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Graphene oxide sheets involved in vertically aligned zinc oxide nanowires for visible light photoinactivation of bacteria

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ABSTRACT

Vertically aligned ZnO nanowires (NWs) hybridized with reduced graphene oxide sheets (rGO) were applied in efficient visible light photoinactivation of bacteria. To incorporate graphene oxide (GO) sheets within the NWs two different methods of drop-casting and electrophoretic deposition (EPD) were utilized. The EPD method yielded effective penetration of the positively charged GO sheets into the NWs to form a spider net-like structure, whereas the drop-casting method resulted in only a surface coverage of the GO sheets on top of the NWs. The electrical connection between the EPD-incorporated sheets and the NWs was checked by monitoring the electron transfer from UV-assisted photoexcited ZnO NWs into the GO sheets, during photocatalytic reduction of the sheets. The obtained rGO/ZnO composites were applied in visible light photoinactivation of *Escherichia coli* bacteria. The ZnO NWs could inactivate only ~58% of the bacteria, while both drop-casting and EPD-prepared GO/ZnO composites exhibited strong antibacterial activities (especially the EPD sample with ~99.5% photoinactivation), under visible light irradiation for 1 h. In fact, the visible light photocatalytic activity of the EPD-prepared GO/ZnO NW composite was found ~1.9 and 6.2 folds of the activity of the GO/ZnO composite prepared by drop-casting method and the bare ZnO NWs.

1. Introduction

Bio-properties and applications of graphene (as a single- and/or multi-layer of graphitized carbon atoms with unique properties) and graphene-based nanomaterials have attracted many attentions in recent years [1,2]. For instance, graphene has successfully been applied in ultra sensitive biosensing [3], neural cell differentiation [4–6], network regeneration [7–9] and tissue engineering using stem cells [10–12], drug delivery [13,14], inactivation of bacteria [15,16], and tumor imaging, targeting and therapy [17–22].

Incorporation of graphene in composite materials is also known as one of the most effective methods which can reveal the unique properties of graphene [23–27]. For example, graphene sheets as excellent electron acceptors with ballistic electron mobility (>15,000 $m^2 V^{-1} s^{-1}$) and extraordinary effective surface area (~2600 m^2/g) along with the capability of physicochemically bonding to metal oxides, can work as highly efficient sensitizer dopants and/or supports in improving the performance of metal oxide semiconductor photocatalysts such as TiO_2 [26,28–30], ZnO [31–33], WO_3 [34] and $ZnFe_2O_4$ [35,36].

ZnO is one of the most interesting metal oxide semiconductor photocatalysts (n-type semiconductor with band-gap energy of 3.1–3.4 eV), because it can easily be formed in various nanostructured morphologies providing high effective surface area and novel applications beside graphene [37]. Concerning this, many investigations about fabrication of graphene–ZnO composites and their various applications have been reported [38–41]. Among the various applications, visible light-driven photocatalytic activity of graphene–ZnO composites has attracted much attention [42,43]. However, these investigations restricted to photodegradation of only some dyes using graphene–ZnO photocatalyst, while ZnO-based nanostructures can effectively be utilized in antibacterial applications [44–49], due to the oxidative stress [50] and/or Zn^{2+} ion release [51,52] mechanisms resulting in membrane damage of bacteria. Nevertheless, there is only one report about antibacterial property of graphene–ZnO nanoparticle hybrid, under a long time (12 h) UV irradiation (rather than visible light irradiation) [53]. This means that no investigation about visible light-driven antibacterial activity of graphene/ZnO nanostructured hybrids has been reported yet.

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Recently, it was also reported that proliferation of bacteria on surface of graphene oxide sheets can reduce the oxide sheets to bactericidal reduced ones in a self-limiting manner [54]. On the other hand, it was demonstrated that the extremely sharp edges of vertically aligned graphene sheets (graphene nanowalls) can physically damage the cell wall membrane of bacteria [55,56]. One of the ways for obtaining graphene nanowalls is incorporation of graphene sheets within the vertically aligned ZnO nanowires (NWs), although deposition of graphene sheets on top of the vertically aligned NWs is also possible.

In this work, vertically aligned ZnO NWs (synthesized by using a one-step anodization method) were used as nanostructured templates for deposition of GO sheets on the top of the NWs (using a drop-casting method) and for incorporation of GO sheets (as nanowalls) within the vertically aligned NWs (using electrophoretic deposition (EPD) method). After a UV-assisted photocatalytic reduction of the GO contents of the composites, the obtained reduced GO (rGO)/ZnO composites were used as efficient visible light photocatalysts in photoinactivation of *Escherichia coli* (*E. coli*) bacteria. A mechanism describing the visible light photocatalytic activity of the composites was also proposed.

2. Experimental

2.1. Synthesis of GO

An improved Hummers' method was utilized to prepare graphite oxide suspension, as its details were previously reported elsewhere [57]. In summary, at first, 1 g graphite (TIMREX® KS6, TIMCAL) was added in 50 mL H_2SO_4 (Merck, 96%) at room temperature and the mixture was stirred (400 rpm). Then, it was put in an ice bath for 10 min and 6 g $KMnO_4$ (Merck) was slowly poured into it while being stirred which caused it warm up to room temperature. The suspension was stirred continuously (800 rpm) in an oil bath at 35 °C for 2 h. Then, the prepared suspension was diluted by 100 mL deionized (DI) water. Care was taken lest the temperature of the suspension become higher than 60 °C. Finally, 200 mL DI water and 6 mL H_2O_2 (Merck, 30%) was added in order to reduce residual permanganate to soluble manganese ions, corresponding to a sudden change in the color of suspension from chocolate brown to bright yellow and stopping of the gas evolution. The residual acids and salts of the graphite oxide suspension were removed by centrifugation at 6000 rpm for 60 min (4 times). The graphite oxide was dispersed in DI water to obtain an aqueous graphite oxide suspension with yellow-brownish color. After ultrasonication at frequency of 40 kHz with power of 150 W for 30 min, the aqueous suspension was centrifuged at 2000 rpm for 15 min to remove any unexfoliated graphitic plates to obtain a transparent and stable aqueous suspension of GO.

2.2. Fabrication of ZnO NWs

The high purity (99.9%) zinc foils were obtained from Goodfellow Cambridge Limited. The thickness of foils was 0.2 mm and they were cut into rectangular shape with the area of 2×2 cm^2. Prior to anodization, the samples were cleaned successively with acetone and ethanol by ultrasonic bath. Subsequently, they were rinsed with DI water and dried in a nitrogen stream. The zinc foils were then electropolished in a 1:1 solution of phosphoric acid and ethanol at 20 V for 5–10 min while vigorously stirred. As a result, surface of the Zn foils became smooth and mirror-like. The anodized samples were rinsed using DI water and dried at 80 °C in air. It should be noted that the electrolyte of the anodization was 10–20 mM $KHCO_3$ aqueous solution. The electrochemical cell was a two-electrode system consisting of the zinc foil as the working electrode and a graphite plate acting as the counter electrode. The distance between the two electrodes was 9 cm.

2.3. Electrophoretic deposition of GO within ZnO NWs

Since EPD method can provide vertically aligned deposition of GO sheets on a substrate [3,55], the GO sheets were deposited within the ZnO NWs using this method. Hence, a two-electrode cell in which a graphite plate served as cathode and the ZnO NW sample acted as anode was used. The electrolyte of the EPD was prepared through mixing 20 mL of the GO suspension (1 mg/mL) with 2 mL $Mg(SO)_4$ solution (10 mg/mL) followed by stirring and sonication for 15 min. A DC voltage (20 V) applied into the electrode of the cell for 2 min for performing the EDP. Meantime, in order to compare the efficiency of the EPD method in fabricating the GO/ZnO NW composite, the same composite was fabricated simply by drop-casting the aqueous GO suspension on surface of the ZnO NWs.

2.4. Material characterization

Surface topography of the GO sheets was studied using atomic force microscopy (AFM, Park Scientific CP-Research model (VEECO)) in tapping mode at frequency of 320 kHz. The samples for the AFM imaging were prepared by drop-casting a diluted GO suspension onto a freshly cleaved mica surface followed by drying in air. X-ray photoelectron spectroscopy (XPS) was utilized to study the chemical state of the GO and GO reduced by the ZnO NWs through a photocatalytic reduction. The data were

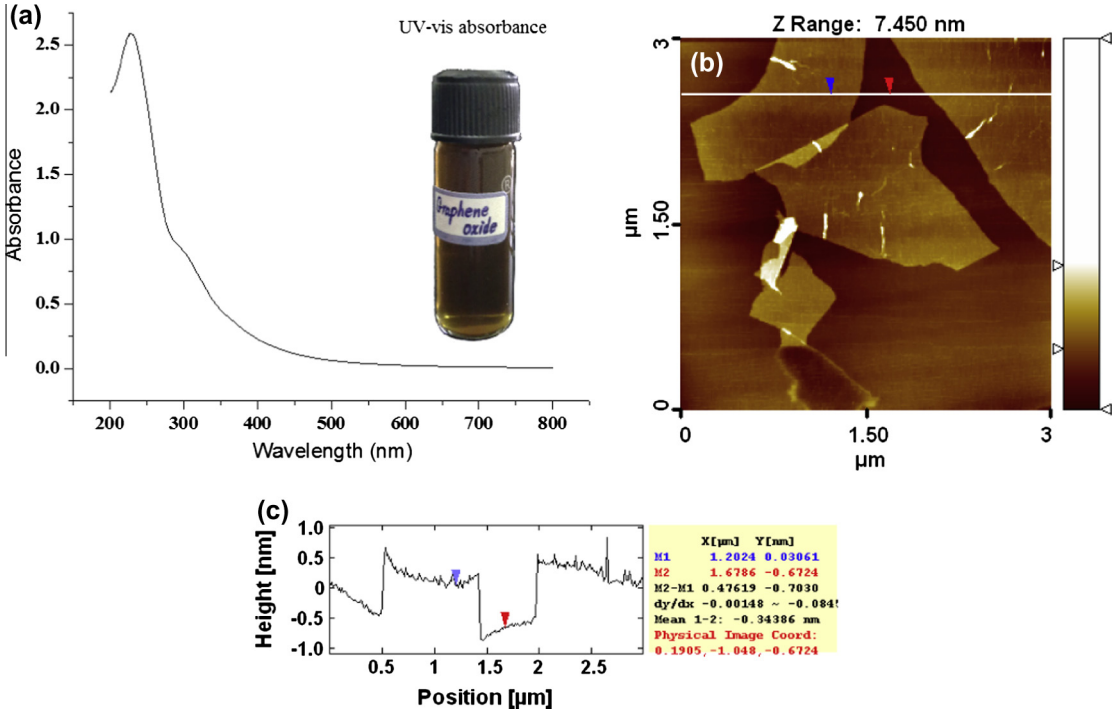

Fig. 1. (a) UV–vis spectrum of GO aqueous suspension (0.2 mg/mL). The inset of (a) shows digital image of the GO suspension (2 mg/mL), (b) AFM image of GO sheets deposited on freshly cleaved mica surface, and (c) height profile of the line marked in (b).