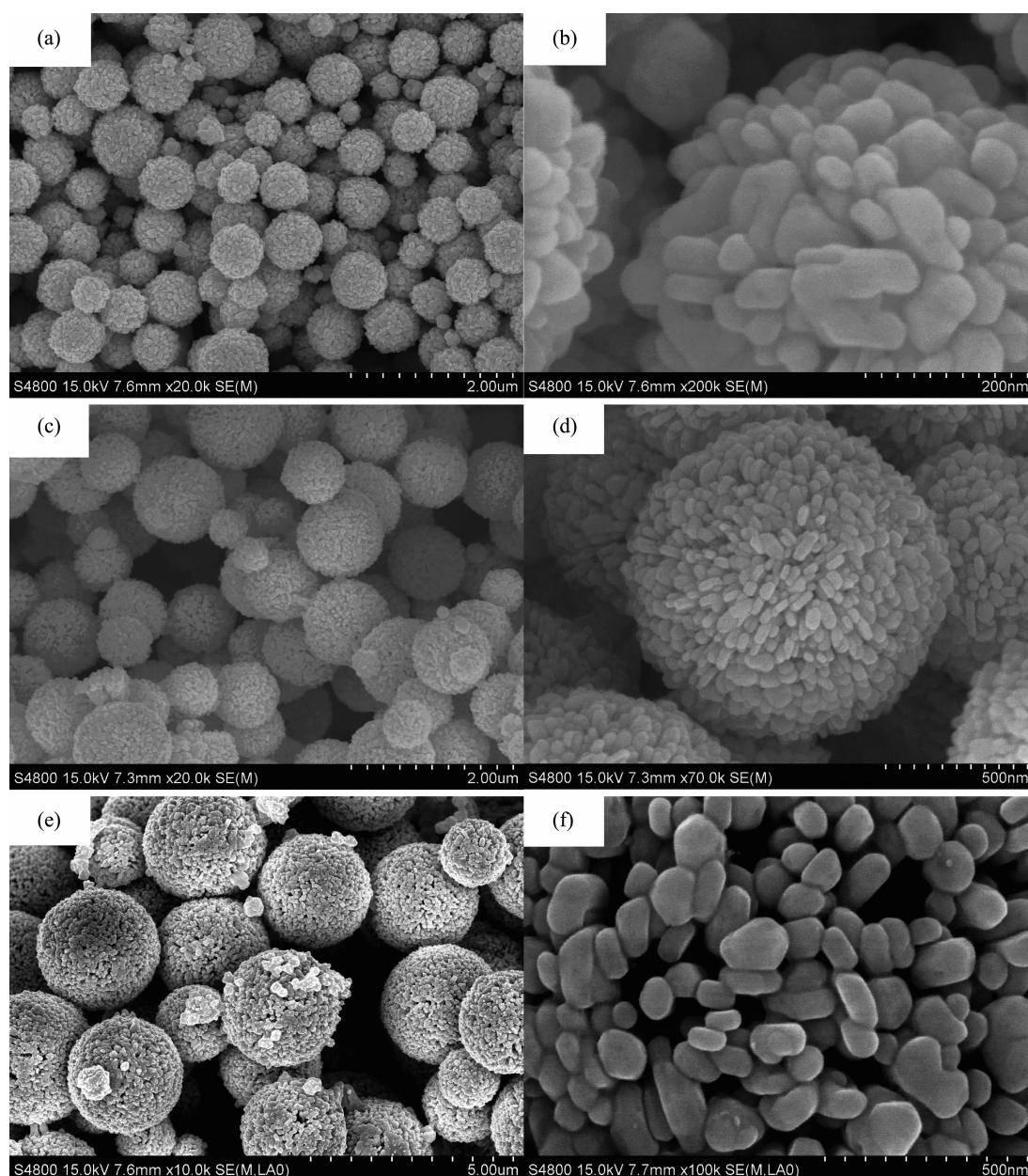


Fig.4 FESEM images of as-prepared Ag products prepared with different ratios of silver nitrate to ascorbic acid (a, b) 1:4 (c, d) 1:2 (e, f) 2:1

become nanocube with mean size of 80 nm (Fig.4e and f).

2.2.3 Effect of reaction time on the size and the morphology of the as-prepared HSNs.

Fig.5 shows the FESEM images of the as-prepared HSNs obtained at different reaction times. Many white precipitates are obtained before adding ascorbic acid. After adding ascorbic acid for 1 min, the solution changes from white to dark and HSNs are found (Fig.5a and b). Reaction time has little effect on the spherical morphology and the whole size. However, we could find that the surface of these silver microspheres becomes loose with the increasing

reaction time (Fig.5c and d). After 1 h, the surface of these HSNs remains unchanged (Fig.5e and f).

2.3 Formation mechanism of the as-prepared HSNs

The FTIR analysis of the as-prepared products further reveals the detailed evolutionary process. Fig.6 shows the IR spectra of the products obtained before and after adding ascorbic acid. Fig.6a shows that the FTIR spectra of white precipitates are obtained before adding ascorbic acid. The obvious two strong peaks at $1\,354$ and $1\,583\text{ cm}^{-1}$ indicate that the precursor is formed by the coordination reaction between silver nitrate and diammonium hydrogen citrate. In Fig.6b,

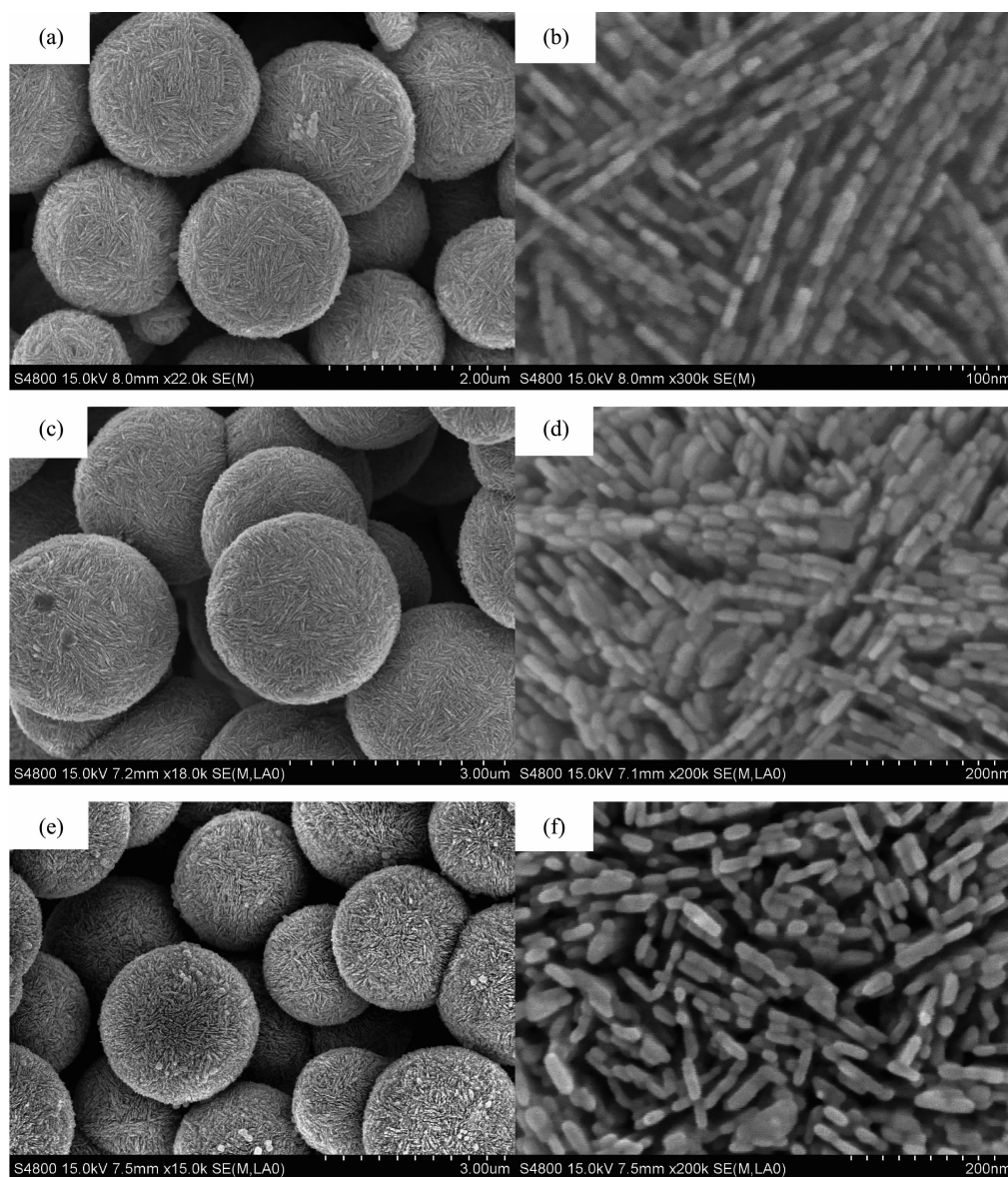


Fig.5 FESEM images of Ag spheres after adding ascorbic acid for different times (a, b) 1 min (c, d) 10 min (e, f) 30 min

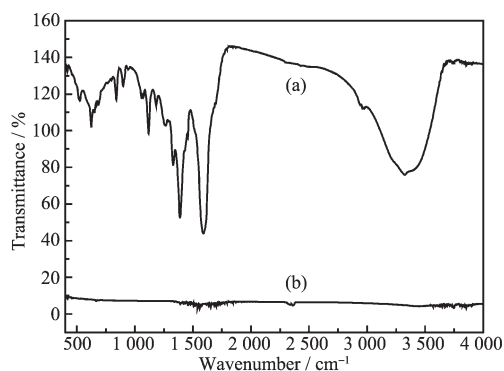


Fig.6 FTIR spectra of (a) white precipitates obtained before adding ascorbic acid and (b) Ag spheres after adding ascorbic acid for 10 min

all absorption bands vanish after adding ascorbic acid for 10 min, indicating the reduction of the precursor and formation of the HSNs.

The evolution process is similar to the formation process of the Ag superstructures reported previously by our group^[29]. In this reaction process, $C_6H_5O_7^{3-}$ acts as an appropriate complexing agent with Ag^+ to form the coordination compound (white precipitates). After adding ascorbic acid, the precursor is reduced *in situ* into Ag nucleation clusters which will aggregate to form larger 3D spheres in order to reduce surface energy. With further extending reaction time, these nucleation clusters are reduced completely and well-defined 3D Ag nanostructures are formed via Ostwald ripening. In comparison with the other direct reaction process, our complex reaction method could regulate the nucleation kinetics and growth of the products and efficiently control the morphology and the structure of the final products.

2.4 Optical property of the as-prepared HSNs

UV-Vis spectra of nanostructures strongly depend on the morphology. Fig.7 shows the UV-Vis spectra of the obtained HSNs. The HSNs have broad absorptions ranging from about 410 nm to near-infrared for the dispersion of the HSNs in ethanol. The broad absorptions in UV-Vis spectra of the HSNs are attributed to the SPR properties of such special structures.

2.5 SERS performances of the as-prepared HSNs

Well defined Raman signals of R6G are

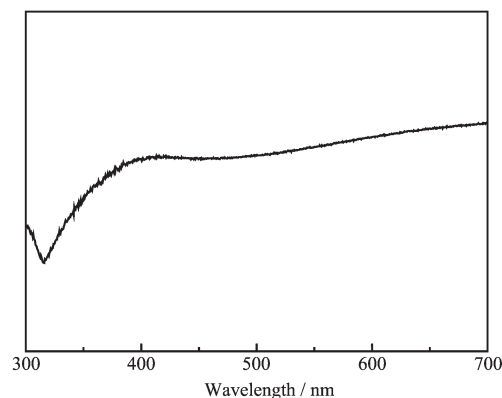


Fig.7 UV-Vis spectrum of the as-prepared HSNs

demonstrated in Fig.8. The spectral intensities are decreased by diluting the concentration of R6G (Fig. 8a~c). According to early reports, the strong peaks at about 1 610, 1 569, 1 483, 1 443, and 1 371 cm^{-1} are assigned to the aromatic C-C stretching modes, and the band centered at about 1 261 cm^{-1} is assigned to the C-C bridge-bands stretching, while the bands centered at about 1 187 and 1 129 cm^{-1} are assigned to the C-H in-plane bending of the aromatic ring moiety of the molecule^[30]. R6G@glass sample are shown in Fig.8d. The enhancement factor EF for the substrate is estimated using the following expression^[31]:

$$EF = \frac{I_{SERS} C_{Ads}}{I_{Raman} C_{Bulk}} \quad (1)$$

where I_{SERS} and I_{Raman} are intensities of a vibrational mode in SERS and Raman spectra. C_{bulk} is the concentration of analyte used in the Raman

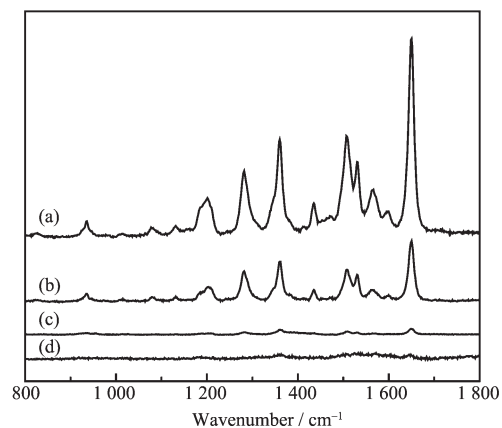


Fig.8 SERS spectra of different concentrations of R6G dropped on HSNs (a) $10^{-4} \text{ mol} \cdot \text{L}^{-1}$, (b) $10^{-5} \text{ mol} \cdot \text{L}^{-1}$, (c) $10^{-6} \text{ mol} \cdot \text{L}^{-1}$, (d) Raman spectrum of pure R6G ($10^{-1} \text{ mol} \cdot \text{L}^{-1}$)

measurements for bulk samples. For our measurement, $10^{-1} \text{ mol} \cdot \text{L}^{-1}$. C_{ads} is the concentration of the analyte used for SERS activity measurement, which is $10^{-6} \text{ mol} \cdot \text{L}^{-1}$ R6G for this study. Using the intensity ratio of the vibrational mode at $1\,651 \text{ cm}^{-1}$ and the molarity ratios (10^{-5}), the enhancement factor is 2.9×10^5 .

Fig.9 describes the SERS spectra of different concentrations of RB absorbed on the HSNs. Vibrations at $1\,187$, $1\,311$, $1\,363$, $1\,509$, and $1\,651 \text{ cm}^{-1}$ are assigned to C-H in-plane bending, C-O-C stretching, and C-C stretching of the aromatic ring^[32-33]. The spectral intensities are also decreased with the concentration of RB (Fig.9a~c). Clearly, the HSN can be used as a SERS substrate for the detection of organic pollutants.

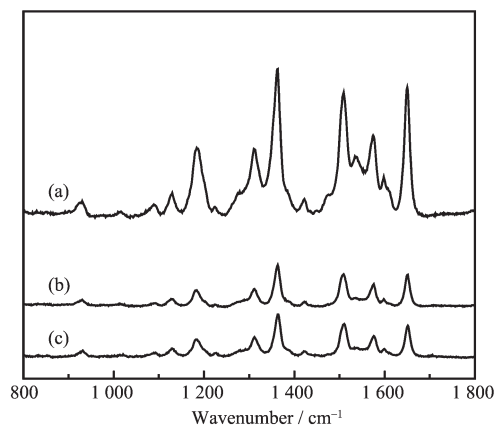


Fig.9 SERS spectra of different concentrations of RB dropped on HSNs (a) $10^{-4} \text{ mol} \cdot \text{L}^{-1}$, (b) $10^{-5} \text{ mol} \cdot \text{L}^{-1}$, (c) $10^{-6} \text{ mol} \cdot \text{L}^{-1}$

3 Conclusions

Three-dimensional (3D) hierarchical silver nanostructures (HSNs) were synthesized via the reaction between silver nitrate and ascorbic acid in the presence of diammonium hydrogen citrate and characterized by XRD, FESEM, TEM, HRTEM, SAED, FTIR and UV-Vis spectroscopy. The proposed method is simple, mild and cheap, and thus it is suitable for industrial production of the HSNs. The HSNs exhibit high SERS activity on R6G and RB.

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