

Preparation and characterization of tin oxide, SnO₂ nanoparticles decorated graphene

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Abstract

SnO₂ nanoparticles/graphene (SnO₂/GP) nanocomposite was synthesized by a facile microwave method. The X-ray diffraction (XRD) pattern of the nanocomposite corresponded to the diffraction peak typical of graphene and the rutile phase of SnO₂ with tetragonal structure. The field emission scanning electron microscope (FESEM) images revealed that the graphene sheets were dotted with SnO₂ nanoparticles with an average size of 10 nm. The X-ray photoelectron spectroscopy (XPS) analysis indicated that the development of SnO₂/GP resulted from the removal of the oxygenous groups on graphene oxide (GO) by Sn²⁺ ions. The nanocomposite modified glassy carbon electrode (GCE) showed excellent enhancement of electrochemical performance when interacting with mercury(II) ions in potassium chloride supporting electrolyte. The current was increased by more than tenfold, suggesting its potential to be used as a mercury(II) sensor.

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1. Introduction

Metal oxide nanomaterial/graphene nanocomposites synthesis is fast becoming a research trend amongst scientists from all over the world. Nanomaterials are defined as materials with at least one dimension having a length of less than 100 nm, which can be categorized into two-dimensional (2-D), one-dimensional (1-D) and zero-dimensional (0-D) nanomaterials. Previously, we have produced 0-D Ni₃Se₂ nanoparticles [1], 1-D PbS nanorods [2], 2-D ZnO nanoplates [3] and magnetic Fe₃O₄/ZnO core/shell nanocrystals [4]. Nanostructured materials of metal oxide offer high surface area, non-toxicity, biocompatibility, ease of fabrication and excellent electrochemical catalytic activity [5].

Tin oxide is an n-type semiconductor with a large band gap of 3.6 eV [6]. SnO₂, in particular, is very stable, has got high carrier density and supports enormous concentration of intrinsic and stoichiometry-violating vacancies, which is correlated to its electrical conductivity [7]. It has a wide range of applications as optoelectronic devices, dye-based solar cells, catalysts, gas sensors, electrochromic devices and electrode materials [6–9]. SnO₂ nanoparticles are widely applied for gas sensing application due to their high mobility of conduction electrons, and good chemical and thermal stability under the operating conditions of sensors [10].

Graphene, a single-atom thick 2-D sheet of sp² bonded carbon, is experimentally discovered in 2004 [11]. It is the building block for all graphitic materials such as 0-D fullerenes, 1-D single-walled carbon nanotubes (SWCNTs) and three-dimensional (3-D) graphite. Graphene has attracted substantial interest and imagination of the scientific community arising from its remarkable electronic [11], optical [12], mechanical

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[13], thermal [14] and electrochemical properties [15]. Graphene offers a unique 2-D environment for electron transport and fast heterogeneous electron transfer at their edges [16], as opposed to SWCNTs uniaxial electron conductivity and heterogeneous electron transfer at their two ends [17]. While graphite is brittle, graphene's flexibility is beneficial for use in adaptable electronic and energy storage devices [18]. Graphene exhibits a surface area of $2630 \text{ m}^2 \text{ g}^{-1}$, which is ~ 260 times greater than graphite and twice that of CNTs [19].

With large surface area and the aforementioned unique properties, graphene has been an attractive choice as the matrix for nanocomposites [20]. Functionalization of graphene sheets with various nanoparticles can further enhance the properties of graphene. Heterostructures consisting of nanoparticles distributed on the surface of graphene could potentially display not only the unique properties of nanoparticles [21,22] and those of graphene [11,23,24], but also additional novel functionality and properties due to the interaction between the materials. Many exciting applications can be envisioned for these novel heterostructures, such as in chemical sensors, biosensors, nanoelectronics, photovoltaic cells, hydrogen storage, energy storage and photocatalysts [25].

Many types of metal oxide/graphene nanocomposites have been widely reported including Ag_2O /graphene [26], CuO /graphene [27], Cu_2O /graphene [26], CoO /graphene [28], Co_3O_4 /graphene [26], Fe_2O_3 /graphene [29], Fe_3O_4 /graphene [30], Mn_3O_4 /graphene [31], NiO /graphene [32], SnO_2 /graphene [33–35], TiO_2 /graphene [36,37], and ZnO /graphene [26]. These hybrids were fabricated using various approaches such as gas/liquid interface reaction [30,33], hydrothermal [27,29,32,37], in situ chemical synthesis [35], in situ oxidation route [26], laser irradiation [28], microwave [34], sonochemical [36] and ultrasonication [31].

Mercury is one of the most toxic heavy metals known to organisms and the environment as even a trace amount of the element is potentially disastrous when ingested [38,39]. The United Nations Environmental Programme (UNEP) estimated that an annual release of mercury was 4400 and 7500 metric tonnes [40] as a result of natural sources and human activities, respectively [41], which contaminates the food chain and the environment. Hence, detection of mercury is very important from the environmental safety aspect.

In this paper, we report on the synthesis of tin oxide nanoparticles/graphene nanocomposite using a facile microwave method. The prepared nanocomposite was characterized using an XRD, FESEM and XPS. Electrochemical analysis was performed on the nanocomposite to investigate its ability to demonstrate determination of mercury(II) ions in potassium chloride supporting electrolyte.

2. Experimental

2.1. Materials

Graphite flakes were purchased from Ashbury Inc., sulfuric acid (H_2SO_4 , 98%), potassium permanganate (KMnO_4 ,

99.9%), hydrogen peroxide (H_2O_2 , 30%), hydrochloric acid (HCl , 37%) and sodium chloride (NaCl , 99.5%) were purchased from Merck. Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 98%) and ammonia solution (NH_3 , $\sim 25\%$) were purchased from R&M Chemicals. Sodium hydroxide (NaOH , 99.99%), potassium chloride (KCl , 100%) and mercury(II) chloride (HgCl_2 , 98%) were purchased from HmbG Chemicals, J.T. Baker and Fischer General Scientific, respectively. Distilled water was used throughout the sample preparation.

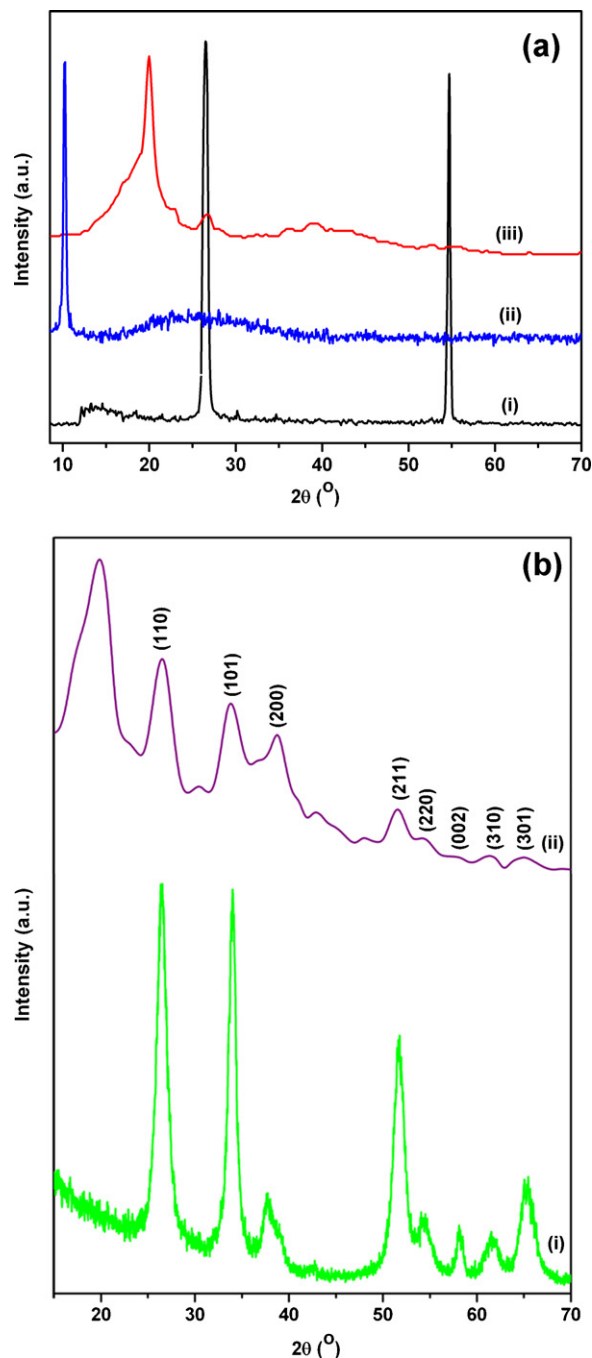


Fig. 1. XRD patterns of (a) graphite (i), GO (ii) and rGO (iii) and (b) SnO_2 nanoparticles (i) and SnO_2 /GP nanocomposite (ii).

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