

## Preparation of Platinum Nanoparticles-Graphene Modified Electrode and Sensitive Determination of Paracetamol

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Only three graphene (GR) based chemical sensors were reported for the determination of paracetamol (4'-hydroxyacetanilide, *N*-acetyl *p*-aminophenol, acetaminophen) (PCT). Kang's group investigated the electrochemical behaviors of PCT on GR-modified electrodes by cyclic and square-wave voltammetry. The results showed that the GR modified electrode exhibited excellent electrocatalytic activity to PCT in alkaline medium (pH=9.5) [1]. Bahramipur and Jalali investigated the electrochemical behavior of PCT at the GR paste electrode [2]. Yin and co-workers fabricated the GR-chitosan composite film modified glassy carbon electrode and used to determine PCT [3]. In this study, aminopolysaccharide chitosan was used as a polymer binder in order to improve the film adhesion to the substrates. However, the electrochemical behavior and voltammetric detection of PCT using noble metal nanoparticle GR/GC modified electrode has not yet been reported. Metal nanoparticles, especially the noble-metal nanoparticles, have attracted considerable attention in constructing electrochemical or optical sensors due to their novel chemical and physical properties [4,5]. Previous studies have recommended that Pt nanoparticles have a good electrocatalytic activity among other metal nanoparticles.

First, a graphene-modified glassy carbon electrode was fabricated by a simple drop-casting method. Then, Pt nanoparticles were electrodeposited on this electrode surface to form a Pt nanoparticles/graphene modified electrode (Pt/GR/GC), and used in the electrochemical detection of PCT. The electrochemical behaviors of PCT on Pt/GR/GC modified electrodes were investigated by cyclic voltammetry and square-wave voltammetry (SWV). A cyclic voltammetry (CV) was used to investigate the electrochemical behavior of PCT on the bare GCE, GR/GCE and Pt/GR/GCE in 0.1 M ammonia buffer solution at a scan rate of 100 mV s<sup>-1</sup>, respectively. Fig. 1 depicts cyclic voltammograms of PCT on the bare GCE, GR/GCE and Pt/GR/GCE in 0.10 M ammonia buffer solution (pH 9.5). On the bare GCE (Fig. 1blue), PCT shows an irreversible redox behavior with small and undefined redox signals. At a bare GCE, PCT shows a quasi-reversible behavior with relatively weak redox current peaks at  $E_{pa} = 0,389$  V and  $E_{pc} = -0,72$  V (vs. SCE). The peak potential separation ( $\Delta E_p = E_{pa} - E_{pc}$ ) was as large as 317 mV. On the GR/GCE, the anodic and cathodic peak currents of PCT are significantly increased. According to the experimental results, the oxidation peak of PCT shifted negatively to 375 mV, and the reduction peak shifted positively to -44 mV at the GR/GCE (Fig. 1red). The value of  $\Delta E_p$  decreased to 331 mV, clearly indicating that the oxidation of PCT become more reversible at the GR/GCE. Further, Pt nano particles were electrodeposited onto surface of GR/GCE. The oxidation peak of PCT shifted negatively to 264 mV, and the reduction peak shifted positively to 186 mV at the GR/GCE (curve black). It can be seen that the oxidation overpotential of PCT becomes lower than that on GR/GCE with a negative shifted of 78 mV. So, significantly increased redox peak currents, reduced oxidation potential and greatly increased electron transfer rate of of PCT at the Pt/GR/GCE. As can be seen in Fig 1, oxidation peak signal significantly increases to 36  $\mu$ A,

which is 2.6 ( $36:14=2.6$ ) times higher than that on GR/GCE. These results demonstrated that the electrochemical reactivity of PCT is remarkably improved on the Pt/GR/GCE.

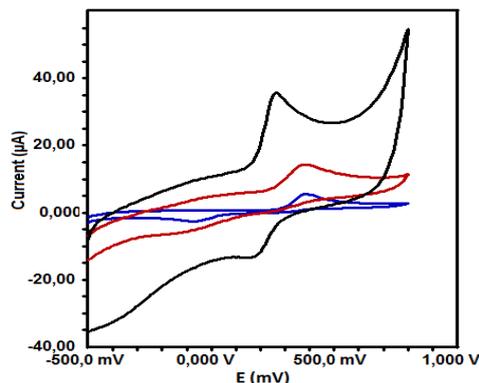


Fig. 1 Cyclic voltammograms of PCT on the bare GCE (blue), GR/GCE (red) and Pt/GR/GCE (black) in 0.10 M ammonia buffer solution (pH 9.5).

The voltammetric determination of PCT was carried out using square-wave voltammetry (SWV). The calibration curve for PCT shows two linear segments: the first linear segment increases from 0.04 to 1.0 and second linear segment increases up to 10  $\mu\text{M}$ . The detection limit was determined as  $2.0 \times 10^{-9}$  mol L<sup>-1</sup> using SWV. Finally, the proposed method was successfully used to determine PCT in pharmaceutical preparations. The developed method can be used for the detection of PCT and *p*-aminophenol simultaneously without interference of each other.

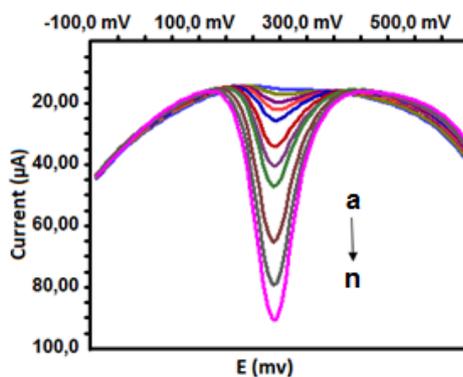


Fig. 2. Square wave voltammograms of Pt/GR/GCE in 0.1M pH 9.5 acetate buffer solution containing different concentrations of PCT (a–n): 0.04, 0.06, 0.08, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0,6.0,8.0,10  $\mu\text{M}$ ).

## References

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