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Ultrathin platinum-group metal coated hierarchical flowerlike gold microstructure: Electrochemical design and characterization

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Abstract

The deliberate tailoring of hierarchical flowerlike gold microstructure (HFGMs) at the ultrathin level is an ongoing challenge and could introduce opportunities for new fabrication and application in many fields. In this paper, a templateless, surfactantless, electrochemical strategy for fabrication of ultrathin platinum-group metal coated HFGMs is proposed. HFGMs were prepared by simple electrodeposition on an indium tin oxide (ITO) substrate. The resulting HFGMs enables the deposition of an ultrathin overlayer through copper underpotential deposition (UPD), followed by spontaneous replacement of the copper with the platinum-group metal to yielded a uniform and ultrathin Pt-group metal layer on the HFGMs surface. Thus prepared bimetallic "core-shell" sample has been characterized by cyclic voltammetry, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray maps and X-ray diffraction (XRD). This is a very general and powerful technique for the fabrication of hierarchical, ultrathin coating, bimetallic "core-shell" microstructure, which, in turn, opens up the possibility of building more complex multicomponent hierarchical microstructure with potential application, such as electrocatalysis, biosensors and nanodevices, etc.

Keywords: Gold; Platinum; Palladium; Hierarchical structure; Underpotential deposition

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1. Introduction

Hierarchical micro/nanostructures assemblies using nanoparticles, nanorods, nanobelts as building blocks and complex nanocrystals with well-defined shape and inner structure are of great significance for the realization of nanodevices and have been obtained through different strategies, such as hydrothermal strategy and electrochemical method, etc. [1–9]. Some semiconductor materials, such as ZnO, CuO, MnO_2, Bi_2S_3, with flowerlike nanoarchitectures (FNs), have been fabricated by a mild hydrothermal strategy [10–15]. However, fabrication of metallic FNs is still a challenge, and especially, the study of FNs' morphology dependent properties is to be conducted. In addition, FNs growing on a substrate directly, which is difficult for hydrothermal strategy, is of importance for some special applications, such as surface-enhanced Raman scattering (SERS) active substrate, superhydrophobicity, and the nanodevice realization [10].

Electrochemical tactic might be a good alternative approach for meeting this matter. Several electrochemical methods are employed to prepare complex hierarchical gold micro/nanostructures, most of which are synthesized in the presence of organic additives or surfactants [10], and others are based on template [16]. Recently, we have reported a facile and low-cost electrochemical approach to prepare diameter-controlled hierarchical flowerlike gold microstructures (HFGMs) with "clean" surface without introducing any template or surfactant and the diameter of HFGMs can be easily controlled via simply controlling the time of electrodeposition [17].

There is currently considerable interest in the preparation and application bimetallic "core-shell" nanostructures in part by specific applications in catalysis, sensors and microelectronics [18–20]. Among various alternative candidates, Pt-group metal are of great significance in chemical catalysis [21] and also have attracted extensive attention in the application of surface enhanced Raman spectroscopy (SERS) [22,23]. Since surface-catalyzed reactions are extremely sensitive to the atomic-level

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details of the catalytic surface, the deliberate tailoring of the Pt-group metal nanostructured catalysts is an ongoing challenge and could lead to new electronic and catalytic properties. On the other hand, Pt-group metal micro/nanostructure with sharp tips may exhibit especially high SERS activity [24].

Herein a promising electrochemical strategy for fabrication of ultrathin Pt-group metal coated HFGMs is proposed. Uniform and ultrathin Pt-group metal coating on Au or Pt nanoparticles can be achieved, which involves redox replacement of an underpotential deposition (UPD) ultrathin level layer by more noble metal cations that could be reduced and simultaneously deposited [25,26]. Similar tactics can now be harnessed to prepare HFGMs modified with uniform Pt-group overlayers. Thus prepared bimetallic "core-shell" HFGMs material with sharp tips could be expected to exhibit excellent catalytic properties and especially high SERS activity [24,27]. To the best of our knowledge, attempt to the preparation of ultrathin Pt-group metal coated three-dimensional (3D) HFGMs has not yet been exploited. Although 1D gold nanorod and 2D nanoporous gold nanorod have been exploited to be coated with ultrathin Pt layer based on the UPD technique, the strategy must use template [27]. However, the use of hard templates may complicate the synthetic procedure and limit the synthesis of micro/nanostructured materials in large quantities [28,29]. The newly electrochemical design presented here is a very general and powerful technique for fabrication of hierarchical, ultrathin coating, bimetallic "core-shell" microstructure, which, in turn, opens up the possibility of building more complex multicomponent hierarchical microstructure with potential application, such as electrocatalysis, biosensors and nanodevices, etc.

2. Experimental

2.1. Reagents

$HAuCl_4$, $CuSO_4$ and H_2SO_4 were purchased from Beijing Chemical Factory (Beijing, China). $PdCl_2$ and K_2PtCl_4 were purchased from Chinese Chemical Reagent Companies (Shanghai, China). Tin-doped indium oxide on glass (ITO) was purchased from Shenzhen Hivac Vacuum Photo-electronics Co. Ltd (Shenzhen, China). Other chemicals were of analytical grade and were used without further purification. All solutions were prepared with deionized water treated in a Millipore water purification system (Millipore Corp.).

2.2. Electrochemical fabrication of the HFGMs

The electrochemical fabrication HFGMs was prepared according to our recent report [17]. For a typical electrochemical fabrication of HFGMs, 24.3 mM of $HAuCl_4$ aqueous solution was used as the source of Au and also as electrolyte. ITO was used as working electrode. Before used, ITO was cleaned by sonicating sequentially for 10 min each in acetone, 10% NaOH in ethanol and distilled water. The clean platinum wire and Ag/AgCl (sat. KCl) electrodes were used as counter and reference electrode, respectively. Amperometric *I–t* curve technique was employed to electrochemical deposition HFGMs with the potential of 0.5 V and the deposition time was 30 min.

2.3. Electrochemical design ultrathin Pt-group metal coated HFGMs

UPD-redox replacement reaction technique was adopted to fabricate ultrathin Pt-group metal coated HFGMs. The typical experiment for fabricating ultrathin Pd coated HFGMs is as follows: a UPD ultrathin of copper was formed on the HFGMs by holding the potential at 0.01 V in deaerated 0.1 M H_2SO_4 containing 1 mM $CuSO_4$ for several minute, then transferred to a solution of 5 mM $PdCl_2$ in deaerated 0.1 M $HClO_4$. The electrode was left in this solution at an open circuit for 10 min to ensure complete redox replacement of the UPD Cu, then rinsed and dried with N_2. The procedure involved spontaneous redox replacement of the Cu layer by the Pt-group metal, similar to that as described previously [21–23,26,27]. The electrochemical fabrication ultrathin Pt coated HFGMs processing was similar to that of Pd and just 5 mM K_2PtCl_4 replaced the 5 mM $PdCl_2$.The value of this method is that it provides epitaxial Pt-group layers on the HFGMs. Thus prepared ultrathin Pd and Pt coated HFGMs were used for further characterization.

2.4. Characterization of the ultrathin Pt-group metal coated HFGMs

Electrochemical experiments were performed with a CHI 832 electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). A conventional three-electrode cell was used, including a Ag/AgCl (saturated KCl) electrode as reference electrode, a platinum wire counter electrode and a HFGMs or Pt-group metal coated HFGMs modified ITO as working electrode. The morphology of the HFGMs and Pt-group metal coated HFGMs was characterized with a XL30 ESEM FEG scanning electron microscopy (SEM) at an accelerating voltage of 20 kV. This SEM instrument has also been used to determine the chemical composition by energy-dispersive X-ray spectroscopy (EDX) and characterize the elemental map of Au and Pt-group metal of the resulting product. The X-ray diffraction (XRD) analysis of the resulting product was carried out on a D/MAX 2500 V/PC X-ray diffractmeter using Cu (40 kV, 30 mA) radiation.

3. Results and discussion

3.1. SEM characterization of the HFGMs

Fig. 1 is the typical FE-SEM images of the as-prepared HFGMs samples growing on ITO substrate at different magnifications. Low-magnification image (Fig. 1A) indicates that the as-prepared product consists of a large quantity of well dispersed microspheres with the diameter about 5 μm. Higher magnification image (Fig. 1B) demonstrates that these microspheres exhibit flowerlike and planar-dendrite (branched) structure. The growth processing of the HFGMs during this electrochemical approach can be explained by the reaction (or electron transfer)

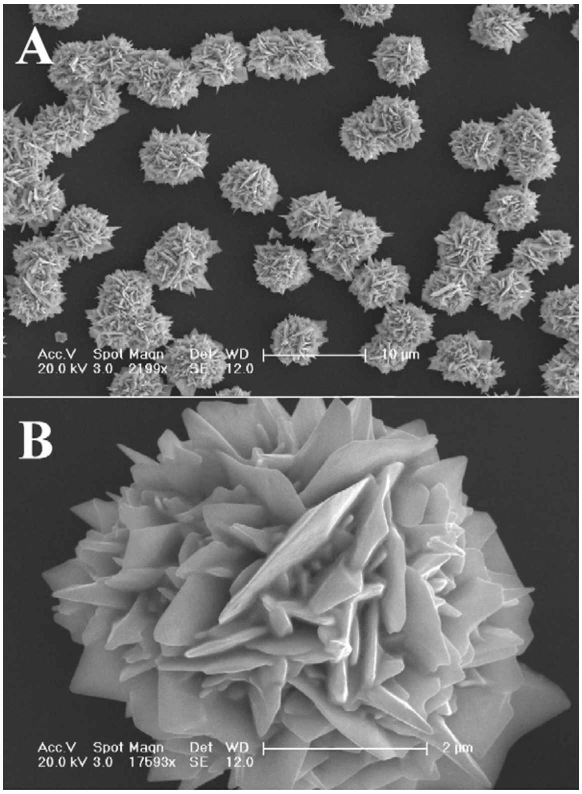

Fig. 1. Typical FE-SEM images of the HFGMs located at ITO substrate at different magnifications. The scale bar is 10 and 2 μM for (A) and (B), respectively.

and crystallization (nucleation and growth) coexist. This result is in accordance with our recent report [17].

3.2. Electrochemical design of the ultrathin Pt-group metal coated HFGMs

The basic electrochemical design protocol employed here entails replacing a UPD metal adlayer on HFGMs template with the desired Pt-group metal via a spontaneous deposition process. The spontaneous redox replacement process, yielding a late Pt-group metal overlayer, is driven by the difference at equilibrium potentials between the Pt-group metal and the UPD metal redox couples. For the system employed, Pd^{2+}/Pd and $PtCl_4{}^{2-}/Pt$, the standard potentials (E^0) of the corresponding half-reaction are more positive than those for the Cu^{2+}/Cu UPD couple [21–23]. So, the spontaneous redox replacement of a previously prepared UPD Cu ultrathin by Pt-group cations can be used to form Pt-group metal deposits, consistent with the anticipated balanced $Cu \rightarrow Cu^{2+}/Pd(II) \rightarrow Pd$ and $Cu \rightarrow Cu^{2+}/Pt(II) \rightarrow Pt/Pt(II)$ electron charge flow.

After the initial preparation of the HFGMs template, a UPD copper ultrathin was deposited. Fig. 2 shows a representative cyclic voltammogram (20 mV s^{-1}) for HFGMs coated ITO in a deaerated 1 mM $CuSO_4$ + 0.1 M H_2SO_4 solution. On the forward (i.e., negative-going) sweep, two main cathodic features (a and b) are observed at about +0.22 and −0.07 V, respectively. Feature a is consistent with the formation of UPD copper, while feature b refers to bulk copper deposition [21,23]. As expected, two anodic peaks (b′ and a′) are obtained on the return (positive-going) sweep, corresponding to dissolution of bulk and UPD copper, respectively. The electrode was immersed in the copper solution at a potential (∼0.01 V) just above that where bulk deposition commences, to ensure full ultrathin coverage, and was then transferred to a deaerated solution containing the Pt-group cation of interest (typically 5 mM Pt and Pd salt in 0.1 M HClO4, respectively). The electrode was left in this solution at open circuit for 10 min. This period of time was chosen to ensure complete redox replacement of UPD Cu and ordering of the resulting Pt and Pd overlayer. The electrode was either transferred to the electrochemical cell for voltammetric scrutiny or to be used for further characterization, as discussed in the next section.

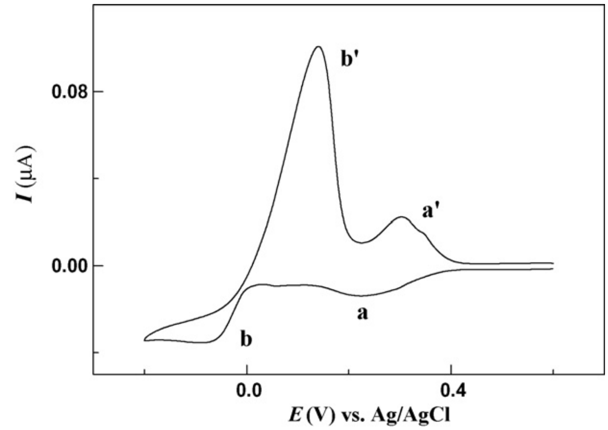

Fig. 2. Cyclic voltammograms for HFGMs modified ITO substrate in deaerated 1 mM $CuSO_4$ + 0.1 M H_2SO_4. Scan rate is 50 mV s^{-1}.

3.3. Electrochemical characterization of the ultrathin Pt-group metal coated HFGMs

Representative cyclic voltammograms obtained (at 50 mV s^{-1}) from −0.2 to 1.5 V versus Ag/AgCl electrode (saturated KCl) for the fabricated HFGMs modified ITO in 0.1 M H_2SO_4 are shown in Fig. 3 (dash traces). The presence of a wide “double-layer” region below ca. 0.7 V and the anodic formation and cathodic removal of oxide at higher potentials are familiar features of gold electrochemistry [21,22]. The solid traces in Fig. 3A and B are corresponding voltammograms obtained after the deposition of ultrathin palladium and platinum, respectively, using essentially the UPD procedure described in Ref. [22]. Significantly, the resulting cyclic voltammograms provide clear evidence that the HFGMs surface is modified essentially by the Pt-group metal. Thus the anodic–cathodic current profiles, comprised of near-reversible peaks associated with hydrogen desorption–adsorption and the irreversible features corresponding to the formation and removal of surface oxide, are characteristic of conventional Pd and Pt surfaces [22], even though only ultrathin level films are apparently present. In particular, the presence of the Pt-group metal oxide reduction peak at ca. 0.32 V, along with the near-absence of the corresponding gold oxide feature at ca. 0.87 V, shows that few exposed Au sites remain, which

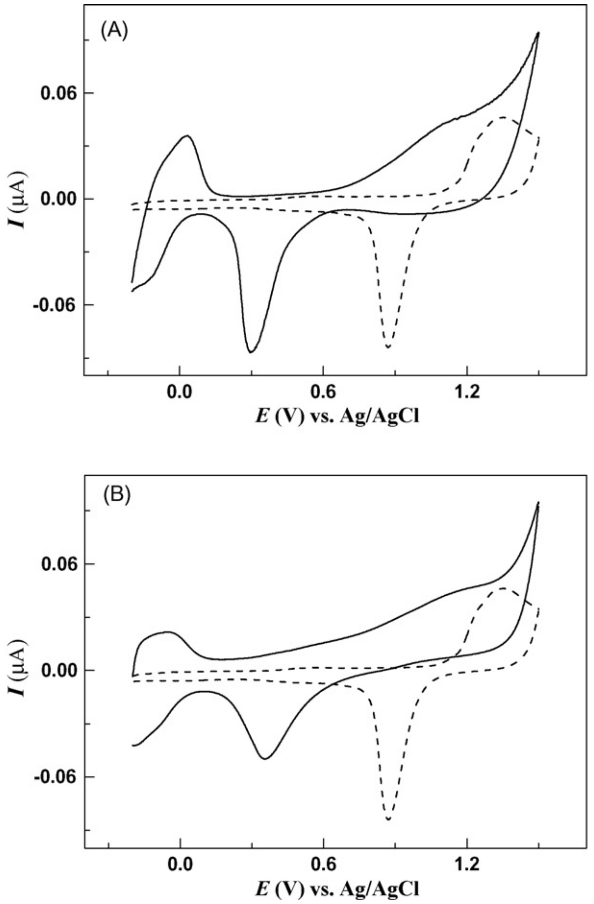

Fig. 3. Cyclic voltammograms for HFGMs modified ITO substrates in deaerated 0.1 M H_2SO_4 before (dash trace) and after (solid trace) coating with ultrathin Pd (A) and Pt (B). Scan rate is 50 mV s^{-1}.

also indicating the essentially “pinhole-free” nature of the ultrathin Pt-group metal coating [21–23]. The uniformity of such Pt-group metal overlayers on a gold nanoparticle surface formed with Pt-group metal is indeed confirmed previously by SERS, employing carbon monoxide as a “probe” chemisorbate [22,23].

3.4. SEM, EDX, X-ray map and XRD characterization

Fig. 4 is the typical FE-SEM images of the as-prepared ultrathin Pd coated HFGMs samples growing on ITO substrate at different magnifications. Low-magnification image (Fig. 4A) indicates that the as-prepared product consists of a large quantity of well dispersed microspheres with the diameter about 5 μm. Higher magnification image (Fig. 4B) demonstrates that these microspheres exhibit flowerlike structures. Local magnification (Fig. 4C) reveals that ultrathin Pd coated HFGMs are still built with many 2D nanoscaled flakelike or pricklike building blocks, showing branched structure. Compared with SEM images of bare HFGMs (Fig. 1), after coating with ultrathin Pd, there was neither a morphology change nor a significant diameter variation. This observation is indicative of the homogeneity of the Pd coating and ultrathin nature.

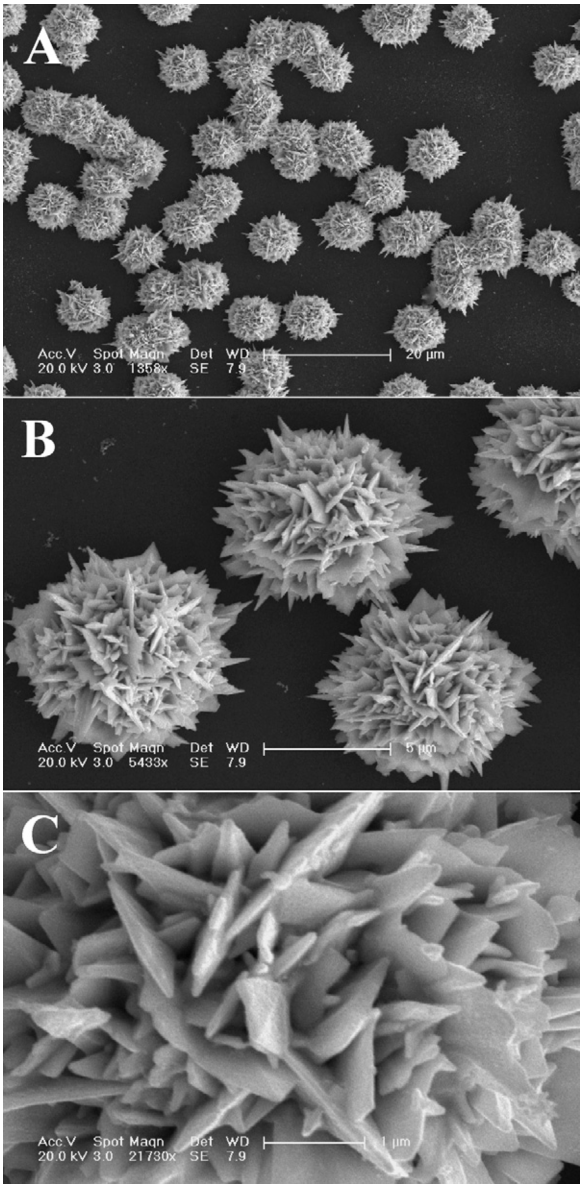

Fig. 4. Typical FE-SEM images of ultrathin Pd coated HFGMs located at ITO substrate at different magnifications. The scale bar is 20, 5 and 1 μM for (A), (B) and (C), respectively.

The chemical composition of the ultrathin Pd coated HFGMs was determined by EDX and X-ray maps analysis of the products coated on an ITO glass slide (Fig. 5). The EDX spectrum (Fig. 5A) testified the existing of the Au and Pd element, in which the peak of the corresponding element Au and Pd was distinct (other peaks originated from the substrate). The corresponding X-ray maps (Fig. 5B–D) reveal that the Pd element is relatively uniform distributed in these microstructures. These results are consistent with the electrochemical results.

Representative SEM images obtained for ultrathin Pt coated HFGMs are confirmed no visible change and variation of the morphology and diameter of the HFGMs can be observed after being coated with ultrathin Pt films (data not shown). EDX analysis and X-ray maps of the Pt coated sample reveal Pt element is relatively uniform distributed in HFGMs (Fig. 6). Furthermore,

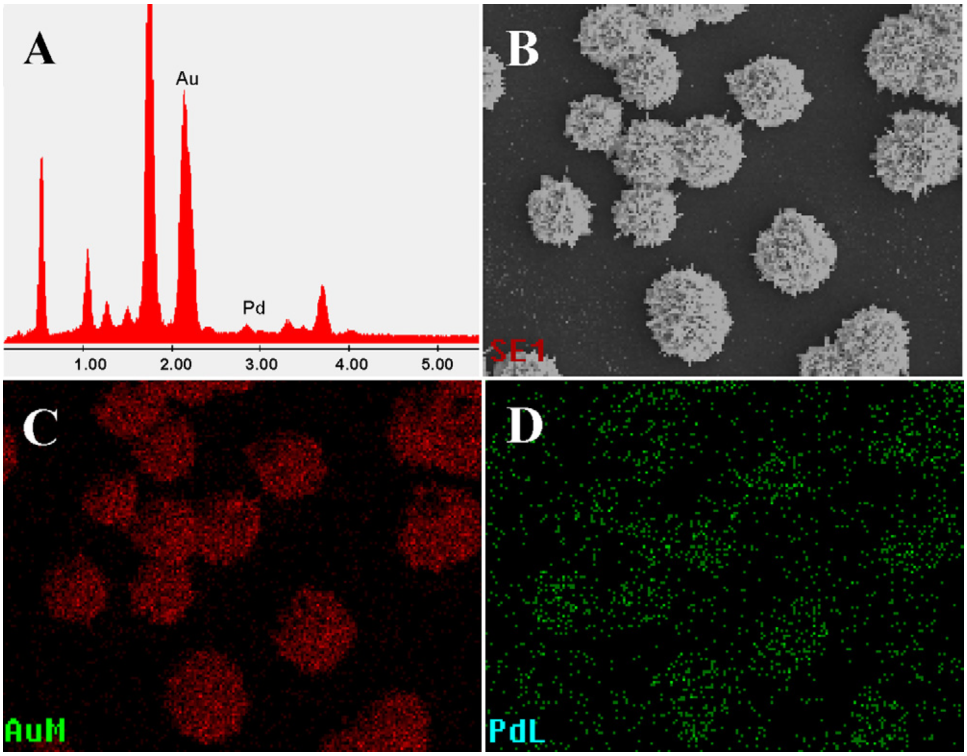

Fig. 5. (A) EDX analysis in a selected domain of ultrathin Pd coated HFGMs sample, (B) the morphological image of the as-prepared sample and X-ray maps of Au (C) and Pd (D), respectively, corresponding to (B).

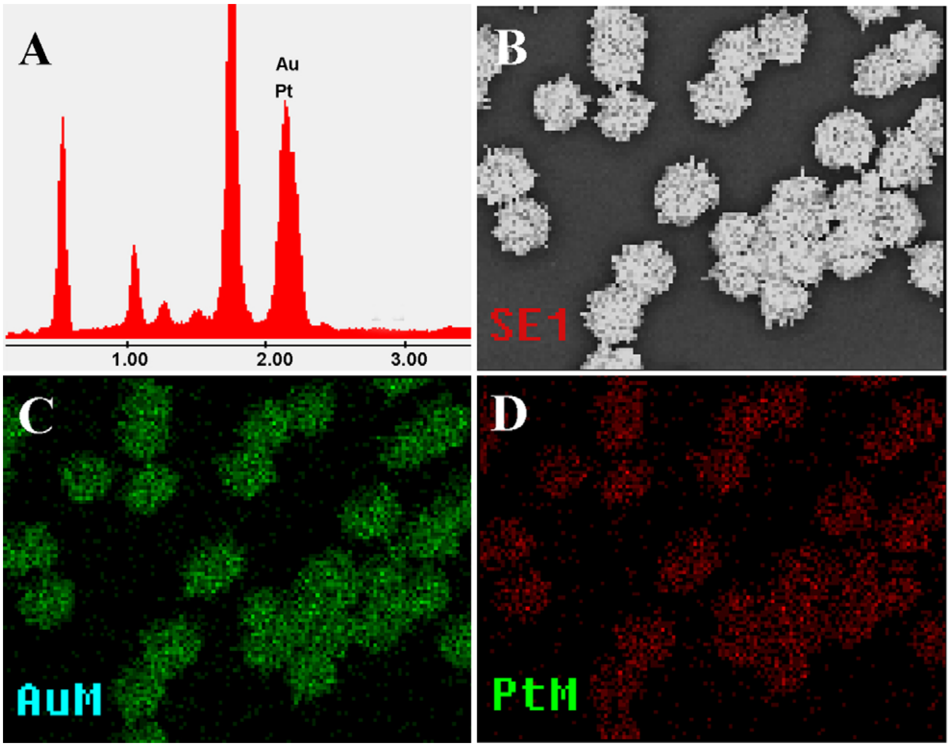

Fig. 6. (A) EDX analysis in a selected domain of ultrathin Pt coated HFGMs sample, (B) the morphological image of the as-prepared sample and X-ray maps of Au (C) and Pt (D), respectively, corresponding to (B).

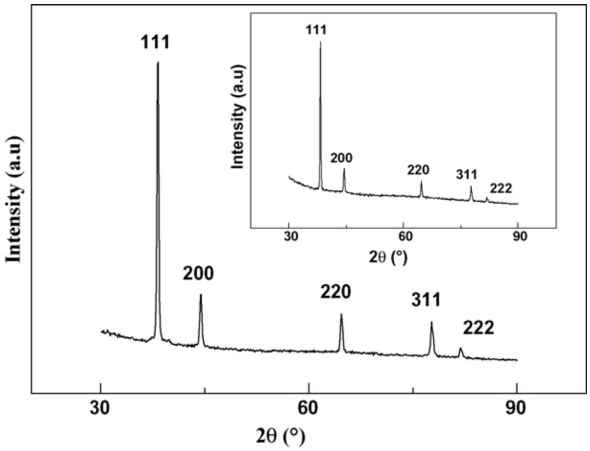

Fig. 7. XRD pattern of ultrathin Pt coated HFGMs sample. The inset is XRD pattern of the HFGMs sample.

XRD was used to characterize the structure of the ultrathin Pt coated HFGMs. Fig. 7 shows the XRD pattern obtained for the Pt coated sample. Compared with the XRD pattern of bare HFGMs (Fig. 7, inset), the peaks number and the location are not changes, only increase of the peak intensity was observed, but the relative intensity between each peak is nearly consistent with that of the bare HFGMs. XRD analysis provided clear evidence that the Pt coating has not interfering with the HFGMs structure and provided more evidence that the Pt coating is relatively uniform and ultrathin. The similar XRD analysis also obtained for Pd coated HFGMs (data not shown), which demonstrates the same conclusion for Pd coated HFGMs. According to our previously report [17], the peaks located at 38.2°, 44.5°, 64.6°, 77.6° and 81.8° were assigned to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) faces of HFGMs, respectively.

4. Conclusion

Overall, the present results demonstrate a very simple, templateless, surfactantless, electrochemical strategy for fabrication of ultrathin platinum-group metal coated HFGMs. Thus prepared bimetallic "core-shell" hierarchical microstructure has been well characterized by electrochemical method, SEM, EDX, X-ray map and XRD, which testified the Pt-group coating holding the "pinhole-free" nature while the HFGMs still keep its morphology. The advantages of the strategy are obvious. First, such bimetallic "core-shell" HFGMs with sharp tips and edges may exhibit better enhancement in SERS compared to analogous nanoparticles with smooth surface [17,24]. Second, it is grateful to design catalysts for practical application since it is possible to save precious metal, e.g., Pt. Furthermore, given the availability of well-developed strategies for preparing HFGMs, together with the diversity of overlayer materials (metal, semiconductors, etc.) that can be electrodeposited on gold [22], there is clearly tremendous scope for generating a myriad of hierarchical microstructure materials by the present means. The further applications of such electrochemical design technique in the development of biosensors are currently underway.

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