

Templateless, surfactantless, simple electrochemical route to rapid synthesis of diameter-controlled 3D flowerlike gold microstructure with “clean” surface†

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We report for the first time a simple low-cost electrochemical route to synthesis of diameter-controlled hierarchical flowerlike gold microstructures with “clean” surfaces using gold nanoplates or nanopricks as building blocks without introducing any template or surfactant.

At the present time, considerable interests have been focused on the design of rational methods for synthesizing higher ordered inorganic crystals with specific sizes, shapes and hierarchies because of the potential to design new materials and devices in various fields.¹ Hierarchical micro/nanostructures, assemblies using nanoparticles, nanorods and nanobelts as building blocks,^{2–4} and complex nanocrystals with well-defined shape and inner structure^{5–7} have received great interest and been obtained through different strategies.

Hierarchical gold micro/nanostructured materials have recently attracted intensive research interests because of their important potential applications in catalysis, biological labeling, optics and electronics. Several methods are employed to prepare complex hierarchical gold micro/nanostructures, most of which are synthesized in the presence of organic additives or surfactants.^{8,9} However, the use of surfactants or directing agents may introduce heterogeneous impurities. Although templates with complex functionalization patterns^{10,11} can direct the growth of gold crystals with controlled morphologies and architectures, the preparation of templates is tedious and post-synthetic treatments are needed to remove them from the products, which might destroy the as-prepared hierarchical nanostructured materials.

So, it is interest to introduce a simple, rapid, controllable method to produce well-defined uniform hierarchical gold microspheres to meet the requirements for potential application in several fields such as nanodevices and nanosensors, *etc.* In this communication, we report, for the first time, a novel low-cost electrochemical approach to diameter-controlled hierarchical flowerlike gold microstructures (HFGMs) with “clean” surfaces using gold nanoplates or nanopricks as building blocks without introducing any template or surfactant. We can easily control the diameter of the HFGMs *via* simply controlling the time or

potential of electrodeposition. The as-prepared HFGMs have very “clean” surfaces, excellent surface chemistry and unique local morphology, all of which will make them find applications in biosensors, surface enhanced Raman spectroscopy (SERS), and as superhydrophobic materials. As an initial application of these HFGMs, we investigated their SERS activity using 4-aminothiophenol (4-ATP) as probe molecule.

For a typical synthesis of HFGMs, 24.3 mM of HAuCl₄ (Beijing Chemical Factory, Beijing, China) aqueous solution was first prepared using the reagent-grade chemical with distilled water. Tin-doped indium oxide on glass (ITO; Shenzhen Hivac Vacuum Photo-electronics Co. Ltd.), used as working electrode, was cleaned by sonicating sequentially for 10 min each in acetone, 10% NaOH in ethanol, and distilled water. Clean platinum wire and Ag/AgCl (sat. KCl) reference electrodes were used as counter and reference electrodes, respectively. The amperometric *i-t* curve technique was employed for electrochemical deposition of HFGMs with the potential set at 0.5 V. For SERS studies, 10 μl of a 0.1 mM 4-ATP ethanol solution was dropped on the as-prepared HFGM modified ITO electrode for drying. After washing the ITO with ethanol and drying by N₂, FT-SERS spectra were recorded using a FT-Raman spectrometer (Thermo Nicolet 960) equipped with an InGaAs detector and a Nd/VO₄ laser (1064 nm) as an excitation source.

The morphology of the resulting precipitates was characterized with a XL30 ESEM FEG scanning electron microscope (SEM) at an accelerating voltage of 15 kV. Fig. 1 shows typical SEM images of the as-prepared sample (deposition time = 30 min) at different magnifications. A low-magnification image (Fig. 1(A)) indicates that the as-prepared product consists of a large quantity of monodisperse microspheres with diameter of 5 μm. Higher magnification images (Fig. 1(B), (C)) demonstrate that these microspheres exhibit flowerlike structures. Local magnification reveals that the HFGMs are built with many 2D nanoscaled flakes or 1D nanopricks as building blocks, showing planar-dendrite (branched) structure. It can be estimated that the nanoflakes are of about 50 nm in thickness.

The chemical composition of HFGMs was determined by energy-dispersive X-ray spectroscopy (EDX). The EDX spectrum (Fig. 2(A)) with only one peak (other two peaks from ITO substrate) corresponding to Au revealed that the HFGMs were pure metallic Au. X-Ray diffraction (XRD) analysis of the resulting product was carried out on a D/MAX 2500 V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation. Fig. 3(A) shows the XRD pattern obtained. The peaks located at 38.0, 44.2, 64.5, 77.5 and 81.7° are assigned to (111), (200), (220), (311) and (222)

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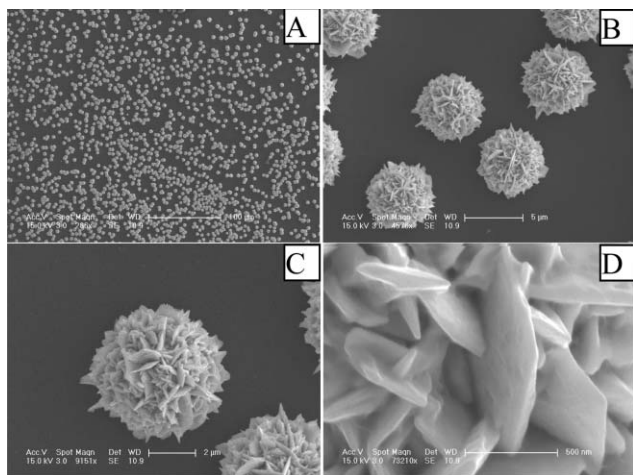


Fig. 1 Typical FE-SEM images of the HFGMs located at ITO substrate at different magnifications (deposition time = 30 min; concentration of $\text{HAuCl}_4 = 24.3 \text{ mM}$); The scale bars for (A), (B), (C) and (D) are 100 μm , 5 μm , 2 μm and 500 nm, respectively.

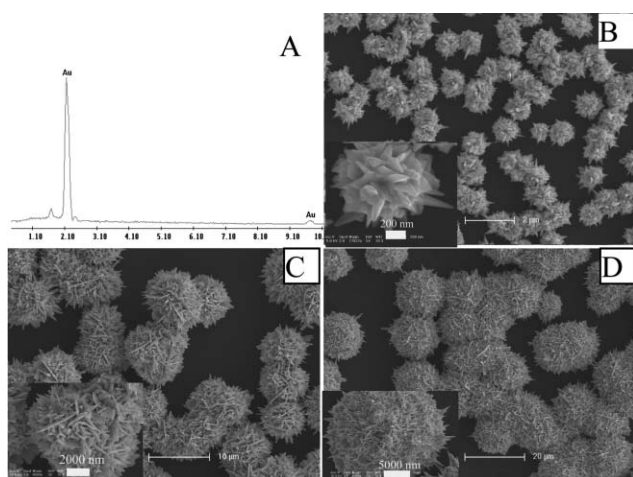


Fig. 2 The EDX image (A) of the HFGMs and typical FE-SEM images (B–D) of the HFGMs located at the ITO substrate. The deposition times for (B), (C) and (D) are 2 min, 2 h and 6 h, respectively. The concentration of HAuCl_4 is 24.3 mM; The scale bars for (B), (C) and (D) are 2 μm , 10 μm and 20 μm , respectively.

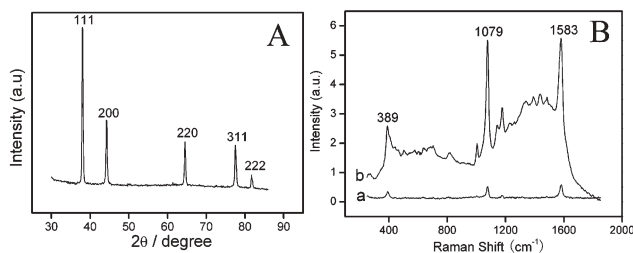


Fig. 3 XRD pattern (A) of the HFGMs and FT-SERS spectra (B) of 4-ATP adsorbed on a $\sim 25 \text{ nm}$ gold nanoparticle film (a) and sample 1 (b). Sample 1 was prepared *via* a deposition time of 30 min and deposition potential of 0.5 V.

faces of the HFGMs, respectively. The intensity ratio (2.2) of the $\{111\}$ to the $\{200\}$ diffraction line is higher than that (1.9) of the standard diffraction of gold powder, indicating that the deposited gold structure has a tendency to grow with the surfaces dominated by the lowest energy $\{111\}$ facets.¹²

To further study the growth process of HFGMs on the ITO surface, the morphologies of HFGMs obtained at different deposition times were characterized through SEM. Fig. 2 shows the SEM images of HFGMs obtained at 0.5 V for 2 min (B), 2 h (C) and 6 h (D). When the deposition time was 2 min, HFGMs with diameter of about 1 μm were obtained. It is noted that several pricklike nanostructures protruded from the HFGMs. On further increasing the deposition time to 2 h, the size of the HFGMs was increased to 9 μm and a higher density of nanoplates or nanopricks was observed in the individual HFGMs. After 6 h of deposition, the ITO surface was coated by the nanostructures with a higher density of building blocks. The size of the HFGMs further increased, and the average size was about 18 μm . Thus, the size and morphologies of the HFGMs can be easily controlled *via* changing the deposition time.

During the electrodeposition process, the electrodeposition potential also affects the morphologies of the nanostructures. The microstructures obtained at a different potential (0.7 V) for 30 min were also examined, as shown in Fig. S1(A) (ESI[†]). These microstructures still exhibit obvious flowerlike structures. However, the diameter of these HFGMs was about 2 μm , which is smaller than that obtained by electrodeposition at 0.5 V. So, changing the electrodeposition potential can also adjust the size of HFGMs. In addition, the concentration of HAuCl_4 (5 mM) was also investigated at the electrodeposition potential of 0.5 V. However, no HFGMs were observed (Fig. S1(B)) (ESI[†]) and only some irregular nanoparticle aggregates were obtained. So the concentration of HAuCl_4 plays a key role in the HFGMs obtained.

Based on the above facts, a plausible formation process is briefly presented as follows: in this approach, the electrochemical reaction (or electron transfer) and crystallization (nucleation and growth) coexist. When the process of electrodeposition happened initially, gold atoms will be produced on the ITO substrate by the electro-reduction of AuCl_4^- . The gold nuclei on the ITO surface will undergo crystal growth into small gold nanoparticles. As shown in Fig. 1(A), a high density of HFGMs was observed, which directly indicates that a great number of small gold nanoparticles should be deposited on the ITO surface at the beginning. In this case, these small nanoparticles on the ITO surface can act as nanoelectrode ensembles. As is known, the diffusion of species to the nanoelectrodes is of spherical type. A diffusion shielding effect between the nanoelectrodes will be produced when the distance between nanoelectrodes is close.¹³ In our system, the diffusion shielding effect of nanoelectrode ensembles probably occurs due to the high density of small gold nanoparticles, which can be judged from the SEM image (Fig. 1(A)). This will lead to an inhomogeneous distribution of AuCl_4^- around the small gold nanoparticle surfaces in subsequent electrochemical reactions. Some positions of gold nanoparticles are at a higher concentration of AuCl_4^- because the diffusion of AuCl_4^- is radial and fast at the nanoelectrode whereas others show lower concentration of AuCl_4^- because the diffusion of AuCl_4^- is planar and slow in the diffusion shield region of nanoelectrode ensembles. Thus, non-uniform distribution of AuCl_4^- on individual gold nanoparticles in the diffusion process

probably plays an important role in this electrochemical synthesis system. In addition, from the XRD data, it is noted that {111} facets dominated. In the growth process, *in-situ* produced Cl^- probably adsorbs onto {111} facets on the surface of nanoparticles, which will result in a very slow growth along the $\langle 111 \rangle$ orientation. Combined diffusion shield effects of nanoelectrode ensembles and Cl^- preferentially adsorbed into {111} facets will lead to the HFGMs. HFGMs were not obtained at low concentrations of HAuCl_4 because the concentration of Cl^- produced *in-situ* is low, making it hard to adjust the growth of certain facets of Au. So the concentration of HAuCl_4 plays an important role in this synthesis system. In addition, several literature reports indicate that anisotropic nanostructures such as nanoplates and nanobars could be readily obtained by operating at a slow reduction rate (under kinetic control).^{14,15} As is known, the standard reduction potential of $\text{AuCl}_4^-/\text{Au}$ is 0.802 V vs. Ag/AgCl (sat. KCl), which is slightly higher than the potential range employed (0.5–0.7 V). Thus, the reduction of AuCl_4^- will occur slowly in this case. It is observed that the HFGMs are built with many 2D anisotropic nanoscale flakes or 1D nanopricks as building blocks. Furthermore, the size of HFGMs obtained at 0.5 V is larger than that obtained at 0.7 V for the same electroreduction time. Both observations indicate the electrochemical preparation of HFGMs is also probably affected by kinetic control. However, the detailed formation mechanism of HFGMs in this synthesis is not very clear at the present time and needs further investigation.

The interesting hierarchical structure of the HFGMs may make them attractive for use as SERS substrates. The FT-SERS spectrum of 4-ATP adsorbed on the film of the HFGMs (deposition time = 30 min) is shown in Fig. 3(B)(b). The SERS signal from this nanostructure is enhanced much more than that from a typical 25 nm gold nanoparticle film (Fig. 3(B)(a)). It is noted that the spectra were dominated with the a_1 vibration modes (in phase, in-phase mode), such as $\nu(\text{C}-\text{C})$ at 1583 cm^{-1} and $\nu(\text{C}-\text{S})$ at 1079 cm^{-1} . The band at 389 cm^{-1} was assigned to one of the vibration modes of the C–S bond,¹⁶ and the disappearance of the most intense band at 464 cm^{-1} was in good accord with that obtained by Zheng *et al.*¹⁷ To elucidate the enhancement effect of 4-ATP on the HFGMs quantitatively, the EF value of 4-ATP in the HFGMs film was calculated according to ref. 18. The enhancement factor (EF) at the HFGMs for the ν_{8a} (a_1) band (1583 cm^{-1}) can be calculated to be as large as 2.2×10^5 at 1064 nm excitation, 22 times higher than that on the aggregated gold nanoparticles modified SERS substrate (See ESI† for detailed calculation of EF). Observing the HFGMs obtained here, it can be concluded that the strong SERS effect for the HFGMs should be related to their particular geometry. Compared to a $\sim 25\text{ nm}$ nanoparticle film, a great many band gaps have been constructed between many of gold nanoplates or nanopricks located in the

individual HFGMs. In addition, the nanopricks (see Fig. 1(D)) can be more advantageous for local intense field because local values of $|E|^2$ at the tips¹⁹ can be as high as 500 times that of the applied field, and therefore lead to a superior SERS effect relative to a $\sim 25\text{ nm}$ nanoparticle film.

In conclusion, HFGMs with “clean” surfaces using nanoplates or nanopricks as building blocks were prepared by a simple low-cost electrochemical approach. The diameter of the HFGMs can be easily controlled *via* simply controlling the deposition time or the deposition potential. The study is of significance in the shape controlled synthesis of metal nanomaterials. More importantly, such HFGMs have particular morphologies and “clean” surfaces, which will find other applications in bioelectrochemistry, superhydrophobic materials, *etc.*

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