SUPPORTING INFORMATION

Ultrasensitive surface-enhanced Raman scattering detection of urea by highly ordered Au/Cu hybrid nanostructure arrays

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Materials and methods

The porous AAO templates used in this work were fabricated by employing a well-known twostep anodization process.¹ The starting material used is 0.5 mm thick aluminum foil with ultrahigh purity (99.999%). The thickness of the walls and the diameter of the nanochannels are about 40 and 20 nm, respectively. By simply immersing the AAO templates in a 5 % H₃PO4 for a certain amount of time, the diameter of the nanochannels can be easily adjusted. In this work, 15 mins of immersion time was used to make the diameter of the nanochannels around 45 nm. The Cu nanorod arrays were made using an aqueous bath containing 0.2 M CuSO₄, 0.1 M H₂SO₄ and 0.1 M H₃BO₃. The pH of the solution was about 4.5. The electrodepostion of Cu was carried out at a constant potential of 0.1 V (vs Ag/AgCl) at room temperature. A platinum wire was used as the counter electrode. By controlling the charged passed, the length of the nanorods can be adjusted. According to previous research, 200 nm is thought to be the optimal length for metal nanorods to generate the highest SERS signal, and the SERS intensity diminishes at lengths longer than this.¹² This is so because with increasing the length of the nanorod up to 200 nm, the total surface area continues to increase, thus significantly enhancing the SERS intensity. However, when the length is longer than 200 nm, the electromagnetic field generated at the bottom of the metal nanorods becomes negligible. Further increasing the length of the nanorods also leads to disorder in the nanostructure. Therefore, the length of Cu nanorods in the present experiments was adjusted to around 200 nm. When the electro-deposition was done, the samples were cleaned with deionized water and ethanol. After that, a very thick layer of copper was deposited on the backside of the samples to prevent the Cu nanorods from disintegrating after the full removal of the AAO membrane. Finally, the samples were immersed in 5% H₃PO₄ at 30°C for 2h to completely remove the AAO membrane. A Q-150TS sputtering machine was employed to coat Au nanoparticles on top of the Cu nanorod arrays. By controlling the sputtering coating time, the gap size between neighbouring nanorods was effectively adjusted. All chemical reagents used in this study were of analytical grade and were supplied by Sigma-Aldrich (Australia).

The structure and morphology of the samples were characterized by scanning electron microscopy (SEM, Nova 450), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD, BRUKER D8-ADVANCE PXRD) and transmission electron microscopy (TEM, Tecnai T20), The SERS measurements were conducted using urea as the analyte. Following the literature methodology, 10 ul of the analyte of different concentrations was dropped on the surface of the Au/Cu hybrid nanostructure arrays.² Then the substrates were put in the oven at 50°C for 20 mins to dry the substrates prior to the SERS measurement. A confocal Raman spectrometer (RENISHAW Invia Raman Microscope) was employed to detect the SERS spectra. All the Raman spectra were collected from a 1 μ m² area of the samples excited at 532 nm with a laser power of 1.7 mW. The exposure time for urea detection was 10 s.



Fig. S1 SEM images of AAO membranes prepared in sulfuric acid electrolyte with different

pore sizes.







Fig. S3 EDS of the Au/Cu hybrid nanorod arrays.



Fig. S4 SERS spectra of pure Cu nanostructured arrays loaded with urea with different concentrations.



Fig. S5 Reusability test of Au/Cu hybrid nanostrucuture arrays by using 0.03 M urea as an analyte. This concentration was chosen because it gives relatively strong signals while all peaks can be observed.



Fig. S6 Raman signal variations under different conditions over time using 0.1 M urea as an analyte. This concentration was chose because it gives relatively strong peaks, which makes it easy for the comparison of the peak intensities.

- 1. J. L. Abell, J. D. Driskell and Y. Zhao, *Chemical Communications*, 2014, **50**, 106-108.
- 2. J. Feng, X. Wu, W. Ma, H. Kuang, L. Xu and C. Xu, Chemical Communications, 2015, 51, 14761-14763.