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Short Communication

A Selective Electrochemical Sensor based on TiO_2/reduced graphene for Efficient Determination of Methanol

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Titanium dioxide (TiO_2) nanoparticles-reduced graphene oxide (rGO) nanocomposite modified glassy carbon electrode (GCE) were produced by drop casting and electrochemical reduction for the sensitive determination of methanol. The as-prepared TiO_2-rGO composite was characterized by X-ray diffraction and scanning electron microscopy. The electro-catalytic performance of electrochemical methanol sensor was evaluated by amperometry and cyclic voltammetry techniques in alkaline media. The electrochemical results indicated that the TiO_2-rGO/GCEs enhanced the electrochemical active surface area for the prepared electrode and significantly improved the electrochemical responses to methanol. This electrochemical methanol sensor revealed excellent stability and reproducibility with 0.7 µM limit of detection and sensitivity of 0.026 $\mu A/\mu M cm^2$ which showed that TiO_2-rGO/GCE electrode had an excellent electro-oxidation to the methanol solution.

Keywords: Titanium dioxide nanoparticles; reduced graphene oxide; Methanol detection; Amperometry technique; cyclic voltammetry

1. INTRODUCTION

Methanol is commonly used organic solvents, mainly in household and industrial products [1]. It is also very valuable as a substitute fuel. However, exposure to methanol through inhalation and absorption into the skin may lead to toxicity from headaches to blindness through direct digestion and even death [2]. Thus, facile analysis methods are important for determining the concentration of methanol in the environment, clinical diagnostic measurements and for alcoholic beverages [3]. Many different instrumental techniques are used for methanol detection, including fluorescence, GC-FID, HPLC with electrochemical, FTIR and UV–visible detection [4-7]. An alternative electrochemical methods is to use an amperometric sensor that detects methanol [8].

In electrochemical methanol oxidation, the type of electrode materials is an important parameter required for a highly efficient electro-catalyst. In recent years, graphene has received significant attention due to its high electrical conductivity, mechanical strength and large surface area [9, 10], which have been used in different fields containing sensor, nanoelectronics and supercapacitor [11-13]. However, the graphene applications were investigated via irreversible agglomeration both in common solvents and in drying state, which significantly decreased its efficiency [14]. It was found that the combination of nanomaterials in graphene sheets may prevent the agglomeration of graphene. In this method, nanomaterials play the role of bridges to accelerate the transfer of electrons between graphene sheets. It can also efficiently prevent the irreversible accumulation of graphene sheets. Nowadays, the common nanocomposites including AuNPs/graphene, $NiFe_2O_4$/graphene, carbon nanotubes/graphene, Co_3O_4/graphene and MIP/nano-Fe_3O_4/SiO_2 have been used to enhance the electrochemical sensor [15-17]. Newly, nanoparticles with novel chemical and physical properties were advanced. Compared to metallic nanoparticles, the metallic oxide nanoparticles involving ZnO nanostructures, SnO_2, and WO_3 nanostructures indicated special performances including improved compatibility, promoted electron transfer high surface area, and enhanced conductivity [18-20].

TiO_2 is well-known electrode material which is widely employed in electrochemical applications. Furthermore, TiO_2 has been mainly used in electrochemical biosensors to detect various analytes with lower concentration because of its good catalytic properties and biocompatibility [21]. Although the use of metal-oxide semiconductor nanostructures for the determination of methanol have many advantages, no study has been conducted on the TiO_2-reduced graphene oxide (TiO_2-rGO/GCEs) based electrochemical sensor. Here, a novel electrochemical TiO_2-rGO/GCEs based sensor was prepared to determine methanol. The electro-catalytic performance of proposed methanol electrochemical sensor was evaluated by amperometry and cyclic voltammetry techniques in alkaline media.

2. MATERIALS AND METHOD

Graphene oxide (GO) was prepared from graphite consistent with a Hummers' technique [22]. The GO powders were dissolved in deionized water at 3 mg/ml concentration. Before reduction, 5 ml of GO suspension was prepared as mixed with DMF (35 ml). Then, the aqueous hydrazine (N_2H_4) was added into the suspension under stirring. The prepared solution was transferred into the water bath at 70 °C for 7 hours. Then, it was sonicated for 1h to homogenize and stabilize the graphene distribution into the DMF solution.

The surface of glassy carbon electrode (GCE) was cleaned with 0.3 µm alumina for half an hour. Then, GCEs was sonicated in distilled water and ethanol for 10 min. The substrates were then posited into an oven at 70 °C. The GO layers were prepared by airbrush spray coating of the GO suspension on the GCE. The air brush was held at a distance of 10 cm from the surface of GCE. Then, the substrate was placed into the hot plate at 110 °C.

TiO_2 NPs (2 mg) was added to GO suspension solution (5 mL) under 2 h ultrasounds to attain the TiO_2-GO composite. Then the TiO_2-rGO/GCEs were prepared using a drop-casting technique followed by an electrochemical reduction procedure through drop-casting of 5 µL TiO_2-GO dispersion onto the surface of GCE. Finally, the reduction process was done by electrochemical technique under the 1.2 V potential for 2 min to form TiO_2-rGO/GCE electrode.

The morphological studies of TiO_2-rGO nanocomposite were performed by field emission scanning electron microscope (FESEM). The structural properties of the samples was carried out by X-ray diffraction analysis (XRD, Philips diffractometer PW 103/00) in 2θ range from 10–60° by Ni-filtered CuKα radiation.

Cyclic voltammetry (CV) were done by a standard three-electrode electrochemical method. The rGO based electrodes were utilized as working electrode. A saturated Ag/AgCl and platinum electrode acted as reference and counter electrodes, respectively. Fresh phosphate buffer (0.1 M) was employed as a supporting electrolyte in all electrochemical experiments. All electrochemical tests were recorded at 0.1V/s scan rate. To determine the electrode sensitivity to methanol, the solutions including different contents of methanol, were measured by the peristaltic pump which the detection method was completely presented in previous studies [23].

3. RESULTS AND DISCUSSION

FESEM analysis was used to characterize the surface morphology of the prepared GO/GCE and TiO2-rGO/GCE electrodes. Figure 1a shows the FESEM image of GO on GCE electrode. Since graphene oxide is composed of stacked layers of graphite, the white lines are observed on the image indicating its folding structure.

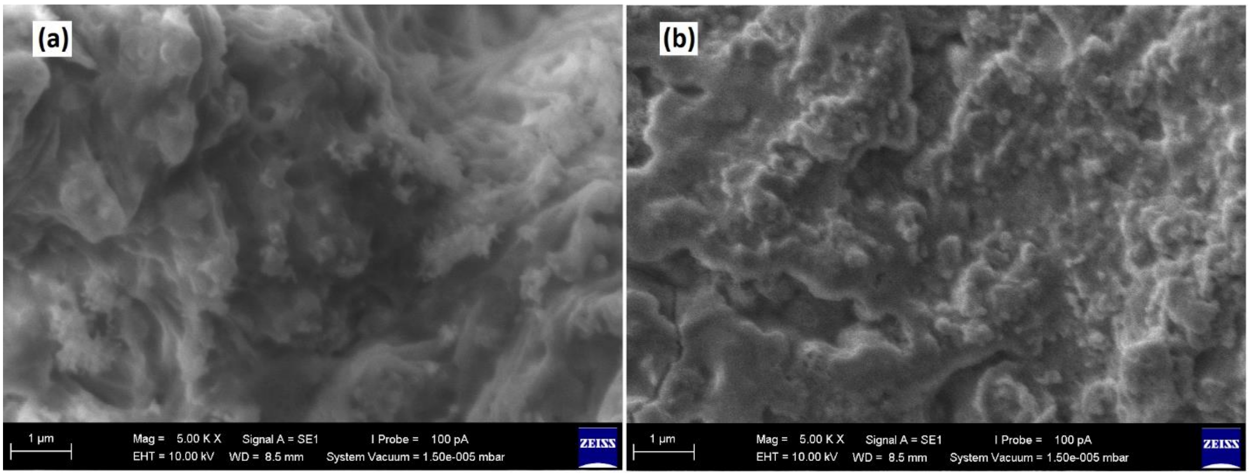

Figure 1. Surface morphologies of (a) the GO/GCE and (b) TiO_2-rGO/GCE electrodes

The distances between all the white lines are not the same, which clarify that GO does not have a special lateral size. As indicated in Fig. 1b, The TiO_2 nanoparticles aggregated together, and therefore their dispersibility can be improved. Furthermore, GO sheets were clearly observed around the TiO2 nanoparticles, revealing the TiO_2 nanoparticles were well composed with the GO nanosheets. The average diameters of these nanoparticles were approximately 100 nm.

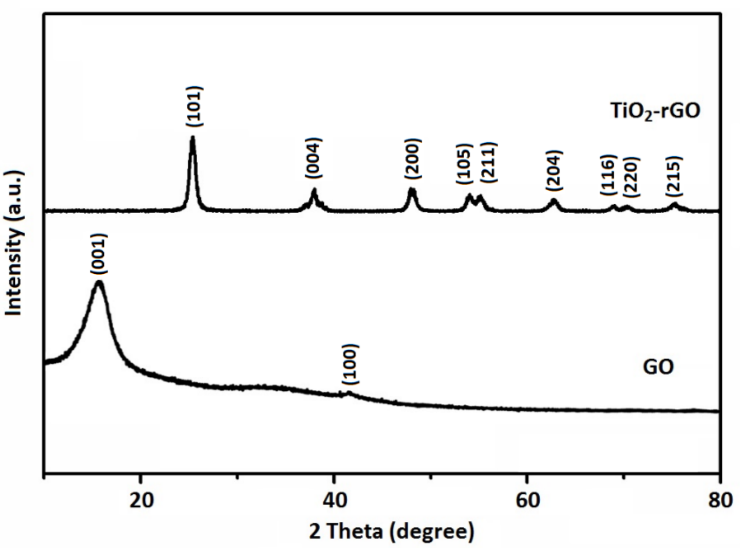

Figure 2. XRD pattern of GO and TiO_2-rGO nanocomposites

Figure 2 indicates the XRD pattern of GO and TiO_2-rGO. As shown in Fig. 2, the GO has the most intense peak at 12 °, according to the (001) plane. The peaks observed at 25.2 , 37.7, 48.2, 54.1, 55.2, 62.4, 68.6, 70.1, and 75.3 are consistent with (101), (004), (200), (105), (211), (204), (116), (220), and (215) of anatase TiO_2 (JCPDF-1272). Furthermore, the diffraction peak of GO disappeared, showing that GO can be reduced to rGO during the hydrothermal reaction.

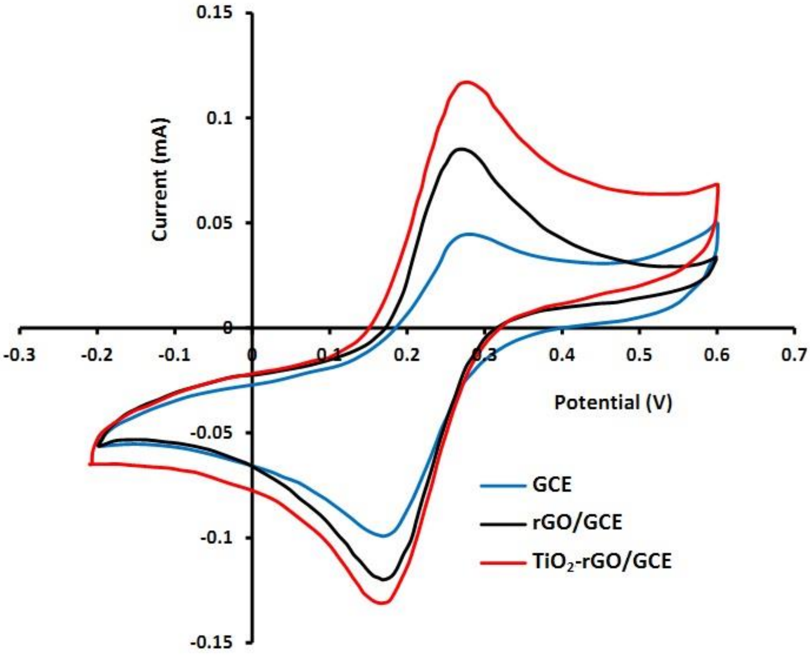

Figure 3. The CV curves of GCE, rGO/GCE and TiO2-rGO/GCE electrodes in 0.1 mM/L PB solution

The CV curves of GCE, rGO/GCE and TiO_2-rGO/GCE electrodes in 0.1 mM/L PB solution are indicated in Fig.3. As shown, all of the electrodes reveal a pair of redox peaks. However, the peak intensity values of redox at TiO_2-rGO/GCE have increased more than the other electrodes. Once the GO was reduced to the rGO, the redox peak improved significantly due to the restoring of the conjugated networks of the conductive carbon and large surface area. On the other hand, the rGO was composed with TiO_2 nanoparticles, Redux's peak current had increased further due to a synergistic enhancement between TiO_2 nanoparticles and rGO sheets. The electrode areas were calculated using the Randles–Sevcik equation [24], which were 0.069, 0.138, and 0.192 cm^2, for GCE, rGO/GCE and TiO_2-rGO/GCE electrodes, respectively. The electroactive area of TiO2-rGO/GCE was bigger than the other electrodes which can be attributed to the large-surface area of rGO and TiO2 nanoparticles. A large electroactive area of the TiO_2-rGO/GCE electrode enhanced the adsorption capacity of methanol and suggested more catalytic sites for methanol oxidation.

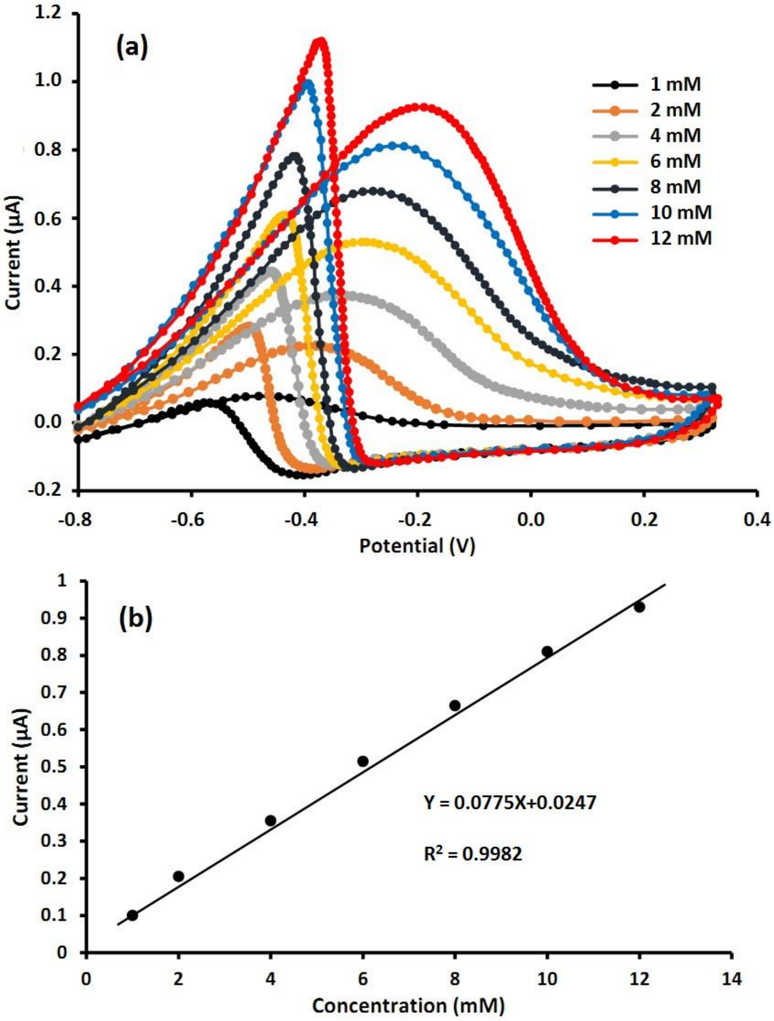

Figure 4. (a) The CV plots of TiO_2-rGO/GCE electrode in 0.1 M PB solution in successive additives of 2 mM methanol solution (b) the plot of calibration graphs

In the methanol sensing process, the optimal potential range of -0.8 to 0.2V was selected to reduce the redox reaction interferences of oxygen, OH^- and Ti that dissolved in the solution [25], also the oxidation peak currents may be applied as methanol detection criteria [26]. The primary volume of every samples was 30 ml of 0.1 M PB solution in the electrochemical cell. Figure 4 indicates the CV responses of TiO_2-rGO/GCE electrode in 0.1 M PB solution with methanol concentration of 1, 2, 4, 6, 8, 10 and 12 mM. As shown in figure 4, the oxidation peak current increases from 0.1 to 0.91 µA. Furthermore, the oxidation peak potentials were shifted from -0.46 V to -0.19 V when the content of methanol increased which can be attributed to the methanol concentration [27]. Hence, the relationship between the methanol concentrations and oxidation peak current may be used to identify methanol. As revealed in figure 4b, the regression equation was found to be $Y = 0.0775X+0.0247$, with a correlation coefficient of $R^2 = 0.9982$. The sensitivity was 0.077 $\mu A/mMcm^2$, and detection limit value was estimated 0.4 µM.

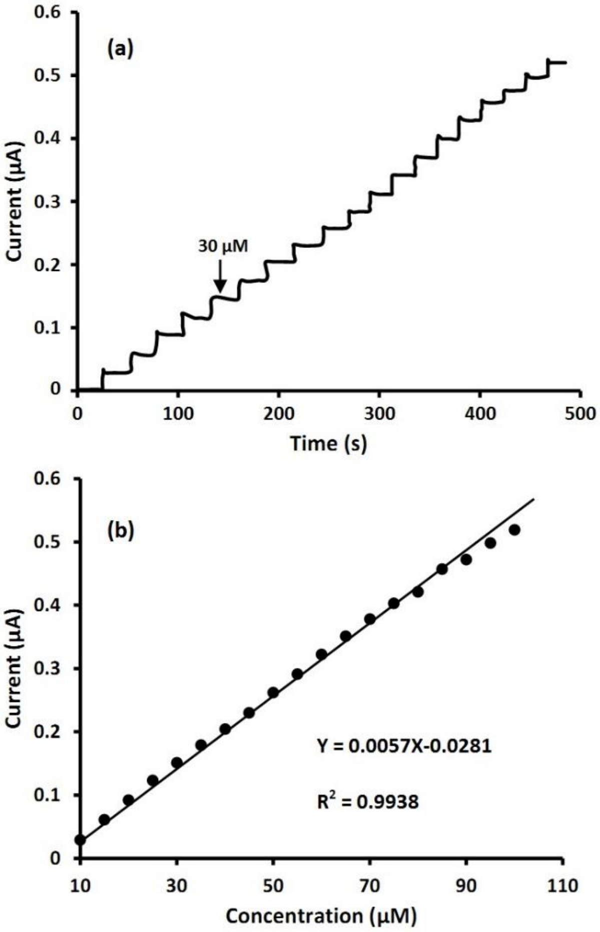

Figure 5. The amperometric performance of TiO_2-rGO/GCE electrode in 0.1 M PB solution in successive additives of 5 µM methanol solution (b) the plot of calibration graphs

Given that amperometry technique is much more sensitive to CV in stirred condition, this method was used to evaluate the low-level methanol content. Amperometry method was applied to investigate the detection limit and sensitivity in 0.1 M PB solution. Figure 5 indicates the amperometric response of TiO_2-rGO/GCE electrode in successive additions of 5 µM methanol solution. As indicated in figure 5a, an excellent response is found for the subsequent additives of methanol. This data shows an efficient and stable catalytic property of TiO_2-rGO/GCE electrode. There is a linear relation between methanol concentration and response current in the range 10 to100 µM. Furthermore, in methanol concentration above 85 µM, a reduction in response current can be found, which can be related to the electrode process transfer from a controlled mass-transport to a surface-reaction [28]. The sensitivity and detection limit were found to be 0.026 $\mu A/\mu Mcm^2$ and 0.7 µM, respectively.

A comparison study in the performance of methanol electrochemical sensors is indicated in Table 1. The results show that TiO_2-rGO/GCE electrode has excellent electro-oxidation to the methanol solution. The performance of methanol oxidation mostly because of the interaction effect among TiO_2 and rGO. The TiO_2 nanoparticles act as an effective alternative material for efficient catalyst dispersion, which seems a promising study.

Table 1. Comparison of TiO_2-rGO/GCE performance with other electrochemical methanol sensors.

Method	Electrodes	detection limit (µM)	Sensitivity ($\mu A/\mu Mcm^2$)	Ref.
AMP	CEF-Ni(II)/Chitosan/GCE	5.2	0.002	[29]
AMP	Pd–Ni/SiNWs/GCE	25	0.48	[30]
AMP	NiOOH/EPGC	10	7.26	[31]
AMP	Modified copper electrode	100	0.015	[32]
CV	Pt/CNTs	60	0.006	[33]
AMP	TiO_2-rGO/GCE	0.7	0.026	This work

4. CONCLUSIONS

Here, TiO2-rGO/GCE electrochemical sensor were produced by drop casting and electrochemical reduction for the sensitive determination of methanol. The as-prepared TiO_2-rGO composite was characterized by X-ray diffraction and scanning electron microscopy. The electro-catalytic performance of the proposed methanol electrochemical sensor was evaluated by amperometry and CV techniques in alkaline media. The CV characterization of various electrodes revealed that a large electroactive area of the TiO2-rGO/GCE electrode enhanced the adsorption capacity of methanol and suggested that more catalytic sites for methanol oxidation. The electrochemical results indicated that the TiO_2-rGO/GCEs enhanced the electrochemical active surface area for the prepared electrode and significantly improved the electrochemical responses to methanol. This electrochemical methanol sensor revealed an excellent stability and reproducibility with 0.7 µM limit of detection and sensitivity of 0.026 µA/µMcm^2 which showed that TiO_2-rGO/GCE electrode has excellent electro-oxidation to the methanol solution.

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