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Efficient synthesis of silver-reduced graphene oxide composites with prolonged antibacterial effects

Danxia Gu [a], Xueting Chang [a,*], Xinxin Zhai [b], Shibin Sun [b,**], Zhongliang Li [a], Tao Liu [a], Lihua Dong [a], Yansheng Yin [a]

[a] Institute of Marine Materials Science and Engineering, College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai 201306, China
[b] College of Logistics Engineering, Shanghai Maritime University, Shanghai 201306, China

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ABSTRACT

In this work, we successfully synthesized the silver-reduced graphene oxide (Ag-rGO) composites based on the *in situ* growth of Ag nanoparticles (NPs) on the surfaces of the GO sheets through a one-pot solvothermal method without using any surfactants or modifiers. The as-synthesized Ag-rGO composites have been characterized by X-ray diffraction, X-ray photoelectron spectrometry and electron microscopy. Results showed that high-density Ag NPs and dots with uniform size distribution were grown on the surfaces of the GO sheets, accompanied by the reduction of GO to rGO. By simply changing the concentration of Ag^+ ions in the solvothermal reaction system, the size and distribution of the Ag nanocrystals could be controlled. The antibacterial properties of the Ag-rGO composites were investigated by combined techniques of inhibition zone method, plate colony-counting method and bacterial growth curve. The Ag-rGO composites have been found to exhibit excellent antibacterial properties with long-term effects, which could effectively inhibit the growth of bacteria of *Vibrio natriegens* and *Bacillus sp. 1NLA3E*. The strongly-coupled interaction between the Ag nanocrystals and the rGO supports as well as the presence of the Ag dots contributed equally to the prominent long-term antibacterial performance of the Ag-rGO composites. The present Ag-rGO composites may find important environmental applications.

1. Introduction

With antibiotics widely used, antibiotic-resistant bacterial and pathogens are becoming more and more serious to human health. Both the pharmaceutical and material scientist around the world have been searching for new antibacterial agents with enhanced functionality in the past few decades. Since the early 1990s, nanotechnology has emerged as a promising strategy for developing new antibacterial agents and efforts have been focused on the production of nanomaterials with antibacterial performance. After years of endeavors, numbers of nanomaterials have been synthesized to meet the increasing demand for the preparation of functional antibacterial agents [1–3]. However, most of the antibacterial nanomaterials reported so far are associated with concerns about toxicity, biological incompatibility, environment pollution and complicated synthesis procedure [4,5]. There still remains challenge for the synthesis of novel, efficient and environmentally friendly antibacterial nanomaterials.

In the past two decades, Ag NPs have attracted tremendous attention in a broad range of applications such as catalysis, optics, sensing, imaging, surface-enhanced Raman scattering, and fluorescence due to their prominent optical, electrical and magnetic properties [6–10]. Importantly, the Ag NPs were demonstrated to exhibit excellent antibacterial activity and have been increasingly used in detergents, plastics, food storage containers, antimicrobial paints, and so on [11–13]. Although the antibacterial properties of the Ag NPs have been extensively studied and reported, the mechanism is not completely known yet. At present, it is generally accepted that the Ag NPs could release Ag^+ ions and/or producing reactive oxygen species (ROS), which could destroy the respiratory system of bacteria and inhibit their growth [11,14,15]. It should be noted that the Ag NPs tend to be agglomerated due to their high surface activity, reducing their antibacterial activity. Additionally, excessive exposure of the Ag NPs to external environment could promote the release of Ag^+ ions significantly, thereby depressing their long-term antibacterial activity. To address these issues, an alternative strategy is to form encapsulated structure by embedding the Ag NPs in mesoporous silica nanoparticles (MSN), fiberglass, and polymers [16–19]. For example, Nangmenyi et al. prepared the Ag-nanoparticle-impregnated fiberglass and investigated its antibacterial property against *Escherichia coli* [17].

* Corresponding author.
** Corresponding author.
E-mail addresses: xtchang@shmtu.edu.cn (X. Chang), sunshibin@shmtu.edu.cn (S. Sun).

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Agarwal et al. prepared the silver-impregnated polymeric films using a layer-by-layer deposition method, which have been found to exhibit excellent antimicrobial activity without cytotoxicity [18]. However, it should be noted that the release of Ag^+ ions from the Ag-based composites with encapsulated structure is strongly limited, leading to the fact that the antibacterial effects of these materials are very weak in the early stage.

In recent years, significant research attention has been drawn towards the coupling of the Ag NPs with GO sheets. GO sheets, exfoliated from graphite oxide, are characterized by the dominant presence of oxygenated functional groups such as epoxy, hydroxyl and carboxyl groups [20–25]. These functional groups provide chemically reactive sites for the growth of inorganic nanostructures. The Ag–GO (or chemically reduced GO, *i.e.* rGO) antibacterial composites have been widely reported over the past few years, and have been found to possess several advantages compared with free Ag NPs [26–32]. First, the morphology, size, and dispersion of the Ag NPs could be effectively tuned with the GO sheets as supports, leading to the formation of Ag–GO composites with high degree of adaptability for many applications. Second, strong interaction (or chemical interaction) between the Ag NPs and the GO sheets usually occurred, which could availably control the diffusion of the Ag NPs and decrease the environmental influence associated with the Ag NPs. Third, the GO sheets with large specific surface area could sufficiently capture the bacteria, increasing the contact opportunity of the Ag NPs with bacteria. Xu et al. prepared a uniform and water-soluble Ag@rGO nanocomposite by a facile deposition method, which display superior antibacterial properties against *Escherichia coli* to that of pure Ag NPs synthesized by microwave irradiation [26]. Cai et al. prepared a hybrid composite by anchoring the Ag NPs on the polyethyleneimine-modified graphene oxide surface [27]. They found that the hybrid not only exhibited ideal antibacterial property, but also possessed excellent antibacterial water-solubility and lower cytotoxicity, making it suitable candidate as a sprayable graphene-based antibacterial solution. de Faria et al. studied the anti-biofilm activity of the Ag–GO nanocomposite toward *Pseudomonas aeruginosa* adhered on stainless steel surfaces. Results showed that the Ag–GO nanocomposite could effectively inhibit the growth of microbial adhered cells, suggesting that the Ag-rGO composite could also be applied as anti-adhesion agents for coating applications [30]. Yu et al. reported a sandwich-like Ag/halloysite nanotubes/rGO (Ag/HNTs/rGO) antibacterial reagent constructed through the direct growth of Ag NPs on the surface of GO-based HNTs nanosheets, which possessed enhanced antibacterial activity compared to both Ag NPs and rGO sheets [31].

Up to now, research work has been simply focused on the synthesis and antibacterial properties of the Ag–GO composites, as well as the structure regulation of the Ag NPs grown on the GO surfaces. Little attention has been devoted to the long-term antibacterial effects of the Ag–GO composites and the related mechanism. Indeed, this is closely related to the practical application of the Ag-based antifouling agents and needs to be investigated. In this study, we successfully fabricated the Ag-rGO composites through a one-step solvothermal method with silver nitrate as precursor, GO sheets as supports, and ethanol as solvent. After the solvothermal reaction, high-density, uniform Ag NPs and dots were formed and anchored onto the surfaces of the GO sheets with strongly-coupled interaction. Simultaneously, the GO sheets were reduced to the rGO sheets, leading to the formation of the Ag-rGO composites. The as-prepared Ag-rGO composites have been found to exhibit excellent antibacterial performance against bacteria of *Vibrio natriegens* and *Bacillus sp. 1NLA3E (bacillus)* with long-term effects. We expect the Ag-rGO composites may find important environmental applications.

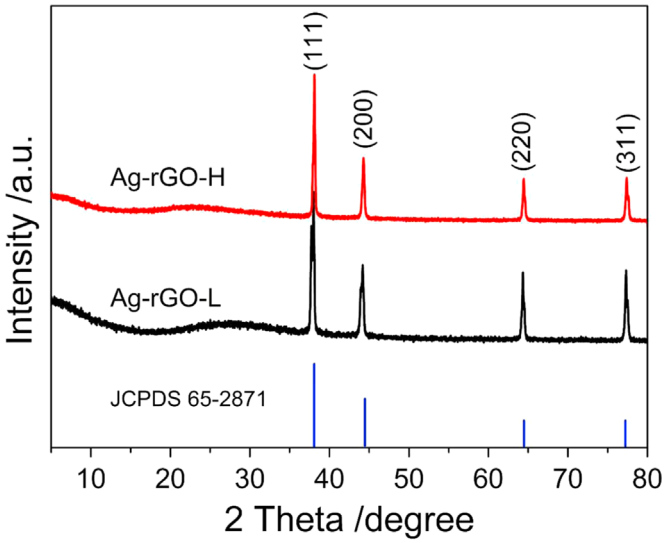

Fig. 1. XRD patterns of Ag-rGO composites.

2. Experimental

2.1. Chemicals

Silver nitrate ($AgNO_3$, > 99.8%), ethanol (EtOH) and deionized (DI) water were purchased from Sinopharm Chemical Reagent Co., Ltd. Graphene oxide (GO, > 98.5%) sheets, produced by using the modified Hummers method, were provided by Sinocarbon™ Graphene Marketing Center. All chemicals were used as-purchased without further purification.

2.2. Synthesis of the Ag-rGO composites

The Ag-rGO composites were synthesized by using a solvothermal route with $AgNO_3$ as precursor, GO sheets as supports and EtOH as solvent. In a typical synthesis, 5 mg of GO powder was ultrasonically dissolved in 30 ml of EtOH in a beaker for 1 h to generate a yellow solution. 50 mg of $AgNO_3$ was dissolved in 3 ml of DI water in a glass pipe for 30 min in dark. Then, the aqueous $AgNO_3$ solution was added to the ethanol solution with a pipette. The mixed solutions with an $AgNO_3$–GO weight ratio of 10 were subsequently transferred into a Teflon-lined high-pressure reaction vessel. The reaction vessel was sealed in a stainless autoclave and heated at 200 °C for 6 h in a drying oven. After naturally cooled to room temperature, the final products were washed with water several times and collected by centrifugation with ethanol. To better understand the influence of the precursor concentration on the morphology and antibacterial activity of the final products, one other Ag-rGO composite was also obtained by increasing the amount of $AgNO_3$ from 50 mg to 75 mg (corresponding to an $AgNO_3$–GO weight ratio of 15) while keeping the procedure unchanged. For convenience, the Ag-rGO composites synthesized with an $AgNO_3$–GO weight ratio of 10 and 15 were denoted as Ag-rGO-L composite and Ag-rGO-H composite, respectively.

2.3. Characterization

The crystal structure of the as-synthesized products was characterized by X-ray diffraction on a D/MAX-2500 X-ray diffractometer, with a Cu Kα radiation and a step size of 0.02° in the 2θ range of 5–80°. The morphology and microstructure of the resultant products were analyzed by using a JSM 2100F transmission electron microscope (TEM), operated at an accelerated voltage of 200 kV. The TEM samples were prepared by depositing the Ag-rGO