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Microwave-assisted synthesis of Bi_2WO_6 flowers decorated graphene nanoribbon composite for electrocatalytic sensing of hazardous dihydroxybenzene isomers

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ABSTRACT

A microwave-assisted synthesis is described for the preparation of bismuth tungstate/graphene nanoribbons (Bi_2WO_6@GNRs) nanocomposite as cost-effective alternative to existing hydrothermal method. HR-TEM, XRD, XPS, EDX, BET and Raman characterizations reveal the incorporation of Bi_2WO_6 flowers on GNRs. The electrochemical and interfacial properties of the composite were probed by voltammetry and impedance studies. The electrocatalytic ability of the composite was assessed by studying the redox reactions of hazardous dihydroxybenzene isomers. Bi_2WO_6@GNRs modified screen-printed electrode was found to distinguish the voltammetric signals of catechol and hydroquinone (separation gap of 140 mV, vs. Ag|AgCl), minimizes reaction overpotentials, and amplifies the electrochemical current signal. The effects of concentration scan rate and cross-reactivity are studied. Bi_2WO_6@GNRs incorporated sensor displayed detection limits of 5.31 nM and 7.24 nM for catechol and hydroquinone, respectively. The method was found to be practically applicable in the determination of catechol and hydroquinone in water samples and face cream sample, respectively.

1. Introduction

Development of advanced nanocomposites is necessary to fabricate sensitive and reliable electrochemical sensors for food, drug, water and environmental analysis [1–3]. Over the past decade, graphene based nanocomposites are developed and extensively applied in a variety of electrocatalytic sensing and sensing applications [4–6]. The extraordinary physicochemical properties of graphene and its synergic combination with the properties of associated materials prompted the researchers to use these composites in catalysis and sensing [7–9]. Besides, the modification of graphene nanocomposite on the electrode surface enables enormous signal amplification that helps to achieve high level of detection sensitivity in real samples [10–12].

Graphene nanoribbons (GNRs) are narrow strips of graphene. Along with interesting properties of graphene, it featured with additional properties such as, open band gap, high edge density, rich edge defects, and extra catalytic sites [13–15]. On the other hand, bismuth tungstate (Bi_2WO_6) is a semiconductor material known for its photocatalytic properties; but, it requires a suitable support to endow its maximum catalytic potential [16]. The incorporation of Bi_2WO_6 on GNRs could produce a Bi_2WO_6@GNRs nanocomposite, which is expected to have significantly improved electrocatalytic as well as photocatalytic properties, useful for multipurpose applications. The catalytic performance of Bi_2WO_6 is majorly depending on its crystallinity and morphology which are controllable by carefully designed preparation protocols [16,17]. Although, procedures are available to prepare Bi_2WO_6@graphene nanocomposite through hydrothermal methods, the method requires the use of expensive autoclave instrument [18–20]. Besides, the focus was solely on exploring photocatalytic applications of Bi_2WO_6; none of the report explores electrochemical sensing applications of Bi_2WO_6@GNRs.

In recent years, microwave (MW)-assisted synthetical strategy is

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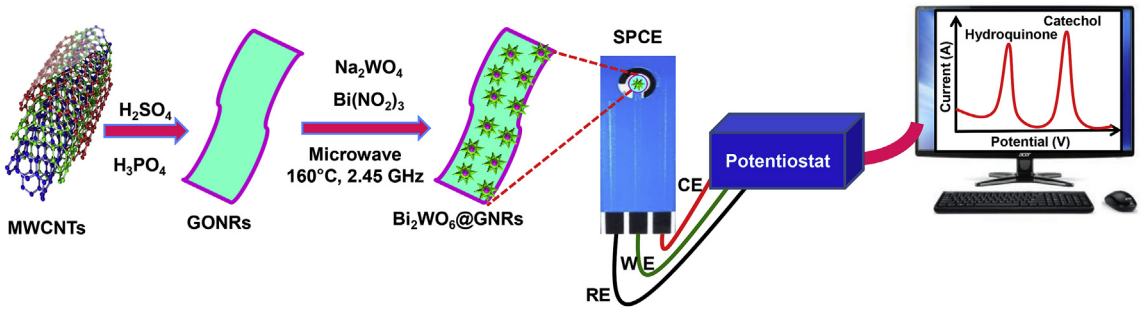

Scheme 1. Schematic illustration for the preparation of Bi_2WO_6@GNRs nanocomposite for sensing dihydroxybenzene isomers in water samples and face cream sample. WE = Working electrode, RE = Reference electrode, CE = Counter electrode.

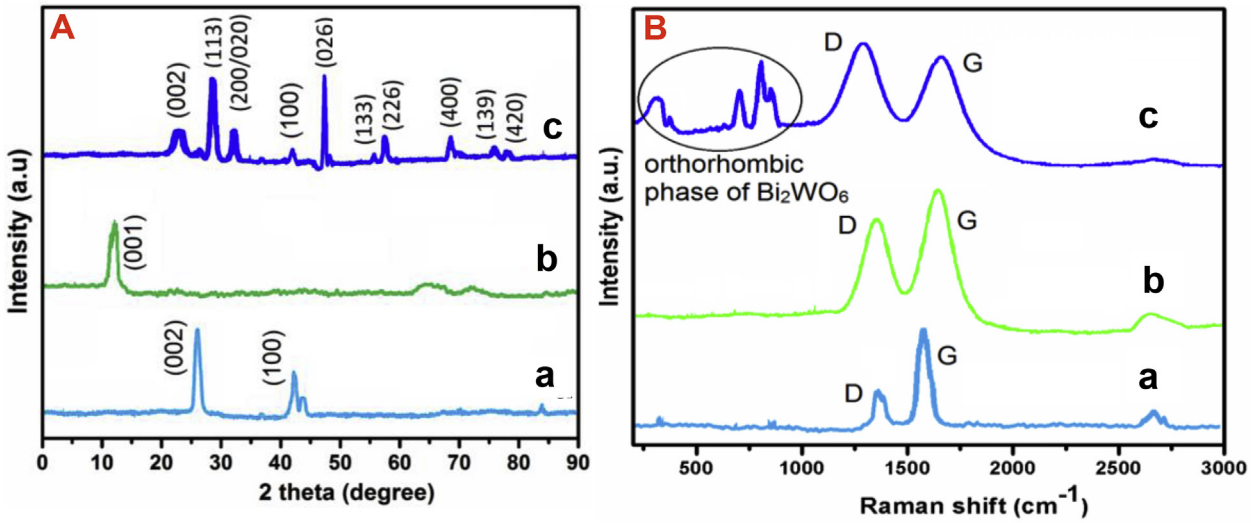

Fig. 1. (A) XRD patterns and (B) Raman spectra of (a) MWCNTs, (b) GONRs, and (c) Bi_2WO_6@GNRs.

emerging as a sustainable green method for nanomaterial synthesis. It is fast, user-friendly, scale-up suitable, cost-effective and can be used safely to substitute the conventional heating techniques such as hydrothermal method [21]. Here, we describe a simple microwave-assisted synthetical route to prepare nanocomposite of GNRs and Bi_2WO_6 flowers by treating the mixture of sodium tungstate, bismuth nitrate, and graphene oxide nanoribbons (GONRs) (Scheme 1). The electrocatalytic properties of the resulting nanocomposite are investigated using dihydroxybenzene isomers as model [22–24]. Dihydroxybenzene isomers such as, catechol (CC) and hydroquinone (HQ) are widely used in the production of cosmetics, dyes, pesticides, and medicines [25]. However, their presence at high concentrations in cosmetics or food samples is toxic to health (biological toxicity) and hence their rapid and sensitive determination is highly important [26].

The main objective of this work is to establish a microwave-assisted synthetical route for Bi_2WO_6@GNRs nanocomposite synthesis and to explore electrocatalytic-sensing use of the nanocomposite. The nanocomposite was prepared, characterized and modified on the screen-printed carbon electrode (SPCE) and our study reveals the excellent electroanalytical features of the modified electrodes towards detection and quantification of HQ and CC even in real samples.

2. Experimental

2.1. Chemicals and instrumentation

Multiwalled carbon nanotubes (MWCNTs) (95%, O. D × I.D × length = 7–15 × 3–6 × 0.5–200 μm), $Na_2WO_4{\cdot}2H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$, CC, HQ and all other reagents were purchased from Sigma-Aldrich. All the reagents used were of analytical grade and used without further purification. The supporting electrolyte used for the electrochemical studies was 0.1 M phosphate buffer, prepared using Na_2HPO_4 and NaH_2PO_4 and the pH was adjusted either using H_2SO_4 or NaOH. The SPCEs were purchased from Zensor R&D Co., Ltd., Taipei, Taiwan.

The morphology of the materials was investigated by high resolution (HR) transmission electron microscopy (TEM; H-7600, Hitachi-Japan) operating at 200 kV. The X-ray diffraction (XRD) patterns were recorded in a diffractometer XPERT-PRO (PANalytical B.V., The Netherlands) using Cu Kα radiation (λ = 1.54 Å). Elemental compositions of the samples were analyzed with an energy-dispersive X-ray (EDX) spectra assessed using HORIBA EMAX X-ACT (Sensor + 24V = 16 W, resolution at 5.9 keV). Raman spectra were acquired using Micro-Raman spectrometer (RENISHAW in via system, U.K) by a 514.4 nm He/Ne laser. X-ray photoelectron spectra (XPS) were obtained using XPS, PerkinElmer PHI–5702. Electrochemical impedance spectroscopy (EIS) studies were carried out using EIM6ex Zahner (Kronach, Germany). Electrochemical measurements were conducted in a CHI 1205c electrochemical workstation at ambient conditions. Three-electrode system comprised printed carbon as working (area 0.071 cm^2) and counter electrodes, and silver as a reference electrode is used.

2.2. Preparation of graphene oxide nanoribbons

GONRs are prepared via unzipping MWCNTs by following previous method [27]. 200 mg of MWCNTs were added to 100 mL mixture of H_2SO_4 and H_3PO_4 (4:1 vol ratio) and stirred for 30 min. The mixture