Fabrication of Au-nanoparticle-Decorated Cu mesh/Cu(OH)$_2$ @HKUST-1 Nanorod Arrays and Their Applications in Surface-Enhanced Raman Scattering

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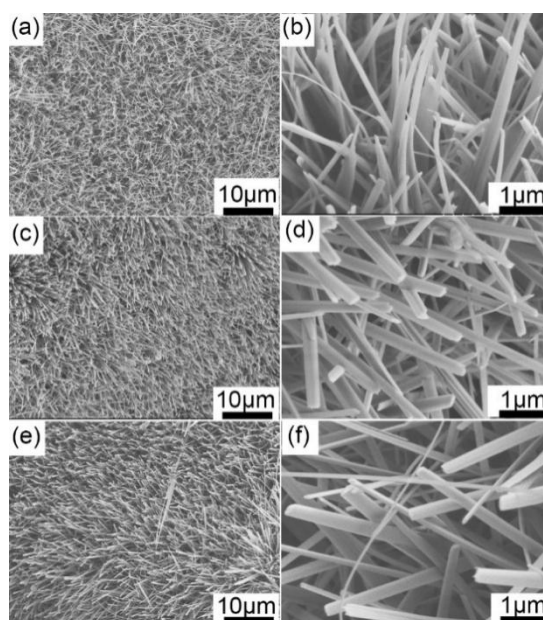
Part I：Figure S1 to S8

Figure S1. SEM images of Cu(OH)$_2$ nanorods prepared under different reaction durations: (a-b) 10 mins; (c-d) 20 mins; (e-f) 30 mins.

Figure S1 is the SEM images of Cu(OH)$_2$ nanorods obtained under different

reaction durations. When the deposition duration is relatively short, such as 10 mins, the $Cu(OH)_2$ nanorods or nanocones with a small diameter were deposited on the surface of the Cu mesh, and they collapsed on top of each other (Figure S1a-b). As the deposition duration increases to 20 mins, a large-area uniform $Cu(OH)_2$ nanorods stand vertically on the surface of the Cu mesh and the length of the $Cu(OH)_2$ nanorods is about 3-4 μm and the diameter of the $Cu(OH)_2$ nanorods is about 150-200 nm (Figure S1c-d). As can be seen from Figure S1e-f, when the deposition duration is further increased to 30 mins, $Cu(OH)_2$ nanorods can grow continuously and produce larger sizes (5-6 μm in length, 200-300 nm in diameter) and denser $Cu(OH)_2$ nanorods.
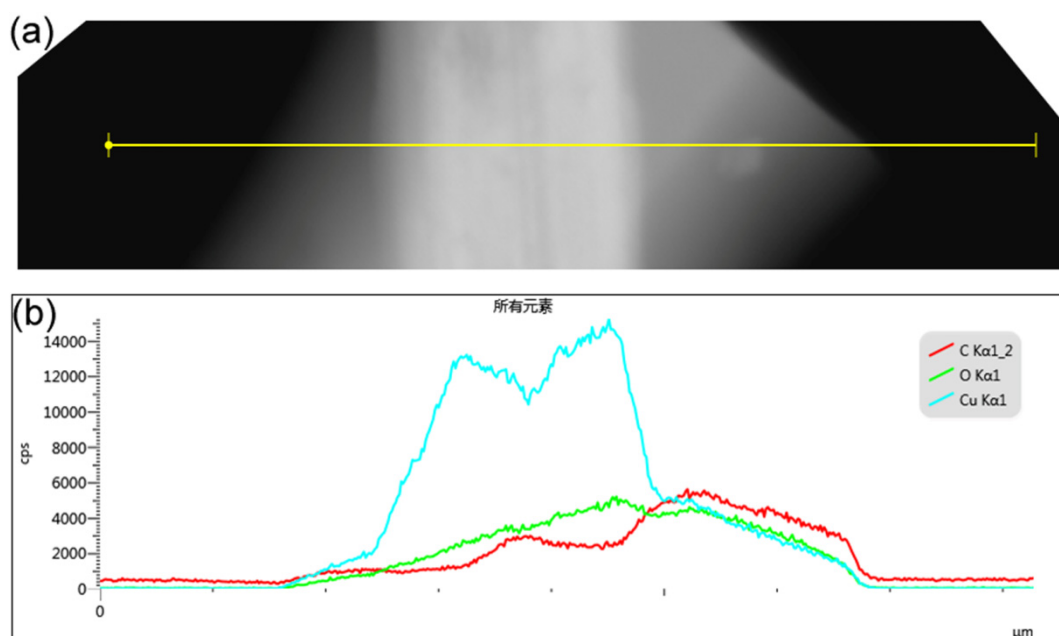

Figure S2. An EDX line on a single $Cu(OH)_2$@HKUST-1 nanorod shown by a yellow line (a) and the resultant compositional profile(b).
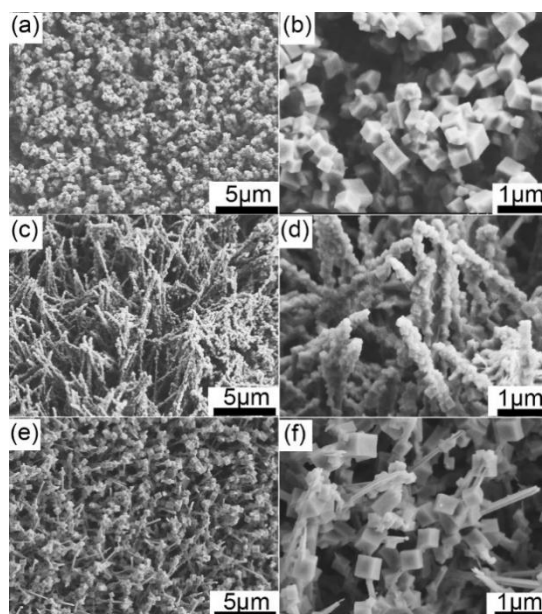
Figure S3. SEM images of Cu mesh/Cu(OH)$_2$ nanorods prepared under different reaction durations: (a-b) 10 mins; (c-d) 20 mins; (e-f) 30 mins.

Figure S3 reveal the morphological evolution of Cu(OH)$_2$@HKUST-1 nanorods obtained by immersing Cu(OH)$_2$ nanorods in the mixed solution of 1,3,5-trimellitic acid and PVP for different deposition duration. Once the Cu(OH)$_2$ nanorods were immersed in the 1,3,5-trimellitic acid solution, the Cu(OH)$_2$ nanorods will react with the 1,3,5-trimellitic acid, and the dissolved Cu ions will combine with the ligand to produce HKUST-1 nanocrystals. As shown in Figure S3a-b, when the reaction duration is 10 mins, it can be observed that a large number of cube-shaped crystals that are stacked on the Cu(OH)$_2$ nanorods to form HKUST-1 nanorods. These high-density nanocubes with a side length of 250 nm are close to each other. With the increase of the deposition duration to 20 mins, the number of the HKUST-1 nanocubes which were only assembled around Cu(OH)$_2$ nanorods was gradually decreasing (Figure S3c-d). When the reaction duration is further extended to 30 mins, the number of HKUST-1 nanocubes is further reduced, and only a small amount of HKUST-1 nanocubes were attached to the surface of the Cu(OH)$_2$ nanorods (Figure S3e-f). This phenomenon may be attributed to etching of 1,3,5-trimellitic acid continuously, which causes the HKUST-1 nanocubes to continuously fall off.
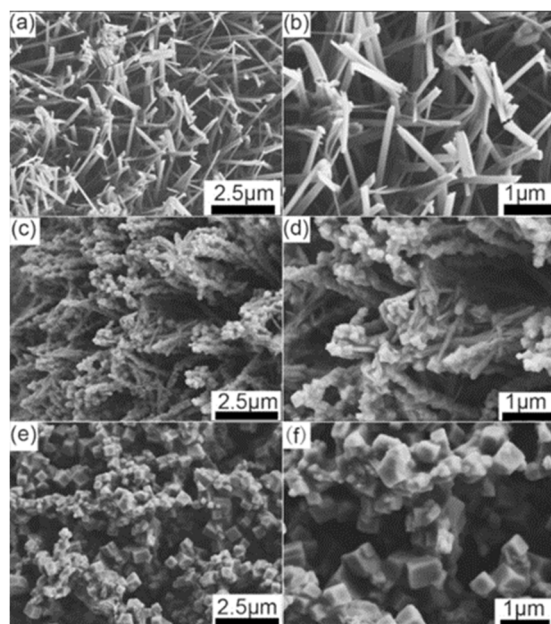
Figure S4. SEM images of Cu mesh/Cu(OH)$_2$@HKUST-1 nanorods prepared with different concentrations of 1,3,5 trimesic acid: (a-b) 1 g/L; (cd) 2 g /L; (e-f) 4 g/L.

On the basis of HKUST-1 nanorods was synthesized by the coordination of organic ligands 1,3,5 trimesic acid and Cu ions, the concentration of trimesic acid has a significant influence on the morphology of HKUST-1 nanorods. Figure S4 are the SEM images of the samples obtained by changing the concentration of 1,3,5-trimellitic acid while keeping other experimental conditions unchanged. When the concentration of 1,3,5-trimellitic acid was 1g/L, it can be seen that the obtained product has a smooth rod-like structures which are densely distributed on the surface of the copper mesh, and there is no obvious HKUST-1 nanocubes assembled on the surface of nanorods (Figure S4a-b). When the concentration of 1,3,5-trimellitic acid was increased to 2 g/L, nanorods with a rough surface was obtained. The surface of the nanorods with an average diameter of about 150 nm are covered with many HKUST-1 nanoparticles with uneven morphology. The adjacent nanoparticles-assembled HKUST-1 nanorods are cross-linked together (Figure S4c-d). Further increase of concentration of 1,3,5-trimellitic acid to 4g/L resulted in the formation of HKUST-1 nanocubes assmbled nanorod arrays with an average diameter of about 250 nm (Figure S4e-f). Cu(OH)$_2$ nanorod arrays can be etched by 1,3,5-trimellitic acid, which promotes the dissolution of Cu ions and the complexation of ligands to form HKUST-1 nanocubes. Therefore, as the concentration of

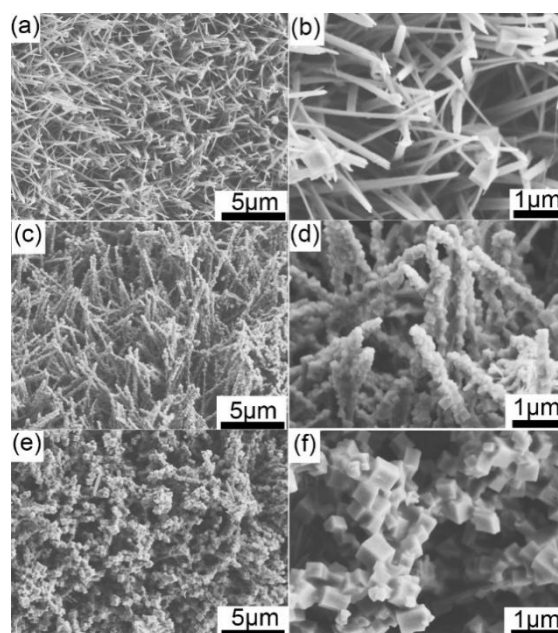1,3,5-trimellitic acid increases, HKUST-1 nanocubes are easier to obtain.

Figure S5. SEM images of Cu mesh/Cu(OH)$_2$@HKUST-1 nanorods prepared with different concentrations of PVP: (a-b) 10 g/L; (c-d) 20 g/L; (e-f) 40 g/L.

Figure S5 is the SEM images of the samples obtained with different PVP concentrations under other experimental conditions unchanged. When the PVP concentration is 10 g/L, a dense 3D nanorod arrays with smooth surface were achieved on the Cu mesh. Only a very small amount of HKUST-1 nanocubes were attached to the surface of Cu(OH)$_2$ nanorod arrays (Figure S5a-b).When the PVP concentration increases from 10g/L to 20g/L, a large number of uniform HKUST-1 nanocubes (the side length of the square is about 300 nm)were attached to the surface of Cu(OH)$_2$ nanorods (Figure S5c-d). As the PVP concentration continued to increase to 40 g/L, the number of HKUST-1 nanocubes increased with the increase of PVP concentration, and the HKUST-1 nanocubes with increased size and sharp corners became clearer (Figure S5e-f).
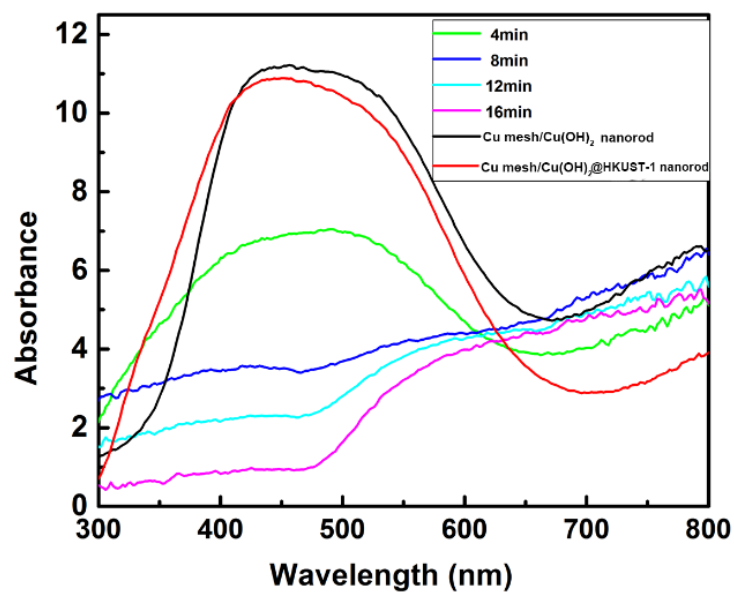
Figure S6. UV–vis absorption spectra of the Cu mesh/Cu(OH)$_2$ nanorod arrays, Cu mesh/Cu(OH)$_2$@HKUST-1 nanorod arrays,   Cu mesh/Cu(OH)$_2$@HKUST-1@Au nanorod arrays with different Au-sputtering durations
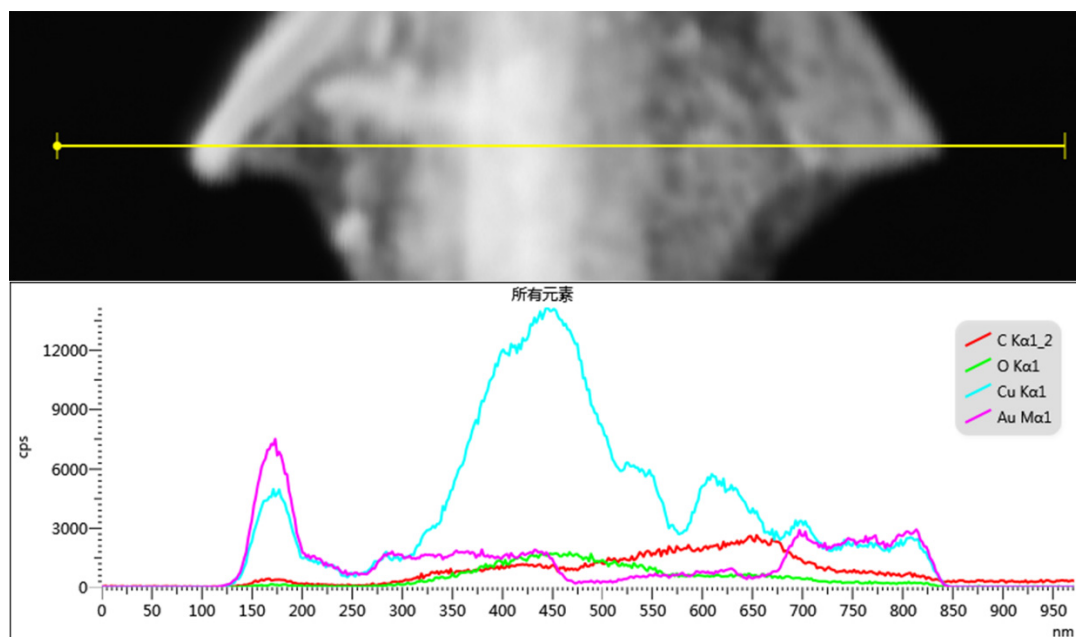

Figure S7. An EDS line on a single Cu(OH)$_2$@HKUST-1@Au nanorod shown by a yellow line and the resultant compositional profile.
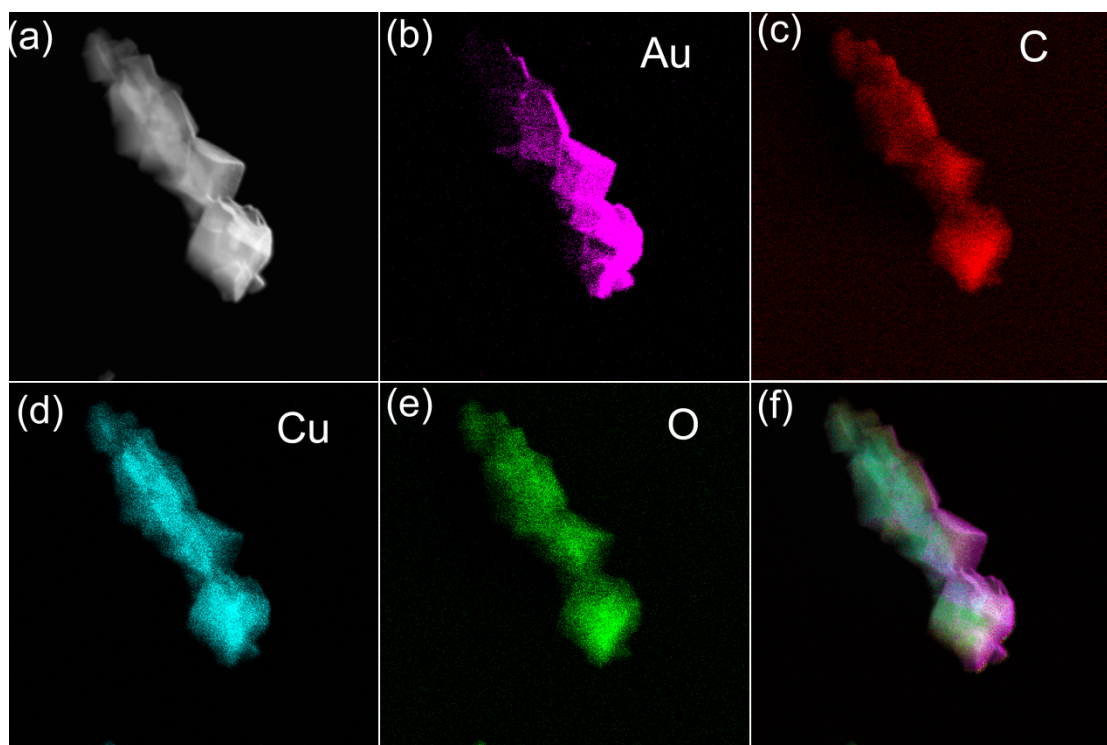
Figure S8. EDS map from a single Cu(OH)$_2$@HKUST-1@Au nanorod.

Part S2: Estimation of enhancement factor

We used the peak at 1078 cm^{-1} (for 4-ATP) to estimate the enhancement factor (EF). The EF can be calculated by:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{Ref}/N_{Ref}} = \frac{I_{SERS}}{I_{Ref}} \times \frac{N_{Ref}}{N_{SERS}}$$

Where N$_{SERS}$ and N$_{Ref}$ are the number of molecules probed on the Cu mesh/Cu(OH)$_2$@HKUST-1@Au nanorods and on the Si wafer, respectively. I$_{SERS}$ and I$_{Ref}$ correspond to SERS signal and the un-enhanced normal signal intensities, respectively. Herein, a certain volume (V$_{SERS}$) and concentration (C$_{SERS}$) 4-ATP ethanol solution was dispersed to an area of S$_{SERS}$ at the Cu mesh/Cu(OH)$_2$@HKUST-1@Au substrate. For non-SERS Raman spectra, a certain volume (V$_{Ref}$) and concentration (C$_{Ref}$) 4-ATP ethanol solution was dispersed to an area of S$_{Ref}$ at a clean Si substrate. Both the substrates were dried in the air. Considering the area of laser spot is the same, the foregoing equation thus becomes:

$$EF = \frac{I_{SERS}}{I_{Ref}} \bullet \frac{C_{Ref}V_{Ref}}{C_{SERS}V_{SERS}} \bullet \frac{S_{SERS}}{S_{Ref}}$$

In our experiment, 2 μL of 1×10^{-8} M 4-ATP ethanol solution was dispersed to an area of 42 mm^2 for the Cu mesh/Cu(OH)$_2$@HKUST-1@Au substrate and 2 μL of 1×10^{-3} M 4-ATP ethanol solution was dispersed to an area of 42 mm^2 for the Si wafer.

For the band at 1078 cm^{-1}, I_{SERS}/I_{Ref} was $\dfrac{2854}{263}$ =10.9. Therefore, average enhancement factor for the band at 1078 cm^{-1} is calculated to be 1.09×10^6.

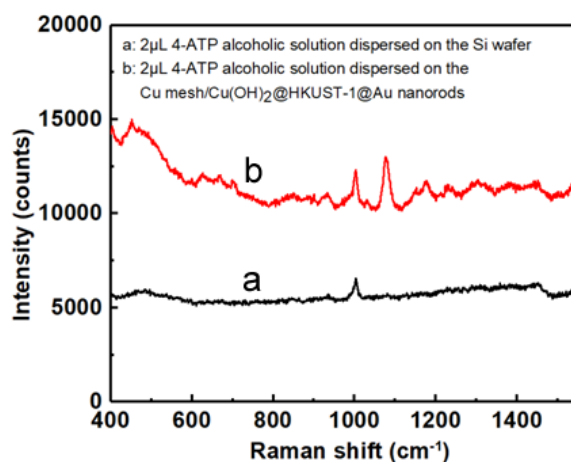**Figure for estimation of enhancement factor:**

Figure S9. (a) Raman spectrum of 4-ATP obtained by dispersing 2 μL 10^{-3} M 4-ATP alcoholic solution on 42 mm^2 Si wafer. (b) SERS spectrum of 2 μL 10^{-8} M 4-ATP alcoholic solution dispersed on 42 mm^2 Cu mesh/Cu(OH)$_2$@HKUST-1@Au nanorods. The exposure time was 2 s. Laser power was 0.1 mW.