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Facile synthesis of thermally reduced graphene oxide-sepiolite nanohybrid via intercalation and thermal reduction method

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ABSTRACT

Hybrid thermally reduced graphene oxide-sepiolite (TRGO-Sep) nanocomposite has been synthesized using via the intercalation of cetyltrimethylammonium chloride (CTAC) with sepiolite (Sep) and graphene oxide (GO) followed by thermal reduction. The physico-chemical characterization of the hybrid was evaluated by wide angle X-ray diffraction (WAXRD), X-ray photoelectron spectroscopy (XPS) and scanning & transmission electron microscopy. The existence of characteristic (110) reflection of sepiolite at $2\theta = 7.48°$ confirmed the presence of Sep in the TRGO-Sep hybrid. BET analysis resulted that the surface area of the hybrid material was found to 128.2 m^2/g. TEM analysis confirmed that the stacking of one dimensional Sep on the graphene sheets.

1. Introduction

Recently, development of hybrid materials with multi-dimensional architecture has gained widespread research attention due to synergistic combination of properties (Lee et al., 2013; Vinayan et al., 2015; Kim et al., 2016). The hybrid nanomaterials have been fabricated via physical or chemical methods using combinations of different materials viz. graphene, nanotubes, silicate clays, etc. (Dong et al., 2011; Tang et al., 2013; Zhang et al., 2014; Li et al., 2015). Specifically, clay minerals have been widely used as a supporting material for the development of hybrid nanomaterials, due to the quality of these silicates to assemble with different types of active species at nanoscale levels (Son et al., 2010; Burridge et al., 2011; Křišťan et al., 2013; Cristina et al., 2014; Dutta and Dutta, 2014; Martınez et al., 2015). Sepiolite possess large surface area and porosity as well as fibrous one-dimensional (1D) structure (Suarez et al., 2009). Due to its large textural properties and surface activity, it can also act as a structure directing agent for the preparation of conducting carbon materials from the organic precursors (Darder and Ruiz-Hitzky, 2005; Avile's et al., 2007, 2010; Hitzky et al., 2011). Sepiolite has been self-assembled with metal oxides, carbon nanotubes, graphene nanomaterials via intercalation as well hydrophobic interaction mechanisms (Suarez et al., 2009; Garcıa et al., 2013; Orozco et al., 2014). In recent years, graphene based hybrid materials have received much research attention due to tailored properties and potential applications in various fields (Chang and Wu, 2013; Li et al., 2014a, b). More specifically, graphene based hybrid nanocomposites such as metal oxides, conducting fibers, metal nanoparticles, etc. have been prepared (Xu et al., 2011; Ren et al., 2011; Kwon et al., 2015). The main advantage of hybridizing graphene with various 1D and 2D materials is to avoid the stacking between the graphene sheets. More specifically for graphene-clay hybrids, Garcıa et al. (2013) developed clay-supported graphene materials from sucrose with montmorillonite and sepiolite and studied hydrogen storage application. Cheng et al. (2013) reported graphene oxide nanosheets supported on sepiolite for the application of uranium adsorption in aqueous medium. Spyrou et al. (2014) also developed the graphite oxide (GO)-clay nanocomposites by the intercalation of cage-shaped adamantylamine (ADMA) molecules into the interlayer space of GO and alumino-silicate clay. Nethravathi et al. (2008a, b) prepared graphene-smectite clay nanocomposites via delamination and co-stacking methods and also developed graphene-inorganic material nanocomposites from the decomposition of graphite oxide-intercalated anionic clay.

In the present work, 1D Sep has been hybridized with 2D graphene sheets in equal mass ratio. It is well known that the CTAC can intercalate both the GO and the nano-clay (Liu et al., 2012; Li et al., 2014a, b). The GO and Na^+-Sep materials were hybridized simultaneously via intercalation as well as the hydrophobic interaction mechanisms. Subsequently, the intercalated GO-Sep hybrid complex was thermally reduced at high temperature to generate graphene-sepiolite hybrid material. The structural properties of the graphene-clay hybrid are reported along with the mechanism of the graphene-clay hybrid formation.

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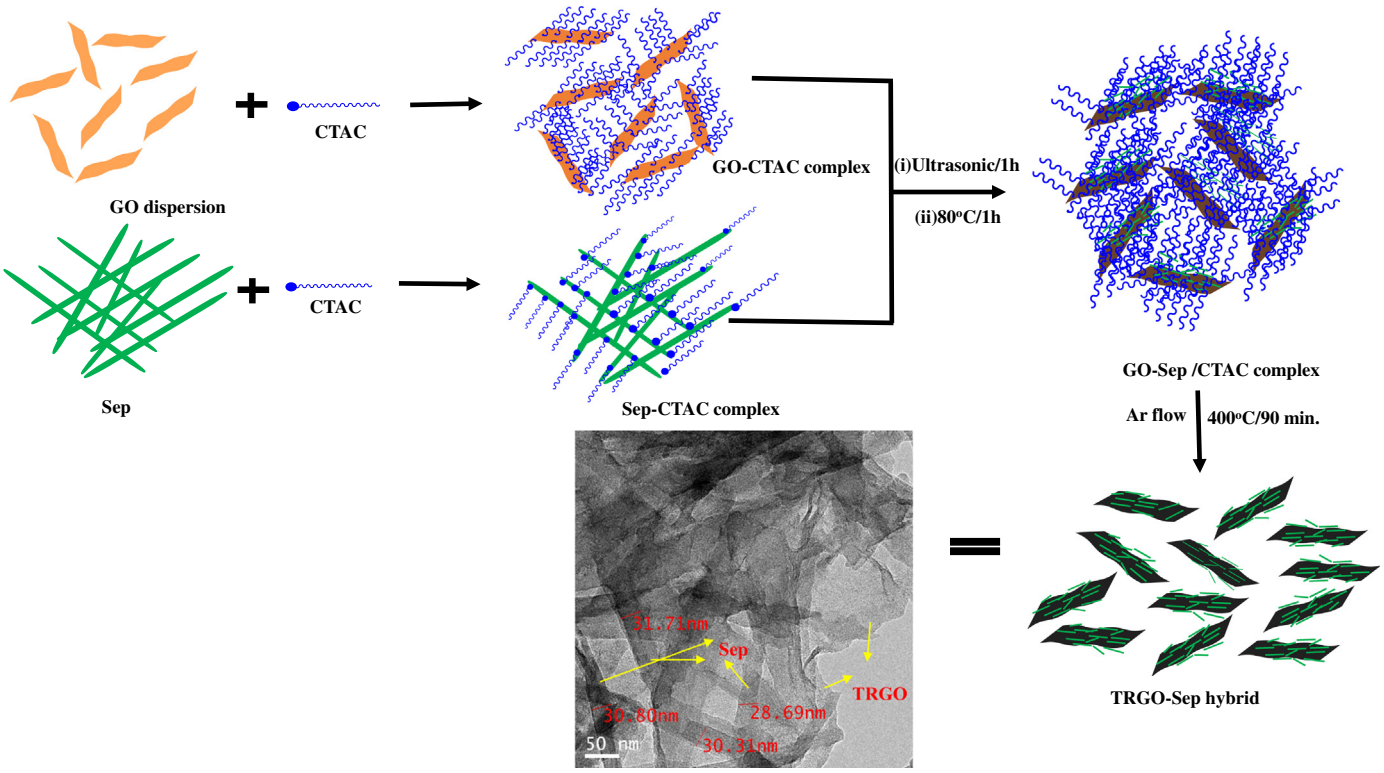

Scheme 1. Schematic representation of formation of TRGO-Sep hybrid.

2. Experimental

2.1. Materials

Orthophosphoric acid, potassium permanganate ($KMnO_4$), conc. sulfuric acid (H_2SO_4) and cetyltrimethylammonium chloride (CTAC) were purchased from Sigma-Aldrich and were used without purification. Graphite powder was purchased from Sigma-Aldrich with particle size of 10 μm. Sepiolite clay mineral was purchased from Sigma-Aldrich and was further purified using NaCl solution, as reported elsewhere (Nagendiran et al., 2008).

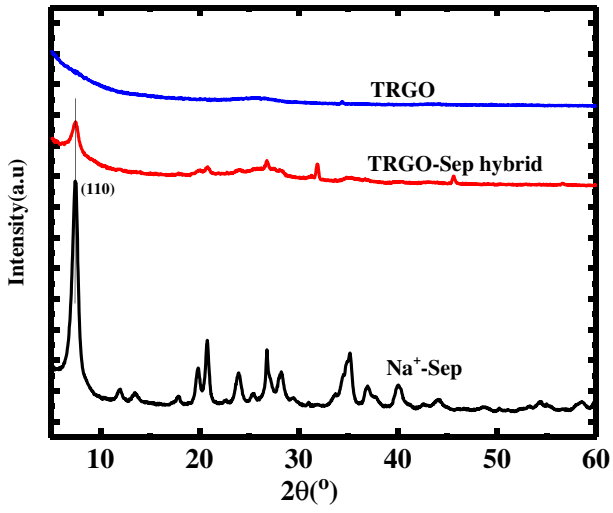

Fig. 1. XRD spectra of Sep, TRGO-Sep hybrid and TRGO.

2.2. Synthesis of GO

Graphite oxide was synthesized by improved Tour's method (Marcano et al., 2010). Briefly, 300 mL of conc. H_2SO_4 and 75 mL of orthophosphoric acid were mixed together. Subsequently, 10 g of graphite powder was added. The contents were stirred for 45 min at 30 °C. $KMnO_4$ (58 g) was added slowly to the mixture and the mixture was allowed to stir for 72 h at 25–30 °C. Afterwards, 1500 mL of 5% H_2O_2 solution was added to the mixture and stirred for 2 h at 25–30 °C. The content was allowed to settle and was then centrifuged to remove the superannuated solution. The residue was washed with 1 M HCl followed by deionized (DI) water. The residue was further purified using cellulose membrane for one week in DI water medium. The purified GO solution was freeze dried to obtain solid graphite oxide.

2.3. Preparation of GO-sepiolite (GO-Sep) hybrid

500 mg of Na^+-Sep was added into 500 mL of GO dispersion in DI water (1 mg/1 mL). The mixture was further dispersed using ultra-sonication bath at room temperature for 2 h. 50 mL of 10% CTAC solution was slowly added to the mixture for 30 min under vigorous stirring conditions (1000 rpm). The mixture was further stirred for 16 h at 30 °C and the excess surfactant was removed via cellulose membrane. The final colloidal mixture was frozen at −20 °C and dried under vacuum.

2.4. Preparation of graphene-sepiolite hybrid (TRGO-Sep)

The dried GO-Sep hybrid was thermally reduced at 400 °C for 90 min using a heating rate of 5 °C/min in a tube furnace with nitrogen flow gas medium. The black powdered material was collected from the furnace after cooling down to room temperature.

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