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Regular Article

Novel electrochemical synthesis of copper oxide nanoparticles decorated graphene-β-cyclodextrin composite for trace-level detection of antibiotic drug metronidazole

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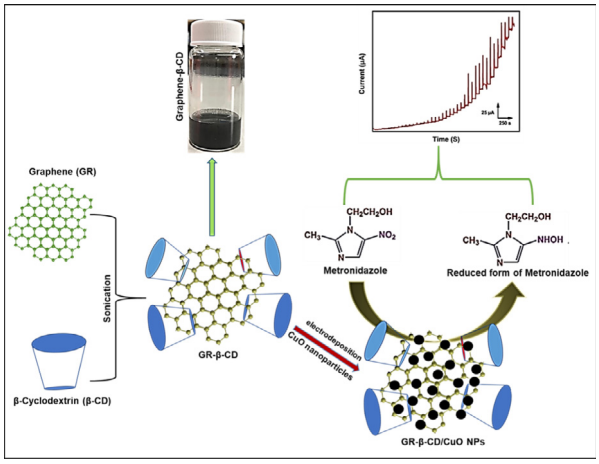
GRAPHICAL ABSTRACT



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ABSTRACT

Over the past decades, the synthesis of inorganic and organic nanocomposites has received much attention in the range of fields including electroanalysis of organic chemicals. In this regard, we have prepared copper oxide nanoparticle (CuO NPs) decorated graphene/β-cyclodextrin (GR-β-CD) composites using a simple electrochemical methodology, where the CuO NPs are electrodeposited on GR-β-CD composite modified electrodes. A stable GR-β-CD composite was prepared by sonication of GR in β-CD aqueous solution. As-prepared GR-β-CD/CuO NPs composites were characterized by the high-resolution scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. Cyclic voltammetry results reveal that the GR-β-CD/CuO NPs composite modified electrode exhibits an excellent catalytic activity and lower reduction potential towards the electrochemical detection of metronidazole (MTZ) over other modified electrodes including GR, GR-β-CD, and CuO NPs. Under optimized conditions, amperometry was used for

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Chemical sensor
Metronidazole

the determination of MTZ using GR-β-CD/CuO NPs composite modified electrodes. The response of MTZ using the composite electrodes was linear over the range from 0.002 to 210.0 μM. This sensor showed the lowest limit of detection of 0.6 nM and was much lower than the previously reported MTZ sensors. In addition, the sensor is highly sensitive, selective and durable in the presence of a range of potentially interfering electroactive compounds.

1. Introduction

Recent advancements of graphene-based composites have gained much attention in different applications including electrocatalysis [1]. Graphene (GR) has been widely known as a building block of all graphitic carbon forms, has a high theoretical surface area, mechanical strength and electrochemical activity over other carbon materials such as carbon nanotubes and C60 [2,3]. However, the stability of GR is poor in aqueous solutions due to the strong π-π stacking of individual GR sheets into graphite [4]. Henceforth, the different nano or micro materials including, but not limited to carbon nanomaterials [5,6], metal/metal alloy nanoparticles [7,8], supramolecular adducts [9], conducting polymer [10,11] and metal oxides [12,13] have all been used to prevent the π-π stacking of GR sheets. Furthermore, these GR based composites have shown an improved surface area and electrochemical activity over than of pristine GR. The GR based composites have also been used as an advanced electrode material for detection of toxic environmental pollutants in real systems [14–18]. Different polymer and nanomaterial supports have been used with GR to improve the dispersion ability and catalytic activity of GR. More recently, we have used β-cyclodextrin (β-CD) as a suitable dispersing agent for GR [19], which has dramatically improved the dispersion ability of GR in aqueous solution and prevent the re-stacking of GR sheets. Despite the exciting characteristics of β-CD (hydrophobic inner cavity and a hydrophilic exterior) that enables to form the stable composite with GR. In addition, the intercalation of unique properties of β-CD can enhance the catalytic activity of the GR. On the other hand, cupric oxide (CuO) has received significant attention in the scientific community due to its large surface to volume ratio and high catalytic activity and non-toxicity [20,21]. Despite these unique properties, CuO has been widely used in different applications including sensors [22], photocatalysis [23] and energy storage [24]. In comparison to other available methods, the electrodeposition of CuO has distinct advantages such as low operating temperatures and cost-effectiveness. In addition, the electrodeposition method can control the growth, morphology, structure, and orientation of CuO. Consequently, the integration of CuO with GR-β-CD composite could further improve the electrocatalytic activity of GR. Hence, in the present work, we have prepared CuO nanoparticle (CuO NPs) decorated GR-β-CD composites via a simple electrochemical methodology.

Metronidazole (MTZ) is an antibiotic drug and has been widely used for the treatment of pelvic inflammatory disease, endocarditis, and bacterial vaginosis [25,26]. However, the overdose and long-term use of MTZ will result in leucopenia, neutropenia, increased risk of peripheral neuropathy, and central nervous system toxicity [27]. Therefore, the accurate monitoring of MTZ concentrations in real samples is of significant interest. To date, the range of analytical methods has been used for the determination of MTZ such as high-performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC–MS), liquid chromatography-mass spectrometry (LC-MS) and electrochemical methods. In comparison with available spectrophotometry and chromatography traditional methods [28], electrochemical methods are found to be simple and cost-effective and offer more sensitivity and selectivity towards the determination of MTZ [29]. Unmodified graphite or glassy carbon electrodes are not suitable for determination of MTZ due to their low sensitivity, low selectivity and fowling or drifting of electrochemical signals. Hence, different micro or nanomaterial-modified electrodes have been used for the sensitive and selective detection of MTZ [30]. In the present work, the as-prepared GR-β-CD/CuO NPs composite was used as a sensitive and lower potential electrode material for detection of MTZ for the first time. In addition, a simple electrochemical method was used for the decoration of CuO NPs on pristine GR-β-CD composite modified glassy carbon electrode (GCE).

2. Experimental section

2.1. Materials

Graphene nanoflakes (thickness = 8 nm) and metronidazole (analytical standard) were purchased from Sigma-Aldrich. β-cyclodextrin, $CuCl_2$, KCl and other chemicals were obtained from Sigma-Aldrich. All chemicals were of standard analytical grade and used as received. The stock solutions and electrolyte solutions were prepared using double distilled (DD) water without any further purification. The pH 7.0 (phosphate buffer) was used as a supporting electrolyte, and was prepared using 0.1 M Na_2HPO_4 and NaH_2PO_4 in DD water. The pH of the solution was adjusted using either 0.1 M NaOH or diluted H_2SO_4. DC150H Ultrasonicator from Taiwan Delta New Instrument Co. Ltd. with an operating frequency of 40 kHz and ultrasonic power output of 150 W was used for sonication.

2.2. Characterization methods

High-resolution scanning electron microscopic (SEM) images were taken by Hitachi S-4300SE/N High-Resolution Schottky Analytical VP electron microscope. The elemental spectral analysis (EDS) of the GR-β-CD/CuO NPs composite was analyzed using BRUKER AXS elemental analyzer with Hitachi S-4300SE/N High-Resolution Schottky Analytical VP SEM. The Zetasizer Nano ZS90 (Malvern Panalytical) was used for the Zeta potential and hydraulic diameter measurements. Raman spectrum was acquired by a Dong Woo 500i Raman spectrometer from Korea. X-ray diffraction (XRD) analysis was performed using XPERT-PRO diffractometer from PANalytical B.V., The Netherlands.

2.3. Electrochemical measurements

Cyclic voltammetry and amperometry experiments were performed using CH750A electrochemical workstation from CH Instruments, USA. GR-β-CD/CuO NPs composite modified GCE (the geometric surface area = 0.8 cm^2) was used as a working electrode, and saturated Ag/AgCl and a platinum wire were used as the reference and auxiliary electrodes, respectively. The electrochemical measurements were carried out at room temperature in an N_2 atmosphere unless otherwise stated.