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Article

Preparation and surface characterization of nanodisk/nanoflower-structured gallium-doped zinc oxide as a catalyst for sensor applications

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ABSTRACT

Nanostructured gallium-doped zinc oxide (GZO) thin films were fabricated on piezoelectric substrates. The GZO thin films with nanodisk/nanoflower morphologies were prepared by a simple spin-coating process followed by one-step hydrothermal treatment. Addition of polymer during hydrothermal treatment resulted in nanodisk and nanoflower morphologies. The morphology, microstructure and chemical composition of thin films prepared under different conditions were examined by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Raman spectroscopy. The XRD and FE-SEM investigations confirmed that the GZO nanodisks, nanorods and nanoflowers formed on the AlN/Si substrates were all wurtzite phase. Green fluorescent protein (GFP) was immobilized on the as-synthesized GZO nanostructured materials by a dipping process. Atomic force microscopy (AFM) and fluorescence spectroscopy measurements were conducted to confirm the surface binding nature of GFP on the GZO nanostructures to determine their suitability for use in sensor applications and bioimaging techniques. Trace-level addition of GFP to the GZO nanostructures resulted in a fluorescence response, revealing good activity for ultraviolet light sensor applications.

1. Introduction

Gallium-doped zinc oxide (GZO)-based nanostructured thin films have recently been prepared by different methods and applied in important research areas such as photocatalysis, sensors and dye-sensitized solar cells [1–4]. Nanocomposites of ZnO are providing better results than pristine ZnO or ZnO/graphene. For example, graphene decorated with manganese-doped ZnO nanoparticles exhibited enhanced visible-light photocatalytic activity for industrial textile waste water treatment [5]. However, it is challenging to form ordered nanostructures to achieve higher activity in catalysis and solar cell applications [2,3]. The biological properties of protein-immobilized ZnO and GZO nanostructures have not been studied in detail. ZnO nanomaterials in the form of quantum dots (QDs) or nanoparticles are potentially applicable in biological cell-labeling and sensor applications [6–8]. GZO nanorods and nanostructured materials have also shown promise for use in the fields of light-emitting diodes and optical devices [8]. The main advantage of GZO and undoped ZnO is that they are relatively nontoxic compared with other semiconductor materials like cadmium-based compounds, which are harmful

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to human beings and the environment because they do not biodegrade [7]. Nanostructured ZnO materials are also attractive for application in gas sensors and biosensing because of their high aspect ratio, polar surface along the *c*-axis, and high electron mobility. Notably, the isoelectric point of ZnO is high (around 9.5), which is favorable for immobilization of biological species with low isoelectric point, such as enzymes and proteins, assisted by electrostatic attraction at suitable pH [9].

In the past decades, ZnO nanomaterials with different morphologies like porous films, nanoparticles, and nanorods have been developed for biosensing applications involving detection of proteins, uric acid, cytochrome c, [10–15], glucose [16,17], and phenolic compounds [18]. An advantage of doping the ZnO lattice with Ga is that it causes the electron conductivity of ZnO to increase by three times compared with that of pristine ZnO [19]. In 2013, Jothi Ramalingam's group [19] fabricated GZO nanodisks by a spin coating process followed by hydrothermal treatment with polymer assistance. Nanodisk formation depended on the preparation methodology and presence of an aluminum coating on the piezoelectric substrate. Inorganic nanomaterials with added polymer are important nanocomposites to develop low-cost sensor devices for environmental gas monitoring. Some of these nanomaterials possess specific properties such as piezoelectricity, which has allowed the development of transducers using either surface or bulk acoustic waves to measure perturbation in fundamental frequencies by the added mass on their surface. Recent biosensor research indicates that the crystalline form of SiO_2, a piezoelectric crystal with an inert surface, is a potential candidate for the immobilization of proteins for biodetection [20]. Recently, Xu et al. [21] reported a photoelectrochemical electrode containing ZnO with an inverse opal structure for α-fetoprotein (AFP) detection and glucose oxidase (GOD) sensor applications. Uniform CdS QDs were synthesized by a hydrothermal method followed by binding of AFP and GOD to form an AFP-CdS-GOD composite. A competitive immunosensor consisting of AFP and the AFP-CdS-GOD composite with anti-AFP antibodies immobilized on an FTO/ZnO electrode was used to detect AFP molecules. The CdS QDs broadened the absorption range of visible light and GOD acted as a catalyst for glucose, providing electrons and increasing the photocurrent. The developed immunoassay achieved high sensitivity for AFP. In another example, Brince Paul et al. [22] used a self-assembled monolayer-modified copper-doped ZnO nanofiber interface to detect plasmodium falciparum histidine-rich protein-2 with the goal of diagnosis of malarial infections. Incorporation of copper into ZnO not only increased the conductivity of the nanofibers but also pre-concentrated the target analyte (protein) onto the nanofiber surface because of the inherent electric field produced at the CuO/ZnO heterojunction interface.

The present study describes preparation methodology to make GZO nanostructures like nanodisks and nanoflowers with good conductivity. The nanostructures are characterized by various surface techniques like X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and Raman spectroscopy. Green fluorescent protein (GFP) is immobilized on the GZO nanodisk and nanoflower materials, as confirmed by florescence spectroscopy. The prepared materials show promising activity as sensors in the presence of UV irradiation.

2. Experimental

2.1. Preparation of GZO thin films

GZO coating solutions were prepared by mixing zinc acetate dihydrate, methoxyethanol, gallium(III) nitrate, and monoethanolamine, which were A. R. grade and used without further purification. Appropriate quantities of the precursors were stirred with a magnetic stirrer at 70 °C for 2 h. Polyethylenimine (non-ionic) polymer solution was purchased from TCI chemical (30% dissolved in water). GZO containing (1, 2 and 3) mol% gallium, which is designated as 1% GZO, 2% GZO and 3% GZO, respectively, was prepared by a reported procedure [19]. The prepared GZO solutions were coated on AlN/Si substrates by spin coating at 1000–2500 r/min. After each deposition, the films were heated on a heating plate at 300 °C for 10 min. Four to six layers of each GZO thin film were deposited to obtain a thickness of 300–350 nm. Following spin coating, the samples were annealed in a furnace at 500 °C for 3 h.

2.2. GZO nanostructure formation by the hydrothermal method

The GZO films on AlN/Si substrates were hydrothermally treated in the presence of 3% polymer solution to fabricate GZO nanodisks or nanoflowers. GZO nanorods as a reference compound were prepared by performing the hydrothermal process without adding polymer solution. In the hydrothermal process, equal volumes of zinc nitrate and hexamethylenetetramine solutions (40 mL) were mixed with 3% polymer solution (10 mL) for a few minutes, and then the mixture was transferred into a Teflon-lined autoclave. A 1% GZO film on an AlN/Si substrate was fixed vertically in a holder inside the autoclave. Nanodisk structures were grown at 90 °C for 20 h. In the case of nanoflower formation, the GZO-coated substrate was kept in a horizontal position instead of vertical inside the Teflon-lined autoclave. The same procedure was repeated using 2% GZO- and 3% GZO-coated substrates.

2.3. Protein immobilization on GZO nanostructures

A solution of GFP (5 μmol/L, 1 mL) in Tris-HCl buffer medium (pH = 7.0) was incubated at 37 °C with a GZO-coated substrate in a 5-mL vessel for time intervals ranging from 15 to 60 min. The substrates were dried at room temperature for further analysis. The structure and morphology of the substrates were characterized by XRD and FE-SEM. The crystalline phases of the samples were analyzed by XRD analysis with a Rigaku ultra-X diffractometer (Cu K_α radiation, 40 kV, 120 mA). FE-SEM and energy-dispersive X-ray spectroscopy (JSM-6500F, JEOL) and AFM (PARK SYSTEM XE 100 E) were used for surface analysis. Raman spectroscopic characterization (Confocal Raman Microscope alpha 300R) was conducted with a laser energy source of 532 nm at a fixed temperature. An Olympus