

## Supporting Information

### One-step Electrodeposition of MOF@CCQDs/NiF Electrode for Chiral Recognition of Tyrosine Isomers

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## 1. Experimental

### 1.1 Reagents and Chemicals

All the chemicals were of analytical grade and used as received unless otherwise specified. All solution were prepared using deionized (DI) water.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , D/L-Tyrosine (Tyr), sodium dihydrogen phosphate, hydrochloric acid, potassium phosphate monobasic, dibasic sodium phosphate, fluoroboric acid were obtained from Aladdin, Shanghai. Ethanol, dimethyl sulfoxide, n n-dimethylacetamide were purchased from Tianjin Fuyu Fine Chemical Co, Ltd.

### 1.2 Apparatus and Characterization

Scanning electron microscopy (SEM) images were recorded on a FEI QUANTA FEG250 scanning electron microscope at 15.0 kV, which were taken on a Hitachi S4800. XRD patterns were recorded on a Bruker SMART APEX CCQD-based diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418\text{\AA}$ ). Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet iS50 spectrometer. UV/vis absorption spectra of samples were recorded by using UV-2550 UV/visible spectrophotometer (Shimadzu Company). The samples were tested in a 1 cm quartz cell. The fluorescence spectra were acquired by a RF-5301pc luminescence spectrometer (Shimadzu

Company). The excitation wavelengths for the emission spectra were fixed at 270 nm. A standard three-electrode cell connected to the CHI 660E (Shanghai Chenhua) was used for electrochemical measurements. Electrochemical impedance spectroscopy (EIS) were carried out in 1 M KOH solution, while the applied perturbation amplitude was 5 mV and the frequency swept from 1 to  $10^5$  Hz. The solid state circular dichroism (CD) spectra (KBr pellets) were recorded on a MOS-500 spectrophotometer (Bio-Logic, France) between 200 and 800 nm of scanning spectrum at 1 nm intervals at room temperature.

### 1.3 Synthesis of MOF/NiF and MOF@CCQDs/NiF

Ligand:  $H_6TDPAT$  {2,4,6-tris(3,5-dicarboxylphenylamino)1,3,5-triazine} was prepared according to the literature<sup>1</sup>. 5-aminoisophthalic acid (15.2 g, 0.084 mol), NaOH (5.36 g, 0.134 mol), and  $NaHCO_3$  (8.74 g, 0.104 mol) were added to 140 mL  $H_2O$ . The mixture was stirred at 0 °C for 30 min, with the dropwise addition of cyanuric chloride (3.68 g, 0.02 mol) dissolved in 1,4-dioxane (70 mL). The mixture was heated at 100 °C for 24 h. The resulting solution was adjusted to pH=2 using HCl solution. The solid was collected by filtration, rinsed several times with distilled water, and dried to give  $H_6TDPAT$ .

MOF/NiF: 0.030 g (0.049 mmol) of  $H_6TDPAT$  and 0.164 g (0.68 mmol) of  $Cu(NO_3)_2 \cdot 3H_2O$  were dissolved in 2 mL of DMA, 2 mL of DMSO, 100  $\mu$ L of  $H_2O$  and 0.9 mL of  $HBf_4$ , then, the mixture was put into electrolysis cell. Copper foam (NiF) (5 mm  $\times$  10 mm) was immersed in dilute hydrochloric acid, sonicated for 5 min, and rinsed with deionized water and anhydrous ethanol. Electrolysis was carried out in an electrochemical cell with the treated NiF as working electrode, the platinum plate as counter electrode and the calomel electrode as reference electrode at a voltage of -1.0 V for 10 minutes. Then, the deposited NiF was washed with ethanol, activated at 100 °C for 2 h.

Chiral CCQD: The D-CQD were synthesized by microwave pyrolysis. In the beaker, the solution of 0.15g, 0.3 g, 0.45g or 0.6g D-sorbitol, 0.1 g sodium dihydrogen phosphate and 10 mL deionized water was heated at 750 W for 120 s in a microwave oven to obtain D-CQD solution. After that, a brownish solution was dialyzed by 500 Da dialysis bag for 3 days to remove the smaller molecules. The L-CQD were prepared by a similar process just using L-sorbitol instead of D-sorbitol.

MOF@CCQDs/NiF: 0.068 mmol (0.164 g) of copper nitrate hydrate, 0.049 mmol (0.030 g) of  $H_6TDPAT$  and the above fresh carbon quantum dots (CQD) were dissolved in 2 mL of DMA, 2 mL of DMSO, 100  $\mu$ L of  $H_2O$  and 0.9 mL of  $HBf_4$  in the electrolysis cell. The NiF (5 mm  $\times$  10 mm) was immersed in dilute hydrochloric acid, sonicated for 5 min, and rinsed with deionized water and anhydrous ethanol. The electrodeposition process is the same as synthesis of MOF/NiF.

#### 1.4 Electrochemical measurement of D/L-Tyr Isomers

Electrochemical enantiorecognition of Tyr was carried out in phosphate buffer solution (PH=4.0, 7.0, 8.0) and KOH solution (0.1M) containing L-Tyr or D-Tyr by cyclic voltammetry (CV). All the electrochemical experiments were carried out with three electrode systems, in which MOF/NiF, MOF@CCQDs/NiF were used as the working electrodes, A Pt wire and Ag/AgCl (3M KCl) were utilized as the auxiliary and reference electrodes. CV were recorded from -1.2 V to 0.6 V at a scan rate of 100 mV/s.

#### 1.5 Determination of standard deviation

The detection limits (DL) prescribed by IUPAC<sup>2</sup> is as follows: DL expressed as the concentration  $c_L$ , is derived from the smallest measure  $x_L$ . The value of  $x_L$  is given by the equation  $x_L = x_{bl} + ks_{bl}$ , where  $x_{bl}$  is the mean of the blank measures,  $s_{bl}$  is the standard deviation of the blank measures and  $k$  is a numerical factor chosen according to the confidence level desired. A value of 3 for  $k$  in equation is strongly recommended, thus, the  $c_L$  corresponds to the value calculated by the calibration plot obtained from a given analytical procedure where  $x_L = x_{bl} + 3s_{bl}$ .

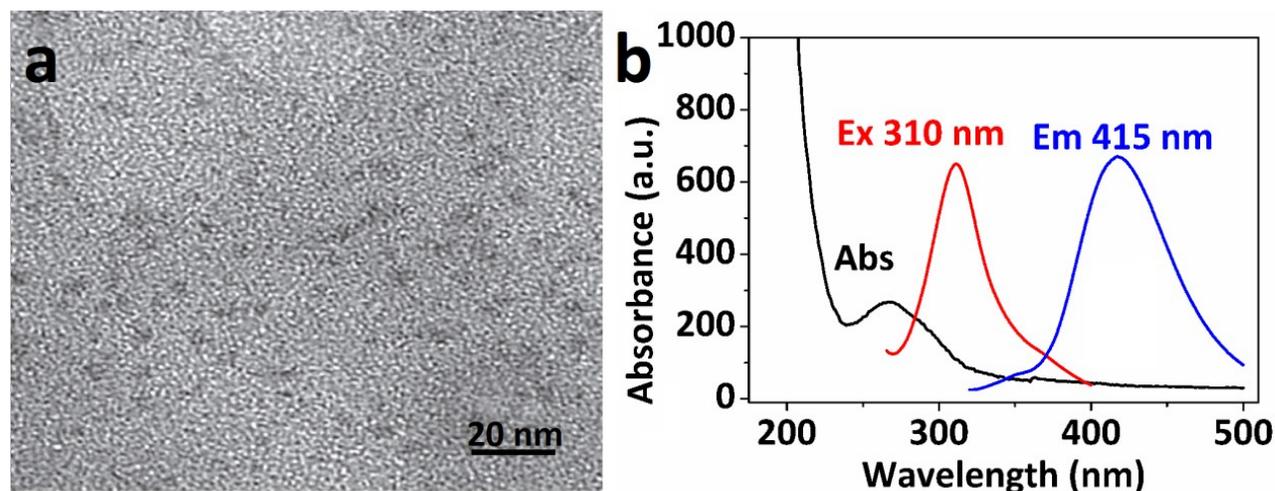


Fig. S1 (a) TEM image of CQD, (b) UV-vis absorption and fluorescence emission spectra of CQD intensity.

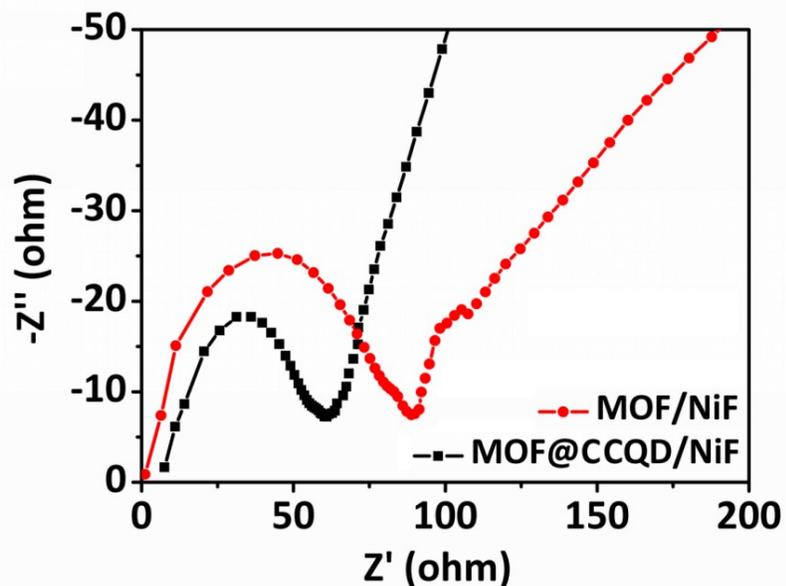


Fig. S2 Nyquist plots obtained at different electrodes MOF/NiF (red line) and MOF@CCQD/NiF (black line) in 0.1 M KCl solution containing 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ .

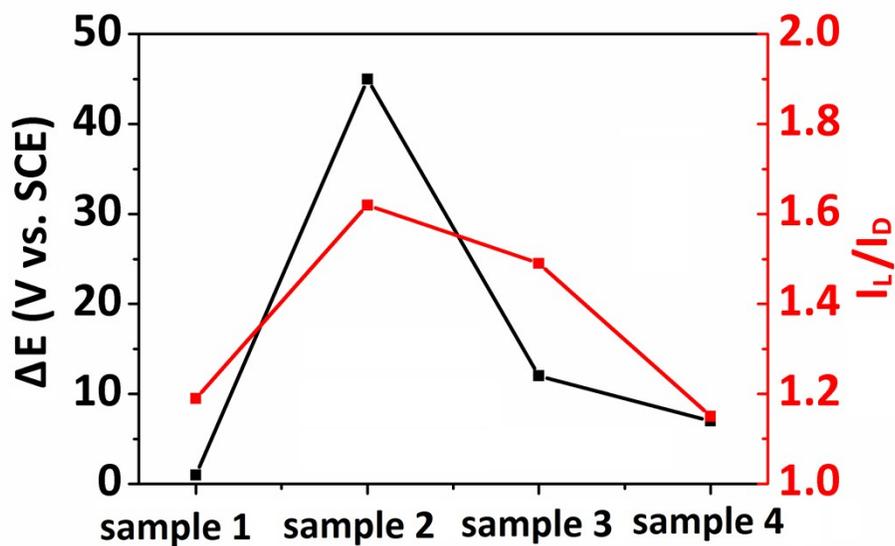


Fig. S3 Recognition ability of MOF@CCQD/NiF prepared by different amount of D-sorbitol (sample1 0.15 g, sample2 0.3 g, sample3 0.45 g, sample4 0.6 g).

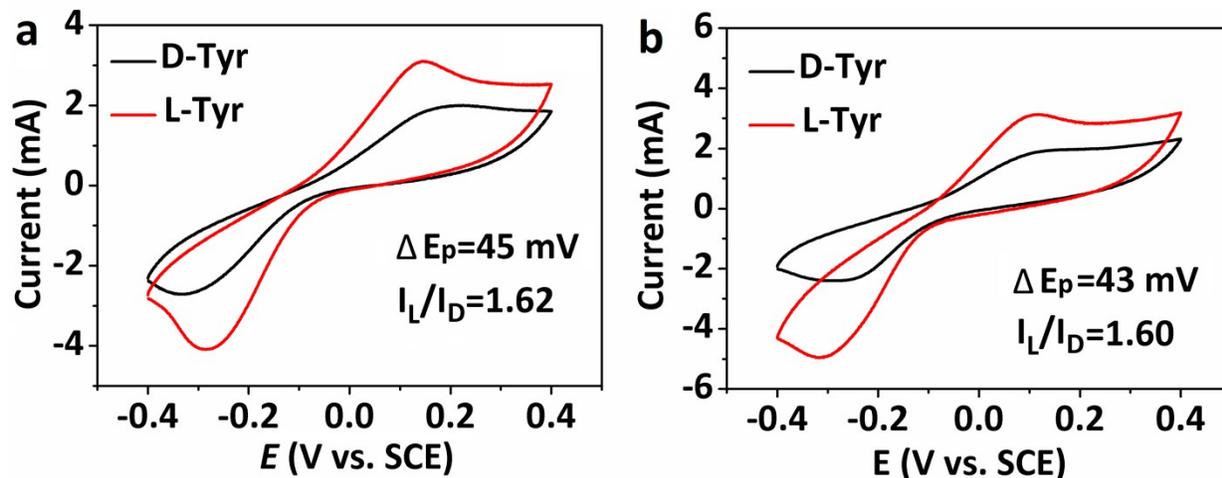


Figure S4. The evaluation of the long-term stability of MOF@CCQD/NiF (a) initial curve and (b) stored at 4 °C for 2 weeks.

## References

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