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Facile fabrication of graphene oxide-wrapped alumina particles and their electrorheological characteristics

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HIGHLIGHTS

- GO wrapped alumina composites are synthesized via a facile titration method.
- Al_2O_3 colloid acts as a titrant, being prepared by adjusting the pH value.
- Negative GO wrapped on Al_2O_3 particles assembly via an electrostatic attraction.
- GO/Al_2O_3 composites reveal electrorheological characteristics under electric field.

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ABSTRACT

Graphene oxide wrapped alumina (GO/Al_2O_3) composites were synthesized by a facile titration method using Al_2O_3 colloid as a titrant. The positively-charged Al_2O_3 particles were prepared by adjusting the pH, followed by wrapping with negative GO particles via electrostatic attractions. Scanning electron microscopy and transmission electron microscopy confirmed that the Al_2O_3 particles were wrapped completely with homogeneous GO sheets, and Fourier transform infrared spectroscopy provided evidence of the coexistence of GO and Al_2O_3 in the composites. The resulting GO/Al_2O_3 composites exhibited electrorheological (ER) properties when dispersed in silicone oil, highlighting the potential engineering applications for GO/metal oxide systems.

1. Introduction

Graphene, a two-dimensional monolayer of carbon, has sparked fascinating research interest because of its excellent mechanical, thermal and electrical properties [1–4]. A range of effective strategies for graphene synthesis, such as mechanical/chemical exfoliation, epitaxial growth and chemical vapor deposition, have been developed for academic research and a wide range of engineering applications [5]. Graphene oxide (GO) is an attractive precursor for producing graphene using a variety of reduction processes [6–8]. GO is a single-layer of graphite oxide with a variety of oxygen functional groups including hydroxyl and epoxy groups on its basal plane, and carboxyl, carbonyl and phenol groups at the edge [9,10]. Compared to graphene, polar functional groups impart hydrophilic properties to GO, enabling it to disperse easily in water and other suitable solvents, facilitating the preparation of GO-based composites [11].

GO/metal (metal oxide) composites have been assessed as suitable materials in a range of applications, such as drug delivery, fuel cells, lithium ion batteries, super capacitors, wastewater treatment, and other electric field responsive characteristics [12–16]. In this study, GO/Al_2O_3 composites were prepared using a simple titration method [17] and their electrorheological (ER) properties when dispersed in silicone oil were studied. The association of GO not only induces its ER characteristics but also improves the dispersion stability of the GO/Al_2O_3 composite-based suspensions.

ER fluids, which are interesting smart materials, are generally composed of polarizable particles with high dielectric constants dispersed in insulating media [18–20]. When applied in an external electric field, the suspended materials become polarized and attract each other to form chain/column-like structures. ER fluids have potential applications as dampers, brakes, shock absorbers, and artificial joints [21,22]. ER suspensions need to have certain properties, such as a high yield stress, good dispersion stability, and

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performance stability over a wide range of temperatures [23–27]. Recently, a range of graphene/GO-based material additives have been evaluated as potential candidates for enhancing the ER properties of a range of suspensions via the adsorption of these sheet materials on semiconducting or insulating particles [28]. These particles included polyaniline, polystyrene, poly(methyl methacrylate) and TiO_2 nanorods [29–32]. This is an effective strategy for solving the agglomeration problem of metal oxides through the addition of a GO suspension in metal oxide colloids. Husin et al. [33] reported a large increase in yield stress by GO in the micron-sized platelet α-Al_2O_3 (alumina) suspensions. Alumina is a typical dielectric material with excellent chemical and thermal stability, relatively low density, good toughness and physical strength. Tangboriboon et al. [34] reported the ER characteristics of alumina/rubber composites, in which the aluminosilicate materials were believed to have strong ER effects because of the movement of metal cations in the structure [35].

2. Experimental

2.1. Preparation of GO sheets

GO was prepared using the improved Hummers method [36]. A mixture of concentrated H_2SO_4/H_3PO_4 (400 mL, 9:1 in volume ratio) was added to graphite powder (3 g, <20 μm, Aldrich), followed by the gradual addition of $KMnO_4$ (18 g, Sigma–Aldrich). The suspension was heated to 50 °C and stirred vigorously for 12 h until graphite oxide was formed. The graphite oxide obtained was cooled to room temperature and treated separately with 400 ml of ice and a 30% H_2O_2 solution. The graphite oxide slurry was finally exfoliated to GO sheets using an ultrasonic generator (28 kHz, 600 W, Kyungil Ultrasonic Co., Korea). The slurry was collected by centrifugation and washed sequentially with 5% HCl and deionized (DI) water.

2.2. Preparation of GO/Al_2O_3 composite

The GO/Al_2O_3 composite was prepared using a titration method [17], in which the surface charge of the Al_2O_3 particles were first made positive by reducing the dispersion pH with a HCl solution. In a separate preparation, the GO sheets were exfoliated separately in DI–water by sonication. The spherical-Al_2O_3 (AO802, Admatech, Japan) powder was dispersed in DI–water (200 mL) and sonicated to obtain a homogeneous suspension at a pH adjusted to 4.5 (same as the prepared GO colloid) using a HCl solution (1 M). The Al_2O_3 colloid was then added dropwise to the GO dispersion with mechanical stirring. The slurry was then separated by a centrifuge and dried in an oven.

2.3. Characterization

The morphology of the particles and their composites was examined by scanning electron microscopy (SEM, S-4300, Hitachi) and transmission electron microscopy (TEM, Philips CM200). The chemical structure, nature of the functional groups and composite particle bonds were analyzed by Fourier transform infrared (FT-IR, VERTEX 80v, Bruker) spectroscopy. The electrical conductivity was measured using a resistivity meter (Mitsubishi Chemical Corporation, MCP-HT 450) and the electrical conductivity of the GO/Al_2O_3 composite was 1.24×10^{-13} S cm^{-1}. The ER characteristics were examined using a rotational rheometer (Physica MCR300, Anton Paar, Germany) equipped with a high-voltage generator (HCN 7E-12 500, Fug, Germany) and a Couette-type sample loading geometry (CC 17, gap distance is 0.71 mm). The ER fluid was prepared by dispersing a GO/Al_2O_3 composite (particle concentration, 20 wt%) in silicone oil (dynamic viscosity of 30 cS, density: 0.955 g ml^{-1}).

3. Results and discussion

Fig. 1(a) shows a SEM image of the GO sheets. A lamellar structure with several layers stacked together was clearly observed. The SEM image of Fig. 1(b) revealed the spherical nature of the pure Al_2O_3 particles with a mean diameter of approximately 0.6 μm. Fig. 1(c) shows the composite GO/Al_2O_3 particles. The Al_2O_3 particles were wrapped densely and uniformly with GO sheets, indicating the good dispersion of GO. In contrast to the white Al_2O_3 particles, the color of the GO/Al_2O_3 composite powder was gray, as shown in the inset image.

Fig. 2(a)–(c) shows TEM images of the pure GO, spherical Al_2O_3 particles and GO/Al_2O_3 composite. The TEM image in Fig. 2(a) confirmed that GO was exfoliated to single or multi-layer sheets. Fig. 2(b) shows the spherical nature of the pure Al_2O_3 particles. The composite particle image in Fig. 2(c) clearly shows that the Al_2O_3 particles were covered uniformly with the GO sheets.

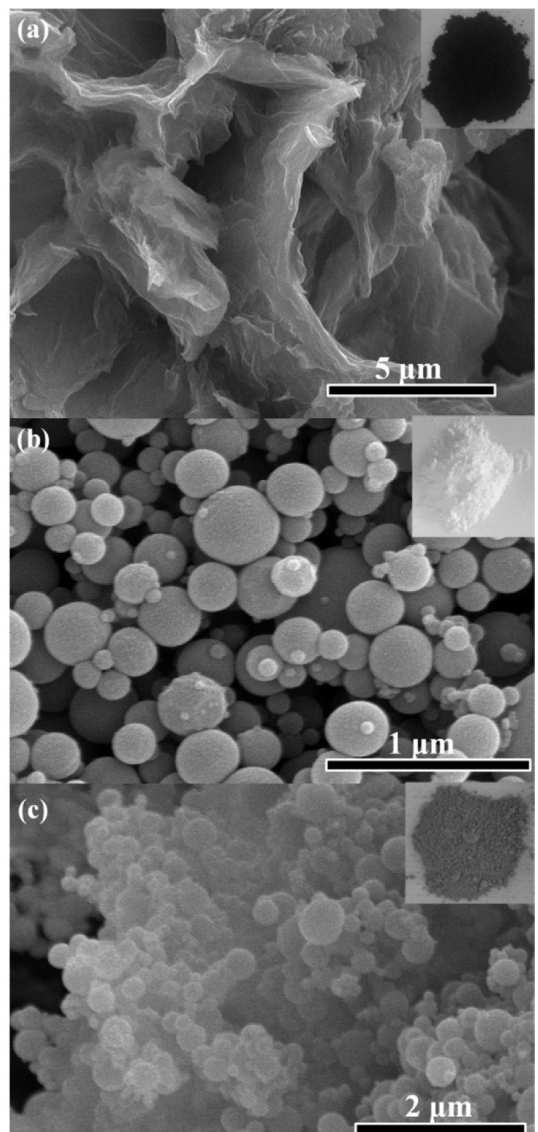

Fig. 1. SEM images of pure GO (a), spherical Al_2O_3 particles (b) and GO/Al_2O_3 composite (c), the insets are pure GO, spherical Al_2O_3 particles and GO/Al_2O_3 composite powders, respectively.