

# Enhanced dielectric performance of polyimide composites with modified sandwich-like SiO<sub>2</sub>@GO hybrids



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## ARTICLE INFO

### Article history:

Received 14 December 2016

Received in revised form 24 March 2017

Accepted 26 March 2017

Available online 27 March 2017

### Keywords:

A. Polymer-matrix composites (PMCs)

A. Graphene

B. Electrical properties

B. Interface

## ABSTRACT

High-dielectric-constant (high-k) polymer nanocomposites are demonstrated to show great promise microelectronics industry. In this work, sandwich-like SiO<sub>2</sub> encapsulated graphene oxide hybrids (SiO<sub>2</sub>@GO) were fabricated through a sol-gel method to enhance the dielectric properties of PI. Series of analysis, such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) demonstrated that SiO<sub>2</sub> were successfully grafted onto the surface of GO and formed a sandwich-like core-shell structure hybrids. Then, polyimide (PI) composites filled with SiO<sub>2</sub>@GO were prepared via in-situ polymerization method. A dielectric constant of 73 (40 Hz) was obtained for SiO<sub>2</sub>@GO/PI composites as the fraction of SiO<sub>2</sub>@GO was 20 wt%. In order to improve the dielectric properties of composite, two kinds of coupling agents, 3-aminopropyl triethoxysilane (APTS) and 3-glycidoxypropyltrimethoxysilane (GPTS), were used to modify the surface of SiO<sub>2</sub>@GO. GPTS-SiO<sub>2</sub>@GO/PI composite had an increased dielectric constant of 79 and a decreased loss of 0.25 at 40 Hz. The significantly enhanced dielectric performance of GPTS-SiO<sub>2</sub>@GO/PI composite was caused by the good dispersion of GPTS-SiO<sub>2</sub>. In addition, the different dielectric performance of composites modified by different coupling agent was also discussed. This work could help researchers further understand the mechanism of fillers' interface on the dielectric properties of composites.

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## 1. Introduction

Flexible polymer composites with high dielectric constant (high-k) are highly desirable for their applications in the modern information and electronics industry, such as charge-storage capacitors, artificial skins and muscles, and flexible electronics [1–5]. Introducing electric conductive fillers to polymer matrix is a promising strategy in preparing composites with advantageous dielectric properties [6–10]. Carbon materials, especially graphene and carbon nanotubes (CNT) are largely used as fillers to form high-k composites due to their excellent electronic conductivity and high aspect ratios [11]. Most of these studies followed the percolation theory, working on development high-k composites with a low percolation threshold [12–15]. For example, Z.M Dang et al. [12] introduced CNT to poly(vinylidene fluoride) (PVDF) getting a very high dielectric constant value of 8000. However, such percolative composites generally presence high dielectric loss (more than

2 at 10<sup>2</sup> Hz) near the percolation threshold [12,16–18]. Such high loss value limits the usage of composites in practice in the microelectronics industry [19]. In order to overcome this disadvantage, many of strategies have been developed [13,14,20–28]. Coating an insulated layer on the surface of graphene or CNT has been proved one of the most effective methods to reduce the dielectric loss, because the presence of insulated shell can prevent the conductive fillers contacting directly. Coating TiO<sub>2</sub> on the surface of graphene or CNT could reduce the dielectric loss of composites [29–33]. For example, Chao Wu et al. [33] prepared graphene-TiO<sub>2</sub> nanorod sheets and added them into polystyrene (PS), the composite exhibited a high dielectric constant and relatively low loss value.

Compared with TiO<sub>2</sub>, SiO<sub>2</sub> has been widely used to fabricate electronics packaging materials for its good properties [34]. To the best of our knowledge, the study of dielectric performances of SiO<sub>2</sub>@graphene/polymer composites has rarely been reported.

Herein, novel flexible composite films that simultaneously possessing high dielectric constant and low loss were produced by incorporating sandwich-like core shell structure SiO<sub>2</sub>@GO hybrids,

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which were prepared via the hydrolysis of TEOS on the surface of GO. The dense  $\text{SiO}_2$  layer grafted on the surface of GO can effectively prevent direct contact of the GO sheets in the composite, thus suppressing the leakage current. As a result, by dispersing 20 wt% of  $\text{SiO}_2$ @GO sheets into a PI matrix, the value of dielectric constant of the composite can up to 73 at 40 Hz, which is 21 times higher than that of pure PI (3.0), and the dielectric loss is only 0.39.

In order to improve the interface compatibility, two kinds of coupling agents were employed, both can decrease the dielectric loss dramatically, however the improvement trend of these fillers on the dielectric constant is  $\text{GPTS-SiO}_2$ @GO (79) >  $\text{SiO}_2$ @GO (73) >  $\text{GPTS-SiO}_2$ @GO (40). This interesting phenomenon was also explained by different interface of those composites. We expect that our strategy of controlling the filler interface will be applied in the future to acquire more polymer composites with high permittivity and low dielectric loss.

## 2. Experimental section

### 2.1. Materials

Natural flake graphite (300 mesh) was obtained from Shuangxing graphite processing plant, China. Tetraethylorthosilicate (TEOS,  $\text{SiO}_2$  content  $\geq 28\%$ ), ammonia, 3-aminopropyl triethoxysilane (APTS, Ar), 3-glycidyloxypropyltrimethoxysilane (GPTS, Ar), potassium persulfate (KPS, Ar), potassium permanganate ( $\text{KMnO}_4$ , Ar), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 95–98%), perhydrol ( $\text{H}_2\text{O}_2$ , 30%), phosphorus pentoxide (PPO, Ar), ethanol (EtOH, 99.5%) and N,N-dimethylacetamide (DMAc, 99.5%) were obtained from Beijing Reagent Co. (Beijing, China). And DMAc was purified by molecular sieves to remove the water before use. 4,4'-Oxydianiline (ODA) and pyromellitic anhydride (PMDA) were obtained from Mitsubishi Gas Chemical Company, INC, Japan.

### 2.2. Preparation of GO, $\text{SiO}_2$ @GO and modified $\text{SiO}_2$ @GO

GO was prepared via a modified Hummers method from a pre-oxidized graphite [35]. 200 mg of dry GO powder was loaded in a 1000 mL of three-necked flask, to which distilled water (50 mL) and ethanol (750 mL) were added. After ultrasonic agitation for 1 h, 10 mL of ammonium hydroxide was added to the solution under stirring [36]. Then 1 mL of TEOS was added dropwise and stirred for 12 h at room temperature. After suction filtering, water washing to neutral and freeze drying, a gray powder was formed, assigned as  $\text{SiO}_2$ @GO.  $\text{SiO}_2$ @GO was further modified with APTS and GPTS, and then noted as APTS- $\text{SiO}_2$ @GO and GPTS- $\text{SiO}_2$ @GO, respectively. For a typical procedure, 10 g of  $\text{SiO}_2$ @GO powders were dispersed in a solution of ethanol (190 mL) and  $\text{H}_2\text{O}$

(10 mL), treated ultrasonically for 30 minutes and then 0.5 g of APTS and 1 mL of ammonia were added and stirred at room temperature for 14 h to complete the coupling reaction.

### 2.3. Synthesis of $\text{SiO}_2$ @GO/PI composites

The  $\text{SiO}_2$ @GO/PI composites films were prepared by in-situ polymerization of ODA and PMDA in the presence of  $\text{SiO}_2$ @GO and then thermal imidization. In a typical procedure, various amounts of  $\text{SiO}_2$ @GO were added to 12 mL of DMAc and ultrasonic for 30 min in a three-necked flask (100 mL). Then 0.632 g of ODA was dissolved in the above suspension in the aid of mechanical stirring. Finally, 0.758 g of PMDA was added in three times within 1 h under ice bath. The mixture was stirred vigorously at 0 °C for 5 h, yielding a viscous mixture, which was casted on a clean glass slide to form a uniform film and subsequently placed in an oven at 80 °C for 2 h, 100, 150, 250 and 300 °C for 1 h respectively to finish imidization. The given  $\text{SiO}_2$ @GO/PI composites were labeled as  $\text{SiO}_2$ @GO/PI-X in which X indicated the percentage content of  $\text{SiO}_2$ @GO in the composites. For example, the sample with 0.2 g of  $\text{SiO}_2$ @GO in 1 g of PI was labeled as  $\text{SiO}_2$ @GO/PI-20.

By similar procedure as above, APTS- $\text{SiO}_2$ @GO and GPTS- $\text{SiO}_2$ @GO was introduced in PI to prepare composite films.

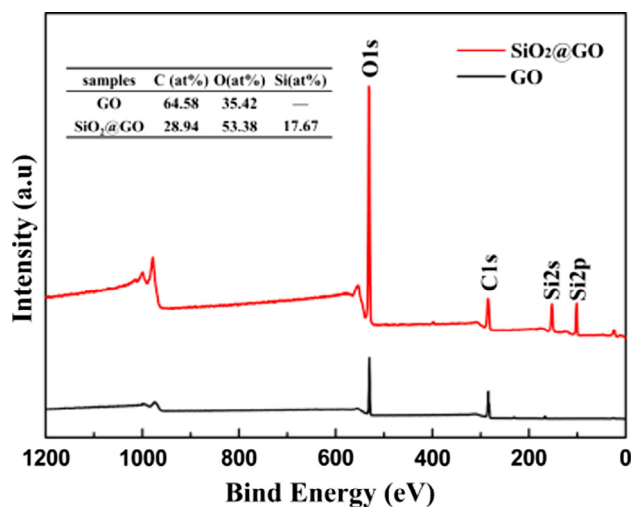


Fig. 2. XPS spectra and elementary composition (the insert table) of GO and  $\text{SiO}_2$ @GO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

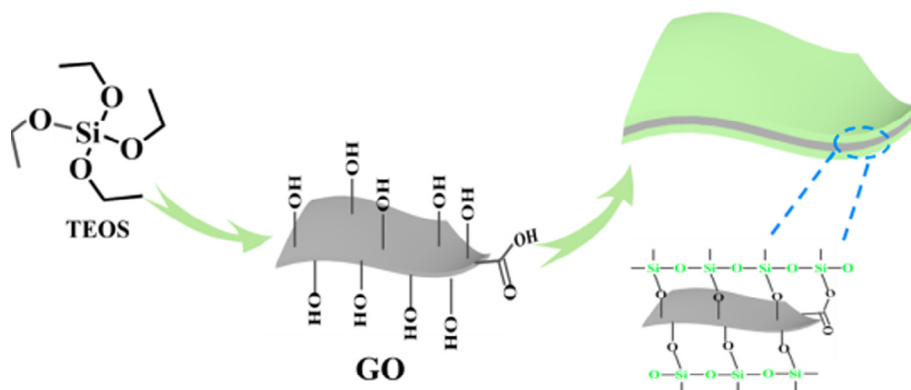


Fig. 1. Preparation procedure of  $\text{SiO}_2$ @GO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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