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A facile one-pot method to two kinds of graphene oxide-based hydrogels with broad-spectrum antimicrobial properties

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HIGHLIGHTS

- Two kinds of GO-based hydrogels (BKB/GOG and BKB/PDA/rGOG) were synthesized.
- The swelling degrees of the GO-based xerogels were calculated.
- Antibacterial experiments were conducted to measure the antibacterial properties.
- The bacterial kinetic test was studied to evaluate the antibacterial activity.

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ABSTRACT

Graphene oxide (GO) has immense potential applications in water purification and biomedical field. Recently, three-dimensional GO-based hydrogels have attracted great attention owing to their advantageous properties. However, it is quite difficult to develop highly efficient, low cost, broad spectrum antibacterial materials that can be easily recycled. In this experimental work, we used a facile one-pot method to synthesize two kinds of GO-based hydrogels: benzalkonium bromide/graphene oxide hydrogel (BKB/GOG) and benzalkonium bromide/polydopamine/reduced graphene oxide hydrogel (BKB/PDA/rGOG). The as-prepared three-dimensional hydrogels were characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), and Raman spectroscopy. The swelling degrees of BKB/GO xerogels and BKB/PDA/GO xerogels with different BKB concentrations were calculated. The maximum value of swelling degree was found to be 95.2 mg/mg. Owing to the synergistic effect of graphene oxide and benzalkonium bromide, the resultant hydrogels exhibited strong antibacterial activities against both Gram-negative and Gram-positive bacteria. The result of bacterial kinetic tests agreed well with that of the qualitative antibacterial experiments. The resultant hydrogels could be easily removed from the solution, which enhanced their potential use in industrial applications. The antibacterial effect of the hydrogel synthesized from benzalkonium chloride (BKC) and graphene oxide was investigated. The findings of this investigation can be beneficial in elucidating the mechanism of synthesis process that involves benzalkonium salts and graphene oxide.

1. Introduction

Graphene oxide (GO) is considered as an emerging star material due to its specific physical and chemical properties. In the near future, graphene oxide could be extensively used in diverse fields, such as water purification, energy storage, drug delivery, surface-enhanced Raman scattering (SERS), and antibacterial fields [1–6]. However, owing to strong Van der Waals interactions between graphene and graphene oxide, there is significant aggregation in their solutions: this practically limits the applications of these novel materials. To avoid the aggregation of graphene and graphene oxide in solutions, certain materials such as Fe_3O_4, chitosan, polydopamine, and TiO_2 were used in the synthesis of materials made from graphene and graphene oxide [7–11]. In particular, the combination of graphene and Ag has drawn immense attention because the resulting synergistic enhancement of this combination is applicable in SERS, catalysis [12,13], and antibacterial fields.

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Recently, Zhang et al. have reported that Ag-polydopamine-graphene hybrid nanosheets exhibited strong antibacterial activities against two types of bacteria, namely, *Escherichia coli* and *Bacillus subtilis* [14]. Nevertheless, it was difficult to recycle the expensive raw materials of these hybrid nanosheets. In other words, these raw materials were not suitable for large-scale production. Since three-dimensional (3D) materials can be recycled easily, they have attracted tremendous attention in multidisciplinary research [15–18]. But, graphene oxide based 3D material has not yet been used in antibacterial fields.

Benzalkonium salts, such as benzalkonium bromide (BKB) and benzalkonium chloride (BKC) are cationic surfactants that have been widely used as antibacterial agents in adhesive and hospital bandages [19]. According to the well-accepted mechanisms that elucidate the action of these antibacterial agents, benzalkonium salts induce membrane permeability changes for bacteria [19,20]. However, research studies have proved that benzalkonium bromide (BKB) and benzalkonium chloride (BKC) can only inhibit heterotrophic bacteria and Gram-positive bacteria. Furthermore, the biocompatibility of benzalkonium salts is reduced when their concentration is increased [21]. Therefore, biomedical scientists are tackling with the issue of devising a method that not only expands the applicability of these antibacterial agents but also enhances their biocompatibility.

To overcome the above-mentioned challenges, we combined graphene oxide and benzalkonium salts for the first time and prepared the 3D graphene oxide-based hydrogels (BKB/GOG or BKC/GOG) using a facile, one-step approach. BKB or BKC were used as cross-linking agents in this experimental study. It has been proved that mussel-inspired dopamine (DA) has good adhesion, biocompatibility, and reducibility. Therefore, at an alkaline pH, mussel-inspired dopamine can self-polymerize to form polydopamine (PDA), which adsorbs on virtually any surface [22,23]. In order to improve the biocompatibility of 3D hydrogels, dopamine was added during the forming process. Dopamine not only acted as the cross-linking agent but also as the reductant in the synthesis of these 3D hydrogels. As a result, we could synthesize two novel graphene oxide-based hydrogels, namely, benzalkonium bromide/polydopamine/reduced graphene oxide gel (BKB/PDA/rGOG) and benzalkonium chloride/polydopamine/reduced graphene oxide gel (BKC/PDA/rGOG). The experimental results indicate that these two types of hydrogels exhibited strong antibacterial activities against both Gram-positive and Gram-negative bacteria. Moreover, these free-standing, graphene-based hydrogels could be easily removed from the liquid bacterial culture.

2. Materials and methods

2.1. Materials

Graphite flake was purchased from Shanghai Yifan Graphite Co., Ltd. Benzalkonium bromide, benzalkonium chloride, and dopamine were purchased from Sigma–Aldrich. All chemical reagents were used without further purification. Deionized water (Milli-Q System, Millipore, USA) was used in all experiments.

2.2. Synthesis of three-dimensional BKB/GO hydrogel and BKB/PDA/rGO hydrogel

GO was prepared using the modified Hummers method [24–26]. BKB/GOG hydrogel was prepared by the following procedure: GO (1 mL, 4 mg/mL) was promptly added into BKB aqueous dispersions (200 μL with different concentrations) under acidic conditions.

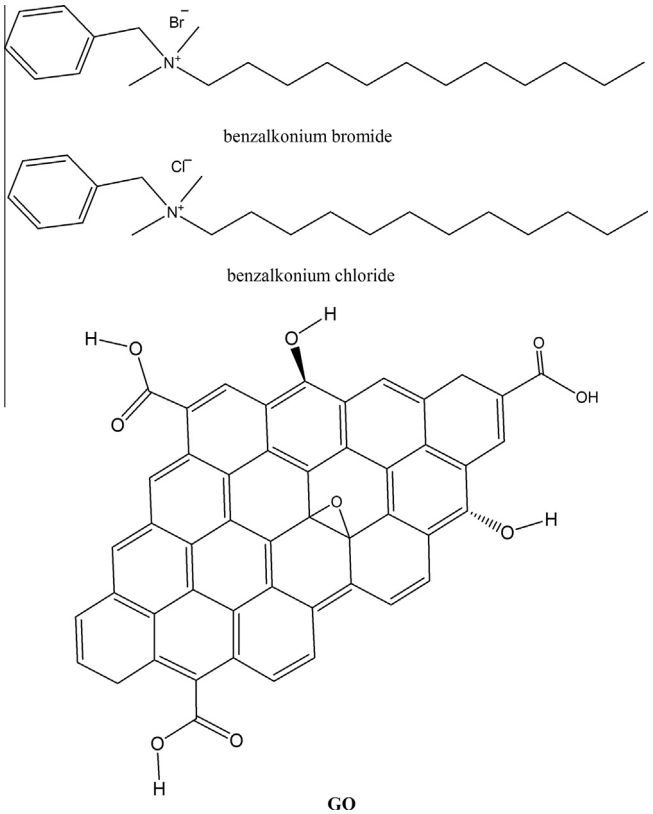
BKB/PDA/rGO hydrogel was prepared by the following procedure: BKB (100 μL) and dopamine (DA, 100 μL) aqueous dispersions were blended. Subsequently, GO (4 mg/mL) was rapidly added into the mixture. Tube inversion method was used to examine the formation of hydrogels.

2.3. Characterization

Transmission electron microscopy (TEM) analysis was performed using JEM-2100HR transmission electron microscopy (JEOL, Japan). This instrument was operated at 200 kV. To characterize the size and thickness of graphene oxide sheet, an atomic force microscope (AFM) was used. Raman spectra were obtained using a confocal Raman microspectrometer (Renishaw InVia, Derbyshire, England): the excitation wavelength of 514.5 nm was generated by an Ar^+ laser. A 20× objective was used to focus the laser beam, and a charge-coupled device (CCD) array was used as the detector. To calibrate this spectrometer, we used the Raman band of a silicon wafer at 520 cm^{-1}. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. The prepared hydrogel was lyophilized for at least 24 h, and then its morphology was examined using a field-emission scanning electron microscope (SEM) (ZEISS Ultra 55). Ultraviolet–visible (UV–Vis) spectra were obtained using a UV–Vis absorbance spectrometer (NanoDrop, ND-1000).

2.4. Determination of the swelling degree

BKB/GO-X xerogels and BKB/PDA/GO-X xerogels (*X* represents the BKB concentration, mg/mL) were produced by freeze-drying the as-obtained hydrogels of different BKB concentrations (50 mg/mL, 30 mg/mL, and 10 mg/mL). These xerogels were weighed and their recorded weight was denoted as m_0. Thereafter,



Scheme 1. Chemical structures of benzalkonium bromide (BKB), benzalkonium chloride (BKC), and GO.