

Supplementary Information

Functionalized MOF PCN-222 loaded CdSe quantum dots as an electrochemiluminescence sensing platform for sensitive detection of p-nitrophenol

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Experimental part

S1. Reagents and apparatus

Selenium powder, sodium borohydride, 3-mercaptopropionic acid, o-nitrophenol, m-nitrophenol, p-nitrophenol, toluene and nitrobenzene were all purchased from Macklin & Company(www.macklin.cn). Cadmium acetate dihydrate($C_4H_6CdO_4 \cdot 2H_2O$) purchased from Shanghai Aladdin Biochemical Technology Co., LTD(www.aladdin-e.com).

anhydrous ethanol and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co.,Ltd.(www.reagent.com.cn).P-nitrotoluene and 1, 4-dimethylbenzene were purchased from TCI Chemical Industry Co.,Ltd.(www.tcichemicals.com).PCN-222 purchased from Shanghai Kaishu Chemical Technology Co., LTD(www.chemsoon.com)。 None of the reagents were further purified.

Scanning electron microscopy (SEM) images were obtained a Hitachi S-4800 scanning electron microscope (Hitachi Co., Japan). Transmission electron microscopy (TEM) was used a JEM-2100 transmission electron microcopy (JEOL Ltd., Japan). X-ray powder diffraction (XRD) was obtained a RigakuD/max-rA X-ray

diffractometer (Japan). X-ray photoelectron spectroscopy (XPS) were obtained on a ESCALAB 250Xi spectrometer (Manufacturer: the United States Electricity Co. , Ltd). Fourier transform infrared spectroscopy (FTIR) were obtained on a Vertex80/Hyperion2000 spectrometer (Bruker, Germany). UV-vis absorption spectra were performed on a UV-1750 UV-vis spectrophotometer (Shimadzu, Japan). All electrochemical measurements were carried out on a CHI 660E electrochemical workstation (Shanghai CH Instrument Co., Ltd., China) and the measurements about electrochemiluminescence (ECL) were taken on a MPI-A analyzer (Xi'An Remax Electronic Science & Technology Co., Ltd., China). Electrochemical impedance spectroscopy (EIS) measurement were carried out on a Thales electrochemical workstation (Zahner-elektrik GmbH & Co., Germany).

S2. Synthesis of CdSe QDs

70.8mg (0.9mmol) selenium powder and 10 mL deionized water was poured into a round bottom flask. In an atmosphere of N₂, 67.9 mg sodium borohydride (1.8mmol) was quickly added to the flask. Then the system was stirred for 2h. The selenium powder dissolved slowly after the addition of sodium borohydride. After 2 hours, selenium powder was dissolved completely and the solution became clear. 320.4 mg (1.2 mmol) cadmium acetate dihydrate (Cd(C₂H₃O₂)₂·2H₂O) and 50 mL deionized water was mixed and ultrasonic dissolved in a three neck flask. After the addition of 0.75 mL 3-mercaptopropionic acid, the solution appeared white turbidity immediately. The system was stirred in N₂ atmosphere, and then the pH value of the solution was adjusted to 9 with 1mol/L NaOH. The white turbidity was disappeared. Finally, the solution was heated to 100°C and stirred for 30min. The precursor selenium was injected to the solution of precursor cadmium, and the color of mixture immediately became red. The mixture was stirred at 100°C for 1h, and then cooled to room temperature. In order to obtain the CdSe QDs, 30 mL ethanol was added to the system and rested overnight. Finally, the powder of CdSe QDs was collected by centrifugation and freeze-drying.

Table-S1. Comparison of this work with the reported method for detecting p-nitrophenol.

Detection Method	Strategy	Linear range	Limit	Ref.
FL	quenching mechanism of neuron cell-analogous carbon-based probes	0.1–50 μM	43 nM	¹
GC	selected ion monitoring	3.0- 681 $\mu\text{g/L}$	1.0 $\mu\text{g/L}$	²
SWASV	NiFe ₂ O ₄ -rGO10/GCE modified for catalysis	0.5 -21.0 μM	45 nM	³
kinetic spectrophotometric	activating effect of p-NP on the oxidation of sulfanilic acid	40–200 ng/mL	8 ng/mL	⁴
NIRDRS	macroporous adsorption resin and PLS method	39.01–117.16 mg /L	39.01 mg /L	⁵
LSV	AgNDs/GCE for extraction	20–1380 μM	1.76 μM	⁶
DPV	Fe ₃ O ₄ @AT-COFs for catalysis	10-3000 μM	0.2361 μM	⁷
CV	L-Cys/Nd ₂ O ₃ /rGO modified GC electrode for analysis	0.05 - 50 μM	0.02 μM	⁸
HPLC	Supramolecular solvent liquid–liquid microextraction combined with HPLC	2-1000 $\mu\text{g/L}$	0.26 $\mu\text{g/L}$	⁹
ECL	Quenched by PCN-222@CdSe QDs/GCE	0.1-100000 $\mu\text{g/L}$	0.03 $\mu\text{g/L}$	This work

Notes and references

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