Available online at www.sciencedirect.com

**ScienceDirect**

RESEARCH PAPER

# Stabilizing graphene layers by intercalating laponite between them

**Jing Li, Jin-can Cui, Zhen-zhen Yang, Han-xun Qiu, Zhi-hong Tang, Jun-he Yang\***

School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

**Abstract:** The reduction of graphene oxide (GO) leads to the re-stacking/agglomeration of graphene layers, which results in their precipitation from an aqueous dispersion. A laponite colloid was used to prevent re-stacking and stabilize an aqueous dispersion of reduced graphene oxide (RGO) by dispersing GO in the colloid, followed by reduction with hydrazine hydrate under microwave radiation. Results indicate that re-stacking is prevented as proven by the disappearance of the RGO (002) peaks in the XRD pattern. A laponite/RGO (w/w: 1:1) dispersion shows the highest stability under centrifugation at 10 000 rpm and the largest Brunauer−Emmett−Teller surface area, which is 17.6% higher than that of RGO and 34.4% higher than laponite. Electrostatic interaction between negatively-charged RGO layers and positively-charged laponite edges lead to an intercalation structure, which is responsible for the non-stacking RGO and its stable dispersion in water. This intercalation method offers an alternative way for the dispersion of graphene layers.

**Key Words:** Graphene; Laponite; Aqueous dispersion; Stability; Intercalation.

## 1 Introduction

Chemical oxidation and reduction method is frequently used for the preparation of reduced graphene oxide (RGO) owing to its high productivity. Graphene oxide (GO), with a large amount of oxygen-containing functional groups on its surface, is readily dispersed in water to form a stable colloid. The reduction of GO partially eliminates the oxygen-containing functional groups and restores the graphitic structure, which recovers the physical properties of graphene to a certain extent. However，the decrease in surface hydrophilicity of RGO leads to its irreversible re-stacking/agglomeration, which sacrifices the geometrical properties of the graphene.

Efforts have been made to create either electrostatic repulsion or steric hindrances between graphene layers, aiming at the dispersion of RGO. A typical strategy is to modify the graphene surfaces through covalent or non-covalent bonding, such as amino-functionalization [1], polymer-grafting [2], coupling treatment [3,4] and surfactant wrapping[5]. Covalent functionalization methods usually involve the formation of aliphatic regions (sp$^3$ carbon atoms), which leads to the changes of the graphene lattice and its electrical properties. Non-covalent surfactant approaches are relatively facile, but organic molecules are left on the RGO surface, which also changes its physical and chemical properties. In this paper, we reported a physical intercalation method to stabilize graphene layers using laponite, a layered silicate nano-particle.

Laponite, a synthetic hectorite, consists of silicate layers bonded by van der Waals forces. The silicate layer has an octahedral magnesia sheet sandwiched between two tetrahedral silica sheets [6]. The substitution of Mg$^{2+}$ in octahedral sites by less charged Li$^+$ is responsible for the negative charge on the layer surface. The electric charge is counterbalanced by the presence of Na$^+$ at interlayer region. The well-defined chemical composition and dimension allow an easy exfoliation into monolayer silicates in water. The exfoliated silicate layers have a negative charge on its surface and a small localized positive charge on its edge, which is generated by absorption of hydroxyl groups.

Loginov et al. demonstrated that laponite can effectively assist the dispersion of carbon nanotubes in water [7]. Alhassan et al. exfoliated and stabilized graphene from the aqueous dispersion of graphite and laponite using a turbulent mixing method, and produced graphene reinforced laponite colloidal glass [8]. Graphene reinforced smectite clay composites were prepared through thermal decomposition of a GO/clay mixture, forming a co-stacking structure, where non-uniform distribution of clay and graphene was observed [9]. Montmorillonite clay was also employed to stabilize RGO in water [10]. In addition, the graphene/clay composites were reported to have multifunction, such as fire-retardant properties [10], oxygen barrier properties [11], selective adsorption of organic pollutants [12], biomedical applications [12], owing to their unique nano-structures. However, the understanding and carefully tailoring of the nano-structure is lacking.

In this paper, the re-stacking of graphene layers and co-stacking between graphene sheets and silicate layers was prevented by a facile physical intercalation method. A stable aqueous dispersion of laponite/RGO was obtained.

## 2   Experimental

### 2.1 Materials

Laponite RD was kindly supplied by BYK Additives & Instruments. As disclosed by the company, the silicate platelets of laponite have a diameter of 25-30 nm and a thickness of 1 nm. As-received laponite powder was mixed with DI water at 5 mg/mL concentration by high shear mixing at 600 rpm for 30 min to obtain a transparent suspension.

GO was prepared by the modified Hummers method, as described previously [4].

### 2.2 Preparation of RGO/laponite suspension

100 mL GO/water solution (1 mg/mL) was mixed with laponite suspension (5 mg/mL). 5 mL hydrazine hydrate (85%) was added to the mixture and was treated under stirring in a microwave reactor (CEM, Discover SP) at 120 °C for 10 min. The unreacted hydrazine hydrate was eliminated by centrifugation. The products were referred as L-RGO, with a blanket followed to indicate the laponite/GO weight ratio.

### 2.3 Characterizations

The suspension stability of all the samples was evaluated by UV–Vis spectroscopy (Perkin–Elmer Lambda 750, USA). Zeta potentials of their aqueous dispersion were measured at room temperature using a zeta-potential analyzer (Nano-zs90, Malvern, UK). Fourier transfer infrared (FTIR, Spectrum 100 Perkin Elmer, USA) spectrometry were used to characterize the surface chemistry of GO, RGO and L-RGO. The surface resistances were measured using a four-point method (DNM-121, Scientific Equipment, UK).

The microstructure of L-RGO was investigated by a X-ray diffractometer (XRD, PANalytical X'Pert Powder, NL), transmission electron microscope (TEM, JEOL 2100F, JP) equipped with an energy dispersive X-ray (EDX) analyser, and surface area and porosity analyzer (Micromeritics ASAP 2020, USA). XRD patterns were obtained using a Cu $K\alpha$ radiation ($\lambda = 0.154\ 056$ nm) with a step size of $0.03^{\circ}$ and at a scanning rate of $0.5^{\circ}$/min, working at 40 kV 40 mA. The scanning $2\theta$ was ranging from $2^{\circ}$ to $40^{\circ}$. TEM images and EDX elementary mapping were obtained at an accelerating voltage of 300 kV. For TEM sample preparation, L-RGO was dispersed in ethanol and sonicated for 5 min, which was deposited on a copper grid with porous carbon film. Brunauer−Emmett−Teller (BET) surface areas of the samples were obtained from nitrogen adsorption isotherms performed at 77 K.

## 3   Results and discussion

### 3.1 Stability of RGO aqueous dispersion

The aqueous suspensions of RGO and L-RGO (1 mg/mL) were prepared with different laponite/GO weight ratios ranging from 0 to 2, and the suspensions were centrifuged at 5000 and 10000 rpm for 30 min, respectively. Fig. 1 shows the UV-vis spectra and the corresponding pictures of the supernatant after centrifugation. After 5000 rpm centrifugation，the supernatant of RGO suspension has the highest transparency because the majority of RGO was precipitated due to its poor suspension stability. L-RGO showed better suspension stability than RGO. The suspension solution remained black and the transparency of visible light was lower than 10% for the L-RGO with laponite/GO weight ratios of 1:1 and 2:1. After 10 000 rpm centrifugation, L-RGO (1:1) showed the highest stability. The supernatant solution remained black and the transparency of visible light was mainly lower than 10%, but all the other supernatants showed much high transparency. The L-RGO (1:1) suspension was stable for months at room temperature without precipitation.

The stability of the L-RGO suspension with different laponite/GO ratios was further confirmed by the zeta potentials, as shown in Fig. 2. All the samples were negatively charged. The zeta potentials of 1 mg/mL GO/water colloid were around -43.1 mV. After the reduction, the RGO was less charged and the zeta potential became -21.1 mV, due to the elimination of the oxygen-containing functional groups. The addition of laponite increased the absolute value of zeta potentials. L-RGO (1:1) showed the highest absolute value of zeta potentials (36.2 mV) among the L-RGO samples, which was consistent with the suspension stability shown in Fig. 1.

Fig. 3 presents the FTIR spectra of GO, RGO and L-RGO with different laponite/GO weight ratios. GO exhibited peaks at 3395, 1734, 1634, 1217 and 1099 cm$^{-1}$ corresponding to –OH stretch, stretching vibration of C=O, graphitic C=C, C–O (alkoxy) and C–O (epoxy), respectively [13]. RGO prepared with the assistance of microwave irradiation showed three peaks at 1590, 1217 and 1099 cm$^{-1}$ with much smaller intensity than the GO, corresponding to graphitic C=C and the remaining C–O (alkoxy) and C–O (epoxy) groups, respectively. It was worth noting that the reduction of GO in this experiment took only 10 min. With conventional heating method, it usually took more than 10 h for the reduction of GO by hydrazine and its derivatives. The difference in the dielectric constants of the solvent and GO led to the selective absorption of microwave energy on GO surface. As a result, energy can be transferred directly to GO surface, causing the effective reduction. Similar with RGO, the FTIR spectrum of L-RGO showed little peaks from 4000 to 1000 cm$^{-1}$, due to the effective reduction of GO. L-RGO (1:1) and L-RGO (2:1) showed a peak at 996 cm$^{-1}$, attributed to the Si-O stretching vibrations of the tetrahedral sheets [14].