Facile synthesis of hydrangea-like copper-tannic acid networks for separation and purification of His-rich proteins with exceptional performance

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Experimental Section

Materials.

Tannic acid (TA) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) were purchased from Aladdin (Shanghai, China). Sodium chloride (NaCl) and 2-methylimidazole were bought from Adamas-beta (Shanghai, China). Sodium hydroxide (NaOH), acetonitrile (ACN), disodium hydrogen phosphate (Na_2HPO_3), sodium dihydrogen phosphate (NaH_2PO_3), hydrochloric acid (HCl, AR, 36%-38%) and nitric acid (HNO_3, AR, 65%-68%) were obtained from Sinopharm (Shanghai, China). Sodium dodecyl sulfate (SDS) and hexadecyl trimethyl ammonium bromide (CTAB) were purchased from Sigma-Aldrich (Shanghai, China). Bovine hemoglobin (BHb), bovine serum albumin (BSA), lysozyme (Lyz) and cytochrome c (Cyt C) were bought from Lanji (shanghai, China). Bovine whole blood were obtained from Dingguo (Fujian, China). Deionized water (18.2 $M\Omega\ cm^{-1}$) was purified with Milli-Q water system (Millipore, USA). All reagents listed above were of analytical grade or better.

Characterization.

Scanning electronic microscopy (SEM) images were obtained by Zeiss Gemini 300. Transmission electron microscopy (TEM) analysis was conducted by the FEI Tecnai F20 with an accelerating voltage of 100 kV. N_2 adsorption/desorption isotherms was finished on ASAP 2460 (Micromeritics, USA) at 77K. Before analysis, the samples were degassed by vacuum at 100 °C for 10 h. Powder X-ray diffraction (PXRD) patterns were obtained at a scan rate of 5° min^{-1} over a range of 10-80° (2θ) on a X'Pert-Pro MPD (Philips, Holland) power diffractometer with Cu Kα source (λ=1.5418 Å).

Fourier-transform infrared spectra (FT-IR) were analyzed by attenuated total reflectance (ATR) on a Nicolet iS50 spectrometer (Thermo Fisher, USA) in the wavenumber range of 4000-400 cm^{-1}. The X-ray photoelectron spectra (XPS) were analyzed by Thermo Kalpha. Inductively coupled plasma optical emission spectrometer (ICP-OES) analysis was conducted on iCAP 7400 (Thermo Fisher, USA). For the sample preparation, 100.3 mg material was digested in a mixed solution of concentrated HNO_3 (2 mL) and HCl (6 mL), and then diluted to 50 mL by 5% HNO_3 solution. Finally, the obtained solution was diluted 100 times for further ICP-OES analysis. (TGA) was carried out on a thermal analyzer (STA449F5 Jupiter) at a heating rate of 10 K min^{-1} to 800 °C in air atmosphere at 50 mL min^{-1}. HPLC analysis was performed using a Shimadzu HPLC system (Prominence LC-20A, Kyoto, Japan) and a Ultimate LP-C18 (4.6 mm × 150 mm, 5 μm, 300 Å) column (Welch Tech., Shanghai, China). The proteins were analyzed under gradient conditions: a gradient was used with buffer A (0.1% TFA aqueous solution) and buffer B (0.08% TFA acetonitrile solution); 0–7.0 min, a linear gradient of buffer B from 33 to 70% was used; the flow rate was 1.0 mL min^{-1}; the column temperature was 35 ℃. The injected sample volume was 10 μL, and then was detected by a UV detector at 280 nm for BSA and Lyz, 406 nm for BHb and Cyt C. Electrophoresis of proteins was performed by regular sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) using a Mini-protean II system (Bio-Rad, USA) with 12% running and 5% stacking gels. Proteins were stained with Coomassie Brilliant Blue R-250.

Supplementary figures

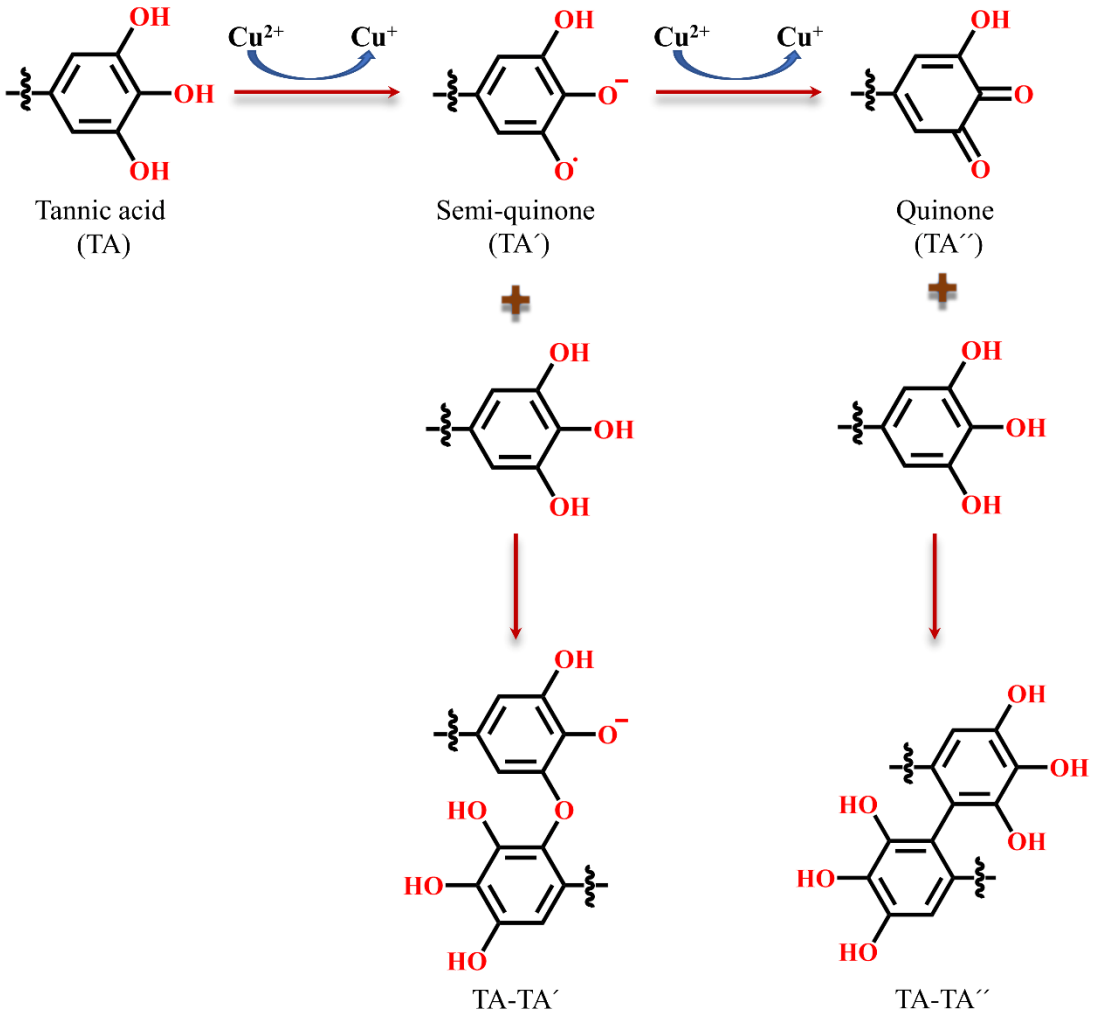

Figure S1 Cu^{2+}-mediated oxidative coupling assembly of tannic acid (TA).

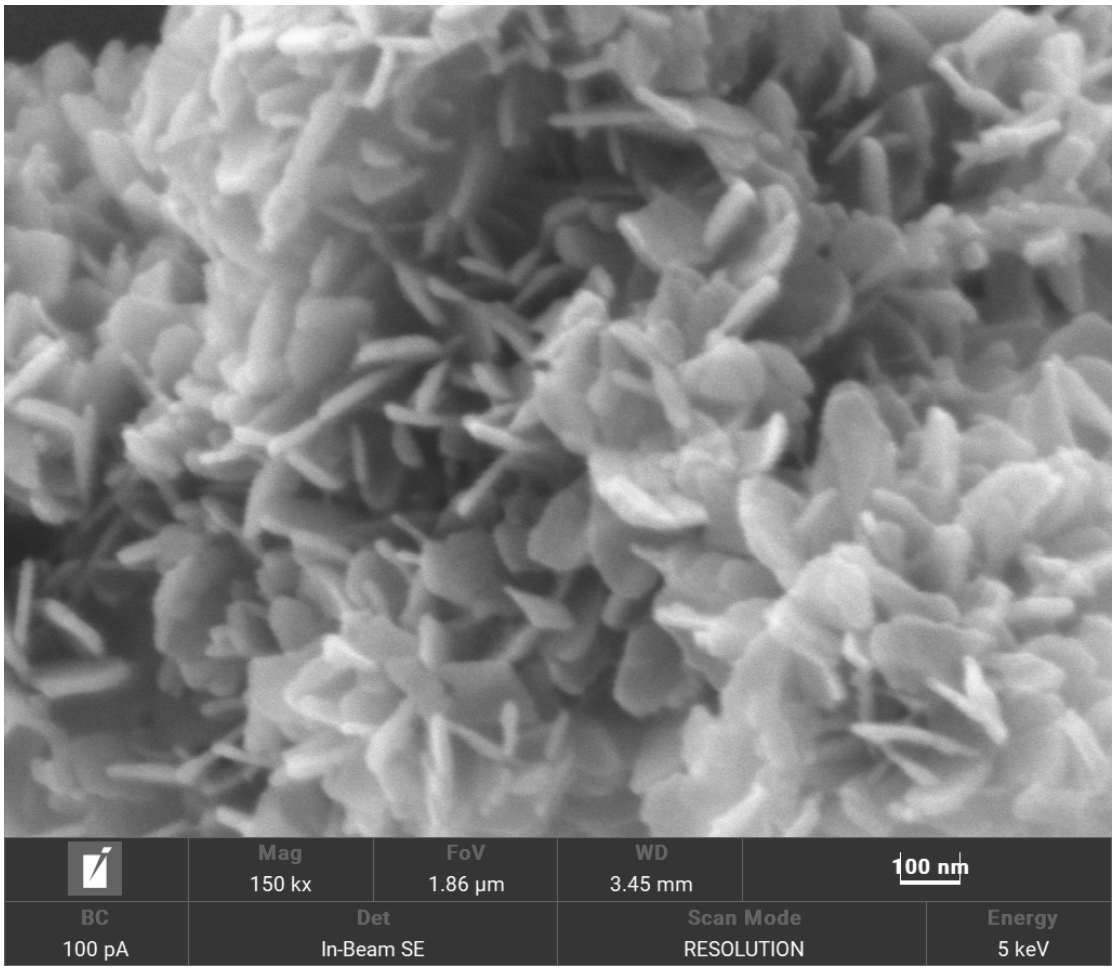

Figure S2 SEM image of hydrangea-like Cu-TA networks.

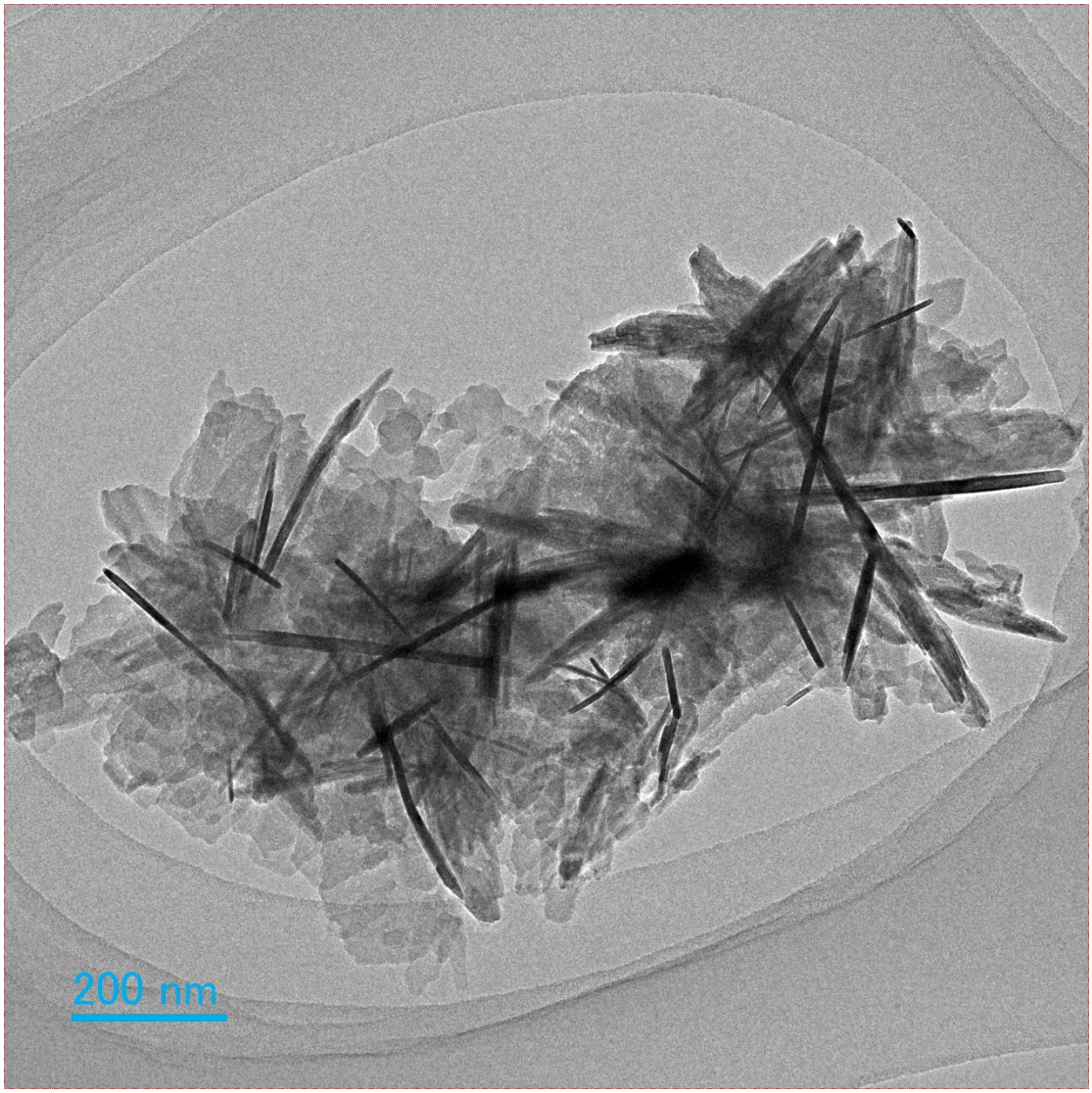

Figure S3 TEM image of hydrangea-like Cu-TA networks.

Table S1 Isothermal parameters for BHb adsorption onto hydrangea-like Cu-TA networks calculated using Freundlich model.

Isothermal model	Freundlich model			
Linear form of equation	$lnQ_e = lnk_F + \frac{lnC_e}{n}$			
Isothermal parameters	k_F (mg/g)	n	R^2	Linear range (mg/mL)
Cu-TA	5568.33	0.782	0.9625	0.1-2.5

Table S2 Kinetic parameters for BHb adsorption on hydrangea-like Cu-TA networks calculated using the pseudo-second order kinetic model and intraparticle diffusion model.

Kinetic model	Pseudo-second-order model			Weber-Morris model		
Linear form of equation	$\frac{t}{Q_t} = \frac{t}{Q_m} + \frac{1}{k_1 Q_m^2}$			$Q_t = k_2 t^{1/2} + C$		
Kinetic parameters	k_1 (g mg^{-1} h^{-1})	Q_m (mg/g)	R^2	k_2 (mg g^{-1} h$^{-1/2}$)	C	R^2
Cu-TA	1.28*10^{-5}	28280.70	0.9991	7792.30	769.08	0.9734
				3111.77	12194.96	0.9615
				1649.15	17392.09	0.9460