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RESEARCH PAPER

Langmuir-Blodgett assembly of transparent graphene oxide-silver microwire hybrid films with an antibacterial property

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Abstract: Silver microwires (AgMWs) were made amphiphilic by non-covalent functionalization with poly (vinyl pyrrolidone) and hexadecyl mercaptan. The Langmuir-Blodgett (LB) technique was used to transfer graphene oxide (GO) and the functionalized AgMWs （F-AgMWs）onto a quartz substrate to obtain GO-AgMW hybrid films. The films had a high optical transparency and an antibacterial property against Escherichia coli (*E. coli*). It is proposed that the GO layer not only acts as an adhesive layer for AgMWs, but also is acidic, which provides an ideal reaction condition for AgMWs to release the Ag^+ ions that fight *E. coli*. The influence of pH value on the antibacterial property of the hybrid films was investigated in order to verify the proposed mechanism. Further development of this method may provide a way to produce next generation transparent multifunctional thin films with antibacterial properties.

Key Words: Graphene oxide; Ag MW; *E. coli*; Transparent; Antibacterial

1 Introduction

Antibacterial materials and agents, both organic and inorganic, including antibiotics [1], metal ions [2], and quaternary ammonium compounds [3], are widely used in daily life to protect the public health [4]. However, the above materials are not suitable for the next generation transparent antibacterial coatings [5]. A number of studies have been conducted toward novel, efficient and transparent antibacterial materials based on graphene, graphene oxide (GO), and their hybrid materials [5-7] owing to the unique structural, mechanical, and antibacterial properties of graphene. It was believed that the antibacterial activity of GO or reduced GO (rGO) was attributed to the membrane stress induced by their sharp edges,which may result in physical damages on cell membranes and thus lead to the loss of bacterial membrane integrity [8]. However, the antibacterial performance of the individual GO sheets is limited as compared with silver [8-11]. Moreover, in contrast to the sliver metal or silver salt, silver micro-wires (Ag MWs) releases the silver slowly [5]. Since GO is shown to be able to control the release of Ag^+ [12], it is supposed that the synergistic effect of the GO and Ag MWs is able to enhance their antibacterial performance.

To hybridize these two kinds of antibacterial materials, there has been several well-established techniques including bar coating [13], dry transfer [14], spray coating [15] and spin coating [12]. However, most of these approaches yield agglomerates and overlapping of the GO sheets, leaving the film with folds and wrinkles during solvent evaporation stage [16, 17]. Besides, these techniques could hardly be used to prepare films at the molecular level [18]. Langmuir Blodgett (LB) method, which is known to be the only technique that can realize the layer-by-layer manner, can be used to accurately control the GO surface structure in molecular level[19].

In this study, we demonstrate a general strategy for assembling transparent antibacterial GO-Ag MW hybrid films. To realize the hybridization via the LB assembly, Ag MWs were functionalized with poly (vinyl pyrrolidone) (PVP) and hexadecyl mercaptan ($C_{16}H_{34}S$) so that they are able to be floated on the water surface. Antibacterial experiments showed the improved performance of the GO-Ag MW hybrid films.

2 Experimental

2.1 Preparation of graphene oxide

The process used to prepare monolayer GO sheets is essentially similar to our previous reports [20, 21]. The preparation and deposition of GO and Ag MWs on quartz substrates is schematically illustrated in Figure 1.5 g of natural graphite （NG） flakes (Asbury Graphite Mills, US) and 150 mL sulfuric acid (H_2SO_4, 95.5%-96.5%, General

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Chemical) was mixed together and stirred in a round bottom flask at a speed of 200 rpm. The mixture was kept at room temperature and stirred for 24 h after 50 mL of fuming nitric acid (Fisher) was added. Then, 200 mL of de-ionized (DI) water was poured slowly into the mixture. After washed for three times using DI water, followed by centrifugation and drying at 60 °C for 24 h, the graphite oxide was obtained. The dried graphite oxide powder was then thermally expanded at 1050 °C for 15 sec to obtain expanded graphite (EG). A mixture of 1 g of EG and 200 mL of H_2SO_4 was stirred in a three neck flask. After 10 g of potassium permanganate was added to the mixture drop wise with stirring, the mixture was then kept at 60 °C and stirred for 24 h. 200 mL of DI water and 50 mL of hydrogen peroxide (H_2O_2) were poured slowly into the mixture and the color turned into light brown in an ice bath. The GO particles were washed and centrifuged with HCl solution three times, then centrifuged again and washed with de-ionized water until the pH of the solution became about 5 to 6. The obtained GO particles thereby were diluted using DI water (~1 mg/ml) and delaminated by gentle shaking.

2.2 Functionalization of Ag MWs

Firstly, in the traditional process of synthesis of Ag MWs, poly (vinyl pyrrolidone) (PVP) is used as a dispersing agent. Hexadecyl mercaptan ($C_{16}H_{34}S$) with a long-chain, is one kind of hydrophobic surfactant which combines well with PVP. We choose PVP (Aladdin) and $C_{16}H_{34}S$ (Alfa Aesar, 90%) as the modification agents to convert the hydrophobic Ag MWs (Xianfeng Nano, Nanjing, China) to amphiphilic ones. 0.25 g of PVP was dropped into 25 mL Ag MW solution (2 mg/mL) and stirred at room temperature for 5 h. Then, 0.5 mL $C_{16}H_{34}S$ was added into the mixture and kept stirring for 24 h. Then the floated functionalized Ag MWs (F-Ag MWs) on the ethanol solution was obtained.

2.3 Preparation of antibacterial GO-Ag MW hybrid films

Quartz slides were used as substrates for LB deposition of GO films. To remove any organic contamination, 15 mm×15 mm square slides were washed in an acetone bath under ultrasonication. The vacuum dried quartz substrates were then immersed in a piranha solution (V_{H2SO4}: V_{H2O2}=7:3) for 1 h, followed by rinsing with DI water and drying in a vacuum oven for 30 min. For the LB assembly of GO, the LB trough (Medium LB Deposition Trough, KSV-NIMA Co, Ltd.) was carefully cleaned with ethanol and then filled with the water-methanol mixture. GO solution was slowly spread onto the water surface dropwise using a glass syringe. The GO solution was spread with a speed of 100 μL/min up to a total of 7 mL and the monolayered GO sheet was formed. Then it was stabilized for about 20 min before compression. A tensiometer attached to a Wilhelmy plate was used to monitor the surface pressure. Then the GO sheet was compressed by moving barriers at the speed of 10 mm/min. By the end of the compression, a GO film with a faint brown color could be observed. The GO monolayer was transferred to a substrate at a surface pressure of 10 mN/m. The substrate was then dipped into the trough and slowly pulled up at a speed of 0.1 mm/min followed by drying in a vacuum oven at 60 °C for 30 min.

The F-Ag MW solution was then dissolved into DI water with a concentration of 1 mg/mL. After the F-Ag MW solution was deposited onto the LB trough with a speed of 50 μL/min up to an amount of 5 mL, the as-prepared GO-coated quartz substrate was dipped into the trough again and then pulled up at a speed of 0.1 mm/min with the surface pressure varying from 1 mN/m to 15 mN/m, followed by drying in air for 2 h. As expected, with the increase of surface pressure, the amount of Ag NWs increased and the samples were denoted as GO-Ag MW-x (x is the surface pressure of the F-Ag MW solution).

2.4 Bacterial adhesion experiment

To prepare a culture medium, a mixture of 18 g nutrient broth (Qingdao hope bio-technology co., Ltd) and 1000 mL distilled water was stirred with a sterilized glass rod, followed by sterilization in a sterile furnace at 120 °C for 20 min. After the hybrid films were put into the separated culture medium, followed by direct inoculation of the pro-cultivated Escherichia coli (*E. coli*) with an inoculating loop, the medium was placed in an incubator at 37 °C for 24 h. The *E. coli* was heated for 30 s. The substrates were held with a forceps above the sink followed by the Gram’s stain process. Firstly, the surfaces of the substrates were flooded with a crystal violet stain, followed by rinsing with DI water. Secondly, the substrates were flooded with a Gram’s iodine, followed by rinsing with DI water. Thirdly, the substrates were flooded with a Gram’s decolorizer followed by rinsing with DI water. Finally, the substrates were flooded with the counterstain and Safranin, followed by rinsing with DI water.

2.5 Characterization

A scanning electron microscope (SEM, FEI CO, LTD Quanta FEG) was used to characterize the structure and morphology of NG, EG and F-Ag MWs. The molecular structure of GO sheets, and F-Ag MWs was characterized by a high resolution transmission electron microscope (TEM, FEI TGF 30). The UV-Vis spectra of the transparenct GO-Ag MW hybrid films were measured by a Perkin Elmer Lambda 750 UV-Vis spectrometer. An optical microscope (Nikon, ECLIPSE 90i) was used to characterize the antibacterial property. The automated colony counter (RTAC-03, Ruitao Technology Company in Hefei) was used to count the number of the colonies.