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Liquid crystallinity driven highly aligned large graphene oxide composites

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ABSTRACT

Graphene is an emerging graphitic carbon materials, consisting of sp^2 hybridized two dimensinal honeycomb structure. It has been widely studied to incorporate graphene with polymer to utilize unique property of graphene and reinforce electrical, mechanical and thermal property of polymer. In composite materials, orientation control of graphene significantly influences the property of composite. Until now, a few method has been developed for orientation control of graphene within polymer matrix. Here, we demonstrate facile fabrication of high aligned large graphene oxide (LGO) composites in polydimethylsiloxane (PDMS) matrix exploiting liquid crystallinity. Liquid crystalline aqueous dispersion of LGO is parallel oriented within flat confinement geometry. Freeze-drying of the aligned LGO dispersion and subsequent infiltration with PDMS produce highly aligned LGO/PDMS composites. Owing to the large shape anisotropy of LGO, liquid crystalline alignment occurred at low concentration of 2 mg/ml in aqueous dispersion, which leads to the 0.2 wt% LGO loaded composites.

1. Introduction

Graphene is an emerging graphitic carbon material consisting of monolayer sp^2 hybrid carbon atoms packed into two-dimensional honeycomb lattice [1]. Its unique material properties, including outstanding carrier mobility ($\sim$15,000 $cm^2\,V^{-1}\,s^{-1}$) and Young's modulus ($\sim$1 TPa) has gathered tremendous research attentions for the utilization in various fields, such as transparent electrodes [2–4], flexible substrates [5], energy storage devices [6–9], carbon composites and so on. Among them, Graphene/polymer composites are a promising candidate for near future practical application. In contrast to the traditional micrometer scale fillers, very low loading level of graphene with extremely large shape anisotropy effectively reinforces the mechanical property [10,11], electrical conductivity [12–14], and thermal stability of a composite structure [15]. In the composite applications, orientation control of graphene flakes within polymer matrix may significantly influence on the anisotropic material properties such as Young's modulus, gas permeability and so on [16,17]. To date, a few methods have been developed for effective orientation control of graphene fillers. Shear induced arrangement is one of the most common methods [18]. However, rapid increase of shear viscosity along with graphene composition may bring about flow instability in a composite structure. Layer-by-layer assembly [19] and vacuum assisted self-assembly [20] also provide highly ordered graphene composites but those approaches are generally time-consuming and require complicated processing equipment.

Recently, graphene oxide (GO) has been reported to show colloidal nematic liquid crystalline behavior in various solvents, including water [21–23]. GO is a chemically modified graphene decorated with hydrophilic oxygen functional groups, such as epoxy, hydroxyl, and carboxylic groups [24,25]. Those hydrophilic functionalities mediate spontaneous dispersibility in water and polar organic solvents [26]. In a stable dispersion, its two-dimensional discotic shape with large shape anisotropy gives rise to the formation of nematic liquid crystal. The molecular scale alignment of a liquid crystal is known to be readily tunable by external perturbation [27,28].

Here, we introduce highly aligned LGO composites fabrication by means of GO liquid crystallinity. LGO with lateral size larger than 20 μm, shows stable nematic liquid crystalline phase at a very low concentration of $\sim$0.8 mg/ml aqueous solution, due to its extremely high aspect ratio. In the nematic phase concentration, LGO flakes are uniaxial aligned within thin parallel gap confinements. The highly aligned state can be transferred into polymer matrix after freeze-drying and subsequent polymer infiltration. Scanning electron microscopy (SEM) and Raman spectroscopy confirmed the successful production of highly aligned LGO composite structures.

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2. Result

2.1. Synthesis of LGO

LGO was synthesized by the modified Hummers method [29,30]. Instead of commonly used sonochemical exfoliation step, we introduced mild mechanical shacking to avoid the damage of basal plane and maintain the large lateral size over 20 μm. Despite the large size of LGO, sufficient dialysis minimizes the screening effect from electrostatic repulsion among GO flakes for stable dispersion. Morphology of LGO was observed with an SEM. Fig. 2a shows the broad lateral size distribution of GO flakes from 1 to 100 μm.

2.2. Liquid crystalline property

To confirm the liquid crystalline phase formation, LGO dispersions are diluted to 0.1–1 mg/ml and immobilized for several weeks. LGO dispersions exhibit typical phase separation into low density isotropic phase and high density nematic phase. Fully nematic phase dispersion is observed above the concentration of 0.8 mg/ml (Fig. 2b). The liquid crystalline behavior was also confirmed by viscosity measurement at a shear rate of $10^{-1}\ s^{-1}$. In a dilute dispersion, shear viscosity monotonically increases along with the concentration. By contrast, shear viscosity suddenly decreases between 0.3 and 0.5 mg/ml range due to the formation of nematic phase. It is well-known that viscosity of nematic phase is generally lower than isotropic phase due to molecular alignment [31]. Bare eye observation shows that 1 mg/ml LGO dispersion exhibits chocolate-milk-like appearance, while bright and dark brushes of Schlieren texture were observed between two cross polarizers (Fig. 2b inset). In this work, large flakes were used for low loading, easy processible two dimensional aligned graphene/polymer composite relying on their much lower critical concentration for nematic phase formation [21].

2.3. Morphology characterization of LGO/PDMS

Fig. 1 shows schematic procedure for highly aligned LGO/PDMS composites. First, LGO aqueous dispersion was dropped onto a confined tray and covered with a flat lid. The confined geometry was immobilized for 1.5 h for the spontaneous orientation of LGO flakes parallel to the confinement surface. The aligned dispersion was freeze-dried to maintain the LGO alignment in the resultant porous LGO aerogel structure. The aerogel was gently immersed in a mixture of PDMS base and curing agent (10:1 w/w) and maintained until LGO aerogel absorbs the PDMS fluid completely. After the curing of PDMS infiltrated LGO aerogel, the resultant LGO/PDMS composite film is peeled off from bottom substrate and reduced with hydrazine vapor to restore the electrical and mechanical properties [32].

To confirm the liquid crystalline alignment effect in composite structures, we diluted LGO dispersions into 0.5, 1 and 2 mg/ml. While 0.5 mg/ml dispersion shows isotropic-nematic biphasic behavior, 1 and 2 mg/ml dispersions exhibit fully nematic phase in Fig. 2b. After those dispersions are aligned between gap confinement and freeze dried, cross sections of each aerogel were observed with SEM (Fig. 3). In the 0.5 mg/ml LGO aerogel, flakes show randomly oriented morphology without any significant influence from freeze-drying process [33]. We could not get free-standing aerogel due to the low content of LGO and significant volume shrinkage during drying process. In the 1 mg/ml dispersion with fully nematic phase, greatly improved LGO orientation was observed. By contrast, freeze-dried aerogel prepared from 2 mg/ml dispersion shows high aligned LGO flakes over entire thickness of the gel structure. By contrast, when the thickness of LGO aerogel was increased to 1.5 mm by controlling the gap distance between two flat confinements, typical nematic defect structures of disclinations were observed in the middle of aerogel (Fig. 3h). Relatively weak alignment effect in the middle of sample should be responsible for such defect formation. Taken together, LGO concentration and aerogel thickness are crucial parameters for the high alignment of LGO flakes.

In this work, we selected PDMS as a matrix for LGO composites principally due to easy infiltration. It is noteworthy that due to the hydrophobic character of PDMS, LGO aerogel does not collapse during infiltration. It should be considered that PDMS with high gas permeability would be beneficial for the gas phase reductant treatment, such as hydrazine vapor [34]. In Fig. 4a, an optical image of highly aligned reduced LGO (rLGO) composite is shown. rLGO is well-integrated within PDMS matrix without apparent mechanical damage upon

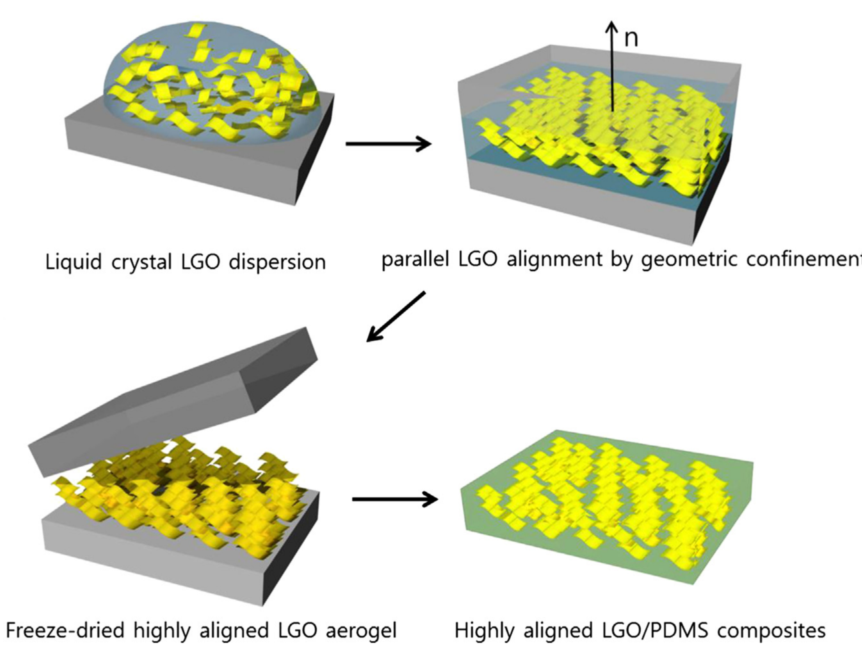

Fig. 1. Schematic procedure for liquid crystal aligned LGO/PDMS composite fabrication.