Supporting Information

A synergistic approach to enhance the photoelectrochemical performance of carbon dots for molecular imprinting sensor

Lebao Mao, Xinyi Wang, Yun Guo, Linli Yao, Xiaojie Xue, Hang-Xing Wang,* Chengyi Xiong, Wei Wen, Xiuhua Zhang* and Shengfu Wang

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules & College of Chemistry and Chemical Engineering, Hubei University, Wuhan, Hubei 430062, PR China.

CORRESPONDING AUTHOR

Dr. Xiuhua Zhang, E-mail: zhangxh@hubu.edu.cn.

Dr. Hang-Xing Wang, E-mail: wanghx@hubu.edu.cn.

Tel: 86-27-8721-7886, Fax: 86-27-6875-4067.

Address: College of Chemistry and Chemical Engineering, Hubei University, Wuhan, Hubei 430062, PR China.

This material includes:

1. Experimental section

Chemicals. Sodium hydroxide (NaOH), Ascorbic acid (AA), Chitosan (CS), glucose (GLU), Dopamine (DA), copper(II) phthalocyanine (CuPc) were obtained from Aladdin Industrial Coperation (Shanghai.China). Citric acid dihydrate (99.9%), L-cysteine (97.0%), Methacrylic acid (MAA), Ethylene glycol dimethacrylate (EDMA), Azodiisobutyronitrile (AIBN) were purchased from Sigma-Aldrich. Fumonisin B_1 (FB_1), ochratoxin A (OTA), ochratoxin B (OTB), deoxynivalenol (DON), Zearalenone (ZON) and Patulin (PAT) were bought from cayman chemical company (United States). And the rice was bought from the local supermarket. All other chemical reagents were of analytical grade, and millipore ultrapure water with a certain resistivity >18.2 MΩ cm was used throughout the experiment. The working solution was using a homemade phosphate buffer solution (pH 7.4, KH_2PO_4-Na_2HPO_4, PBS) with 0.1 mol·L^{-1} for MIP-PEC detection.

Apparatus. PEAC 200A PEC reaction instrument (Tianjin Aidahengsheng Science-Technology Development Co., Ltd., China). PEC signals were carried out by CHI660C electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) with a three-electrode system, and Indium tin oxide (10×45×1 mm) (South China Science & Technology Co., Ltd., China) was served as working electrode. High speed freezing centrifuge (Beijing BMH Instuments Co.Ltd., shanghai, China). The zeta potential was characterized using a Zetasizer (Nano-ZS90, Malvern, U.K.). Scanning electron micrographs (SEM) were measured on a ZEISS SIGMA 500 scanning electron microscope (Germany), Transmission electron microscopy (TEM) images were employed to HITACHI H-7000FA and JEOL 2100F transmission electron microscope. The UV−vis spectra were obtained in a Shimadzu UV-2700 spectrometer and the fluorescence spectra were obtained from Shimadzu RF-5301pc spectrometer. UV polymerization was achieved by ZF-I UV analyzer (Shanghai Guanghao Analysis Instrument Co., Ltd., shanghai, China).

Preparation MIP-PEC and non-MIP (NIP-PEC) sensor. The method is based on the literature.[1] Firstly, the ITO electrode surface cleaned with a sequential employing acetone, ethanol, and ultrapure water by ultrasonic treatment in turn and then dried it. Then, the original N,S-CDs/CuPc was fully mixed with 1 wt % chitosan after it was diluted 20 times. Subsequently, the ITO surface (modified area of 1.00 cm^2) was coated with 100 μL of N,S-CDs/CuPc mixture, and dried at 60 ℃ for 2 h. After that, the original solution of MIP included OTA, MAA, EDMA and AIBN, and 20 μL of the original solution was dropped on modified area. Finally, the MIP-PEC sensor was obtained by ultraviolet initiated polymerization for 15 min. As a control, the NIP-PEC sensor was prepared in the same way except the template molecules. The MIP-PEC and NIP-PEC sensors were eluted with ethanol for 20 min for further detection.

Photoelectrochemical measurement. The proposed MIP-PEC sensor was carefully cleaned with ultrapure water and then incubated in OTA solution for 15 min. The photocurrent responses were gained in PBS solution (0.1 M, pH = 7.4) containing 30 mM AA with a three-electrode system illuminated by white light. The light was switched on 30 s and off 20 s in turn, and the applied potential was 0 V.

EIS characterization of the prepared MIP-PEC sensor. The capability of electron transfer of the electrodes modified with different materials was investigated by EIS 0.1 M KCl solution containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$, the potential was 0.208 V and frequency range was from 10 mHz to 100 kHz.

Standard recovery test of the MIP-PEC in real samples. OTA was processed in rice samples following the reporting method with a slight change.[1] Rice was dispersed in ethanol with ultrasonic extraction. The supernatant which had been centrifuged was diluted with PBS (pH 7.4) for additional use. Then the recovery experiment was performed with various concentrations of standard OTA. As showed in table 1, the recoveries were between 97.33% and 102.0% with the RSD between 1.8% and 5.6%, which indicated that the prepared sensor equipped with a good detection effect for OTA.

2. Figures

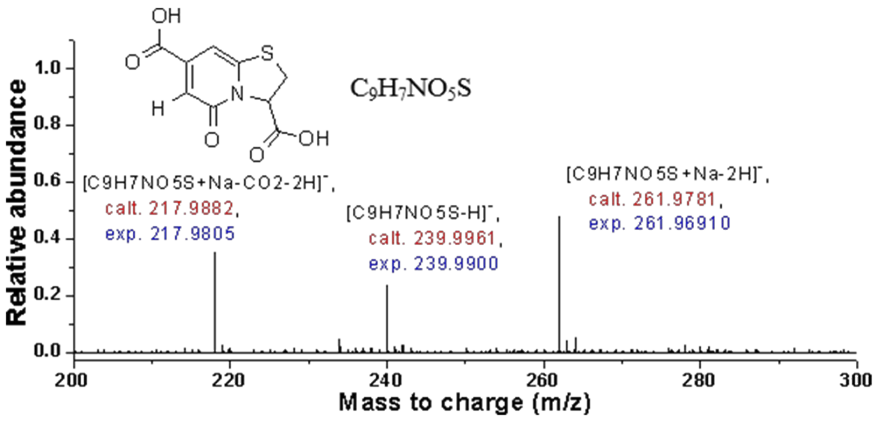

Fig. S1 LC-MS spectra of TPA.

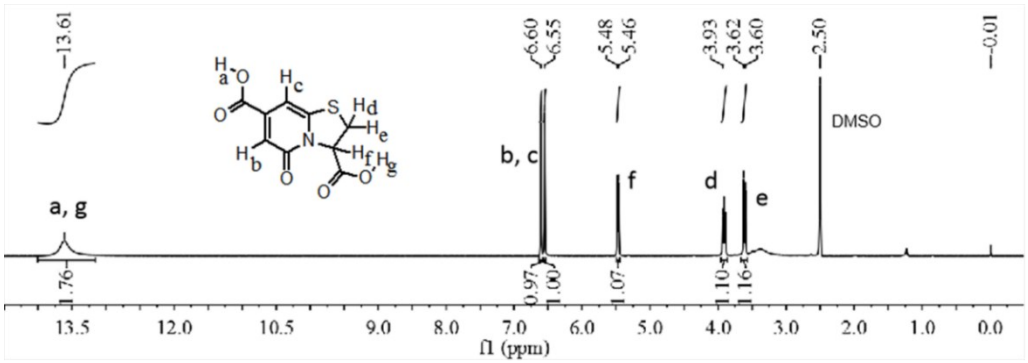

Fig. S2 ^{1}H-NMR spectra of TPA.

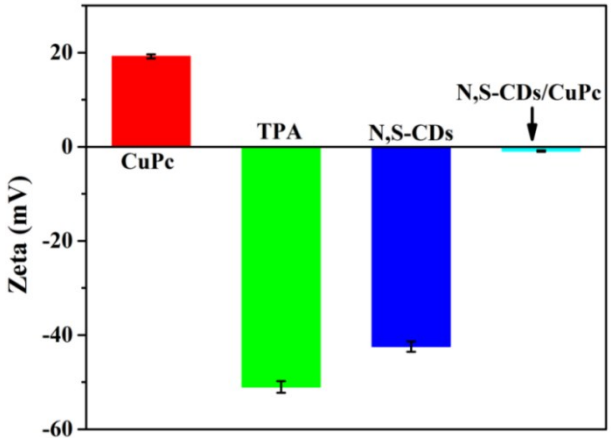

Fig. S3 Zeta potential of CuPc,TPA, N,S-CDs and N,S-CDs/CuPc.

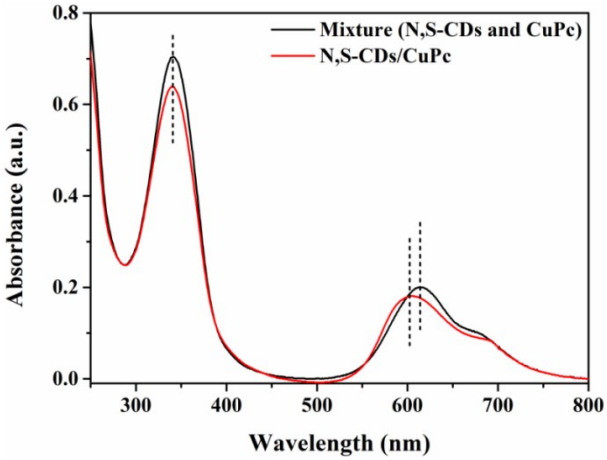

Fig. S4 UV-vis absorption spectra of Mixture (N,S-CDs and CuPc) and N,S-CDs/CuPc.

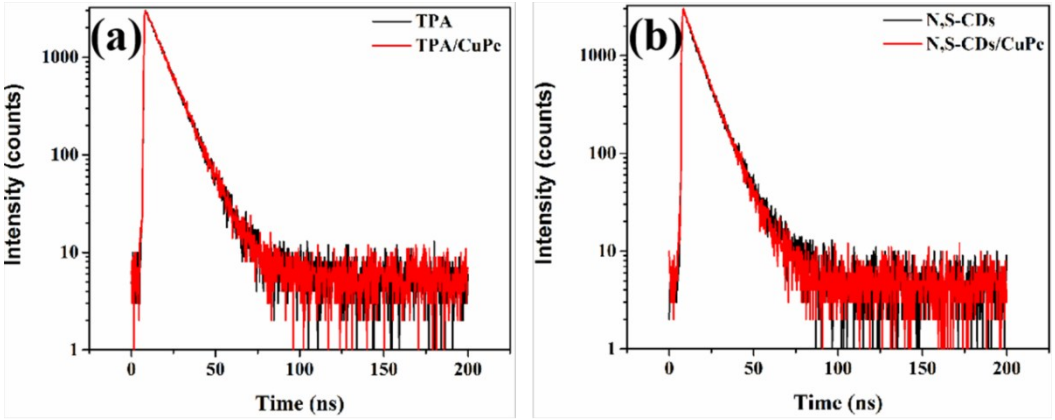

Fig. S5 Time-resolved fluorescence spectra of (a) TPA and TPA/CuPc, (b) N,S-CDs and N,S-CDs/CuPc.

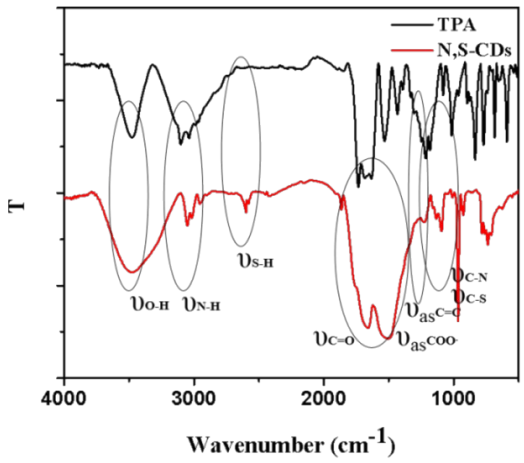

Fig. S6 FTIR spectra of TPA and N,S-CDs.

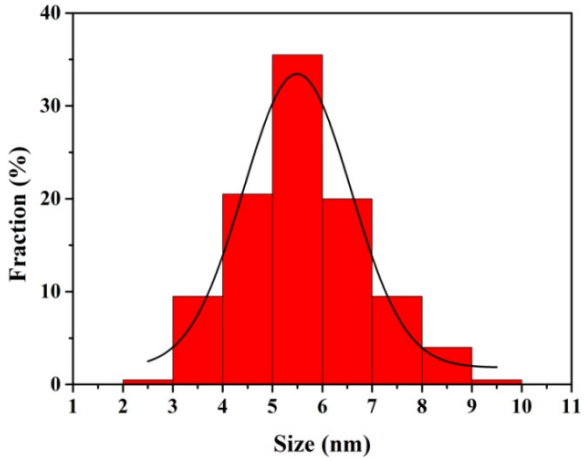

Fig. S7 Size distribution of the N,S-CDs.

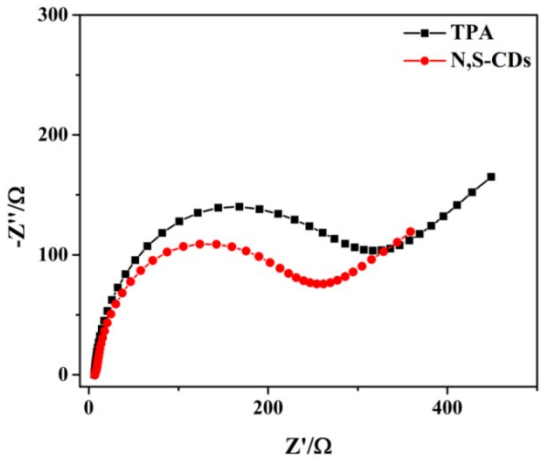

Fig. S8 EIS of TPA/ITO and N,S-CDs/ITO.

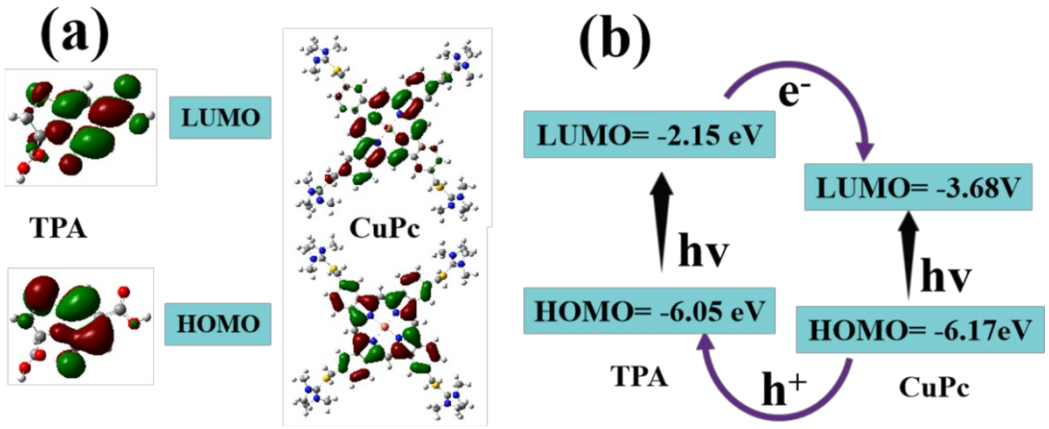

Fig. S9 (a) HOMO-LUMO of TPA and CuPc, (b) Electric energy level of TPA and CuPc.

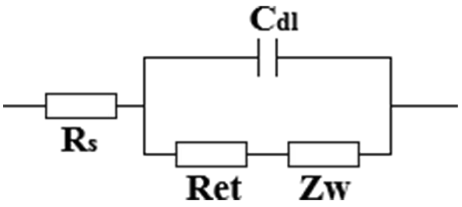

Fig. S10 The Randle's model equivalent circuit.

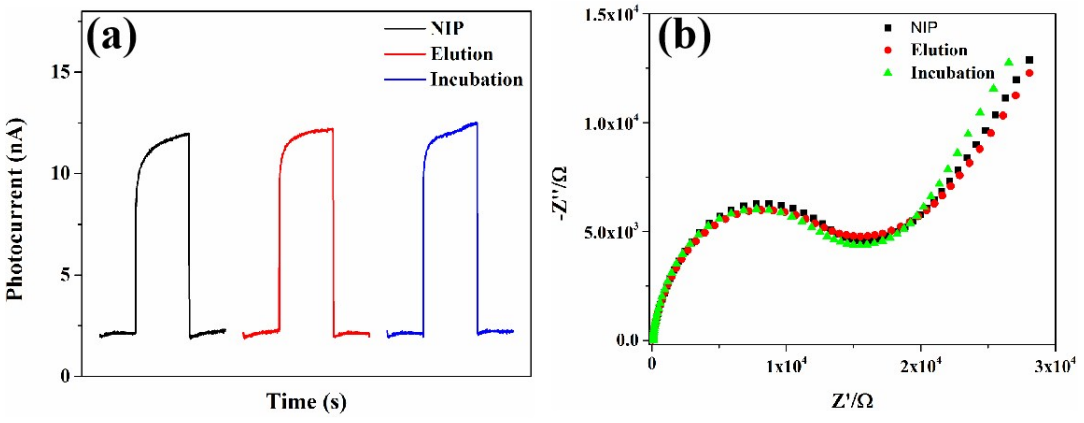

Fig. S11 (a) photocurrent responses of NIP/N,S-CDs/CuPc/ITO before template eluted, NIP/N,S-CDs/CuPc/ITO after template eluted and NIP/N,S-CDs/CuPc/ITO after template incubated, (b) EIS of NIP/N,S-CDs/CuPc/ITO before template eluted, NIP/N,S-CDs/CuPc/ITO after template eluted and NIP/N,S-CDs/CuPc/ITO after

template incubated.

3. Table

Table S1. Decay parameters for TPA, TPA/CuPc, N,S-CDs and N,S-CDs/CuPc.

	TPA	TPA/CuPc	N,S-CDs	N,S-CDs/CuPc
τ (ns)	10.49	10.51	9.07	9.10

Table S2. Comparison of the proposed sensor with other methods in OTA detection.

Detection method	Linear range ($ng \cdot mL^{-1}$)	Detection limit ($pg \cdot mL^{-1}$)	References
FL	0.05–100 ng mL^{-1}	20 $pg \cdot mL^{-1}$	[2]
DPV	0.005–10 ng mL^{-1}	1.0 $pg \cdot mL^{-1}$	[3]
SWV	0.01–10 ng mL^{-1}	5 $pg \cdot mL^{-1}$	[4]
CV	0.1–20 ng mL^{-1}	30 $pg \cdot mL^{-1}$	[5]
CL	0.001–50 ng mL^{-1}	0.3 $pg \cdot mL^{-1}$	[6]
ECL	0.001–10 ng mL^{-1}	0.5 $pg \cdot mL^{-1}$	[7]
PEC	0.001–100 ng mL^{-1}	0.51 $pg \cdot mL^{-1}$	This work

4. References

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