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Very sensitive electrochemical determination of diuron on glassy carbon electrode modified with reduced graphene oxide–gold nanoparticle–Nafion composite film

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ABSTRACT

In this work, a very sensitive electrochemical sensor based on glassy carbon electrode (GCE) modified with reduced graphene oxide–gold nanoparticles/Nafion (rGO–AuNPs/Nafion) composite film was applied to determine diuron. Synthesized GO was characterized using X-ray diffraction (XRD) and UV–visible spectroscopy. The surface morphology of the rGO–AuNPs/Nafion film was also characterized using scanning electron microscopy and electrochemical impedance spectroscopy. Cyclic voltammetry (CV) and adsorptive differential pulse voltammetry (AdDPV) were applied to investigate the electrochemical response of the diuron on the modified electrode. The electrode showed a linear response at $1.0 \times 10^{-9} - 1.0 \times 10^{-7}$ M and a detection limit of 0.3 nM under the optimized conditions. The effect of some other species on the determination of diuron was investigated and the sensor showed good selectivity for determination of diuron. The constructed sensor was applied to determine diuron in enriched samples of orange juice, mineral and tap water which statistical t-test showed accuracy of method. Also the sensor was applied to obtain diuron content in the tea sample. The reliability of the proposed sensor was confirmed after comparing the results with those obtained using high performance liquid chromatography (HPLC) as a comparative method.

1. Introduction

Diuron (N-(3,4-dichlorophenyl)-N,N-dimethylurea) as a herbicide is frequently used for weed control of crops such as citrus fruits, rice, cotton, soybeans, sugarcane, potato, wheat, tea and coffee, as well as along airport runways, railways, and pipelines. It is one analytical target due to its stability in water and soil and so can cause to environmental impacts for plants and mammals. In plants, it is adsorbed via root of plants and then reaches to stem and leaves and finally can prevent from photosynthesis. In human, it can be led to the formation of methemoglobin in the blood, as well as liver and spleen abnormalities and also problems in processes of release and transport of natural hormones in the body (Wong et al., 2013). Therefore sensitive, selective and simple determination of diuron is very important to protect ecology and environment. Some analytical methods were reported for determination of diuron, such as chromatography (Lourencetti et al., 2008; Rodrigues et al., 2007), fluorescence spectroscopy (Sharma et al., 2010) and electrochemical methods (Mani et al., 2015; Mugadza and Nyokong, 2010b; Sharma et al., 2011; Wong et al., 2013, 2015; Wong and Sotomayor, 2014). The electrochemical methods have advantages such as high sensitivity, stability, and selectivity especially when the electrodes is modified with nanomaterials (Kor and Zarei, 2013; Zarei et al., 2015), graphene (Li et al., 2012), Nafion (Zarei and Helli, 2015), polymers (Kor and Zarei, 2014; Zarei et al., 2014) and imprinted polymers (Kor and Zarei, 2016). The materials that were selected for this work are reduced graphene oxide, gold nanoparticles and Nafion.

One of the most important derivatives of graphene is reduced graphene oxide (rGO). It has high thermal and chemical stability, large surface area, superior biocompatibility, and excellent conductivity (Pang et al., 2016). Therefore it can be applied for construction of new chemical sensors.

Gold nanoparticles (AuNPs) have unique optical, physical and chemical properties such as strong adsorption ability, large surface-to-volume ratio, small particle size and good electrical properties. Therefore, they have been extensively used in many sensors and biosensors (Ma and Zhang, 2011).

Nafion as a perfluorinated sulphonated cation exchanger has properties of excellent antifouling capacity, chemical inertness and high permeability to cations. Nafion has been widely used as an electrode modifier (Anandhakumar and Mathiyarasu, 2013; Liu et al., 2011; Senthil Kumar et al., 2012; Wang et al., 2006; Yang et al., 2010; Yin et al., 2010; Zarei and Helli, 2015).

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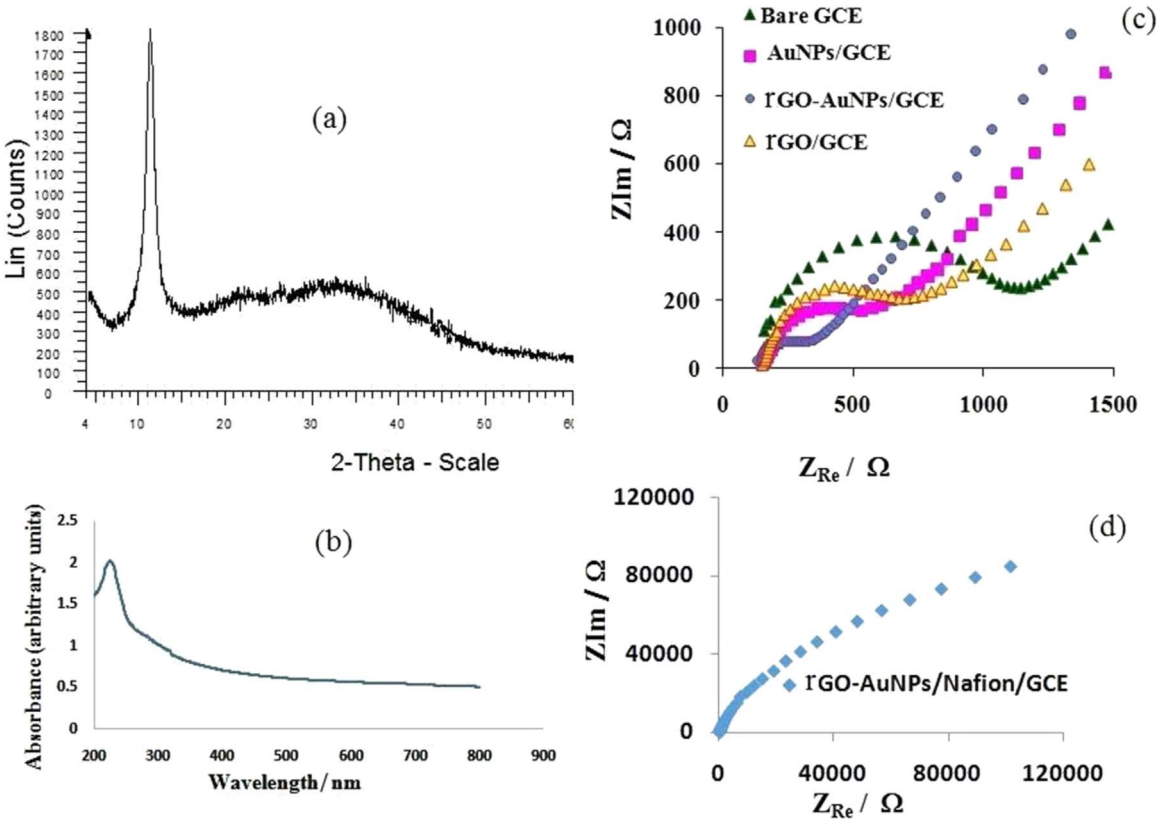

Fig. 1. XRD spectra (a), UV–vis spectra of GO (b) EIS of bare GCE, rGO/GCE, AuNPs/GCE and rGO-AuNPs/GCE (c) and rGO-AuNPs/Nafion/GCE (d) in 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in 0.1 M KCl. Applied AC voltage: 5 mV, frequency: 0.1 Hz to 100 kHz.

In this work, the reduced graphene oxide–gold nanoparticles/Nafion (rGO–AuNPs/Nafion) film modified glassy carbon electrode (GCE) was constructed and applied for the electrochemical determination of diuron using adsorptive differential pulse voltammetry (AdDPV).

2. Experimental

2.1. Apparatus

A PAR (Princeton Applied Research) electrochemical analyzer model 394 and an Autolab electrochemical system with PGSTAT 12 (EcoChemie, Utrecht, Netherlands) and FRA 4.9 software, were used for voltammetric and impedance experiments, respectively. Three-electrode system consisted of a rGO–AuNPs/Nafion/GCE as the working electrode, Ag/AgCl electrode (KCl saturated) as the reference electrode and a platinum wire as the auxiliary electrode. For impedance measurements, the frequency range of 0.10 Hz to 100 kHz was employed. The AC voltage amplitude used was 5 mV.

Diuron, Nafion (5%) and $HAuCl_4$ were provided from Sigma–Aldrich. Graphite oxides were prepared from graphite powder by Hummers method (Hummers and Offeman, 1958).

The stock 1.0×10^{-3} M diuron solution was prepared by dissolving the required amount of diuron in 15% methanol to water. All other reagents were of analytical grade and used as received. All solutions were prepared with redistilled water.

2.2. Preparation of rGO–AuNPs/Nafion composite modified electrode

Before modification, the GCE was polished with 0.3 and 0.05 μm alumina powders using a polishing cloth with water as the lubricant. The electrode was then sonicated in diluted HNO_3, then ethanol and finally distilled water for 10 min.

1.0 mg of the GO was added to 10 ml water and then the mixture was sonicated for 30 min to obtain a uniform modifier suspension. For the preparation of rGO–AuNPs composite, 15 μl $HAuCl_4$ 24.3 mM was added to the above solution and transferred to the voltammetric cell and rGO–AuNPs was simultaneously reduced using cyclic voltammetry. Here, 7 CV scans were performed under magnetic stirring at the potential range of −1.5–0.3 V and scan rate of 26.6 mVs^{-1}. The number of CV cycles can control the thickness of nanocomposite film and therefore it was optimized. After co-reduction of rGO–AuNPs, the electrode surface color changed from black to bright red (color of AuNPs). In this stage, the modified electrode was washed with redoubled distilled water and dried under I.R. lamp. Finally 4 μl Nafion 0.5% was casted on the electrode surface and it remained at room temperature to evaporate the solvent.

2.3. Experimental procedure

The sample solution, containing 2.0 ml 0.1 M $HClO_4$ and a specified volume of diuron was diluted to the mark with water in a 10 ml volumetric flask and the resulting solution was transferred into a voltammetric cell. Accumulation was performed at 0.0 V for 300 s under constant stirring and then stirring was stopped and after 5 s, the voltammogram was recorded by using a positive-going differential pulse scan from 0.4 to 0.7 V versus Ag/AgCl electrode at a scan rate of 33.3 mVs^{-1}. After each measurement, the modified electrode was placed in the blank solution and potentials of 1.0 V and −1.0 V was applied to the electrode for 4 min and 1.0 min, respectively, to remove any memory effect. A blank solution without diuron was used to obtain the blank peak current.