

Supporting information

Highly sensitive and stabilized sensing 6-benzylaminopurine based on NiCo₂O₄ nanosuperstructures

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Reagents

6-benzylaminopurine (6-BAP) was bought from Sinopharm Chemical Reagent Co. (China) (<http://www.instrument.com.cn/netshow/SH101458/about.htm>) and 0.1 mmol/L (mM) of 6-BAP stock solution was prepared by accurately weighing amount of 6-BAP to dissolve in ethanol and stored at 4 °C. Polyethyleneimine was purchased from Sigma-Aldrich (<https://www.sigmaaldrich.com>). The 0.1 M phosphate buffer solution (PBS) of different pH was obtained by mixing 0.1 M Na₂HPO₄ and NaH₂PO₄ with pH meter. Other reagents were analytical grade reagents. The ultrapure water used to prepare solution was purified using a Water purified (China) purification system.

Instruments and measurements

The surface morphologies of the NiCo₂O₄ nanosheets were studied using scanning electron microscopy (SEM, Hitachi S-4800) (<http://www.hitachi.com/>), transmission electron microscopy (TEM, FEI F20 S-TWIN) (<http://www.fei.com>) and X-ray diffraction (XRD, PANalytical X'Pert spectrometer, Co-K_α radiation) (www.panalytical.com). Electrochemical measurements were performed using a three-electrode electrochemical cell, with a modified glassy carbon electrode (3 mm in diameter), an Ag/AgCl electrode (sat. KCl) and a platinum wire were used as working electrode, counter electrode, reference electrode, respectively. Cyclic voltammetry (CV), chronocoulometry (CC), linear sweep voltammogram (LSV), chronoamperometry (CA) were performed using a LK2006 Electrochemical Work Station (Tianjin Lanlike Electronic Co., LTD, Tianjin, China)

(<http://www.instrument.com.cn/netshow/SH100827/>). The pH measurements were carried out on PHS-3C exact digital pH metre (Shanghai Leici Co. Ltd., China), which was calibrated with standard pH buffer solution.

Preparation of samples

250 g bean sprouts were weighed accurately and ground finely with a mortar and a pestle then obtained exact volume of 212.5 mL. Then the mixture was centrifuged at 8000 r for 15 min. Finally, the supernatant liquid was collected for subsequent application. The sample solution was diluted by ethanol, and ultrasonicated in an ultrasonic bath for 30 min. After the sample was dissolved, it was stored at 4 °C in order to slow oxidation.

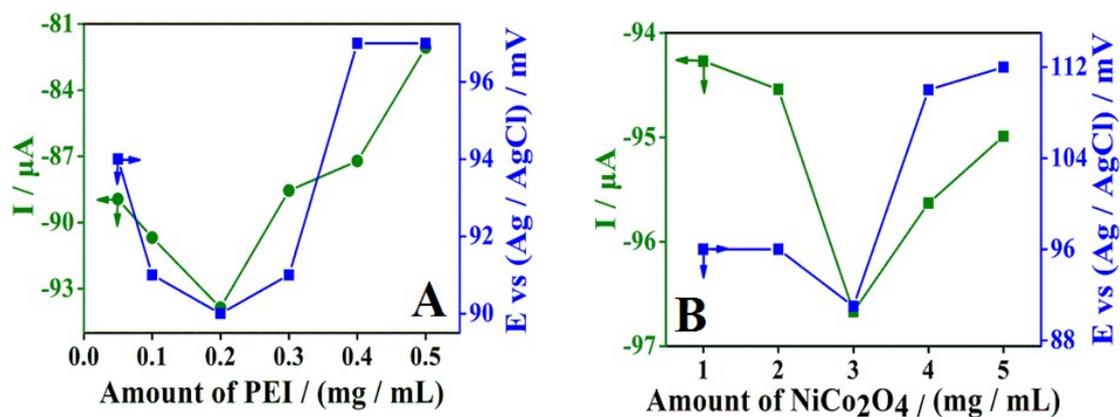


Fig. S1 The relationship between the anode peak currents (green line) and the peak potential differences (blue line) relative to amount of PEI (A), NiCo₂O₄ (B) in 5 mM K₃[Fe(CN)₆] containing 0.1 M KCl range from 0 V to 1.5 V versus Ag/AgCl as reference electrode at 100 mV s⁻¹ scan rate.

In order to obtain the optimization of experimental condition, the effect of amount of PEI in the 5 mM K₃[Fe(CN)₆] solution containing 0.1 M KCl was examined showing in Fig. S1A. It was seen that with increasing the concentration of PEI from 0.05 to 0.2 mg mL⁻¹, the CV peak current of [Fe(CN)₆]³⁻ increased and the peak potential difference declined until the amount of PEI up to 0.2 mg mL⁻¹. And then with the further increasing PEI concentration from 0.2 to 0.5 mg mL⁻¹, the peak current decreased, meanwhile, the potential difference increased and tended to invariableness. The result illustrated that if the PEI film was too thick, it could cause difficult releasing of [Fe(CN)₆]³⁻ from PEI, and the electron transfer of [Fe(CN)₆]³⁻ confined on the modified electrode surface. So the 0.2 mg/mL PEI was chosen as the optimal amount of the PEI to construct electrochemical platform.

With the optimal concentration of 0.2 mg mL⁻¹ of PEI, adding different amount of NiCo₂O₄ into the PEI solution, it was observed that the peak current and the peak

potential difference were also related to the concentration of NiCo_2O_4 in Fig. S1B. There was shown that the most negative peak current reached a maximum and contrarily the peak potential difference reached a minimal value when the amount of NiCo_2O_4 was 3 mg mL^{-1} . Under this amount of 3 mg mL^{-1} , NiCo_2O_4 has much superior electronic conductivity and high electrochemical activity [1]. Whereas, increasing the amount of NiCo_2O_4 from 3 to 5 mg mL^{-1} , its peak current rapidly decreased and the peak potential difference increased, which could block analytic to arrive surface of electrode and enhanced resistance. Therefore, we obtained the optimal concentration of NiCo_2O_4 was 3 mg mL^{-1} .

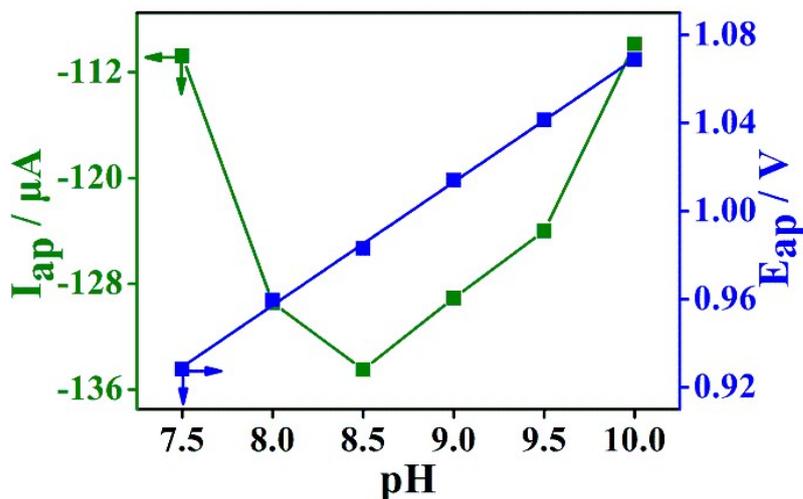


Fig. S2 Effect of solution pH on anodic peak currents (green line) and the peak potential differences (blue line) of PEI-NiCo₂O₄/GCE in 0.1 mM 6-BAP range from 0 V to 1.5 V versus Ag/AgCl as reference electrode at 100 mV s⁻¹ scan rate.

As seen in Fig. S2, the oxidation peak current (I_{pa}) and oxidation peak potential (E_{pa}) varied with pH changing from 7.5 to 10. Accompany increasing the pH, the E_{pa} for 6-BAP oxidation was towards more positive values and it was in good linear relationship with a slope 55.97 mV/pH at the regression equation $E_{pa} (V) = 0.509 - 0.05597 \text{ pH}$ ($R^2 = 0.9988$) which was close to the theoretical value of 57.6 mV/pH in Nernst equation [2] for a redox process including the transfer of an equal number of protons and electrons. The result obviously suggested that the 6-BAP oxidation at PEI-NiCo₂O₄/GCE was pH dependent and hydrogen ion together affected the rate of the oxidation process [3] and this electrode process for 6-BAP might be two-proton coupled two-electron transfer. Additionally, the maximum oxidation peak current is obtained at 8.5 which showed in the green line. Because the current increased with increasing pH until pH=8.5, and then the pH over 8.5, the current decreased. It was chosen pH=8.5 as the optimum pH value for the further studies.

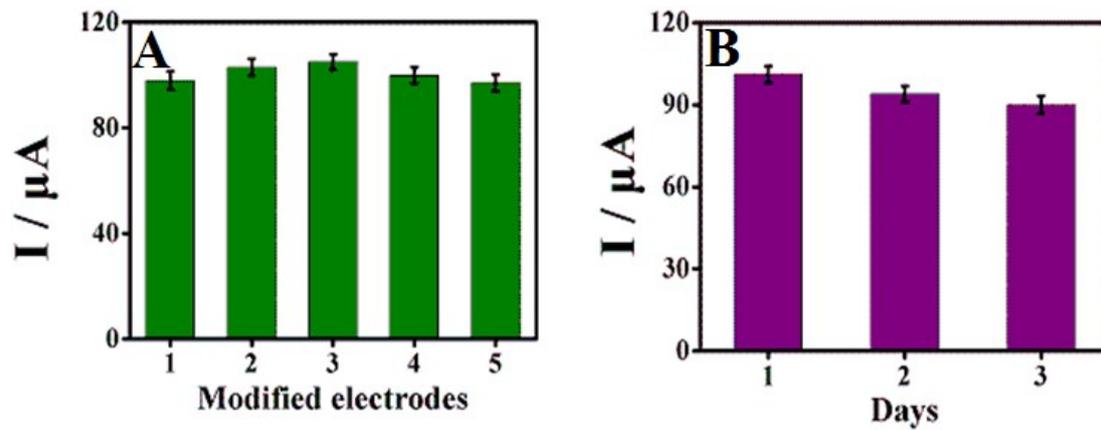


Fig. S3 (A) The reproducibility and repeatability of five PEI-NiCo₂O₄/GCE modified electrodes in 0.1 mM 6-BAP containing 0.1 M PBS (pH 8.5). (B) The stability of the same PEI-NiCo₂O₄/GCE modified electrode at different days.

Table S1 The comparison of developed analytical methods used in detection of 6-BAP.

Method	Linearity range (μM)	LOD (nM)	Reference
Pt/OMCs/GCE	0.05-24	5	[4]
CNTs/GCE	0.04-10	5	[5]
AB-DHP/GCE	0.02-5	5	[6]
PEI-NiCo ₂ O ₄	0.0001-10	0.1	This work

Table S2 6-BAP recovery analysis for bean sprout samples at PEI-NiCo₂O₄/GC electrodes by CC.

Sample	6-BAP concentration			
	Added (ng)	Found (ng)	Recovery (%)	RSD (%) (n=5)
Bean sprout	0.0	0.0	--	--
	1.125	1.0	98.6	4.6
	225	197	89.5	5.2
	2250	2257	100.3	3.5

Reference

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