Nonenzymatic sensing of methyl parathion based on graphene/gadolinium Prussian blue analogue nanocomposite modified glassy carbon electrode

Yuqin Li [b1], Minrong Xu [a1], Peipei Liu [a], Jing Dong [a*], Shiyun Ai [a*]

[a] *College of Chemistry and Material Science, Shandong Agricultural University, Taian, Shandong 271018, China*

[b] *School of Pharmaceutical Science, Taishan Medical University, Taian, Shandong 271016, China*

* Corresponding authors.

Tel: +86 538 8249248

Fax: +86 538 8242251

E-mail address: ashy@sdau.edu.cn (S.Y. Ai)
dongjing@sdau.edu.cn (J. Dong)

[1] These authors are equally contributed to this paper.

1. Synthesis of GO

GO was synthesized from natural graphite powder by a modified Hummers method [1]. Briefly, graphite powder (6 g) was added to an 80 °C mixture solution containing 25 mL of concentrated H_2SO_4, 5 g of $K_2S_2O_8$, and 5 g of P_2O_5. After reaction for 6 h, the mixture was diluted with 1 L of double-distilled water, filtered and washed several times. Finally, oxidized graphite was obtained after being dried in air overnight. For the following oxidation step, the oxidized graphite was added into the 0 °C H_2SO_4 (230 mL) and 30 g of $KMnO_4$ was slowly added under stirring with temperature controlled below 10 °C. The mixture was sequentially stirred for 2 h at 35 °C, after which 460 mL of double-distilled water was added slowly to keep the temperature under 50 °C. 1.4 L of water was added after further reaction for 2 h, and 25 mL of 30% H_2O_2 was added drop by drop. The mixture was filtered and washed with a total of 2.5 L of 10% HCl solution followed by 2.5 L of water to remove the acid and metal ions. Finally, the resulting dark-yellow solid was obtained after vacuum-drying at 60 °C for 12 h and used for further electrochemical reduction.

2.

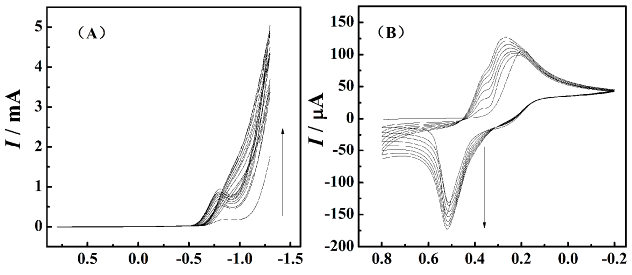

Fig. S1 The typical cyclic voltammograms of GNs (A) and GdHCF (B) deposition process on GCE.

3. FT-IR spectra of GO, GNs and GdHCF/GNs

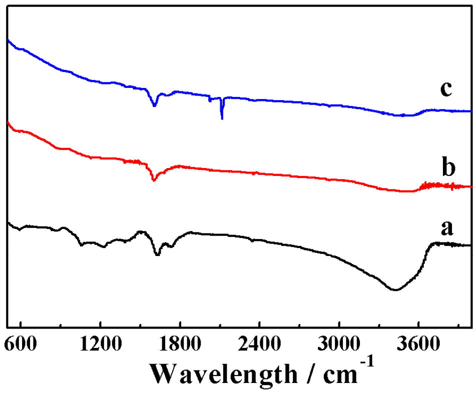

Fig. S2 FT-IR spectra of GO (a), GNs (b) and GdHCF/GNs (c).

The FT-IR spectra of GO, GNs and GdHCF/GNs were recorded to confirm the successful deposition of GNs and GdHCF films in Fig. S2. The characteristic peaks of GO appeared at 1732, 1633, 1417, 1224 and 1055 cm^{-1} (curve a) can be assigned to C=O, C=C, carboxy C–O, epoxy C–O, alkoxy C–O groups situate at the edges of the GO, respectively. After GO was electrochemically reduced on GCE (curve b), the characteristic absorption bands of oxide groups (O–H, C=O, and C–O) decreased distinctly, illustrating the GO has been reduced to GNs. With the deposition of GdHCF on the GNs/GCE (curve c), a strong absorption band at 2118 cm^{-1} was observed, due to the C≡N stretching absorption band in the GdHCF. The FT-IR spectra further proved the GdHCF was successfully electrodeposited on the GNs/GCE.

4.

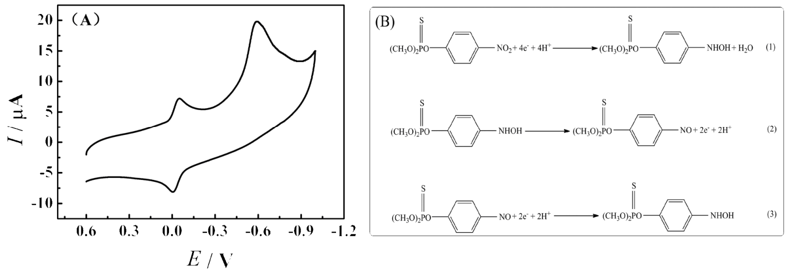

Fig. S3 (A)Cyclic voltammograms of GdHCF/GNs/GCE in the presence of 8 µM MP in 0.1 M PBS (pH 6.0) in the potential range from 0.6 to -1.0 V. (B) Mechanism of the electrochemical reaction of MP on the modified electrodes.

5. UV-vis spectra of MP solution after adsorption by different modified electrodes

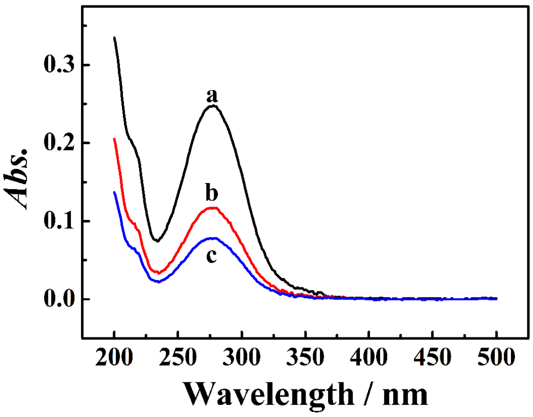

Fig. S4 UV-vis spectra of MP solution before (a) and after adsorption on GNs/GCE (b) and GdHCF/GNs/GCE (c), accumulation time: 5min.

UV-vis spectra were used to prove the efficient adsorption of GdHCF/GNs/GCE for MP. UV-vis spectra of MP solution before (curve a) and after adsorption by GNs/GCE (curve b) and GdHCF/GNs/GCE (curve c) were shown in Fig. S4. 0.5 µM of freshly prepared MP solution showed a maximum absorbance ($\lambda_{\max}$) at 268 nm. After extraction by the GNs/GCE and GdHCF/GNs/GCE for 5 min, respectively, the maximum absorbance of MP solutions significantly decreased due to the adsorption of the two modified electrodes. Compared with GNs/GCE, the maximum absorbance after adsorption by GdHCF/GNs/GCE was smaller than that of GNs/GCE, indicating larger amount of MP was adsorbed on the GdHCF/GNs/GCE. This phenomenon illustrated that the GdHCF/GNs/GCE could serve as a higher-efficiency adsorbent for MP, which may be due to the enlarged surface area, rich π-electron system of GNs and the zeolite-like structure of the GdHCF [2].

6. Optimization of detection conditions for MP at GdHCF/GNs/GCE

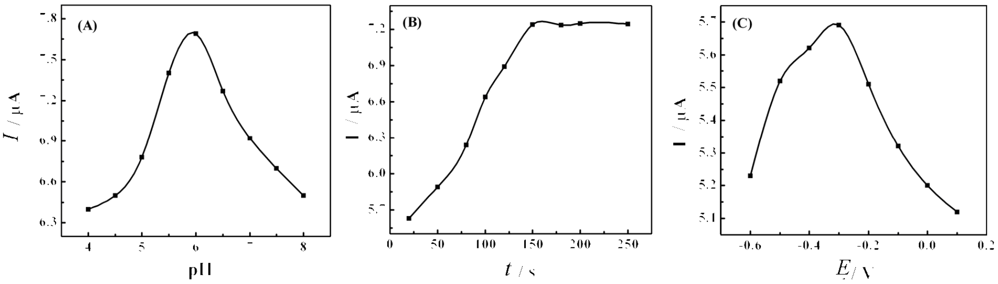

Fig. S5 Influence of pH value (A), accumulation time (B) and accumulation potential (C) on the DPV response of the GdHCF/GNs/GCE to 8 μM MP in 0.1 M PBS.

In order to achieve good performance of stripping analysis for MP, various experimental parameters affecting the stripping currents of MP were optimized including pH, accumulation time and accumulation potential.

The pH is one of the most important affecting factors for the detection of OPs. The influence of pH was evaluated in the range of 4.0 to 8.0. As presented in Fig. S5(A), the stripping currents increased with increasing pH up to 6.0, however, it decreased as pH further increased which was resulted from the decomposition of MP in basic media. H^+ was needed in the irreversible reduction of MP [3]. Considering the sensitivity of the sensor, a pH 6.0 PBS was used in the subsequent experiment.

Accumulation time was also one of the key factors for the stripping currents of MP. The accumulation time dependence of the stripping currents was illustrated in Fig. S5(B), with accumulation time increasing, the stripping currents quickly increased and reached a platform after 150 s. The rapid and high-efficiency adsorption of MP may be due to the large surface area, good conductivity, and strong affinity of GdHCF/GNs/GCE. Thus, 150 s was selected as the accumulation time in the following investigations.

As shown in Fig. S5(C), accumulation potential over the range of 0.1 to -0.6 V was investigated, and the maximum oxidation peak current appeared at -0.3 V. Therefore, the optimal accumulation potential for detection of p-nitrophenol was -0.3 V.

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.* , 1958, **80**, 1339-1339.
2. Y. Jiang, X. Zhang, C. Shan, S. Hua, Q. Zhang, X. Bai, L. Dan and L. Niu, *Talanta*, 2011, **85**, 76-81.
3. D. Du, X. Ye, J. Zhang, Y. Zeng, H. Tu, A. Zhang and D. Liu, *Electrochem. Commun.*, 2008, **10**, 686-690.