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Eco-friendly mass production of poly(p-phenylenediamine)/graphene oxide nanoplatelet composites and their electrorheological characteristics

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ABSTRACT

Poly(p-phenylenediamine)/graphene oxide nanoplatelet (PPDA/GONP) composites were synthesized via in situ oxidation polymerization of p-phenylenediamine (PDA) in graphene oxide nanoplatelets (GONPs) suspension for potential electrorheological (ER) fluid applications. Initially, the mass production of GONPs can be achieved through a simple and green ball milling process of graphite with dry ice. The versatile synthesis methods and multifunctionality of poly(p-phenylenediamine) (PPDA) enable the wide potential applications of PPDA/GONP composites. The π−π stacking interaction between GONP and PDA is a key factor to fabricate PPDA/GONP composite successfully. The ER characteristics of both PPDA/GONP composites and PPDA in silicone oil medium were examined using a rotational rheometer equipped with a high voltage generator. The resultant PPDA/GONP composites exhibited improved typical ER behavior compared with that of pure PPDA, providing a new potential application of the PPDA/GONP composites as an intelligent material.

1. Introduction

Graphene has attracted an enormous interest for various potential applications in capacitors, electronics, composites and sensors owing to its extraordinary structural and electrical properties [1,2]. Accordingly, several techniques including chemical vapor deposition (CVD) [3,4], solution exfoliation [5,6] and micro-mechanical exfoliation of graphite [1] have been developed to produce graphene. Nevertheless, the tedious operation and high cost of the CVD process limit large scale preparation of graphene, meanwhile a series of strong oxidizing and reduction reagents (e.g., hazardous H_2SO_4 and $KMnO_4$, poisonous N_2H_4 etc.) are involved in the cumbersome solution exfoliation of graphite [7,8], while the inadequacy of micro-mechanical exfoliation method is limited due to its low yield. Currently, a ball milling technology has emerged as a facile and eco-friendly mass production method of graphene nanoplatelets (NPs) [9–11]. In general, the ball milling can trigger reactions of graphite with gas, liquid or solid to obtain graphene NPs straightforward. Kinetic energy of high-speed spinning balls is applied to graphite promoting the breakage of chemical bond and effective fracture and exfoliation of graphite into small pieces of graphene NPs during the ball milling process. Recently, Jeon et al. reported the successful preparation of edge-halogenated graphene NPs by ball-milling graphite with chlorine, bromine or iodine and adopted them as counter electrodes [12], electrocatalysts for oxygen reduction reaction [13], high performance electrodes materials for lithium-ion batteries [14]. León et al. also prepared graphene via ball milling of graphite with triazine derivatives [15]. Likewise, Yan et al. prepared hydroxyl-functionalized graphene via ball milling of graphite in the presence of potassium hydroxide [16].

Electrorheological (ER) fluid is a kind of intelligent fluid composed of polarizable particles dispersing in insulating carrier liquid (e.g., silicone oil and paraffin, etc.). The dispersed particles can get polarized and form fibril-like structure reversibly controlled under an external electric field [17], therefore, the ER fluid has

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broad applications in control systems, such as microfluidic chips, microvalves, dampers and tactile display [18–20]. Substantial effort has been made to investigate conducting polymers such as polyaniline [21,22], and polypyrrole [23,24] as well as their composites for ER systems. The structure of p-phenylenediamine (PDA) is close to that of aniline which encourages the ER performance study of its polymer [25]. The ER activity of PPDA suspensions in silicone oil has been reported by Stejskal and his team [26,27]. Moreover, the fact that poly(p-phenylenediamine) (PPDA) possesses very versatile synthesis methods and more multifunctionality than polyaniline will expand its practical applications [25,28–30]. Despite the intense research of PPDA based composites for diverse utilizations, such as PPDA/graphene oxide (GO) hybrids for the detection of dopamine, PPDA/graphene nanocomposites for supercapacitor and PPDA/Fe_3O_4 nanocomposites for antioxidant [31–33], there are few reports about the ER effect of PPDA based composites.

In this article, graphene oxide NPs (GONPs) were prepared via a modified Jeon's method by ball milling of graphite in the presence of dry ice, and the PPDA/GONP composites were fabricated via in situ oxidative polymerization of PDA in the GONPs dispersion, as showed in Scheme 1. Moreover, the specific surface area of the obtained GONPs is 589.7 m^2/g, which is much higher than that of previously prepared using the similar method (389.4 m^2/g) [9,34,35]. The π−π stacking interaction between GONPs and PDA is considered to be one key force to form PPDA/GONP composites successfully. It was found that improved ER properties were obtained with PPDA/GONP composites when compared to that of pure PPDA.

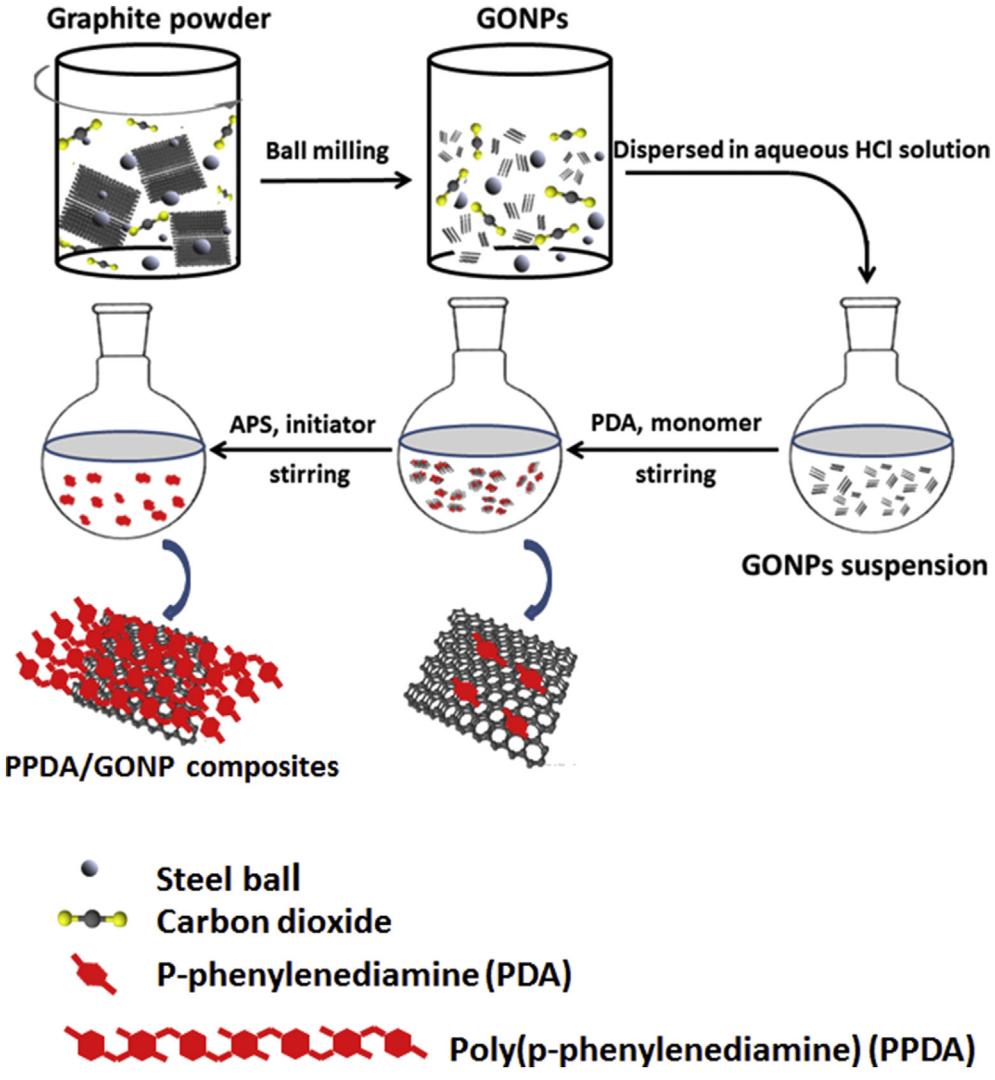
2. Experimental section

2.1. Preparation of GONPs

30 g graphite and 300 g dry ice were added into a grinding bowl (2.5 L) containing stainless steel milling beads of 5 mm and 10 mm in diameter, which was sealed and fixed in planetary ball mill. The internal carbon dioxide released very slowly through a gas outlet valve. GONPs were obtained by ball milling for 48 h at a rotational speed of 300 rpm at room temperature. The GONPs were washed and freeze-dried for 48 h to afford the pure GONPs.

2.2. Synthesis of PPDA and PPDA/GONP composites

The monomer PDA (0.02 mol) was dissolved in 250 ml of GONPs (0.4 g) suspension in HCl (1 M) with sonication for 30 min. The solution of APS (0.02 mol) in 50 ml of HCl (1 M) was added drop-



Scheme 1. A scheme to illustrate the formation of PPDA/GONP composites by in situ oxidative polymerization of PDA in the GONPs dispersion.