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Short communication

## Preparation of polyvinyl alcohol graphene oxide phosphonate film and research of thermal stability and mechanical properties

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## ABSTRACT

In this article, flake graphite, nitric acid, peroxyacetic acid and phosphoric acid are used to prepare graphene oxide phosphonic and phosphinic acids (GOPAs), and GOPAs and polyvinyl alcohol (PVA) are used to synthesize polyvinyl alcohol graphene oxide phosphonate and phosphinate (PVAGOPs) in the case of faint acidity and ultrasound irradiation, and PVAGOPs are used to fabricate PVAGOPs film, and the structure and morphology of GOPAs, PVAGOPs and PVAGOPs film are characterized, and the thermal stability and mechanical properties of PVAGOPs film are investigated. Based on these, it has been proved that GOPAs consist of graphene oxide phosphonic acid and graphene oxide phosphinic acid, and there are C–P covalent bonds between them, and PVAGOPs are composed of GOPAs and PVA, and there are six-member lactone rings between GOPAs and PVA, and the thermal stability and mechanical properties of PVAGOPs film are improved effectively.

## 1. Introduction

Graphene as one of carbon's allotropes has drawn considerable attention because it has the high thermal stability, outstanding conductivity, distinguished Young's modulus and fracture strength [1–4]. So far graphene based materials have potentially applied in the sensor [5], catalyst carrier [6], photovoltaic device [7], fillers [8] and absorbent material [9] owing to their extraordinary characteristics. Among these applications, graphene as the filler into polymer matrix for enhancement of the thermal stability, conductivity, thermal conductivity and mechanical properties has attracted a great deal of attention because they not only have the merits of graphene but also the peculiarities combined with polymer. However, that there are two major problems in the design of optimal graphene based materials need be resolved: 1) to perfectly disperse graphene in polymer matrix in molecular level; 2) to form strong interfacial interaction between graphene and polymer matrix.

In order to solve the problems, the guiding ideology is 1) to functionalize graphene into phosphonic and phosphinic acids, thus make graphene evenly disperse in polymer matrix and forming strong interfacial interaction between graphene and polymer matrix, and 2) to select the appropriate polymer matrix into graphene based materials. As to the graphene functionalized into phosphonic and phosphinic

acids, the graphene chemical modified method [10], thermal annealing method [11], ball-milling method [12] and chemical vapor deposition method [13] have been used. As far as the selection of polymer matrix, PVA with the nontoxicity, water-solubility and abundant hydroxyls has been used, and the simple bottom-up methodology [14], the prolongable solution-mixing method [15] and the direct esterification of PVA and carboxylic acid on the surface of graphene sheet [16] have been also used to synthesize graphene/PVA matrix materials. Throughout the preparations of phosphonic and phosphinic acids and the structure of graphene/PVA matrix materials synthesized by the previous methods, it is considered that the aggressive reaction reagents, time-consuming procedures and complex instrumentation have restricted the massive preparation of them, and the interfacial interaction between graphene and PVA matrix is relatively weak.

The sonochemistry method is an environmentally-friendly, rapid and simple approach. In the ultrasonic-assisted synthesis, whether the heat energy of reaction requirement or the increase of collision frequency between reactants depend on the ultrasonic cavitation [17]. Otherwise, it has been reported that the ultrasound treatment not only affects the surface morphology but also the uniform distribution of polymers and nanofibers [18–23]. Recently, the sonochemistry method has been used to simplify the preparation of graphene oxide phosphonic acid and graphene oxide phosphinic acid (GOPAs) and the syntheses of

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PVAGOPs in our laboratory. After the characterization of GOPAs and PVAGOPs and the investigation of the thermal stability and mechanical properties for PVAGOPs film, it has been attested that the sonochemistry method is very effective in the preparation and the synthesis, and the thermal stability and mechanical properties of PVAGOPs film are improved.

## 2. Experimental

### 2.1. Materials

Flake graphite (Average flake size = 160  $\mu\text{m}$  mesh, Carbon content = 99.00 wt%) was purchased from Man Country, China. Nitric acid (65.00 wt%), peroxyacetic acid (35.00 wt%), acetic anhydride (85.00 wt%), phosphoric acid (85.00 wt%) were purchased from Beijing Huagong Company, Beijing, China. PVA (1799) was purchased from Tianjin, China.

### 2.2. Preparation of GOPAs

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 flask. And then, the flask was placed in the ultrasonic cleaning bath (Nominal power: 250 W). After 35 min of irradiating, the flask was taken out from the ultrasonic cleaning bath. The solid was transferred into the porcelain evaporating dish after the solid and liquid separated. Later, the solid in the porcelain evaporating dish was placed into a drying box and dried at 100  $^{\circ}\text{C}$ . After 30 min of drying, the solid was removed from the porcelain evaporating dish and transferred into the flask. A certain amount of phosphoric acid (flake graphite:phosphoric acid = 10.00:1.00) and acetic anhydride (flake graphite:acetic anhydride = 1.00:1.00) were added in the flask. Then, the flask was fixed in the ultrasonic cleaning bath. After 25 min of irradiating, the solid and liquid were separated. The solid was transferred into another porcelain evaporating dish and dried at 100  $^{\circ}\text{C}$ . After the solid dry completely, the porcelain evaporating dish was transferred into the drying box and heated at 170  $^{\circ}\text{C}$ . After 20 min of heating, GOPAs could be prepared.

### 2.3. Synthesis of PVAGOPs

In accordance with Scheme 1, PVAGOPs were synthesized as follows. 7.00 wt% of GOPAs and 20.00 mL of distilled water were added in a flask installed in the ultrasonic cleaning bath. Later, the flask with GOPAs and the distilled water was irradiated for 1 h. In that time, the gray colloidal suspension that consisted of GOPAs and  $\text{H}_2\text{O}$  formed within the flask, and the stacked GOPAs exfoliated and dispersed in  $\text{H}_2\text{O}$  to form the stable GOPA/ $\text{H}_2\text{O}$  colloidal suspension because the hydroxyls in GOPAs had the hydrophilicity. Next, 1.60 g of white and

viscous PVA solution was slowly added in the stable GOPAs/ $\text{H}_2\text{O}$  colloidal suspension in the case of ultrasound irradiation, which prepared from a certain amount of PVA and distilled water at around 90  $^{\circ}\text{C}$  and then cooled to around 40  $^{\circ}\text{C}$ . After 2 h of irradiating, PVAGOPs with 7.00 wt% of GOPAs could be synthesized.

In accordance with the above procedures, 0.00, 1.00, 3.00 and 5.00 wt% of GOPAs and 1.60 g of white and viscous PVA solution were used to synthesize four PVAGOPs with 0.00, 1.00, 3.00 and 5.00 wt% of GOPAs.

### 2.4. Fabrication of PVAGOPs film

PVAGOPs film was fabricated via solidifying PVAGOPs in a culture dish. PVAGOPs with 7.00 wt% of GOPAs were paved nicely on the bottom of the culture dish via rotating the culture dish again and again. Later, the culture dish with PVAGOPs with 7.00 wt% of GOPAs was placed carefully in a drying box. The temperature of the drying box was adjusted to 60  $^{\circ}\text{C}$  in advance. After 60 min of drying, PVAGOPs film was formed on the bottom of culture dish. Lastly, PVAGOPs film with 7.00 wt% of GOPAs could be obtained after it was peeled carefully from the bottom of culture dish.

In accordance with the above procedures, four PVAGOPs films with 0.00, 1.00, 3.00 and 7.00 wt% of GOPAs were fabricated.

### 2.5. Instrumentation part

#### 2.5.1. SEM and TEM

Scanning electron microscopy (JEM-2100F, Japan) and corresponding energy-dispersive X-ray spectroscopy were used to obtain SEM micrograph and EDS spectrum of GOPAs shown in Fig. 1(a) and (b) and SEM micrographs of PVA and PVAGOPs films. Among them, SEM micrographs of PVA film and PVAGOPs films with 1.00 and 7.00 wt% of GOPAs were shown in Fig. 8. SEM micrographs of PVAGOPs films with 3.00 and 5.00 wt% of GOPAs were shown in Supplementary materials.

Transmission electron microscope (Tecnai G2 20, Holland) and corresponding selected area electron diffraction spectroscopy were used to obtain TEM micrograph and SAED pattern of GOPAs shown in Fig. 1(c) and the upper right corner of Fig. 1(c).

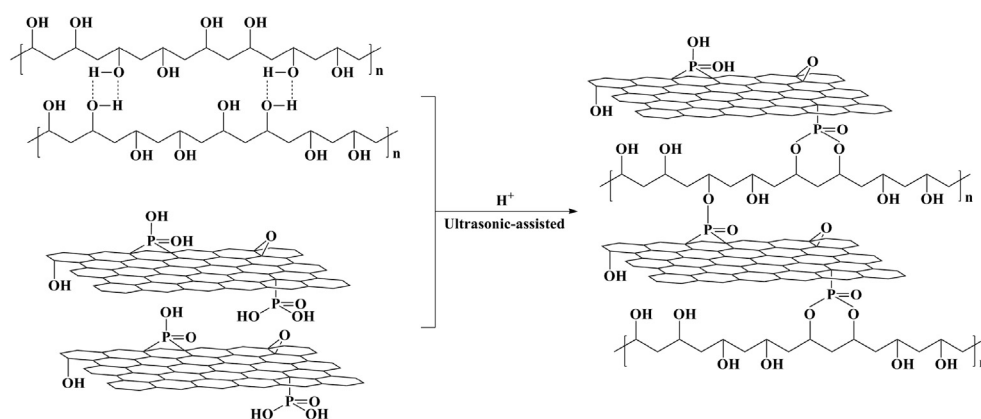
#### 2.5.2. FTIR and Raman

Fourier-transform infrared-9800 spectrometer (Japan) was used to obtain FTIR spectrum of GOPAs shown in Fig. 2 and FTIR spectra of PVA and PVAGOPs film with 1.00 wt% of GOPAs shown in Fig. 6.

Raman spectrometer (France) was used to obtain Raman spectra of GO and GOPAs shown in Fig. 3.

#### 2.5.3. XPS

X-ray photoelectron spectroscopy (XPS) (USA) was used to obtain the surface element information of GO and GOPAs in the case of 200 W



Scheme 1. Syntheses of PVAGOPs in the case of ultrasound irradiation.

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