Supplementary Material

Cu_5Zn_8@SiO_2/NC derived from Cu/ZIF-8 as efficient electrochemical sensor for environmental pollutant detection in water bodies

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S1. Materials and Reagents

All chemicals were of reagent grade and used without further purification. Tetraethyl orthosilicate was purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), Copper nitrate trihydrate($Cu(NO_3)_2·6H_2O$), ethanol (C_2H_5OH), Cetyltrimethyl ammonium bromide(CTAB), 2-methylimidazole and ammonia hydroxide ($NH_3·H_2O$, 32 wt%) were purchased from Sinopharm Chemical Reagent. Nitrobenzene (NB) was obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai China). Sodium chloride, Aqueous electrolytic conductivity-KCl, Sodium phosphate dibasic and Sodium phosphate monobasic dihydrate were provided by Shanghai Bide Pharmatech Co., Ltd. The phosphate buffer saline (PBS pH=7.0, 100 mM) contained 39.00 mM $NaH_2PO_4·2H_2O$, 61.00 mM Na_2HPO_4, 136.75 mM NaCl and 100.00 mM KCl. Ultrapure water was adopted throughout this work (electrical resistivity ≥ 18 MΩ).

S2. Apparatus

X-ray polycrystalline diffractometer (XRD, Smartlab, 9 kW, Japan), X-ray photoelectron spectroscopy (XPS, ES-CALAB 250, United States), scanning electron microscope (SEM, REGULUS8230, Japan), transmission electron microscope (TEM, JEM-2100, Japan). All electrochemical measurements were carried out on a CHI 660E electrochemical workstation (Shanghai CH Instrument Co., Ltd., China). Chemical impedance spectroscopy (EIS) performed on a Thales electrochemical workstation.

During the test, a Ag/AgCl electrode was selected as the reference electrode, a platinum wire electrode as the auxiliary electrode and a glassy carbon electrode (GCE) as the working electrode.

S3. Synthesis of SiO_2 nanospheres

2 mL of tetraethyl orthosilicate and 3 mL of $NH_3 \cdot H_2O$ were added to 50 mL of ethanol and stirred for 24 h at 25°C. The product was centrifuged at 8000 rpm with water and ethanol respectively, and then dried at 80°C for 12 h.

S4. Synthesis of Cu/ZIF-8@SiO_2/PDA

$Cu(NO_3)_2 \cdot 3H_2O$ (96.64 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (178.51 mg), and CTAB (7.5 mg) were dissolved in 10 mL of ultrapure water (A). Next, 2-methylimidazole (4.54 g) was completely dissolved in 70 mL of ultrapure water (B). Solution A was rapidly added to solution B under vigorous stirring at ambient temperature for 1 h. Cu/ZIF-8 was obtained by centrifugation with ethanol at 9000 rpm and drying at 80°C for 12 h. Then, Cu/ZIF-8 (20 mg) and SiO_2 (5 mg) were dissolved in a mixture of 15 mL ultrapure water and 10 mL ethanol. After that, 10 mg of dopamine hydrochloride was added and ultrasound for 15 min. Then added 10 mL of Tris buffer and stirred for 90 min. Finally, the product was centrifuged at 9000 rpm and dried at 80°C for 12 h.

S5. Synthesis of Cu_5Zn_8@SiO_2/NC

The dried material (Cu/ZIF-8@SiO_2/PDA) was carbonized at 700°C for 1.5 h at a ramp rate of 2 °C/min under Ar gas atmosphere, the obtained product was Cu_5Zn_8@SiO_2/NC.

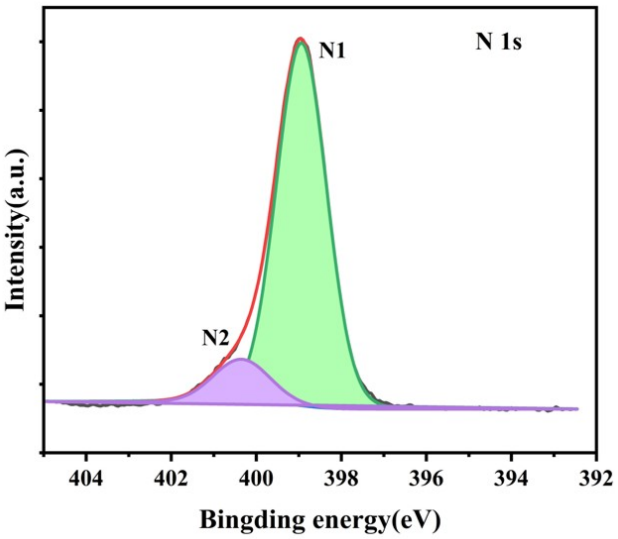

Figure S1. XPS survey spectrum of $Cu_5Zn_8@SiO_2$/NC (N 1s)

Figure S2

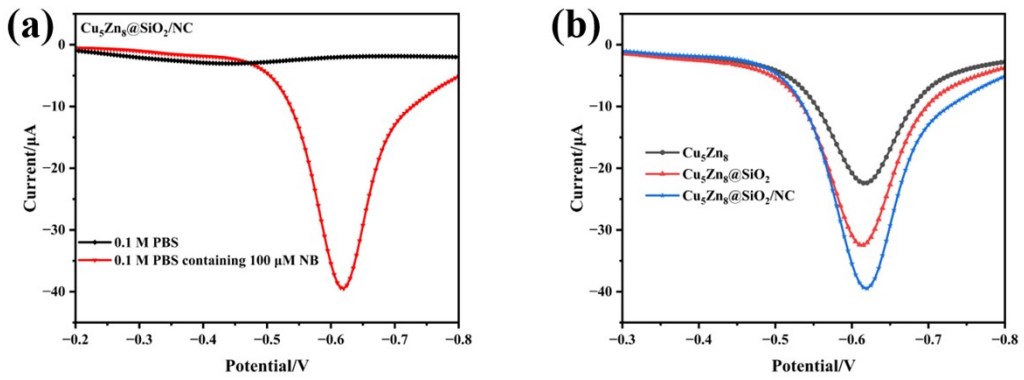

Figure S2. DPV current response curves of $Cu_5Zn_8@SiO_2/NC$ in PBS solution and in PBS solution containing 100 μM NB, respectively (a), $Cu_5Zn_8@SiO_2/NC$, $Cu_5Zn_8@SiO_2$ and Cu_5Zn_8 DPV current response curves in PBS solution containing 100 μM NB (b).

As can be seen from Figure S2(a), $Cu_5Zn_8@SiO_2/NC$ itself has no obvious current signal in the voltage range from -0.2 V to -0.8 V, indicating that the material's own reaction has little influence on the detection of NB within this range. When NB is added, the current response of DPV changes obviously, indicating that $Cu_5Zn_8@SiO_2/NC$ is feasible for the detection of NB. It can be seen from Figure S2(b) that in 100 μM NB, the current response of Cu_5Zn_8 to NB is -22.41 μA. When SiO_2 is combined, the current response of $Cu_5Zn_8@SiO_2$ is increased to -32.47 μA. The resulting composite $Cu_5Zn_8@SiO_2/NC$ has a current response of -39.48 μA. It shows that the current response to NB is higher and higher with the composite of the material. The composite $Cu_5Zn_8@SiO_2/NC$ has good feasibility for electrochemical detection of NB.

Figure S3

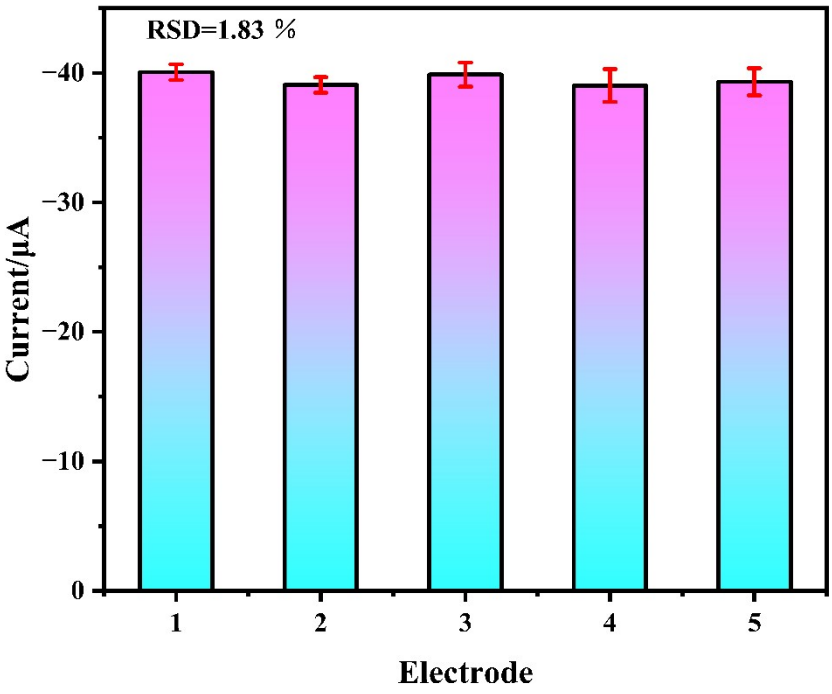

Figure S3. Reproducibility of NB detection by Cu_5Zn_8@SiO_2/NC.

Table S1. Performance comparison of different electrodes for NB detection.

Modified electrode	Detection method	Linear range (μM)	LOD (μM)	Ref.
Ni/Fe(SDS)-LDH	DPV	1-350	0.096	[1]
SNPs/GCE	DPV	5-40	0.027	[2]
Co-NC-800/GCE	DPV	0.1-863	0.086	[3]
ZSO-gCN/GCE	LSV	30-900	2.200	[4]
SANb-BCN/GCE	LSV	2-600	0.700	[5]
GC/Au-MOF-5	CV	20-6000	15.300	[6]
Cu_5Zn_8@SiO_2/NC	DPV	0.2-1000	0.063	This work

Table S2. NB detection results in actual water samples

Real sample	Added (μM)	Found (μM)	Recover (%)	RSD (%)
Tap water	0	0	-	-
	0.5	0.52	103.87	1.66
	50	48.74	97.48	2.17
	500	492.55	98.51	2.5
Lake water	0	0	-	-
	0.5	0.49	98.32	2.24
	50	48.72	97.45	3.25
	500	511.65	102.33	1.11

References

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