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**Fabrication of gold and silver hierarchical micro/nanostructure arrays by  
localized electrocrystallization for application as SERS substrates**

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**Abstract:** A simple and universal method, based on polypyrrole (PPy) through-pore template induced by colloidal monolayer, is developed to fabricate the gold and silver hierarchically micro/nanostructured arrays with hexagonally packed pattern and controllable morphologies through electrochemical deposition. Using polystyrene colloidal monolayer as the first template, a hexagonally packed PPy through-pore thin film was electrodeposited and used as a secondary template to adjust the interface electroconductivity, further to control the localized electrocrystallization process. Final electrodeposition under appropriate conditions can easily lead to several kinds of metal periodic arrays. These hierarchically micro/nanostructured arrays can be used as surface-enhanced Raman scattering (SERS) active substrates. Before use, a certain thickness of gold layer was ion-sputtered onto the periodic arrays to eliminate the interference from PPy film and enhance the substrate SERS activity. Such gold-covering strategy can also provide an effective method to clean the impurity-adsorbed SERS substrate, which is quite important in SERS-based applications.

**Keywords:** Colloidal monolayer, Micro/nanostructured array, SERS, Electrocrystallization

## 1. Introduction

Ordered hierarchically micro/nanostructured arrays have attracted much interest because of their promising applications in a variety of fields, such as surface-enhanced Raman scattering (SERS) active substrates,<sup>1-3</sup> sensors,<sup>4</sup> superhydrophobic surfaces,<sup>5-7</sup> *etc.* At present, there are mainly two methods to prepare the ordered arrays, including the lithography techniques and the template-based techniques.<sup>8</sup> As is known, the lithography techniques, such as photolithography, electron beam lithography *etc.*, have the disadvantages of high costs and low sample throughput. On the contrary, the template-based methods are of simple, effective and low cost advantages. For instance, on the basis of colloidal monolayer templates, by using chemical or physical routes, colloidal lithography has been well developed to create periodic micro/nanostructured arrays. Among them, the electrodeposition method is an effective way to control the structures and morphologies of the as-deposited nanomaterials. For example, based on electrodeposition onto the Au-coated monolayer colloidal crystal template, Liu *et al* fabricated the Ag nanoplate-built hollow microsphere arrays with centimeter-squared scale.<sup>9</sup> Using the polystyrene (PS) monolayer colloidal crystal as template, we had built a kind of gold hierarchically micro/nanostructured pore array.<sup>10</sup> Directly using colloidal monolayer as template, the electrocrystallization sites tend to be on the surfaces of the colloidal spheres or the conductive substrate not covered with spheres (*i.e.* the gaps between the spheres), that is the nanostructures are easy to be built on these locations, and cannot be deposited on the areas where the colloidal spheres contact with the conductive substrate. Through such a route, hemispherical or spherical, or bowl-like arrays are most easily prepared.

In order to get more complicated micro/nanostructures and better regulation of electrocrystallization process, we previously presented a strategy by using self-assembled thiol monolayer as the invisible template to adjust the interface electroconductivity of the electrode, further to regulate the electrocrystallization process, and successfully controlled the electrocrystallization site at the area where the colloidal sphere contact with the substrate.<sup>11</sup> However, for this invisible template method, the adjustable scope of deposition potential is limited, and the morphologies of the arrays cannot be widely regulated.

Here, we further put forward a polypyrrole (PPy) through-pore second template method, and realized a wider adjustable deposition potential and better universality. The PPy film, a conductive polymer layer, is used to replace the thiol self-assembled monolayer to adjust the electroconductivity of the electrode interface. Based on such a strategy, we have synthesized a series of gold and silver hierarchically micro/nanostructured ordered array with controlled structures, and studied the SERS performances of the as-obtained gold and silver array substrate. The experimental results revealed that, the PPy film could produce Raman signal to interference target molecular accurate recognition. We further proposed a gold-covering strategy, not only successfully solved the interference problem, but also improved the substrate SERS activity at the same time. This also provides an effective cleaning treatment strategy for impurity-adsorbed SERS substrates.

## **2. Experimental Section**

### **2.1 Materials**

The 2.5 wt% aqueous suspensions of polystyrene (PS) spheres of 2  $\mu\text{m}$  diameter were purchased from Alfa Aesar Corporation.  $\text{AgNO}_3$ , polyvinylpyrrolidone (PVP) and sodium

citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) were bought from Sinopharm Chemical Reagent Corporation. Chloroauric acid (Shanghai Chemical Reagent Co., Ltd.), pyrrole (Shanghai Kefeng Industry Co., Ltd.), sodium dodecyl benzenesulfonate (Aladdin Chemistry Co., Ltd.) and solvents including acetone and ethanol were used without further purification. Deionized water ( $18.2 \text{ M}\Omega\cdot\text{cm}$ ) was obtained from an ultrafilter system (Milli-Q, Millipore, Marlborough, MA).

## 2.2 Synthesis of hierarchically micro/nanostructured array

The main fabrication process was shown in Fig. 1. First, we used Si wafers as supporting substrates, which were cleaned sequentially for 15 min each in acetone, ethanol, and deionized water in an ultrasonic bath. After drying with high-purity flowing nitrogen, an Au-substrate (*i.e.*, Au/Ti/Si substrate) was prepared by an ion-sputtering deposition method of  $\sim 60 \text{ nm}$  of gold and  $\sim 10 \text{ nm}$  of titanium onto the Si wafer. The thicknesses of the gold and titanium film were fixed in all experiments. And the thickness value was estimated according to the sputtering deposition rate curve provided by the instruction manual of the sputter coater (Emitech K550X). The  $\sim 60 \text{ nm}$  gold film was obtained at 25 mA for 8 min, and the  $\sim 10 \text{ nm}$  titanium layer was obtained at 20 mA for 90 s. Second, by a gas-liquid interface self-assembly method, a large-area uniform PS colloidal monolayer was prepared on the well-cleaned glass slide, as previously described in detail.<sup>10,12</sup> Then, the as-prepared PS colloidal monolayer was integrally transferred onto the Au-substrate by a floating method.<sup>13</sup> After drying at room temperature, the Au-substrate covered with the PS colloidal monolayer (*i.e.*, PS/Au-substrate) was heated in an oven at  $110 \text{ }^\circ\text{C}$  for 10 min so that the PS colloidal spheres had a firm (or an area) contact with the Au-substrate. Third, the electrodeposition of polypyrrole (PPy) layer was carried out in a solution composed of pyrrole (0.1 M) and

sodium dodecyl benzenesulfonate (0.1 M), at a deposition current density of  $0.5 \text{ mA cm}^{-2}$  for 15 s, the as-heated PS/Au-substrate was used as a working electrode, and a graphite flake as a counter electrode.<sup>14</sup> After covering with a PPy layer, the substrate was immersed into methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) solution to dissolve the PS spheres and rinsed with deionized water for several times, the PPy ordered through-pore array was then obtained. Finally, electrodeposition of Au and Ag micro/nanostructured arrays: the electrolytes for Au and Ag were, respectively, pure  $\text{HAuCl}_4$  ( $0.5 \text{ g L}^{-1}$ ) aqueous solution, and a mixed solution composed of  $\text{AgNO}_3$  ( $1 \text{ g L}^{-1}$ ), PVP ( $5 \text{ g L}^{-1}$ ) and  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  ( $1 \text{ g L}^{-1}$ ). The electrochemical deposition current densities are,  $-25 \text{ } \mu\text{A cm}^{-2}$  for Au, and  $-5 \text{ } \mu\text{A cm}^{-2}$  for Ag. All the electrodeposition experiments, including deposition of PPy film and metal arrays, were carried out by the galvanostatic method. The specific electrodeposition parameters for every sample are listed in the figure captions.

### 2.3 Characterization

The morphologies of the as-prepared gold and silver micro/nanostructured arrays were investigated by using a field-emission scanning electronic microscope (FE-SEM, Sirion 200) operated at an acceleration voltage of 10 kV. The Raman spectra were carried out on a confocal microprobe Raman spectrometer (Renishaw inVia Reflex) with a laser beam of 633 nm wavelength and 0.85 mW. A 50x microscope objective was used to focus the laser beam onto a round spot of ca.  $14 \text{ } \mu\text{m}$  in diameter. The integration time was 10 s for each spectrum. Before Raman spectral examination, the samples were immersed in  $10^{-6} \text{ mol L}^{-1}$  rhodamine 6G (R6G) aqueous solutions for 15 min, rinsed with deionized water for several times, and then dried in air.

### 3. Results and Discussion

#### 3.1 Hierarchically micro/nanostructured arrays

Fig. 1 schematically illustrates the main fabrication process of the hierarchically micro/nanostructured arrays. The PS colloidal monolayer was used as the first template. By following electrodeposition of the PPy film and the removal of the PS spheres, the PPy through-pore secondary template was obtained. Herein, the electropolymerized PPy film is used to regulate the interface electroconductivity of electrode. Finally, through choosing the appropriate electrolyte, deposition current density and duration, various metal micro/nanostructured arrays can be synthesized.

According to the fabrication strategy shown in Fig. 1, on the basis of the PS colloidal monolayer and the PPy hexagonally ordered through-pore templates, the gold and silver hierarchically micro/nanostructured arrays were successfully synthesized by further electrodeposition in the corresponding electrolyte. Fig. 2 and Fig. 3 are their typical FESEM images, clearly exhibiting the microscaled units packed in hexagonal pattern, and the period is 2  $\mu\text{m}$ , which is inherited from the as-chosen PS colloidal monolayer template.

Fig. 2 shows the FESEM images of the gold hierarchically micro/nanostructured arrays electrodeposited at  $-25 \mu\text{A cm}^{-2}$  for different times based on the PPy through-pore template (schematically described in Fig. 1e). By electrodeposition for a relatively long time, such as 90 min, from the local magnified image (see the inset in Fig. 2a), we can clearly see the hierarchically micro/nanostructures. The microscaled building unit looks like a flower, which is composed of the rod-like or plate-like nanostructures. Such nanostructures having sharp edges and a lot of nanogaps can dramatically enhance SERS activity of the substrate.



Shortening the deposition time, as shown in Fig. 2c and 2d, the roughness of the hierarchical structure is gradually reduced, while the size of the microscale building cell also becomes smaller.

If choosing the electrolyte contain of  $\text{AgNO}_3$  solution, under an appropriate current density (*e.g.*  $-5 \mu\text{A cm}^{-2}$ ), after optimization of the deposition time (180 min), the silver micro/nanostructured ordered array composed of plate-like nanostructures was obtained, as shown in Fig. 3a and 3b. From the side-view FESEM image in the inset of Fig. 3c, it is obvious that the microstructure unit is approximatively hemispherical. The bottom contact area is correlated with the heat treatment between PS spheres and Au-substrate, and also with the electrodeposition time of PPy thin layer. Fig. 3f shows the structure after deposition for 1 hour, the size of the microscaled building unit becomes smaller, and the nanostructures changed to quasi spherical nanoparticles. To obtain the optimal enhanced Raman active substrate, it should usually choose the plate-like structure with more nanogaps for enhanced “hot spots”.

Above all, using the PS colloidal monolayer as the first template and the PPy through-pore thin film as the secondary template, further electrodeposition of metal can effectively keep the hexagonally periodic pattern. The sizes, morphologies and structures of the arrays are easy to be adjusted by effectively controlling the electrocrystallization process. Through choosing different diameters of the PS spheres and changing the deposition time, the interval distances of micro-structure units could be regulated. Compared to the reported invisible template,<sup>11</sup> this PPy through-pore template can realize a wider range of potential regulation, and thus more metal micro/nanostructured arrays can be prepared.

Comparing the micro- and nano-structures of gold and silver periodic arrays deposited for different times (see Fig. 2 and 3), we can find their growth processes are similar. With increasing the deposition time, the microscaled building unit gradually becomes bigger, and the hierarchical structures become more and more obvious. From the hexagonally packed pattern of the as-prepared gold and silver arrays, we can know the PPy through-pore template played an effective spatial confinement effect in the electrodeposition processes. This is also related to the deposition current density. Under a relatively low current density, in the initial stage, the nucleation preferentially occurs at the better conductive positions of the electrode surface,<sup>11</sup> where are the through-pore locations not covered with PPy thin film, that is also where the PS spheres contacted with the Au-substrate. In the later stage, growth will dominate the electrodeposition process, due to a low deposition current density. As is reported, gold and silver are easy to grow into a nanoplate-built flower-like structure.<sup>9,15,16</sup>

It should be mentioned that, the preparation of the working electrode is very important. The Ti layer deposited between the gold film and the Si substrate is essential to promote adhesion, to prevent the gold film detached from Si surface in the electrodeposition process. In addition, the heat treatment is necessary to create an area contact between the PS spheres and the Au-substrate, which is important for the subsequent formation of PPy through-pore array and create the localized area for the electrodeposition of the metal.

### 3.2 SERS performance

As described above, the as-prepared gold and silver micro/nanostructured arrays with sharp edge or nanogaps, are considered as excellent candidate substrates for SERS applications. Herein, we chose rhodamin 6G (R6G) molecules as probe molecules to study the SERS

performances of the as-prepared substrates. Fig. 4 gives the Raman spectra of the Au and Ag hierarchically micro/nanostructured arrays without any treatment (black curves), and the SERS spectra of R6G molecules absorbed on them (red curves). From these curves, we can find that after absorbing R6G molecules, the SERS spectra are almost not changed, remaining very similar with the Raman spectra directly obtained from the substrates. The obvious peaks mainly appears at  $930\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ , and between  $1000 - 1150\text{ cm}^{-1}$ ,  $1300 - 1400\text{ cm}^{-1}$  also found two obvious bands. Compared to the characteristic vibration peaks of R6G molecules reported in literatures,<sup>17,18</sup> these peaks are clearly not belong to R6G molecules. On the contrary, it is consistent with the Raman spectra of the PPy film. The peak at  $930\text{ cm}^{-1}$  is related to the doping ions, the peak at  $1600\text{ cm}^{-1}$  come from backbone stretching of C=C bonds, and the detail value is related to the electrical conductivity of the PPy film.<sup>19</sup> The double peak at  $1050\text{ cm}^{-1}$  and  $1080\text{ cm}^{-1}$  are assigned to C-H in plane deformation, and  $1320\text{ cm}^{-1}$  and  $1380\text{ cm}^{-1}$  are assigned to the ring stretch mode.<sup>20</sup> These results proved that the PPy through-pore thin film was truly existed, though it is difficult to see on electron microscopy. As it made a great interference on the identification of the target molecules, the as-prepared Au and Ag hierarchically micro/nanostructured arrays are need to be further cleaned before using as SERS active substrates.

As mentioned above, a certain thickness of the PPy through-pore film can be synthesized by electrochemical deposition on Au-substrate, and used as the secondary template for the following deposition of noble metal micro/nanostructured arrays. Further, the Raman experiment results show that the PPy film has strong Raman peak (as shown in Fig. 4) that easily cover up the characteristic Raman peaks of the target molecules, and seriously interfere

the accurate recognition. Thus, how to eliminate this influence or completely remove the PPy film before use as SERS active substrates are the key to the SERS-based application. Here, the electropolymerized PPy film is hard to dissolve in common solvents. According to the reference,<sup>21</sup> heat treatment at 250 °C for a certain time can effectively remove the PPy film. We also conducted the experiments to investigate the effectiveness. Fig. 5 shows the FESEM images of the Au and Ag periodic arrays (the corresponding original morphologies are shown in Fig. 2c and Fig. 3c) after heat treatment at 250 °C for 24 h. We can see that the hierarchical structures of the Au and Ag arrays had been badly damaged. The flower-like Au hierarchically rough microstructures are melted to some particles. The hemispherical Ag hierarchical microstructures are changed to various shapes. These variations make the periodic arrays irregular, and reduce the structure consistency. As the SERS activity is closely related with the surface micro/nanostructures, the SERS activity and uniformity should be affected. The experimental results have proved this point, as shown in Fig. 6. After high temperature treatment, the distinct characteristic Raman peaks of R6G molecules were detected on the Au and Ag micro/nanostructured arrays, which also mean that the heat treatment can effectively eliminate the interference from PPy film. However, we can also see the Raman intensities measured at different points of the same substrate are obviously different, meaning such arrays are not suitable for using as high-quality SERS substrates. In short, PPy through-pore template method, can adjust the deposition potential in a wide range, and through this method a variety of metals such as gold and silver ordered array could be synthesized, but eliminating the influence of PPy film on the target molecule is still a big difficulty for SERS-based detection application.

From above, we knew the heat treatment to remove the PPy film is not a good way to obtain high-quality SERS substrates. As we know, physical deposition techniques, such as the ion-sputtering deposition, seldom introduce other impurities in the process of the deposited metal. Correspondingly, the surface of the deposited metal film is relatively clean. Therefore, in order to better solve the interference problem from PPy film on target molecular recognition, we further put forward a gold-covering strategy, that is sputtering deposition of a certain thickness of gold layer on the micro/nanostructured array to cover the Raman peaks of the PPy film. Fig. 7a shows the SERS spectra of R6G molecules adsorbed on the Au micro/nanostructured array which have been coated a gold layer in ~60 nm thickness by ion-sputtering deposition method. We can see the Raman peak of PPy film is obviously decreased, and the characteristic Raman peaks of R6G molecules are very clear and strong. In addition, we obtained five SERS spectra from five different points randomly chosen on sample surface, as shown in Fig. S1. These spectra have very small differences in intensities (with the measurement errors of 12% for Au-based sample and 10% for Ag-based sample), demonstrating that the gold-covering strategy will not destroy the uniformity of the substrates. Comparing to the high temperature heat treatment, this strategy can not only eliminate the interference from PPy film while keeping the substrate good uniformity, but also enhance the substrate SERS activity. The experiment on the Ag micro/nanostructured array also confirmed it, as shown in Fig. 7b and Fig. S2. These results proved that the as-prepared gold and silver hierarchically micro/nanostructured arrays after coating of gold layer can be used as uniform SERS substrates. To further know these substrates' activities, we roughly estimated the enhancement factor is in the  $10^8$  orders of magnitude according to the method in literature.<sup>22</sup>

The detection limitation of R6G can be to  $10^{-11}$  mol L<sup>-1</sup> when immersing the substrate in R6G solution for long time (such as 2 hours) and the long Raman integration time (20s).

#### 4. Conclusion

In conclusion, we proposed a PPy through-pore secondary template strategy based on colloidal monolayer, and successfully synthesized the large-area periodic gold, silver hierarchically micro/nanostructured arrays. The electropolymerized PPy through-pore array film was used to regulate the interface electroconductivity of the electrode and to control the subsequent localized electrocrystallization process. These as-synthesized hierarchically micro/nanostructured arrays can be used as SERS substrates after surface covering of a gold layer to overcome the interference from the PPy film to the target molecules for recognition of Raman spectra.

#### Acknowledgements

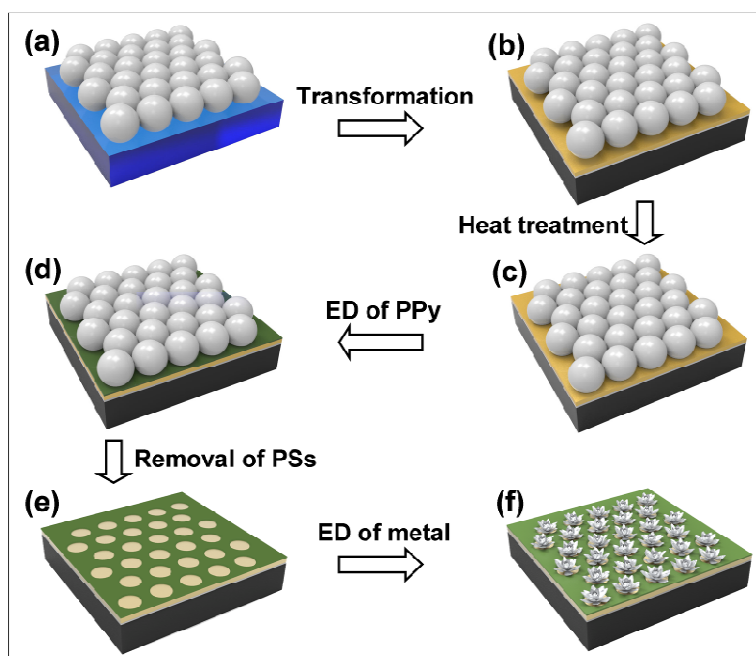
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## References

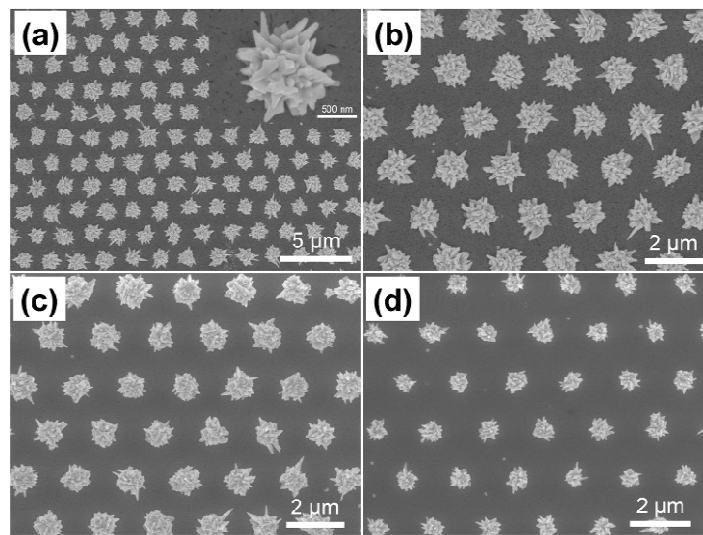
- 1 G. Duan, W. Cai, Y. Luo, Y. Li and Y. Lei, *Appl. Phys. Lett.*, 2006, **89**, 181918.
- 2 P. M. Tessier, O. D. Velev, A. T. Kalambur, J. F. Rabolt, A. M. Lenhoff and E. W. Kaler, *J. Am. Chem. Soc.*, 2000, **122**, 9554-9555.
- 3 G. Liu, W. Cai, L. Kong, G. Duan, Y. Li, J. Wang and Z. Cheng, *J. Hazard. Mater.*, 2013, **248**, 435-441.
- 4 H. C. Jeon, T. Y. Jeon, T. S. Shim and S. M. Yang, *Small*, 2014, **10**, 1490-1494.
- 5 Y. Li, X. J. Huang, S. H. Heo, C. C. Li, Y. K. Choi, W. P. Cai and S. O. Cho, *Langmuir*, 2007, **23**, 2169-2174.
- 6 Y. Li, N. Koshizaki, H. Wang and Y. Shimizu, *ACS Nano*, 2011, **5**, 9403-9412.
- 7 Y. Li, T. Sasaki, Y. Shimizu and N. Koshizaki, *Small*, 2008, **4**, 2286-2291.
- 8 Y. Li, G. Duan, G. Liu and W. Cai, *Chem. Soc. Rev.*, 2013, **42**, 3614-3627.
- 9 G. Liu, W. Cai, L. Kong, G. Duan, Y. Li, J. Wang, G. Zuo and Z. Cheng, *J. Mater. Chem.*, 2012, **22**, 3177-3184.
- 10 J. Wang, G. Duan, G. Liu, Y. Li, Z. Dai, H. Zhang and W. Cai, *J. Mater. Chem.*, 2011, **21**, 8816-8821.
- 11 J. Wang, G. Duan, Y. Li, G. Liu, Z. Dai, H. Zhang and W. Cai, *Langmuir*, 2013, **29**, 3512-3517.
- 12 Z. Dai, Y. Li, G. Duan, L. Jia and W. Cai, *ACS Nano*, 2012, **6**, 6706-6716.
- 13 F. Sun, W. Cai, Y. Li, B. Cao, F. Lu, G. Duan and L. Zhang, *Adv. Mater.*, 2004, **16**, 1116-1121.
- 14 J. Wang, G. Duan, Y. Li, G. Liu and W. Cai, *ACS Appl. Mater. Interfaces*, 2014, **6**,

- 9207-9213.
- 15 S. J. Guo, L. Wang and E. K. Wang, *Chem. Commun.*, 2007, 3163-3165.
- 16 L. Wang, S. Guo, X. Hu and S. Dong, *Electrochem. Commun.*, 2008, **10**, 95-99.
- 17 P. Hildebrandt and M. Stockburger, *J. Phys. Chem.*, 1984, **88**, 5935-5944.
- 18 A. Weiss and G. Haran, *J. Phys. Chem. B*, 2001, **105**, 12348-12354.
- 19 Y. Liu, *J. Electroanal. Chem.*, 2004, **571**, 255-264.
- 20 X. Wan, X. Liu, G. Xue, L. Jiang and J. Hao, *Polymer*, 1999, **40**, 4907-4914.
- 21 M. A. Ghanem, P. N. Bartlett, P. Groot and A. Zhukov, *Electrochem. Commun.*, 2004, **6**, 447-453.
- 22 E. C. Le Ru, E. Blackie, M. Meyer, P. G. Etchegoin, *J. Phys. Chem. C*, 2007, **111**, 13794.

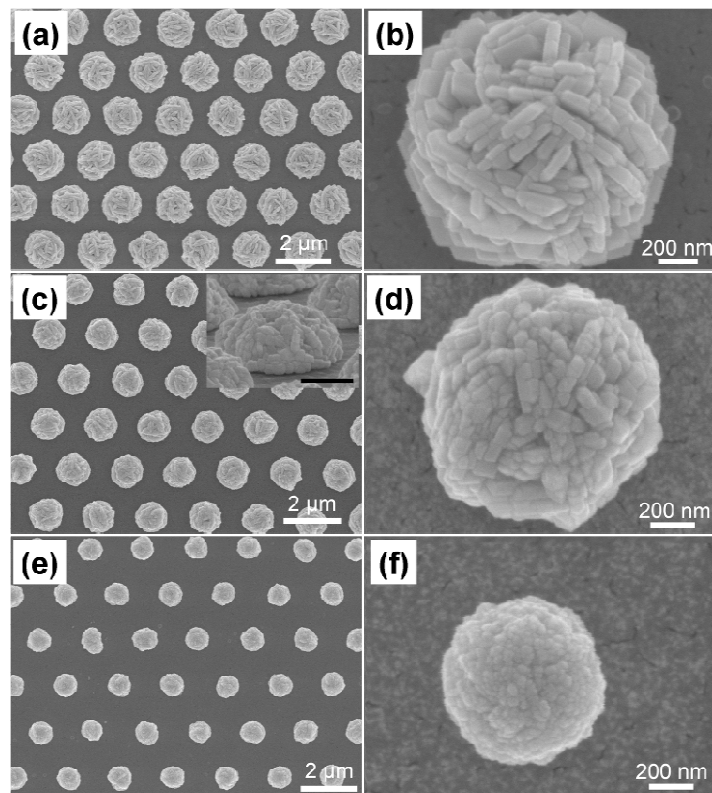


Fig. 1 Jingjing Wang *et al*

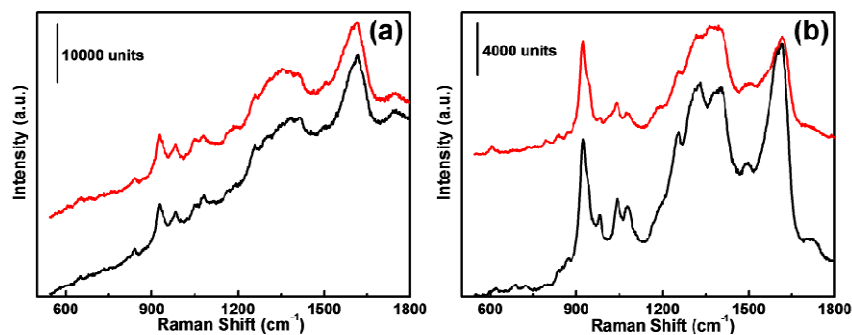
**Fig. 1** Schematic illustration of the fabrication process of the hierarchically micro/nanostructured arrays. (a) Large-area PS monolayer colloidal crystal on a glass slide prepared by an interface self-assembly method. (b) PS colloidal monolayer on an Au-substrate (*i.e.*, Au/Ti/Si substrate) transferred from the glass slide by a floating method. (c) PS monolayer becomes firm (area) contact with the Au-substrate after heat treatment. (d) PPy thin layer is electrodeposited on the heated PS/Au-substrate. (e) PPy through-pore array is formed after removal of PS spheres. (f) Hierarchically micro/nanostructured array is electrodeposited on the PPy through-pore template.

**Fig. 2** Jingjing Wang *et al*

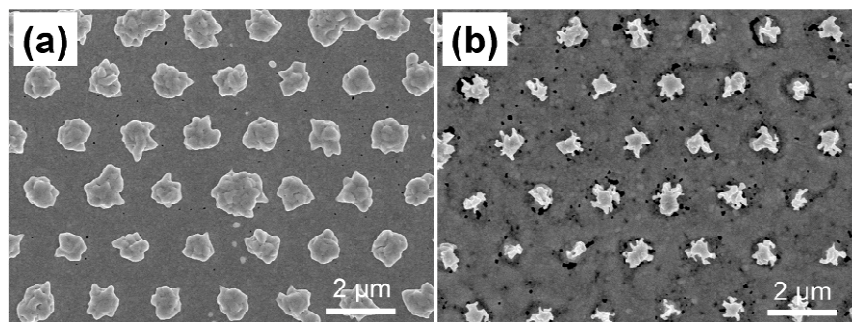
**Fig. 2** FESEM images of Au hierarchically micro/nanostructured arrays electrodeposited at  $-25 \mu\text{A cm}^{-2}$  for different times based on the PPy through-pore template. The deposition times are: (a, b) 90 min; (c) 60 min; (d) 30 min, respectively. The inset in (a) is the corresponding local magnification of (a), and (b), (c), (d) are in the same magnification.

**Fig. 3** Jingjing Wang *et al*

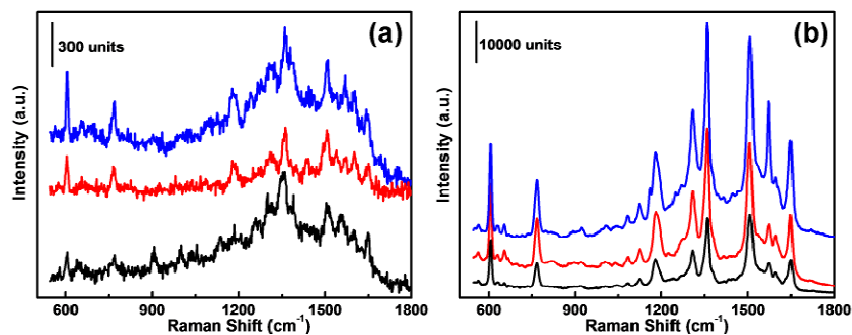
**Fig. 3** FESEM images of Ag hierarchically micro/nanostructured arrays electrodeposited at  $-5 \mu\text{A cm}^{-2}$  for different times based on the PPy through-pore template. The deposition times are: (a, b) 180 min; (c, d) 90 min; (e, f) 60 min, respectively. (b), (d) and (f) are the corresponding local magnification FESEM images of (a), (c) and (e). The inset in (c) is the corresponding side-view FESEM image of (c), and the scale bar is 500 nm.

Fig. 4 Jingjing Wang *et al*

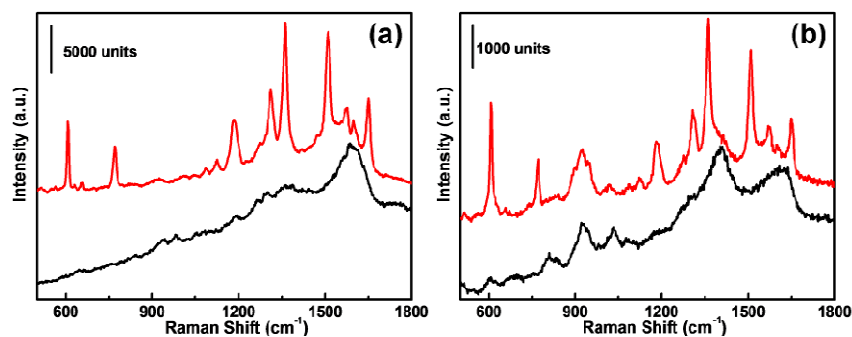
**Fig. 4** Raman spectra of R6G molecules before (black curve) and after (red curve) absorbed on the Au (a) and Ag (b) hierarchically micro/nanostructured arrays without any treatment. The as-used Au sample and Ag sample were shown in Fig. 2c and Fig. 3c. The Raman test conditions are respectively, laser wavelength: 633 nm, laser power: 0.85mW, integration time: 10 s.

**Fig. 5** Jingjing Wang *et al*

**Fig. 5** FESEM images of (a) Au and (b) Ag hierarchically micro/nanostructured arrays after annealed at 250 °C for 24 h. The corresponding original morphologies are shown in Fig. 2c and Fig. 3c, respectively.

Fig. 6 Jingjing Wang *et al*

**Fig. 6** Raman spectra of R6G molecules absorbed on the annealed Au substrate and Ag substrate. The corresponding morphologies are shown in Fig. 5a and 5b, respectively. The three curves in (a) and (b) were measured at different points. The Raman test conditions are respectively, laser wavelength: 633 nm, laser power: 0.85mW, integration time: 10 s.

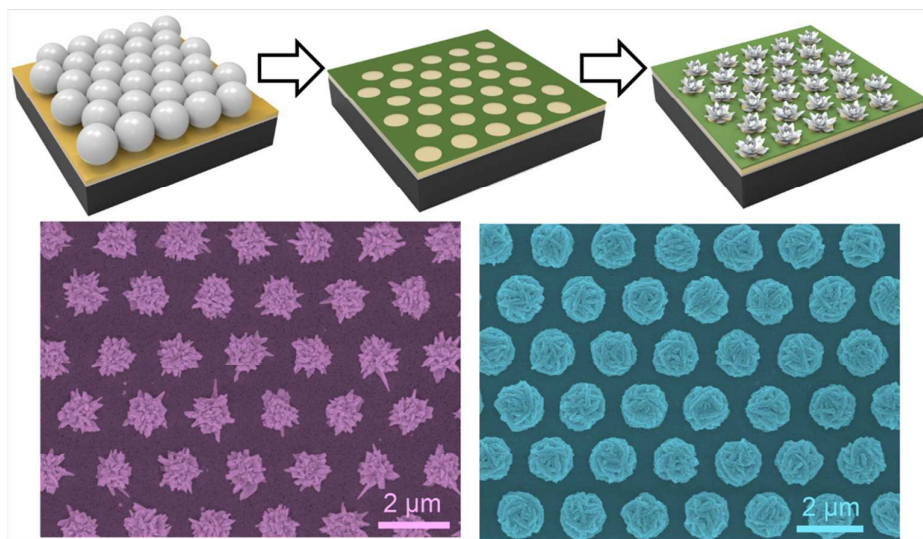
Fig. 7 Jingjing Wang *et al*

**Fig. 7** Raman spectra of R6G molecules before (below black curve) and after (upper red curve) absorbed on (a) Au and (b) Ag hierarchically micro/nanostructured arrays after surface coating of ~60 nm Au film. The Raman test conditions are respectively, laser wavelength: 633 nm, laser power: 0.85mW, integration time: 10 s.





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A method based on polypyrrole through-pore template induced by the colloidal monolayer is developed to fabricate gold and silver hierarchically micro/nanostructured arrays.