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Hydrothermal-hot press processed SiO_2-rGO hybrid with enhanced physical properties

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ABSTRACT

In this study, monoliths of SiO_2-rGO hybrids were obtained with improved physical properties by calcination-hot press processing. It was found that the oxygen-containing groups on graphene oxide were beneficial for the adsorption of ethyl silicate ($C_8H_{20}O_4Si$), leading to the uniform dispersion of rGO with SiO_2, which was obtained by hydrolysis of ethyl silicate during the hydrothermal reaction. The hybrid, which was subsequently calcinated for 1 h showed electrical conductivity of 0.143 S m^{-1} together with higher thermal conductivity (1.612 $Wm^{-1}k^{-1}$), dielectric constant (10^7), BET surface area (712.01 m^2g^{-1}), and higher tensile strength (225.74 MPa). In addition, the enhanced value of electrical conductivity (0.02 S m^{-1}), thermal conductivity (1.439 $Wm^{-1}k^{-1}$), dielectric constant (500), tensile strength (98 MPa), and BET surface area (611.21 m^2g^{-1}) were obtained for the silica-rGO (1.55 wt% rGO) as compared to the bare SiO_2. XRD characterization showed that an increase in calcination temperature and further hot-press processing at 750 °C led to enhanced crystallinity in the SiO_2 spheres in the hybrid, resulting in enhanced physical properties in the hybrids.

1. Introduction

Due to its high electrical conductivity (10^6 S m^{-1}), high thermal conductivity (5000 W/mK), high young's modulus (1 TPa) and high intrinsic strength (130 GPa), graphene is considered as an ideal candidate to improve the electrical, thermal and mechanical properties of polymers, metals and ceramics [1,2]. Among the numerous types of graphene materials [3,4], graphite oxide derived graphene plays a significant role in enhancing the physical properties of hybrids because of its tunable surface functionalization and the potential for large-scale production [5,6]. In inorganic hybrids, rGO has been used for the uniform deposition of Co_3O_4 particles for enhanced catalytic effects for the decomposition of ammonium perchlorate due to the integrated properties of the GO and Co3O4 nanoparticle-components [7]. In another study, rGO was used to enhanced the toughness of bulk silicon nitride by up to ~ 235%, which may be used for high performance structural applications [8]. Polystyrene-reduced graphite oxide (rGO) composites with a low threshold content of rGO of ~ 0.1 vol percent have shown greatly improved electrical conductivity (~ 0.1 S m^{-1}) due to the good dispersion of rGO in the composite [9].

Ceramics usually have a brittle attribute with low strength [10]. Among the numerous ceramics, silica is one of the widely used additive ceramic due to its good functionalized ability and stability [11–13]. Silica has applications in the field of biomedical, polymer and composite engineering [14]. To improve its physical properties, rGO has been used to enhance the thermal conductivity (0.452 Wm^{-1} K^{-1}), storage modulus (3.56) and dielectric constant (77.23) of epoxy-SiO_2-rGO hybrids [15]. 3-D SiO_2-graphene composites have been investigated with improved gas sensing performance and lower BET surface area (6.95 m^2 g^{-1}) which was obtained by an electrostatic self-assembly approach [16]. In another study, silica-graphene oxide nanocomposites were fabricated using the in situ sol gel method which indicated that the presence of rGO is essential to enhance the dispersion, corrosion resistance and barrier properties of hybrids [17]. SiO_2-graphene hybrids shown superior gas sensing response (31.5%) towards 50 ppm NH_3 for 850 s as compared to rGO based sensor (1.5%) [18]. SiO_2-rGO composites obtained via one step hydrothermal method showed enhanced BET surface area (676 m^2 g^{-1}) and 98.8% Cr(VI) adsorption efficiency [19]. SiO_2-polyvinylidene fluoride were reported with high dielectric constant (72.94) and low dielectric loss (0.059) on

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addition of ultrathin graphene [20]. Similarly, epoxy-silica-graphene oxide composites showed enhanced tensile strength (73 MPa), leading to an increase in the Young's modulus and fracture toughness [21,22]. However, in most of the previous reports on silica-rGO, there is no complete systematic study on the physical properties of the SiO_2-rGO such as investigation of dielectric, electrical, mechanical and thermal properties.

Briefly, herein, the monolithic SiO_2-rGO were prepared via hydrothermal-hot press processing. For the first time, this optimized method is adopted to form SiO_2-rGO hybrids. However, in this study, hybrid monoliths were obtained to systematically study the enhanced physical properties of the hybrids. Our goal is to develop a simple and effective method to enhance the physical properties of the hybrid. Furthermore, for the SiO_2-rGO monoliths, the effect of calcination temperature and further hot pressing are discussed.

2. Experimental

2.1. Preparation of SiO_2-rGO hybrid powder

In brief, the preparation of the SiO_2-rGO hybrids was carried out by mixing GO with cyclohexane and ethyl silicate ($C_8H_{20}O_4Si$), followed by a hydrothermal reaction. For the preparation, 0.1 g of GO was first dispersed in 50 mL cyclohexane, following which 5 mL of ethyl silicate ($C_8H_{20}O_4Si$) was added dropwise. The mixture was then stirred at a speed of 1500 rpm at room temperature for several days, until the GO powder was homogeneously dispersed, following which the color of suspension remained constant. Centrifugation was used to separate the products, which were then washed several times with cyclohexane. The solid samples obtained are denoted as $Si(O)_x$/GO. $Si(O)_x$/GO powders were obtained from 0.1, 0.2 and 0.3 g of GO suspensions, respectively. The solid samples were dispersed in 75 mL cyclohexane, and then transferred to a 100 mL Teflon-lined stainless-steel autoclave for hydrothermal reaction. After the reaction was carried out at 420 K for 4 h, the resultant sample was again centrifuged and dried at 303 K, which is denoted as $Si(O)_x$-rGO. SiO_2-rGO was then calcinated at 800 K for 1 h. SiO_2-rGO hybrids consisting of 1.55, 6.75, and 10.82 wt% rGO were obtained using the same method for studing the physical properties. Sample-a, sample-b, sample-c are referred to 1.55%, 6.75% and 10.82% rGO, respectively. The same procedure was also used to form pure SiO_2 (referred as sample-d) without the addition of GO. For analysis of the effect of calcination temperature on crystallinity, the calcination temperature was set as 500 K, 600 K, 700 K and 800 K, for a processing time of 1-h.

2.2. Hotpress processing of SiO_2-rGO hybrid powder

Hot-pressing of the SiO_2-rGO hybrid powder was performed in a vacuum furnace (model number OTF-1200 ×-VHP4). The furnace was integrated with an electric hydraulic press to compress the samples in a graphite pressing die. The temperature was set to increase from room temperature at a heating rate of 10 °C min^{-1} up to 750 °C and then, this temperature was maintained for 50 min. When the temperature reached 80% of the set temperature, pressure of 25 MPa was applied to the hybrids. For analysis of the effect of hot-pressing pressure, pressure was set as 10 MPa, 20 MPa, and 30 MPa.

2.3. Characterizations

Thermogravimetric analysis (TGA) was carried out using a TG analyzer (DTG-60H, Shimadzu) under flowing air from room temperature to 800 °C with a step of 10 °C min^{-1}. Scanning electron microscope (SEM) was performed using JSM-6700F (operated at 10 kV). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were taken on a TEM (JEM-2100F, 200 kV, JEOL). The structure of the hybrids was characterized via X-ray diffraction (XRD) using a powder diffractometer (Smart Lab, Rigaku) and Cu Kα radiation (λ = 0.15414 nm). Raman spectra were recorded using a Raman microscope (inVia, Renishaw, 532 nm laser). Fourier transform infrared spectroscopy (FTIR) spectrum was performed using a Nicolet 8700 (Thermo Scientific). X-ray photoelectron spectroscopy (XPS) was performed using Thermo ESCALAB 250 with an Al K_α radiation (150 W power, 500 μm x-ray beam). The Brunauer-Emmett-Teller (BET) surface area was determined using a Micromeritics Instrument (TriStar II 3020). Electrical conductivity was measured using the 4-probe method with a digital duel measurement system (Gwinstek, GDM-8261A). Thermal conductivity was measured using a laser flash thermal conductivity instrument with an energy pulse of up to 18 J per pulse (Netzsch, LFA457). Dielectric property was measured using an LCR meter (Tonghui, TH2811DN). Mechanical tensile stress-strain curves were obtained with a ramp force of 0.5 N min^{-1} up to 30 N using a dynamic mechanical analyzer (DMA, Q800, TA Instrument). Each physical measurement was carried out 5 times and the average values are shown with error bars in the following sections.

3. Results and discussion

With rGO in the hybrids, the sample powder exhibited a color change after calcination as shown in the optical image in Fig. 1a and b. The optical image of hot pressed SiO_2-rGO, which is obtained with 0.1 g GO, is presented in the inset of Fig. 1b. The TGAs curves of the SiO_2-rGO powder samples show that different GO concentrations (0.1, 0.2, and 0.3 g) led to different concentrations of rGO in the hybrids. The TGAs curves of all the hybrids show a stable weight loss up to 100 °C due to moisture loss, and between 150 and 300 °C as a removal of unreduced GO functional groups. A stable weight loss between 350 and 600 °C is ascribed due to removal of all the carbon related materials and it may be possible because of decomposition of rGO, and other impurities (if any) after heating to 800 °C in air atmosphere [23]. For the samples with a 0.1 g, 0.2 g and 0.3 g GO, the calculated loss was 1.55 wt%, 6.75 wt% and 10.82 wt%, respectively. The samples before calcination but after autoclave heating is denoted as $Si(O)_x$/rGO [24].

For sample a, SEM image [Fig. 2a and c] exhibits a sphere like morphology. Spheres have location side by side with a wide size distribution, ensuring very close contact among SiO_2 spheres in the whole network. The diameter of spheres range from 5 nm to 3 μm. The SEM image [Fig. 2b and d] shows spherical nanocrystals or nanoparticles of bare SiO_2. The rough texture of nanocrystals can also be confirmed by closely observing Fig. 2d. For bare SiO_2, the diameter of spheres range from 1 μm to a few micrometers. TEM is carried out to verify the SEM morphology. The TEM image of sample a is shown in Fig. 2e, where spherical SiO_2 with an rGO layer in the hybrids are observed. After hydrothermal-calcination treatments, sample a indicates the spherical SiO_2 with a very thin rGO layer. In the Fig. 2e, the low-contrast features are actually edges or small portions of the graphene sheet, on which SiO_2 is uniformly distributed. This is a key requirement for good properties in hybrid SiO_2-rGO after calcination. For sample a, the TEM image [Fig. 2e] shows that the diameter of spheres range from few nm to a few micrometers, in agreement with SEM results. For sample a, the selected area electron diffraction pattern presented in Fig. 2e shows the hybrid is composed of SiO_2 and rGO. From SAED pattern, the electron diffraction rings indicate the amorphous nature of SiO_2. TEM image [Fig. 2f] indicates rough texture and the non-uniform surface of bare SiO_2. The diameter of spheres range from 1 μm to a few micrometers. SEM and TEM image for samples b and c are shown in the supporting information (Fig. S1). From morphological analysis, it is found that all hybrid shows sphere-like morphology.

For SiO_2-rGO hybrids, the successful fabrication of the amorphous SiO_2 phase was confirmed from the XRD patterns as shown in Fig. 3a. For sample d, the XRD pattern of the sample without GO confirmed the presence of amorphous SiO_2. In the XRD patterns of all the four