Supporting Information for:

Conversion of Cu_2O nanowires into Cu_2O/HKUST-1 core/sheath nanostructures and hierarchical HKUST-1 nanotubes

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Experimental Section

Chemicals and Materials

Benzene-1,3,5-tricarboxylic acid (H_3BTC) were purchased from Aladdin (Shanghai, China). All solid reagents and solvents used in this study were of analytical grade and used as received from the suppliers without further purification. Ultra-pure water with resistivity larger than 18.0 MΩ was produced from an Ultrapure Water System (Purifier).

Preparation of Cu_2O Nanowires

Single crystalline Cu_2O nanowires with high aspect ratios were synthesized via a modified method described in Li's work[1]. In a typical Cu_2O nanowires synthesis, 0.10-0.20g $Cu(Ac)_2$ and 0.10g polyvinyl pyrrolidone (PVP, Mr = 40000) were dissolved in 35 mL deionized water. Afterward, 10 mL of 0.10M pyrrole aqueous solution was added. The mixture was sealed into a 50 mL autoclave and heated at 125 °C in an oven for 12 h. After cooling to ambient temperature naturally, the products were isolated by pouring off the supernatant. The isolated sediments were washed three times with ethanol and dispersed in 10 mL ethanol for storage and following characterizations.

Preparation of Cu_2O/HKUST-1 Core/Sheath Nanowires and HKUST-1 Nanotubes

For the synthesis of Cu_2O/HKUST-1 core/sheath nanowires, 0.5mL of the above-prepared Cu_2O nanowires dispersed in ethanol was mixed with 0.5mL, 0.16 mol/L H_3BTC ethanol solution. The mixture was diluted to 2mL with ethanol (EtOH)/ N, N-dimethylacetamide (DMA) solution (3:2, v/v,) and then kept at 30°C until the colour of the nanowires becomes light green. After 140 minutes reaction, the Cu_2O/HKUST-1 core/sheath were obtained by centrifuging at 7000rpm for 2 min and washed three times with ethanol. The HKUST-1 nanotubes were obtained by immersing the Cu_2O/HKUST-1 core/sheath in 5mL acetic acid (HAc)/EtOH solution (1:100, v/v) for 24 hours under ambient conditions.

Preparation of the primitive HKUST-1

The primitive HKUST-1 crystals were synthesized by a solvothermal method described in Calero's work[2]. Typically, 0.875 g (3.6 mmol) $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 12 mL deionized water and mixed with 0.42 g (2.0 mmol) H_3BTC dissolved in 12 mL ethanol. The resulting solution was stirred for 30 min, and then heated in an autoclave at 383K for 18 h. The as-synthesized crystalline solid was washed with ethanol for three times and then dried at 60^{o}C for 10 h.

Adsorption and desorption circulatory experiments

In a typical process, 10 mg of HKUST-1 nanotubes or primitive crystals was immersed in 5 mL of aqueous dye (methylene blue (MB), methyl orange (MO), rhodamine B (RhB) and congo red (CR)) solution with various concentrations at room temperature. After 6 min sonication, the solution was separated with the solid via centrifugation and subjected to UV-vis adsorption spectroscopy. The desorption experiments were carried out by re-dispersing the adsorbent saturated by either CR or MB dye into ethanol. After 3 min sonication, the adsorbent was separated by centrifugation and dried before reuse in adsorption experiments.

Characterization

Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance (Cu $K_{\alpha1}$ radiation, λ=1.5406 Å) at a scanning rate of 3°/min. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449 F3 instrument under air atmosphere with a heating rate of 10^{o}C/min. Nitrogen adsorption/desorption isotherm curve was measured at 77 K with a Micromeritics ASAP 2020 analyzer under the degas conditions of 120^{o}C for 8 h. Field emission scanning electron microscopy (FESEM) analysis was conducted with a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) images were captured on an FEI Tecnai F20 transmission electron microscope operating at an accelerating voltage of 200 kV. The UV-vis absorption spectra were recorded using a Varian Cary 50 Conc UV-Visible spectrophotometer.

Supplemental figures

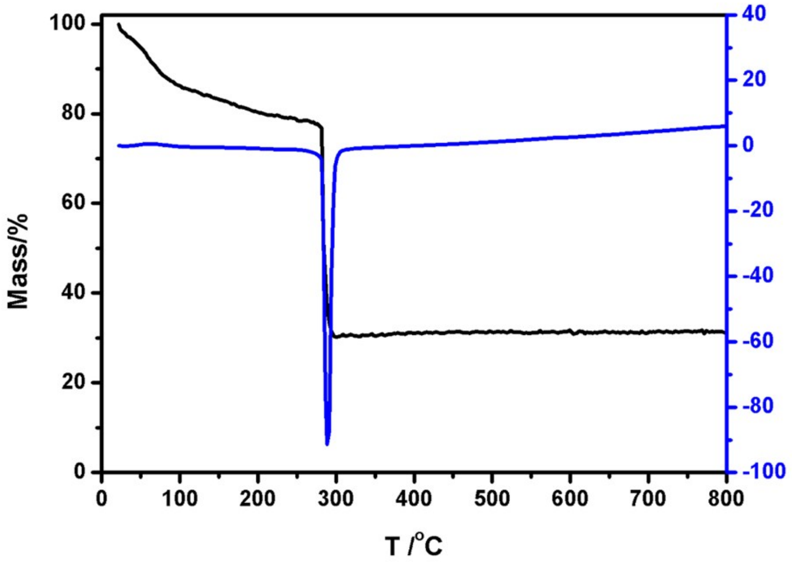

Fig. S1 Thermogravimetric analysis (TGA) curve of the as-prepared HKUST-1 nanotubes.

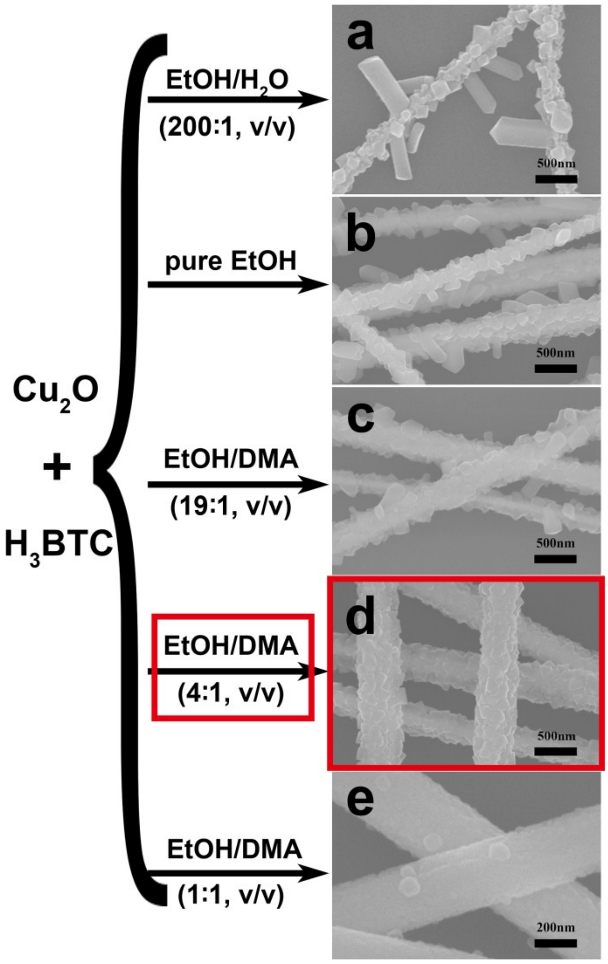

Fig. S2 FESEM images of Cu_2O/HKUST-1 nanowires obtained in different solvent composites of (a), EtOH/H_2O (200:1, v/v); (b), pure EtOH; (c), EtOH/DMA (19:1, v/v); (d), EtOH/DMA (4:1, v/v); and (e), EtOH/DMA (1:1, v/v), respectively.

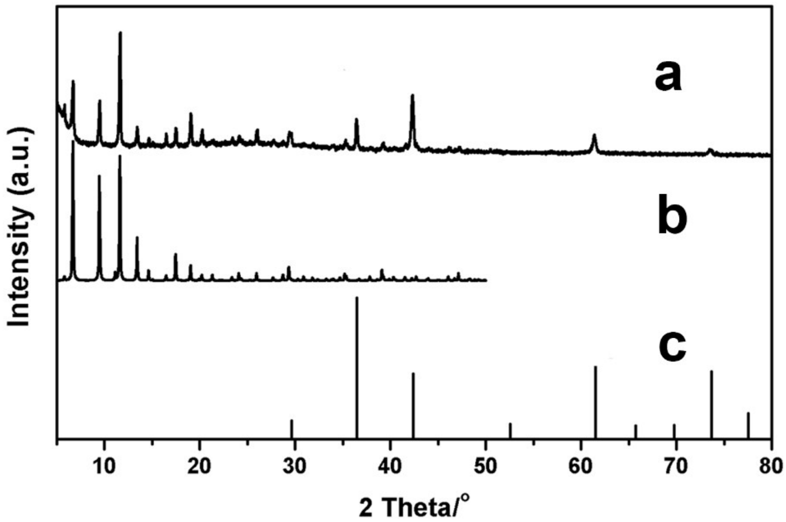

Fig. S3 PXRD patterns of (a) Cu_2O/HKUST-1 core/sheath nanowires covered with octahedral and spike-like particles, (b) simulated HKUST-1, and (c) standard Cu_2O.

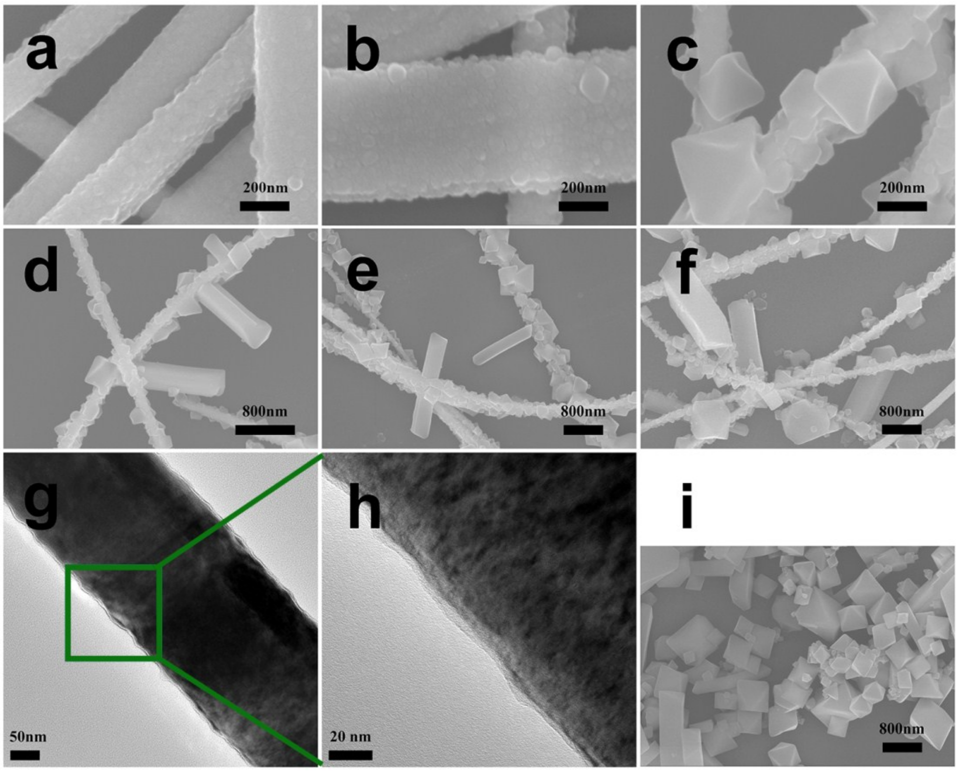

Fig. S4 FESEM images of Cu_2O/HKUST-1 core/sheath nanowires covered with octahedral and spike-like particles by reacting with 2 mL of 0.04M H_3BTC ethanol/water solution with volume ratio of 9:1 for (a) 3 min; (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min and (f, i) 35min,. TEM images obtained after reaction for 3 min (g, h); the green box in (g) is the location of (h) after being magnified.

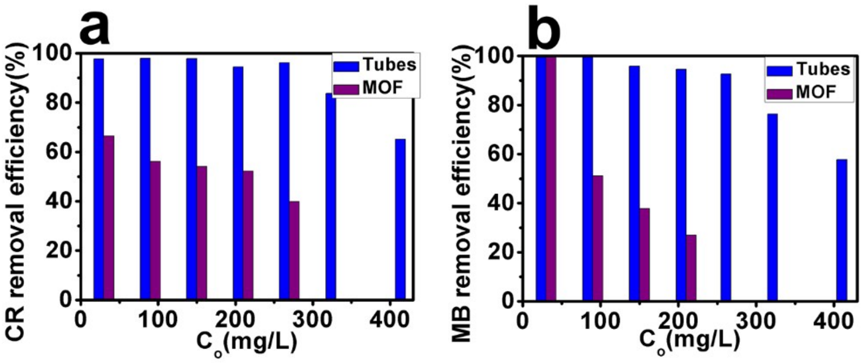

Fig. S5 The uptake percentage of CR (a) and MB (b) dyes by HKUST-1 nanotubes and the HKUST-1 primitive particles

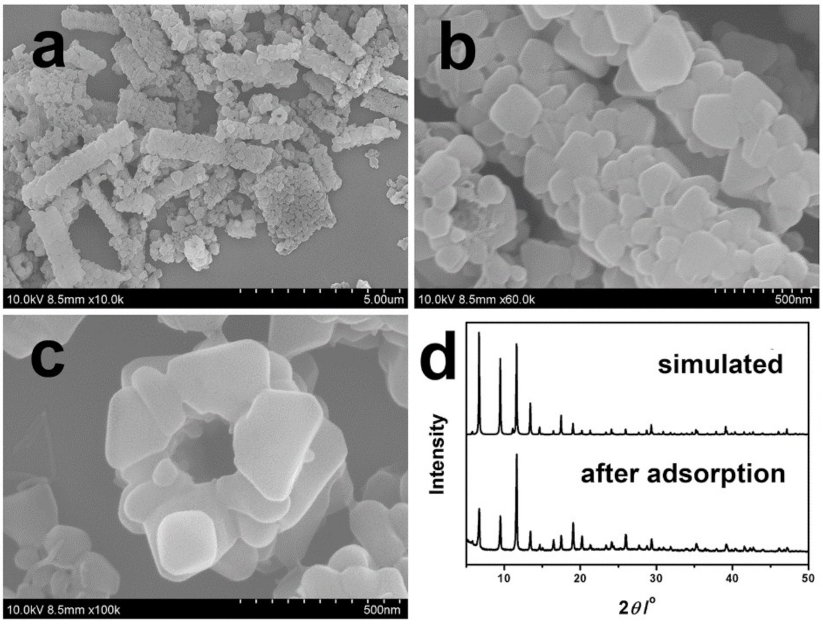

Fig. S6 (a-c) FESEM images and (d) PXRD of HKUST-1 nanotubes after regeneration from the desorption of CR dye.

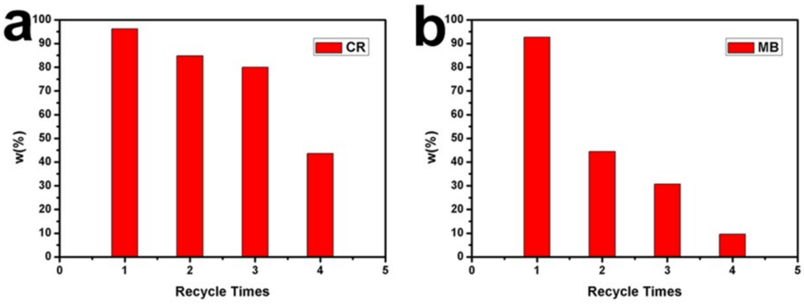

Fig. S7 Cycle measurements of the as-prepared HKUST-1 nanotubes as the adsorbent for (a) CR and (b) MB.

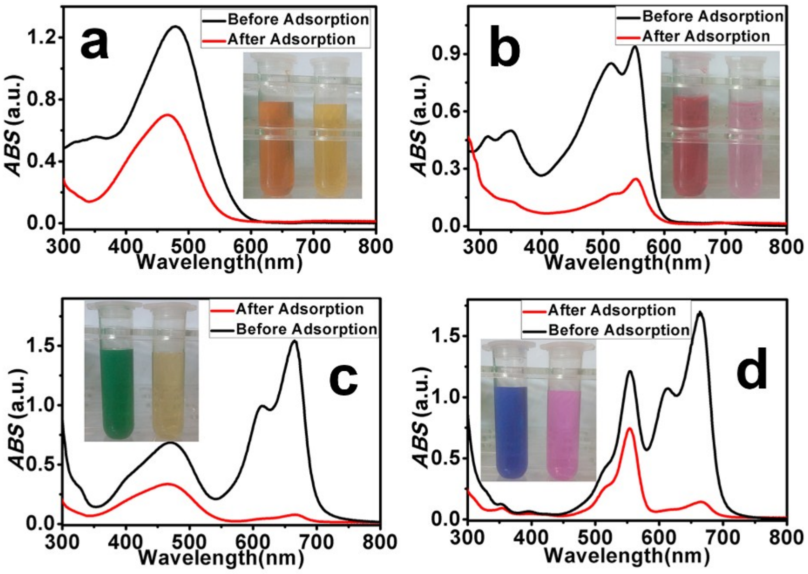

Fig. S8 The selective adsorption capability of HKUST-1 nanotubes toward the mixed dyes: (a) CR and MO, (b) CR and RhB, (c) MB and MO, and (d) MB and RhB. Inset: the color change of the mixed dyes solution before and after adsorption experiments.

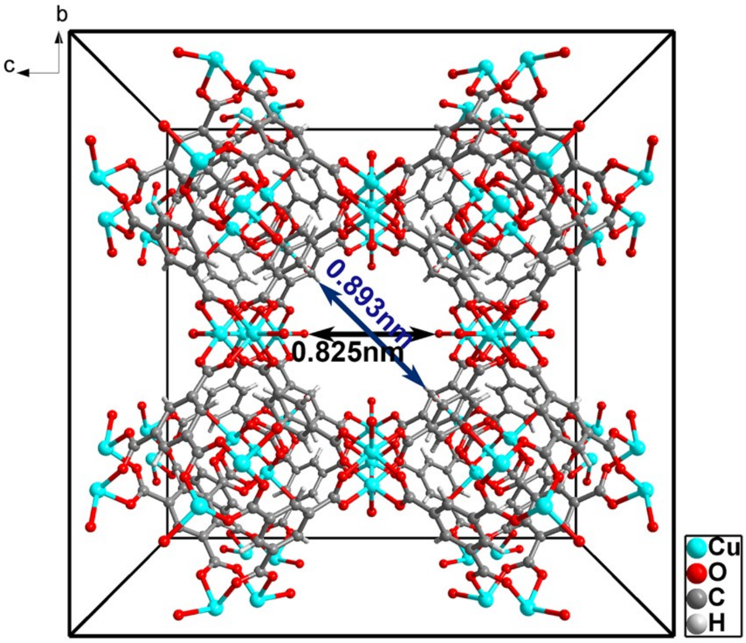

Fig. S9 The environment and size of the 1D micropore in HKUST-1.

Reference:

1. Y. Tan, X. Xue, Q. Peng, H. Zhao, T. Wang, and Y. Li, *Nano Letters*, 2007, 7, 3723-3728.
2. E. García-Pérez, J. Gascón, V. Morales-Flórez, J. Castillo, F. Kapteijn, and S. Calero, *Langmuir*, 2009, 25, 1725-1731.