

## Supplementary Information

### **Hydrophobic AgNPs: *One-step* Synthesis in Aqueous Solution and Its Greatly Enhanced Performance for SERS Detection**

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## **Materials and Methods**

### **Chemicals**

Silver nitrate ( $\text{AgNO}_3$ ) was from Chengdu Chemical Reagent Factory (Chengdu, China). Cetylpyridinium chloride monohydrate (CPC) was obtained from Sigma-Aldrich (St Louis, MO, USA). NaOH and citric acid were from Guangdong Chemical Reagent Engineering Technological Research and Development Center (Guangzhou, China). Petroleum ether (PE), ethanol and dichloromethane were purchased from Chengdu Kelong Chemical Co, Ltd. Rhodamine 6G (R6G) was purchased from Shanghai Chemical industry Park (Shanghai, China). Copper sheet was bought from Shenzhen T2 Red Copper Film Manufacturers (Shenzhen, China). All the chemicals involved in these experiments were of analytical grade and used as received. Deionized water was used in whole experiments.

### **Apparatus**

UV-visible spectra of materials were measured on a Hitachi U-2900 spectrophotometer (Shanghai, China). X-ray diffraction (XRD) measurements were acquired on a Tongda TD-3500 X-ray powder diffractometer (Liaoning, China) with Cu K $\alpha$  radiation in the  $2\theta$  range of  $10^\circ$ - $90^\circ$  with a step size of  $0.05^\circ$ . The Fourier transform infrared (FTIR) spectra were obtained on the Thermo Scientific Nicolet 6700 FT-IR spectrometer (Sugar Land, TX, USA). The transmission electron microscopic (TEM) images of samples were measured on a Tecnai G2 F20 S-TWIN transmission electron microscope (Hillsboro, American) with an accelerating voltage of 300 kV using carbon-coated copper grids. Raman spectra were acquired using a Raman microscope (Oceanoptics Company of American, United States). The structure of o-AgNPs/ $\text{Cu}(\text{OH})_2$  NWs and  $\text{Cu}(\text{OH})_2$  NWs were characterized using FE-SEM, S-4800 (Hitachi, Japan) with an accelerating voltage of 10 kV. The X-ray photoelectron spectra (XPS) were measured on a Kratos AXIS Ultra DLD X-ray Photoelectron Spectroscopy (Kratos, UK) using Mg as the excitation source.

### ***One-step synthesis of hydrophobic AgNPs in aqueous solution***

Typically, 5 mL AgNO<sub>3</sub> (45 mM) was added into the 5 mL CPC (15 mM) aqueous solution, the color of the solution changed from colorless to milky white, After stirring for 30 minutes in dark, 2 mL NaOH (1 M) aqueous solution was added into the above mixture, the color of the solution turned to brown instantly, and then darkened. As the reaction time increasing, a large amount of precipitation was clearly observed in the solution, and the precipitation could then be transferred into upper organic phase with an excellent dispersibility after the addition of petroleum ether into the reaction solution. After separating off the aqueous phase, the o-AgNPs could be obtained by washing with ethanol for three times and dried under vacuum at 35 °C. In addition, o-AgNPs could also be synthesized by using AgCl instead of AgNO<sub>3</sub> as precursor with the same procedure mentioned above.

### **Synthesis of Cu(OH)<sub>2</sub> nanowires**

In this work, Cu(OH)<sub>2</sub>NWs, used as substrate for immobilizing of o-AgNPs, was prepared according to the reported literature.<sup>1</sup> Firstly, a small pieces copper sheet (1.5 cm × 1.5 cm) was cut and ultrasonically washed with acetone, ethanol and water for 10 minutes, respectively. After that, the cleaned copper sheet was further treated with 0.1 M HCl aqueous solution for 1 min to remove the surface oxide layer water, then rinsed with water and dried for further use. The Cu(OH)<sub>2</sub>NWs was prepared by immersing treated copper pieces in an aqueous solution mixture of (NH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (66.5 mM) and NaOH (1.33 M) at room temperature for 4 minutes. After washing with water and drying at nitrogen atmosphere, the hydrophilic Cu(OH)<sub>2</sub> nanowire arrays with vertically growth on copper piece could be obtained successfully.

### **Fabrication of hydrophobic o-AgNPs/Cu(OH)<sub>2</sub>NWs**

The hydrophobic o-AgNPs/Cu(OH)<sub>2</sub>NWs of SERS substrate was prepared by directly dipping Cu(OH)<sub>2</sub>NWs in synthesized o-AgNPs ethanol solution. Briefly, the o-AgNPs ethanol solution (5 mg/mL) was firstly prepared by redispersing synthesized o-AgNPs in ethanol solution. After immersing the synthesized Cu(OH)<sub>2</sub>NWs substrate in the above o-AgNPs ethanol solution for 30 min, the Cu(OH)<sub>2</sub>NWs substrate was then

taken out and dried at nitrogen atmosphere, thus the o-AgNPs could be loaded on the surface of Cu(OH)<sub>2</sub>NWs successfully. After repeating this procedure for several times, the o-AgNPs/Cu(OH)<sub>2</sub>NWs substrate with different amounts of o-AgNPs loading could be obtained.

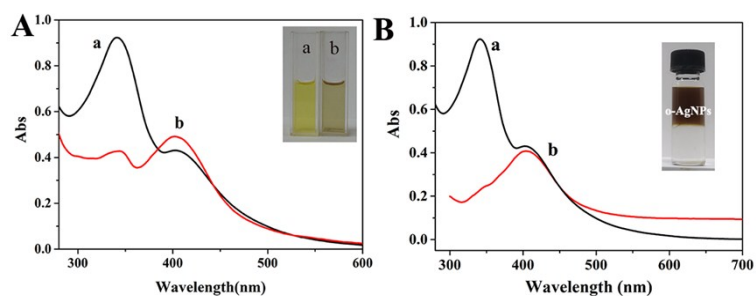
### **SERS test on hydrophobic AgNPs/Cu(OH)<sub>2</sub>NWs**

The SERS properties of constructed o-AgNPs/Cu(OH)<sub>2</sub>NWs was investigated by detecting Rhodamine 6G (R6G) as a mode, which is usually selected as detect target substance to evaluate the performance of SERS substrate. The testing was carried out on a Raman microscope equip a 785 nm diode laser with an 11.3 mW of power and a 40× objective lens. Samples were processed within the range of 200-2000 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup> and the acquisition time of 1 s. All the spectra, unless otherwise stated, were taken at 10 random different points and presented only after baseline and smoothing correction by using the polynomial fitting method with Labspec 6 software.

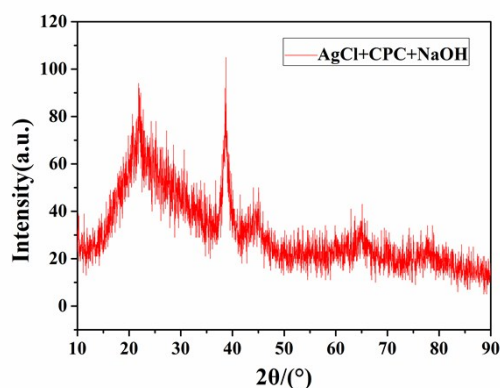
Enhancement factors (EF) for R6G at 1507 cm<sup>-1</sup> was calculated as following equation:

$$EF = \frac{I_{SERS}}{I_{NR}} \times \frac{C_{NR}}{C_{SERS}}$$

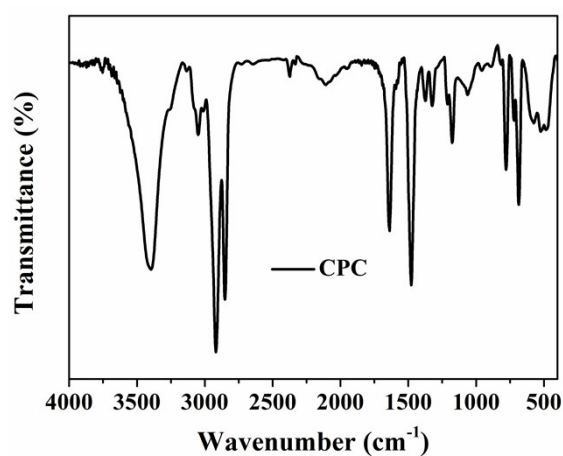
which I<sub>SERS</sub> represents the SERS intensities of the band of 1507 cm<sup>-1</sup> for R6G, I<sub>NR</sub> represents the normal Raman signal for the neat R6G, C<sub>SERS</sub> and C<sub>NR</sub> represent the corresponding concentrations of R6G on o-AgNPs/Cu(OH)<sub>2</sub>NWs and neat R6G.



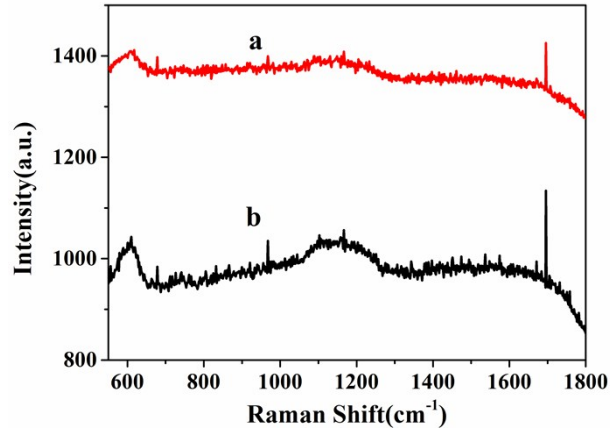
**Fig. S1** (A) The UV-vis spectra of OCDs (**curve a**) and o-AgNPs (**curve b**) dispersed in petroleum ether. Inset: Photographic images of o-AgNPs (**b**) and OCDs (**a**) under daylight. (B) The UV-vis spectra of OCDs (curve a) and o-AgNPs (synthesized under dark, curve b) dispersed in petroleum ether. Inset: photographic images of o-AgNPs dispersed in petroleum ether phase.



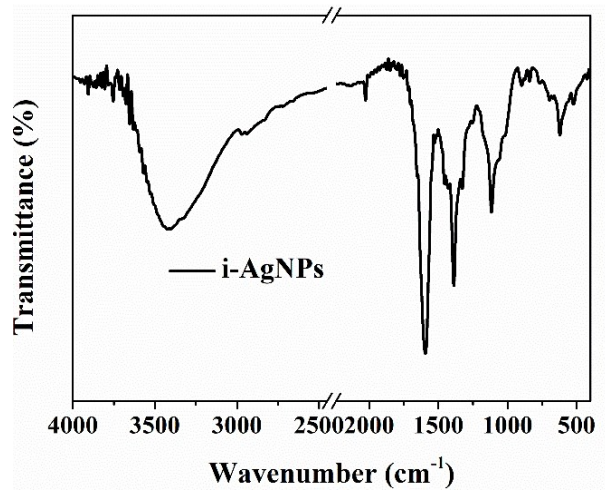
**Fig. S2** The XRD pattern of o-AgNPs synthesized with AgCl as silver precursor.



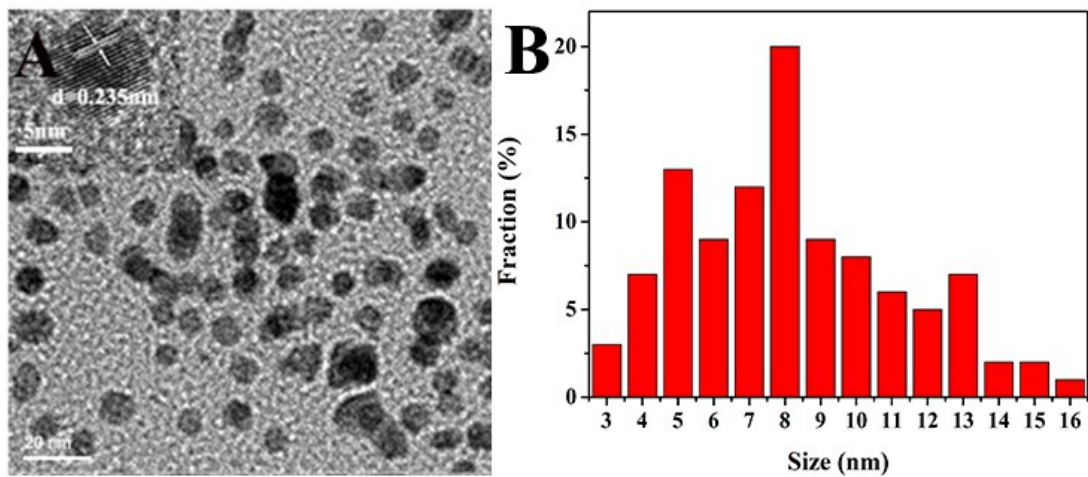
**Fig. S3** The FT-IR spectrum of CPC.



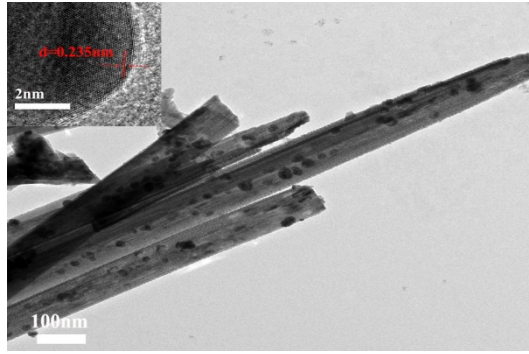
**Fig. S4** The SERS spectra of Cu(OH)<sub>2</sub>NWs (a) and o-AgNPs/Cu(OH)<sub>2</sub>NWs (b).



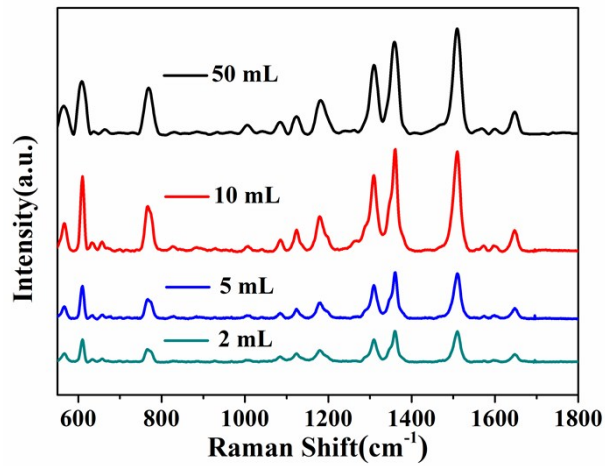
**Fig. S5** The FT-IR spectrum of synthesized i-AgNPs.



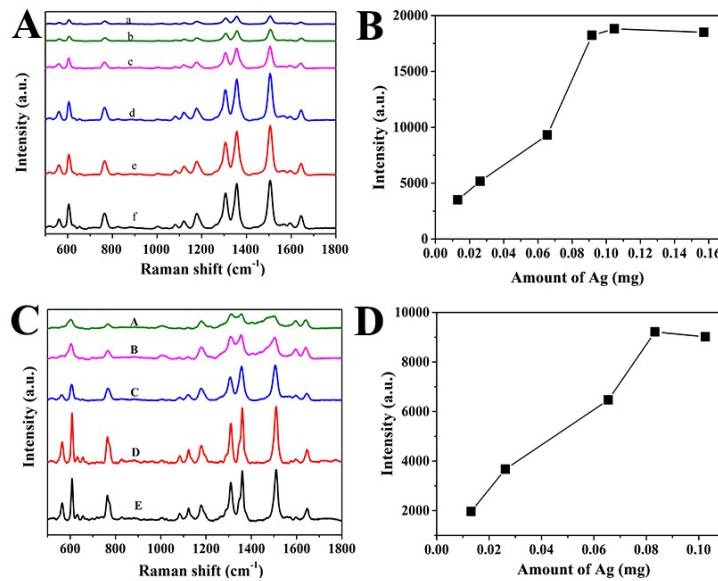
**Fig. S6** The TEM image (A) and size distribution (B) of i-AgNPs.



**Fig. S7** The TEM images of i-AgNPs/Cu(OH)<sub>2</sub>NWs.

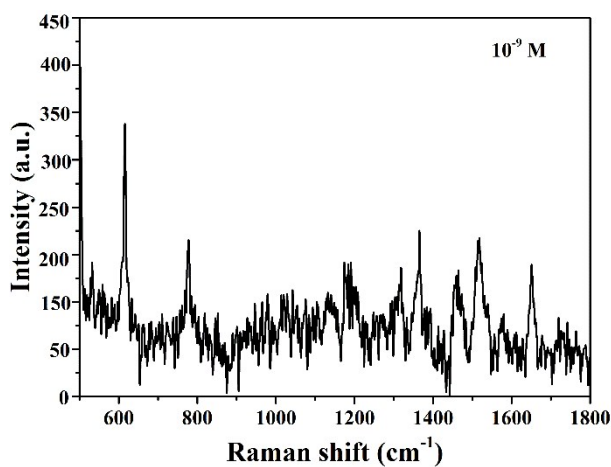


**Fig. S8** The Raman spectra of R6G by immersing o-AgNPs/Cu(OH)<sub>2</sub>NWs substrate in different volume of R6G aqueous solutions (2, 5, 10 and 50 mL).

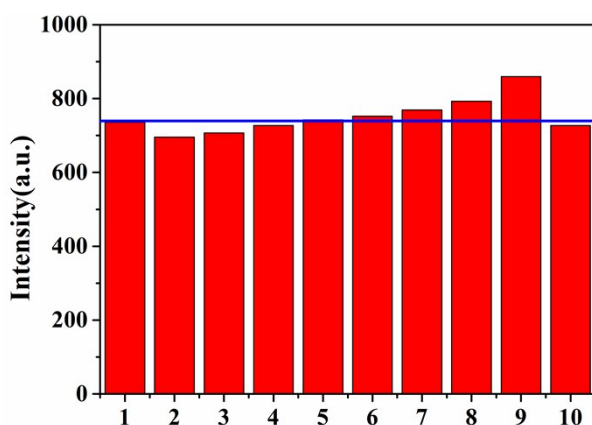


**Fig. S9** The SERS spectra of R6G on the substrates of o-AgNPs/Cu(OH)<sub>2</sub>NWs (A) and i-AgNPs/Cu(OH)<sub>2</sub>NWs (C) with different loading amount of AgNPs, respectively. The Raman

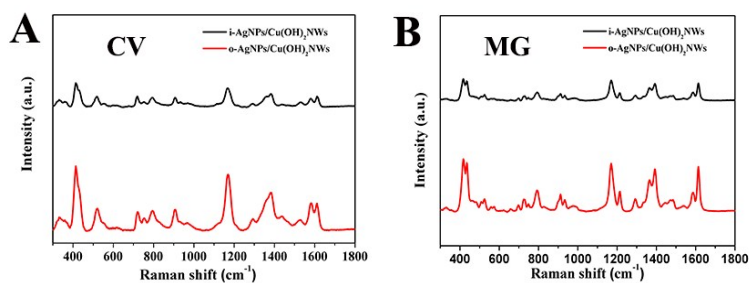
intensity of R6G at  $1507\text{ cm}^{-1}$  as a function of the AgNPs density on o-AgNPs/Cu(OH)<sub>2</sub>NWs (B) and i-AgNPs/Cu(OH)<sub>2</sub>NWs (D), respectively.



**Fig. S10** The SERS spectra of R6G ( $10^{-9}\text{ M}$ ) on the substrates of i-AgNPs/Cu(OH)<sub>2</sub>NWs.



**Fig. S11** Raman intensity of R6G ( $1.0\times 10^{-8}\text{ M}$ ) at  $1507\text{ cm}^{-1}$  acquired from 10 random sites on the o-AgNPs/Cu(OH)<sub>2</sub> NWs SERS substrate.



**Fig. S12** The SERS signals of CV (A) and MG (B) ( $10^{-5}\text{ M}$ ) on the substrates of i-AgNPs/Cu(OH)<sub>2</sub>NWs (black) and o-AgNPs/Cu(OH)<sub>2</sub>NWs (red), respectively.



**Table S1** The amounts of Ag on i-AgNPs/Cu(OH)<sub>2</sub>NWs and o-AgNPs/Cu(OH)<sub>2</sub>NWs measured by ICP-MS.

<b>Substrate (1.5 cm × 1.5 cm)</b>	<b>Concentration of Ag in ethanol solution (ppb)</b>	<b>Amounts of Ag on substrate (mg)</b>
i-AgNPs/Cu(OH) <sub>2</sub> NWs	40.10	0.10
o-AgNPs/Cu(OH) <sub>2</sub> NWs	36.70	0.092

### **References:**

1. M. Ma, K. Djanashvili, W. A. Smith, *Angew. Chem. Int. Ed.* 2016, **55**, 6680-6684.