Electronic Supplementary Material (ESI) for RSC Advances

In situ controlled growth of well-dispersed Au nanoparticles inside the channels of SBA-15 using a simple, bio-inspired method for surface-enhanced Raman spectroscopy

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Experimental Methods

Synthesis of parent hexagonal lamelliform SBA-15 microplates:

The parent SBA-15 microplates was synthesized following a procedure in the literature.[1] In a typical synthesis, the procedures began with dissolving P123 (2.0 g) in a HCl solution (75 ml, 2.0 M) at 45 °C under the stirring rate at 200 r/min. When a homogenous solution formed, tetraethyl orthosilicate (TEOS) (4.3 g) was added into the reaction container dropwise at 45 °C for 24 h. Subsequently, the resultant mixture was hydrothermally aged without stirring at 110 °C for 24 h. The products were filtered and washed with distilled water and then dried at 100 °C for 12 h.

Protection of outer surfaces of SBA-15 microplates:

The as-synthesized parent SBA-15 (0.2 g) was dispersed in dry toluene (20 mL) at 80 °C under flowing N_2, then $(CH_3)_3SiCl$ (TMCS) (1 ml) was added dropwise under stirring and kept stirring overnight. The mixture was filtered with toluene followed by drying in vacuum at 80 °C for 10 h. After modification of the outer surfaces, the surfactant template was removed from the channels by solvent extraction using ethanol refluxing under stirring for 24 h. The SBA-15 with outer surfaces protected by the $–Si(CH_3)_3$ groups (TMCS-SBA-15) was obtained.

Growth of Au nanoparticles inside the channels of TMCS-SBA-15 microplates:

Firstly, the pore surfaces of the outer surface protected TMCS-SBA-15 microplates were grafted with dopamine. Briefly, 200 mg of TMCS-SBA-15 and 200 mg dopamine hydrochloride were dissolved in 50 ml Tris-buffer (pH 8.5) solution, and allowed to proceed for 12 h at room temperature under stirring. The products DPA-TMCS-SBA-15 were washed with ethanol and water several times and dried for further use. Secondly, 200 mg of DPA-TMCS-SBA-15 was added to 60 ml 0.1 mg/ml $HAuCl_4$ solution and allowed to proceed for 12 h at room temperature under stirring. The product of Au nanoparticles inside the channels only (Au-DPA-TMCS-SBA-15) was collected and washed with water and ethanol several times and dispersed into the anhydrous ethanol solution.

Growth of Au nanoparticles on the outer surfaces of SBA-15 microplates:

In order to obtain Au nanoparticles just dispersed on the outer surfaces of SBA-15, 200 mg parent SBA-15 microplates were added into the solution of 200 mg dopamine hydrochloride dissolved in 50 ml Tris-buffer (pH 8.5) and allowed to proceed for 12 h at room temperature under stirring. The product of dopamine on the outer surfaces of SBA-15 microplates (DPA-Template-SBA-15) were washed with ethanol and water several times and dried for further use. Secondly, 200 mg of

DPA-Template-SBA-15 was added to 60 ml 0.1 mg/ml $HAuCl_4$ solution and allowed to proceed for 12 h at room temperature under stirring. The product of (Au(O)-DPA-SBA-15) was collected and washed with water and ethanol several times and dispersed into the anhydrous ethanol solution.

Growth of Au nanoparticles on the outer surfaces and inside the channels of SBA-15 microplates:

In order to obtain Au nanoparticles dispersed on the outer surfaces and inside the channels of SBA-15, 200 mg surfactant template removed SBA-15 microplates were added into the solution of 200 mg dopamine hydrochloride dissolved in 50 ml Tris-buffer (pH 8.5) and allowed to proceed for 12 h at room temperature under stirring. The product DPA-SBA-15 were washed with ethanol and water several times and dried for further use. Secondly, a 200 mg DPA-SBA-15 was added to 60 ml 0.1 mg/ml $HAuCl_4$ solution and allowed to proceed for 12 h at room temperature under stirring. The product of (Au(O+I)-DPA-SBA-15) was collected and washed with water and ethanol several times and dispersed into the anhydrous ethanol solution.

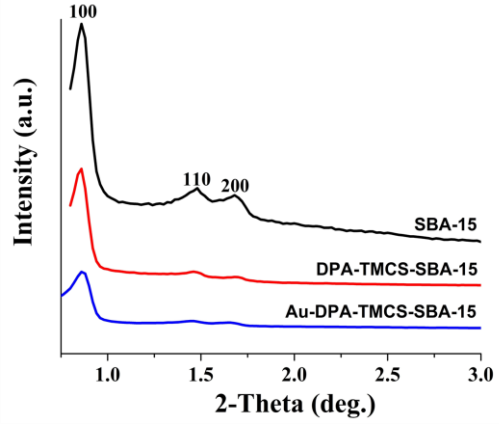

Fig. S1. Small-angle XRD patterns of the parent SBA-15 (SBA-15), dopamine grafted inner surfaces of the outer surface protected SBA-15 (DPA-TMCS-SBA-15), and Au nanoparticles just dispersed inside the channels of SBA-15 (Au-DPA-TMCS-SBA-15).

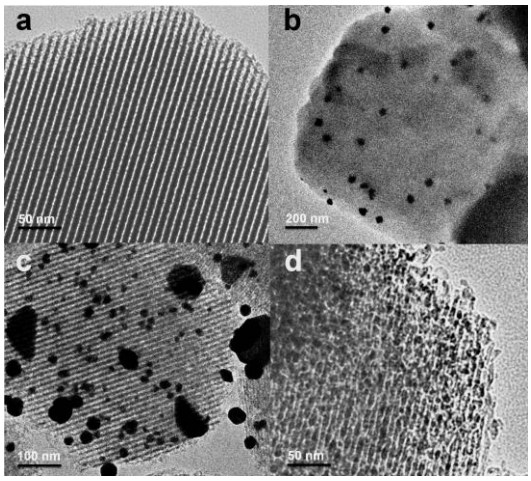

Fig. S2. The TEM images of (a) the parent SBA-15 (SBA-15), (b) Au nanoparticles just dispersed on the outer surfaces of SBA-15 (Au(O)-DPA-SBA-15), (c) Au nanoparticles dispersed on the outer surfaces and inside the channels of SBA-15 (Au(O+I)-DPA-SBA-15), and (d) Au nanoparticles just dispersed inside the channels of SBA-15 (Au-DPA-TMCS-SBA-15).

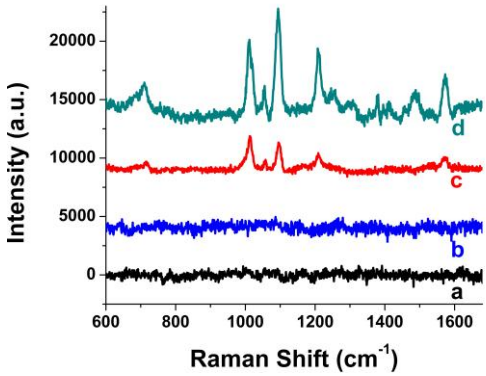

Fig. S3. SERS spectra of 1×10^{-5} M 4-Mpy aqueous solution drop-casted on to the powders of different SBA-15 samples on silicon substrates, including (a) the parent SBA-15; (b) Au nanoparticles just dispersed on the outer surfaces of SBA-15 (Au(O)-DPA-SBA-15), (c) Au nanoparticles dispersed on the outer surfaces and inside the channels of SBA-15 (Au(O+I)-DPA-SBA-15, and (d) Au nanoparticles just dispersed inside the channels of SBA-15 (Au-DPA-TMCS-SBA-15).

References

1. Y. H. Zhu, H. Li, J. Q. Xu, H. Yuan, J. J. Wang, X. X. Li, *CrystEngComm*, 2011, **13**, 402.