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Three-dimensional free-standing ZnO/graphene composite foam for photocurrent generation and photocatalytic activity

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ABSTRACT

A convenient, nontoxic and efficient way is developed for the fabrication of three-dimensional free-standing graphene foam modified with ZnO nanorods arrays. The resulting composite foam (ZnO/rGO foam) has a hierarchical micro-nano structure. The conductive macroporous structure will enhance the light harvesting, the photoinduced electron-hole separation and electrons transport. Moreover, the ZnO nanorods on the graphene surface will act as the active material which show the dramatic improvement in photocurrent generation and photocatalytic activity. This simple and scalable manufacturing technology will open a reasonable design and engineering route for the high-performance photoelectric conversion apparatus and environmental pollutant management.

1. Introduction

Fabrication of macroscopic structures with nanomaterials, while keeping the original properties of nano-building blocks, is of great significance to promote the practical applications. In the field of material science, graphene has received much attention because of its unique structure and its excellent physical and chemical properties, such as mechanical strength, big specific surface area, biocompatibility and chemical stability [1–6]. Integration of two-dimensional (2D) graphene nanosheets into a functional system is indispensable to investigate the advanced properties of individual graphene sheets for macroscopic applications [7–10]. Although many methods have been reported about assembling the graphene nanosheets into films or three-dimensional (3D) structures, interconnected 3D graphene foams have gained tremendous attention recently due to their unique structure and superior physical properties, which inherits from graphene sheets [11,12]. Based on functional graphene foams, many efforts have been made to enhance the performance of applications in sensing, energy conversion, environmental management, and catalysis [13,14]. To harness graphene foams for various applications, several approaches have been developed for fabrication of graphene foams, mainly including hydrothermal reduction of graphene oxides (GO), chemical reduction of GO, and chemical vapor deposition (CVD) growth on nickel foam skeletons [15]. As the precursor of graphene, GO can be obtained easily from graphite powders [16]. The introduced oxygen-containing groups can make pristine graphene water soluble, so that GO is a good candidate for the bottom-up assembly of graphene into macroscale materials [17]. Moreover, the graphene foam can be treated as a conductive 3D network substrate, which can be modified with other active material to meet the needs in different areas [18,19].

Photoelectric research has attracted a lot of attention from academic researchers and industry application engineers [20]. The main objective of photoelectric conversion is to obtain a good solar energy conversion efficiency. There are many factors associated with the efficiency, including light utilization efficiency, band gap of material used to build the device, separation efficiency of photoinduced electron-hole and photoinduced electrons transporting within the material freely, etc. Recently, we found that the 2D bio-inspired graphene composite porous structure were able to achieve high light utilization with low reflection, which resulted in improved photoelectric conversion [21]. The 3D graphene foam has deeper light penetration, and the light will scatter in the foam pore interior, which will reduce the reflective of the incident light. If there are active materials on the surface of the foam scaffold, the incident light will be maximally absorbed. The reasonable design and preparation of composite foams can help promote the sunlight utilization and improve the conversion efficiency. Furthermore, such a composite graphene foam is a good candidate as photocat-

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alyst for the photodegradation of organic pollutants, which cause severe environmental and ecological problems every year [22–24].

Herein, in order to study the performance of the 3D graphene composite foam for photoelectric and photocatalytic application in energy or environment field [25,26], a simple, nontoxic and effective way is proposed to prepare a 3D free-standing composite graphene foam using Ni foam as the template and following a one-step hydrothermal process to form ZnO nanorods arrays capped on graphene surface. ZnO semiconducting material has been considered to be an ideal candidate for photoelectric and photocatalytic application due to its high electron mobility, nontoxicity and chemical stability [27–30]. In particular, the 3D self-supporting and hierarchical porous graphene structure acts as the conductive substrate which would let the solution pass through itself, and ZnO nanorods serve as the active material which can maximum exert dimensions and interfaces optimization. By combining the advantages of interconnected porous network, high conductivity, big surface area, good mechanical strength and thermal stability, the free-standing 3D graphene composite foams show high electrochemical activity and great potentialities for high-performance electrode materials in many energy conversion and photodegradation applications [31–34].

2. Experimental

2.1. Preparation of graphene oxide (GO)

A modified Hummers' method was used to prepare GO from natural graphite powder (Sigma) [35]. Briefly, graphite (1.1 g) was added into a solution of concentrated H_2SO_4 (8.6 mL), $K_2S_2O_8$ (1.8 g), and P_2O_5 (1.8 g). This solution was stirred at 80 °C for 6 h. After washed by deionized water, filtrated, and dried, the powder was added into another solution of concentrated H_2SO_4 (43.2 mL) and $KMnO_4$ (5.4 g). The mixture was stirred at 35 °C for 2 h. Then, 50 mL water was added into this mixture in an ice bath to keep the temperature below 50 °C. After further 2 h stirring, the solution was further diluted using water (100 mL), and then 5 mL of H_2O_2 (30%) was added into this solution to stop the reaction. The crude product was centrifuged and washed by HCl solution (V:V = 1:10, 300 mL), followed by repeated washing with water until the pH value is around neutral. The resulting product is graphite oxide. After ultrasonicated for 4 h, single layer graphene oxide suspensions were obtained by 30 min of 8000 rpm centrifugation.

2.2. Preparation of reduced graphene oxide foam (rGO foam)

The nickel foam (NF) was firstly washed by isopropanol, ethanol and deionized water for 5 min using an ultrasonic cleaner, respectively. In order to get free-standing 3D graphene foam, GO (C_{GO} = 3.1 mg/mL) suspension was dipped on the nickel foam (1.5 cm × 1.5 cm × 0.16 cm). In this step, we must ensure that GO solution was dipped evenly on the nickel surface of nickel foam. After GO/NF dried naturally, nickel foam coated with GO turned to yellow. The reduction of GO to reduced graphene oxide (rGO) was achieved by hydrazine reduced method. Briefly, GO/NF and 10 μL of hydrazine monohydrate were put into the autoclave and then heated the autoclave at 90 °C for 10 h to achieve the reduction of graphene oxide/nickel foam (rGO/NF). Finally, rGO/NF was immersed in the mixture of 0.5 M $FeCl_3$ and 1 M HCl solution for 5 h to remove nickel, and rGO foam was obtained. After washed and dialyzed with water several times, the three-dimensional, free-standing, and light-weight, rGO foam was formed. The pure rGO foam can be transferred onto quartz and ITO substrates for different applications, respectively.

2.3. Preparation of ZnO nanorods modified rGO foam (ZnO/rGO foam)

A modified Pacholski method was utilized to prepare ZnO nanocrystal seed [36]. Briefly, a NaOH ethanol solution (30 mM) and $(CH_3COO)_2Zn$ ethanol solution (10 mM) were mixed together slowly, and then the mixture solution was heated at 60 °C with stirring for 2 h. A few drops of the obtained spherical ZnO nanocrystal seed solution were added onto the rGO foam. After the ethanol solution dried, the ZnO seeds covered on the whole graphene surface of rGO foam. And then rGO foam was heated at 90 °C to make sure the ZnO seeds binding with rGO foam firmly. Then rGO foam which was supported on a substrate was put into an autoclave, at an angle around 30°, with the rGO side facing the bottom. The autoclave was filled with a solution containing $Zn(NO_3)_2{\cdot}6H_2O$ (30 mM) and hexamethylenetetramine (HMTA, 30 mM) and it was heated at 90 °C for 6 h to perform ZnO nanorods growth. After hydrothermal reaction completed, ZnO/rGO foam was rinsed with deionized water and then dried at room temperature.

A ZnO/rGO smooth film was also prepared using similar process. Briefly, GO aqueous solution was casted on a substrate, and dried naturally. After that, the GO film was reduced by hydrazine, and then followed the hydrothermal process to form ZnO nanorods arrays on graphene film surface as same condition as that of ZnO/rGO foam.

2.4. Photocurrent measurements

A three-electrode method was used to study the photocurrent properties with CHI 660D electrochemical station (CH Instruments). Here, rGO foam or ZnO/rGO foam acted as working electrode, Ag/AgCl as reference electrode (3.0 M KCl) and a Pt electrode as counter electrode. A 0.5 M Na_2SO_4 aqueous solution was chosen as electrolyte solution, and before testing, the electrolyte solution was purged for 60 min with nitrogen. A high-pressure Xe lamp was used as light source to simulate solar light. The light intensity was 100 mW/cm^2 and the area of the sample exposed to light was 1.5 cm^2.

2.5. Photocatalytic activity study

Rhodamine B (RhB) was used as a probe molecule to evaluate the photocatalytic activity of pure rGO foam, ZnO nanorod powder and ZnO/rGO foam. The absorbance spectra of RhB was measured with the same time interval, and the characteristic absorption peak of RhB at 554 nm was chosen to monitor the photocatalytic degradation process. The photocatalytic experiment was carried out by the following steps: Firstly, the RhB aqueous solution (5 ppm, 25 mL) was prepared, and then the catalyst was dispersed into this solution. The weight of the catalyst was controlled by the amount of ZnO nanorods, which was adjusted to be 0.2 mg/mL in all the photodegradation experiments. Before the photodegradation experiments, the mixture solution was placed in the dark with stirring for at least 30 min. This step is to sure that the RhB dye molecules are adsorption and desorption equilibrium on the surface of the corresponding catalysts. Secondly, a simulated solar light, whose flux intensity was 100 mW/cm^2, was used to irradiate the mixture solution. At each 10 min, 3 mL of mixture solution was taken out, and centrifuged at 6000 rpm for 10 min to remove the catalysts, and then the UV–vis absorbance spectra of the RhB aqueous solution was measured with a spectrophotometer (Shimadzu 3600). Here, the same amount of ZnO nanorods in the ZnO/rGO foam and pure ZnO nanorods powder was used to achieve the contrast experiments. Before the hydrothermal growth process, the weight of the rGO foam was measured. After the hydrothermal growth process, the weight of ZnO/rGO foam was also measured.