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Research paper

Graphene oxide-Laponite hybrid from highly stable aqueous dispersion

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ABSTRACT

A simple method for preparation of hybrid of graphene oxide (GO) and Laponite (Lap), obtained by solvent evaporation from their highly stable aqueous dispersions is reported. The dispersion up to ~1 mg/ml of GO in 1% Lap dispersion, i.e., 10:1 of Lap:GO was found to be stable without flocculation for several months; lower mass ratios of Lap to GO than this showed marginal flocculation with time. The electrostatic interaction between cations present in the interlayers of Lap and the functional groups of GO is envisaged to be the cause for the stable dispersion, which was confirmed by the presence of cations; viz., Na⁺ and small amounts of K⁺ and Mg²⁺ in the aqueous filtrate of the hybrid. Their interaction was further confirmed by higher absorption of GO in aqueous Lap dispersion than that in water using UV–vis spectroscopy. The resulting hybrid material was found to be partially reduced and self-assembled to form layered structure in its dry state. The hybrids further showed improved electrical conductivity (~0.01 S/cm) upon chemical reduction. The present study demonstrates a facile method for preparation of a new hybrid material and greener pathway for GO reduction; though partially. This hybrid has potential as multifunctional filler for clay polymer nanocomposites.

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1. Introduction

Nanocomposites of carbon and inorganic clay are important materials due to their wide range of applications; such as electrodes for Li ion batteries (Sandí et al., 1999; Duclaux et al., 2000), supercapacitor (Duclaux et al., 2000), electrocatalysis and preparation of carbon nanofibers (Fernández-Saavedra et al., 2004). In these clay polymer nanocomposites (CPN), the inorganic clay mineral (e.g., montmorillonite (Sonobe et al., 1991), taeniolite (Bandosz et al., 1996), sepiolite (Sandí et al., 1999)) is used as a template and the carbon source (e.g., furfuryl alcohol (Sonobe et al., 1991), polyacrylonitrile (Fernández-Saavedra et al., 2004), sucrose (Bakandritsos et al., 2004)) is intercalated into interlayer spaces of the clay mineral and subsequently pyrolyzed to obtain CPN (Sonobe et al., 1991). However, in recent years with the invention of graphene (Novoselov et al., 2004; Geim and Novoselov, 2007) and its derivatives, hybrid materials having graphene as one of the major components have attracted a great deal of research attention due to their versatile and tunable properties (Nethravathi et al., 2008a, 2008b; Nethravathi et al., 2010; Zhao et al., 2012; Dey and Raj, 2013; Wang et al., 2013a, 2013b). Often, these materials exhibit improved catalytic activity (Liang et al., 2011), better sensing properties (Xiao et al., 2012;

Zhang et al., 2015) and improved energy storage (Xiao et al., 2011; Giri et al., 2014), compared to their individual constituents. Evolution of these properties has been attributed to the extraordinary properties of graphene and its chemical coupling with wide range of nanomaterials. The advantages of these nanocomposites are their easier processing methods over their conventional counterparts and moreover in the former nanocomposites, carbon precursor is not required. A significant research effort has been made towards preparing such nanocomposites. For instance, graphene oxide (GO)-silica nanocomposites prepared through sol-gel process and subsequent reduction to graphene-silica nanocomposites were found to exhibit electrically conducting (~0.5 S/cm) and optically transparent coatings on glass substrates (Watcharotone et al., 2007). Clay-graphene nanomaterials were prepared by intercalating liquid caramel into various clay minerals (montmorillonite, sepiolite) followed by heat-treatment at elevated temperatures and the resulting materials showed promising hydrogen storage (Garcia et al., 2013). Adsorption of DNA and Cytochrome C onto the reduced GO-amino clay hybrids, reported by Achari et al. (2013) showed promising catalytic and biomedical applications. Various strategies have been adopted to prepare graphene/metal oxide nanocomposites from GO-layered double hydroxide nanocomposites (Nethravathi et al., 2008a, 2008b; Rajamathi et al., 2010; Zhao et al., 2012; Dey and Raj, 2013; Wang et al., 2013a, 2013b). Exfoliated and porous nanocomposites of GO and smectite was produced by heat-

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treatment followed by leaching out of clay by acid treatment (Nethravathi et al., 2008a, 2008b). Among these, hybrids of GO and clays are particularly important, as these nanocomposites offer a possibility of having a layer-to-layer (LTL) interaction by electrostatic interaction between mobile interlayer cations of clays and polar functional groups of GO. Further, the similarity of their morphology (both having layered structures), intercalation and exfoliation properties may contribute to the LTL interaction. Recently, Yoo et al. (2014) found that a multilayer approach of Lap and GO coating on a polyester transparent sheet significantly lowered oxygen permeability as compared to the coatings made by individual components. However, they did not observe any reduction of GO in presence of Lap. Besides the numerous applications of these hybrid materials, they can also potentially serve as new functional fillers for CPN, which might impart synergistic effects, improved interfacial bonding and multifunctional properties in nanocomposites. It is worth-noting that most of the techniques used for hybrid material preparation involve several steps and are relatively complex in nature. Moreover, the interaction between the constituents of hybrid is not well-understood; particularly between a synthetic hectorite and GO. Here, a simple two-step method was adopted for preparation of Lap-GO hybrid and their chemical interaction was studied.

GO is chemical derivative of graphene and synthesized by well-known Hummers method (Hummers and Offeman, 1958). GO contains a mixture of sp^2 and sp^3 C atoms. The sp^3 C atoms in GO arise due to attachment of functional groups; like phenolic, epoxide, carbonyl, etc. Reduction of GO eliminates the functional groups on graphitic backbone to produce a compound which closely resembles graphene (Dreyer et al., 2011). Reduced graphene oxide (RGO), however due to defects on its graphitic plane, exhibits lower electrical conductivity than the graphene produced directly from graphite. Nevertheless, RGO has been widely studied in the context of various applications; such as polymer nanocomposites (Stankovich et al., 2006), sensors (Wang et al., 2013a, 2013b), supercapacitors (Dreyer et al., 2011) due to its large throughput and ease in synthesis by simple reduction of GO. Significant research efforts have been carried out in the past decade for developing better, greener and newer methods for reduction of GO. Among these, hydrazine treatment of GO perhaps is the most popular method of reduction for its ease and efficacy (Stankovich et al., 2007). Alcohols were also used to prepare RGO in an attempt to make the process greener (Dreyer et al., 2011). Strong reducing agent like sodium borohydride was found to reduce GO effectively with sheet resistance of $2.6 \times 10^3 \Omega/\text{sq}$ and electrical conductivity of 45 S/m (Shin et al., 2009). Successful efforts were also made to reduce GO using hydroquinone (Wang et al., 2008), ascorbic acid (Zhang et al., 2010), formamidinesulfonic acid (Ma et al., 2013), urea (Lei et al., 2012), sulfur containing compounds (Chen et al., 2010), thiourea (Yanzhen et al., 2011), using microwaves (Bourlinos et al., 2009), etc. In this study, a solid non-toxic and environmentally-benign clay mineral was serendipitously found to partially reduce GO.

Lap, a synthetic hectorite with a generic formula: $\text{Na}_{0.7}^+(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4^{0.7}$, disperses easily in water and forms transparent solution at low concentrations below percolation threshold of network formation (Ramsay, 1986). At higher concentrations (>2 wt%) Lap makes a gel with a 3D network of particles (Ruzicka et al., 2010). Lap surface is negatively charged, which is originated by the isomorphous substitution of Mg^{2+} by Li^+ at octahedral sites and the deficiency in positive charges are compensated by the electrostatically bound sodium cations (Na^+) (Pinnavaia, 1983). Lap is used as an additive in cosmetic products, household cleaners, industrial surface, antistatic coatings and agrochemical products, etc. On account of the numerous uses of Lap, its hybrid with GO is further expected to increase its application realm by imparting unique physical and electrical properties. Stabilization of multi-walled carbon nanotubes (CNT) (Loginov et al., 2012) and graphene (Alhassan et al., 2012) by Lap aqueous dispersion has been reported at small mass fractions of CNT and graphene. A significant

research effort has also been devoted to synthesize water soluble graphene or to prepare stable colloidal dispersions of graphene in water (Bourlinos et al., 2009; Alhassan et al., 2012; Achari et al., 2013). In this context, Lap is chosen to be an ideal system to make a hybrid with GO and subsequent preparation of water-soluble RGO by exploiting its unique intercalation and cation exchange properties.

In this article, a two-fold study is reported: (i) the formation of a highly stable graphene oxide-Lap dispersion in water by simple ultrasonication and subsequent hybrid preparation of Lap and GO by solvent evaporation and (ii) chemical reduction of the resulting hybrid in order to produce an electrically conducting hybrid. In this process, a partial reduction of GO in the hybrid is observed. A possible mechanism of the interaction between the layers of GO and Lap is postulated.

2. Materials and methods

2.1. Materials

Lap XLS (Rockwood Additives Ltd., UK) a synthetic clay mineral modified by an inorganic polyphosphate dispersing agent and with an aspect ratio of ~25 was used in this study. The density and surface area of Lap XLS were 1 g/cm^3 and $300 \text{ m}^2/\text{g}$, respectively, as provided by the supplier. The average diameter and thickness of individual layer were ~25 nm and ~1 nm, respectively. GO was prepared using the modified Hummers method from natural graphite (100 μm mesh size, SD Fine Chem. Ltd., Mumbai, India) (Hummers and Offeman, 1958). De-ionized water (Nanopore, 18 M Ω , pH ~5.6) was used throughout the experiments.

2.2. Lap-GO dispersion and hybrid preparations

1 g of Lap was thoroughly mixed in 100 ml of water for 24 h at room temperature using a magnetic stirrer. GO was added to the above Lap dispersion in different mass ratios; such that the final dispersions contained the Lap and GO mass ratios of 10:1, 10:3, 5:2 and 2:1, which correspond to 1, 3, 4 and 5 mg/ml of GO in Lap dispersions, respectively. The above dispersions were ultra-sonicated using a low intensity bath sonicator ($20 \pm 3 \text{ kHz}$, Electrosonic Industries, India) for 1 h. The resulting dispersions were black and uniform in color and they are termed as Lap-GO. About 100 ml of the above dispersions were refluxed with 1 ml of hydrazine monohydrate (Thomas Baker, India) at 80 °C for 20 h in order to prepare reduced Lap-GO dispersion. The dispersions were allowed to keep unperturbed for various time periods and the photographs were taken. Both Lap-GO and reduced Lap-GO hybrids were prepared by evaporating the solvent (water) in an oven at 70 °C. Reduced Lap-GO powder was washed repeatedly with water to ensure complete removal of hydrazine hydrate. The black powder was gently crushed using a mortar-pestle to make fine powder before performing characterizations. The crushing was gentle enough to have minimal mechanical damage to GO sheets. The 10:1 Lap-GO hybrid was characterized by various techniques; because this sample has minimum amount of GO in it; which showed excellent colloidal stability without flocculation for considerable time period, i.e., several months. Other dispersions, which contain higher amounts of GO, i.e., 3, 4, 5 mg/ml in Lap dispersions, showed flocculation with time. The measured pH values for all the dispersions are presented in the Supporting Information (Table S1).

2.3. Ultrafiltration of cations using membrane

Polyether sulfone dialysis membranes (Permionics Membranes Pvt. Ltd., Vadodara, India) of 10 kDa (pore size: 2–3 nm) with permeability of $(3.16 \pm 0.1) \times 10^{-11} \text{ m/Pa}\cdot\text{s}$ were used to filter the loosely bound interlayer cations present in Lap. Small pore size of the membrane ensured that the Lap particles (size ~25 nm) were not filtrated through the membrane. This experiment was performed in order to

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