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Short communication

Ultrasonic-microwave assisted synthesis of three-dimensional polyvinyl alcohol carbonate/graphene oxide sponge and studies of surface resistivity and thermal stability

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ABSTRACT

In the article, graphene oxide (GO) was prepared by flake graphite, nitric acid and peroxyacetic acid via the sonochemical method and characterized, and polyvinyl alcohol carbonate/GO composite (PVAC/GO composite) was synthesized by polyvinyl alcohol (PVA), dimethyl carbonate (DMC) and GO via the approach of transesterification in the case of ultrasonic-microwave synergistic effects and characterized, and three-dimensional PVAC/GO sponge (3D PVAC/GO sponge) was manufactured by PVAC/GO composite via the foaming approach and characterized, and the thermal stability and surface resistivity of 3D PVAC/GO sponge were investigated. Based on those, it had been attested that PVAC polymer was structured by DMC and PVA and had the six-membered lactone rings and the ether bonds, and PVAC/GO composite was constituted by 2D GO lattice and PVAC polymer, and 3D PVAC/GO sponge was constructed by PVAC/GO composite, and the surface resistivity of 3D PVAC/GO sponge with 0.00, 0.60, 1.20, 1.80 and 2.40 g of GO were 9.07 × 10^7, 6.02 × 10^7, 4.65 × 10^7, 2.47 × 10^7 and 1.06 × 107 O/sq, and the thermal stability of 3D PVAC/GO sponge had improved.

1. Introduction

Artificial sponges have supernormal physical properties that include fascinating porosity [1], outstanding mechanical properties [2], extraordinary thermal stability [3] and conductivity [4]. Based on these fascinating characteristics, they can be potentially applied in the field of oil-water separation, energy storage, packaging and catalyst carrier [5-8]. In general, the artificial sponges mainly contain polymer-based sponges [9-14], such as melamine sponge [9,10], polyurethane sponge [11], polyvinyl alcohol (PVA) sponge [12,13] and epoxy resin sponge [14]. Among them, PVA-based polymer matrix has gained the increasing attention in the process of designing high-performance, low-cost three-dimensional polymer sponge (3DPS) as a result of a low-toxic and tractable and easily-obtained macromolecule polymer [15–17]. However, the pure three-dimensional PVA sponge (3DPVAS) can be readily dissolved in water because PVA chain carries abundant hydroxyl functional groups. In view of such, how to evade the dissolution of 3DPVAS in water is a key factor for developing its application in the practical life. So far it has been the better method to decrease the number of hydroxyl functional groups in PVA. In many reactions of hydroxyl functional groups, aldol reaction of aldehydes and PVA can not only produce aldehyde acetal but also decrease the number of hydroxyl functional groups, and aldehyde acetal can also form 3D PVA-based sponges [18,19]. For instance, 3D PVA-formaldehyde sponge and 3D PVA-glutaraldehyde sponge used in the packaging field have been largely produced. Indeed, aldehydes with low molecular weights are very much pernicious with regard to the human health, which remain in the sponges. Thereby, it is necessary to manufacture a new “green” 3D polyvinyl alcohol carbonate sponge (3DPVAS) which does not contain the residual aldehydes with low molecular weights.

Recently 3DPVAS known as 3D PVAC/GO sponge has been synthesized in our laboratory. Compared with the previous 3D PVA-based sponges, dimethyl carbonate (DMC) as raw materials was used to replace aldehydes with low molecular weights [20], and the transesterification between PVA and DMC was used to replace the aldol reaction between aldehydes and PVA in manufacturing 3D PVAC/GO sponge. Otherwise, GO with the low toxicity, thermal stability and favorable biocompatibility [21–23] was also used to construct 3D PVAC/GO sponge. Due to the toxicity of DMC is lower than that of aldehydes with low molecular weights and GO has the low toxicity, thermal stability and electric property, the toxicity of 3D PVAC/GO sponge will be lower than that of the previous 3D PVA-based sponges, and the electric

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property and thermal stability of 3D PVAC/GO sponge will also improve with respect to the previous 3D PVA-based sponges.

2. Experimental

2.1. Materials

PVA (1799, Alcoholysis degree = 99.00%), DMC (98.00 wt%), K_2CO_3 (99.00 wt%), OP-10 (99.00 wt%) and n-pentane (99.00 wt%) were purchased from Tianjin, China. Flake graphite (the average flake size = 160 μm mesh and the carbon content = 99.00 wt%) was purchased from Man Country, China. Nitric acid (65.00 wt%), peroxyacetic acid (35.00 wt%) were purchased from Beijing Huagong Company, Beijing, China.

2.2. Preparation of GO

In accordance with the weight ratio (flake graphite:nitric acid:peroxyacetic acid = 1.00:0.50:1.00), flake graphite, nitric acid and peroxyacetic acid were mixed into a mixture in a conical flask (hereinafter referred to as the flask). And then, the flask was placed in the ultrasonic cleaning bath (Nominal power: 250 W). After 35 min of ultrasonic irradiation, the flask was taken out from the ultrasonic cleaning bath. The liquid was removed from the flask, and the solid was transferred to a porcelain evaporating dish. Later, the solid in the porcelain evaporating dish was placed into a drying box and dried at 100 °C. After the solid dried completely, the porcelain evaporating dish was transferred to the drying box and heated at 170 °C. After 20 min of heating, GO could be obtained.

2.3. Synthesis of PVAC/GO composite

PVAC/GO composite with 0.60 g of GO could be synthesized as follow. 0.60 g of GO and 50.00 mL of distilled water were added in 250 mL of single neck round bottom flask (hereinafter referred to as the flask), and the flask was placed in the ultrasonic cleaning bath. After ultrasonic irradiation for 2 h, a gray colloidal suspension generated within the flask, and a stable and gray GO/H_2O colloidal suspension could be also formed. Next, 2.00 g of K_2CO_3 powders were added in the flask. After ultrasonic irradiation for 2 min, K_2CO_3 powder was dissolved completely in the GO/H_2O colloidal suspension. Then, 9.00 g of PVA was added in the flask. The flask was transferred into the microwave catalytic synthesizer. At the same time, the reflux condenser tube and the probe ultrasonic generator were also installed on the three-pronged dovetail pipe of flask. After 10 min of magnetic stirring and the irradiation produced by the ultrasonic and microwave, PVA would dissolve completely in the GO/H_2O colloidal suspension. Afterwards, 4.50 mL of OP-10 and 5.00 mL of DMC were added into the flask in the case of the magnetic stirring and the irradiation produced by the ultrasonic and microwave. After 2 h of reaction, PVAC polymer was synthesized via the transesterification between PVA and DMC, and GO was evenly dispersed into PVAC polymer to produce PVAC/GO composite.

In addition, PVAC/GO composites with 0.00, 1.20, 1.80 and 2.40 g of GO were also synthesized in accordance with the above procedures.

2.4. Manufacture of PVAC/GO sponge

PVAC/GO sponge was manufactured via a convenient and high-effective foaming approach. The flask containing PVAC/GO composite with 0.60 g of GO was taken out and placed on the test bench. Then, PVAC/GO composite with 0.60 g of GO was cooled in the flask. When the temperature of PVAC/GO composite in the flask dropped to room temperature, 5.00 mL of n-pentane was added in the flask. After 5 min of stirring, PVAC/GO composite and n-pentane could form a mixture. Afterwards, the mixture was quickly transferred to a petri dish, and the petri dish was immediately put in a vacuum drying box. After 10 h of heating at 55 °C, PVAC/GO composite could foam into PVAC/GO sponge.

In accordance with the above procedures, PVAC/GO sponges with 0.00, 1.20, 1.80 and 2.40 g of GO were also manufactured.

Besides, the conventional route and method were also used to synthesize PVAC/GO sponge. In the synthesis, the transesterification between PVA and DMC was completed in the thermostatic waterbath and in the case of agitation (the synthesis procedures have been shown in Supplementary materials). Through the analysis of FTIR spectrum, it was also identified that PVAC/GO composite had been synthesized (FTIR spectrum has been shown in Supplementary materials). Here it should be pointed out that both the conventional route and method and the ultrasonic-microwave assisted synthesis can be used to synthesize PVAC/GO sponge, but they can have the different driving forces that make PVA and DMC to produce the effective collision and disperse GO into PVAC polymer. For instance, the driving forces for the effective collision between PVA and DMC and the dispersion of GO in the conventional route and method may relay on the heat energy produced by the thermostatic waterbath and the agitation, and the ones between PVA and DMC and the dispersion of GO in the ultrasonic-microwave assisted synthesis may depend on the irradiation energy produced by the ultrasonic and microwave. From the influence of the energy on the effective collision and the dispersion, the heat energy produced by the electric heating jacket would hardly change once the adjustable resistance is fixed, and the high temperature and high pressure with the momentary produced by the ultrasonic cavitation effect and microwave irradiation may not act on PVA and DMC, which can increase the effective collision frequency between PVA and DMC and the dispersion of GO in PVAC polymer. Nevertheless, the irradiation energy produced by the ultrasonic and microwave would strengthen with the increase of the reaction time, and the high temperature and high pressure with the momentary property may act on PVA and DMC, which can increase the effective collision frequency between PVA and DMC and the dispersion of GO in PVAC. It is very obvious that the increases of the effective collision frequency between PVA and DMC and the dispersion of GO in PVAC polymer will make for accelerating the transesterification between PVA and DMC and the dispersion of GO in PVAC polymer, and PVAC/GO sponge will also form in the case of the foaming. To contrast these synthetic methods, it is believed the ultrasonic-microwave assisted synthesis has the advantages of short reaction time, quick reaction velocity and no need to control the reaction temperature.

2.5. Characterization

2.5.1. Confirmation of GO

Scanning electron microscopy (JEM-2100F, Japan) was used to obtain SEM micrograph of GO, and the micrograph was shown in Fig. 1(a). Transmission electron microscope (Tecnai G2 20, Holland) and corresponding selected area electron diffraction spectroscopy were used to obtain TEM micrograph and SAED pattern of GO. And then, TEM micrograph was shown in Fig. 1(b) and SAED pattern inserted in Fig. 1(b). X-diffraction spectrometer (Germany) was used to obtain XRD pattern of GO, and the pattern was shown in Fig. 2. Raman spectrometer (France) was used to obtain Raman spectrum of GO, and the spectrum was shown in Fig. 3.

2.5.2. Characterization of PVAC/GO composite

Fourier-transform infrared-9800 spectrometer (Japan) was used to obtain FTIR spectra of PVA and PVAC/GO composite with 0.60 g of GO, and FTIR spectra were shown in Fig. 4.

2.5.3. Characterization of PVAC/GO sponge

X-diffraction spectrometer (Germany) was used to obtain XRD patterns of PVA and PVAC/GO sponge with 0.60 g of GO, and the patterns were shown in Fig. 5. Scanning electron microscopy (JEM-2100F,