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Self-stabilized polyaniline@graphene aqueous colloids for the construction of assembled conductive network in rubber matrix and its chemical sensing application

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ABSTRACT

Facile dispersion and construction of graphene-based 3D conductive network in polymer matrix are highly attractive for the preparation of conductive polymer composites (CPCs) and flexible electronic devices. In this study, a simple and effective strategy for the fabrication of graphene-based assembled conductive network in natural rubber (NR) matrix is reported. Specifically, polyaniline@graphene nanohybrids were prepared by in situ reduction of graphene oxide using aniline as both reducing and stabilizing agents. The resulted self-stabilized polyaniline@graphene nanohybrids could well disperse in aqueous suspension by electrostatic repulsion. When homogenized with NR through latex assembly technique, they could be located in the interstitial space between the NR latex microspheres and organized into a continuous 3D hierarchical network. The as-prepared CPCs with this 3D conductive network exhibited a very low percolation threshold (3-fold lower than that of the conventional NR/graphene blends), enhanced electrical conductivity (up to 6 orders of magnitude improvement) and meanwhile excellent chemical sensing properties. This work provides a feasible approach to stabilize graphene nanosheets in aqueous media without the use of stabilizer or complicated surface modification and extend their applications in the preparation of CPCs as chemical sensing materials.

1. Introduction

Graphene has attracted great attention due to its unique layered structure, remarkable electronic and mechanical properties since its discovery [1–3]. It is well recognized as a promising nanofiller for the preparation of conductive polymer composites (CPCs) [4–6]. The study of graphene-based CPCs is very attractive to worldwide researchers because of their unique advantages, such as electronical properties, good processability, low weight and tunable properties [7,8]. Although some recent studies explored new methods to the preparation of graphene [9], the chemical reduction of graphene oxide (GO), the layered nanosheets exfoliated from graphite oxide, is widely perceived as an effective and scalable method to produce reduced graphene oxide (rGO). Hydrazine and hydrazine hydrate are the most widely used reducing agents for GO because of their high efficiency [10,11], but their highly toxic and explosive nature restricted their large-scale applications [12]. On the other hand, graphene nanosheets tend to aggregate during the synthesis and processing procedure in aqueous or organic media due to their high specific surface area [13], which resulted in poor dispersion in polymer matrix and limited their large-scale application [14,15].

Although severe aggregation could be relieved by adding stabilizers or attaching other molecules onto the graphene sheets, these external additives would exert negative effect to the electrical and mechanical properties of the prepared CPCs. Besides, the used organic surfactants, like 7,7,8,8-tetracyanoquinodimethane [16] or benzylamine [17], could also have potential hazard to the environment. The stabilization of graphene nanosheets in aqueous media without the use of stabilizer or complicated surface modification is still challenging. Li et al. [18] prepared a stable graphene aqueous colloids with excellent processability through electrostatic stabilization. However, costly and time-consuming dialysis treatment was necessary in this approach, which might hinder its large-scale application.

The preparation of CPCs requires a suitable mixing approach to incorporate conductive fillers into the polymer matrix. Generally,

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melt compounding is an effective way to prepare CPCs, but it can hardly reach homogeneous dispersion without breaking down conductive fillers [7]. Recently, latex assembly technique has been proved to be an effective method to prepare CPCs with excellent electrical properties [19–21]. In this process, conductive fillers are homogenized with polymer latex and located in the interstitial space between the polymer latex microspheres and organized into a continuous network. Homogeneous dispersion of conductive fillers in aqueous polymer emulsion is the prerequisite for this strategy. Although there are many studies reported the successful preparation of rGO/polymer composites [22,23], most of these studies directly dispersed GO powders into polymer latex (e.g. polystyrene, natural rubber (NR)) with the assist of ultrasonic irradiation [24]. The GO/polymer latex was in situ reduced by hydrazine hydrate under ultrasonic irradiation to obtain conductive rGO/polymer composites. However, it is difficult to remove the toxic and explosive hydrazine hydrate from this viscous compound.

In this study, polyaniline (PANI)@rGO aqueous colloids with remarkable dispersion stability was prepared using aniline as the reducing agent for the reduction of GO. No extra reducing agents or stabilizers were involved in the synthesis. This elaborate strategy avoided the process of removing reducing agents from the resulted rGO-filled composites. On the other hand, as an intrinsic conducting polymer [25], PANI could also contribute to the electrical properties of the composite. Ma et al. prepared PANI/graphene hydrogel with well excellent capacitance, in which PANI played key roles in the fabrication and the enhancement of stability and capacitance [26]. In our study, the obtained PANI@rGO/NR nanohybrids could be well dispersed in the polymer matrix during the compounding with NR latex and subsequent co-coagulation, and located in the interfaces between NR microspheres assembling into a 3D hierarchical conductive network structure according to our previously reported approach [27–29]. The as-prepared PANI@rGO/NR composites exhibited well enhanced electrical conductivity compared to the conventional mixed PANI/rGO/NR blends with identical filler loadings. Furthermore, the conductive network in the prepared composites is ‘brittle’ and sensitive to chemical solvent due to its ultralow percolation threshold. We demonstrated that the PANI@rGO/NR composites have potential application as chemical sensing materials. This work might provide a simple, green and effective approach for the preparation of CPCs with high performance and functional properties.

2. Materials and methods

2.1. Materials

Graphite powder was purchased from J&K Chemical, Inc. (China) H_2SO_4, H_3PO_4, HCl, aniline, ammonium hydroxide ($NH_3 \cdot H_2O$, 25–28%), toluene (≧99.5%), xylene (≧99.5%), hydrazine hydrate, ammonium persulfate (APS) and $KMnO_4$ were all purchased from Chengdu Kelong Chemical Reagent Company (China) and used without further purification. The NR latex (solid content: 58 wt%) was provided by Chengdu Xinyuanding Co., Ltd (China).

2.2. Preparation of PANI@rGO nanohybrids

GO was prepared according to the improved Hummers method [30]. The graphite powder and $KMnO_4$ was mixed and slowly added into a mixture of concentrated H_2SO_4/H_3PO_4 (9:1, wt%), producing a slight exotherm to about 35 °C. Then the mixture was heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and kept in the ice bath with 30% H_2O_2. The resulted products were purified by repeated centrifuge and dialysis in deionized water.

The PANI@rGO nanohybrids were prepared by combining the reduction of GO with the oxidative polymerization of aniline. In a typical procedure, 200 mg of GO was dispersed in 200 mL of deionized water and 2 mL of aniline monomer was dissolved into 100 mL of aqueous 1 M HCl solution. Then, aniline solution was rapidly added into GO dispersion and stirred vigorously at 70 °C for 24 h. After reaction, the mixture was removed by vacuum filtration, and repeatedly rinsed by 0.1 M HCl solution (1 time) and deionized water until the filtered water became clear. The resulted PANI@rGO nanohybrids was treated with excess 0.5 M $NH_3 \cdot H_2O$ for 1 h to adjust their pH value to 9.0.

2.3. Preparation of PANI@rGO/NR composites

For the preparation of PANI@rGO/NR composites, 8.6 g NR latex was dispersed in 250 mL deionized water and stirred for 5 min to reach uniform dispersion. A desired amount of PANI@rGO nanohybrids suspension and latex dispersion were mixed with stirring for 25 min, reaching a dark blue mixture. The resulted mixture was coagulated by adding 150 mL H_2SO_4 solution (1 M). During this process, PANI was re-doped by H_2SO_4. PANI@rGO/NR composite was separated with filtration and soaked in the deionized water to remove residual H_2SO_4. Then the composite was dried at 60 °C for 12 h to constant weight.

In order to demonstrate the effect of conductive filler dispersion to the electrical conductivity of CPCs, rGO/PANI blend was prepared by direct mixing hydrazine hydrate reduced rGO with oxidative polymerized PANI for comparative analysis. The detailed preparation process is given in the Supporting Information. The ratio of rGO/PANI blend was adjusted to the same as that of PANI@rGO nanohybrids. This blend was mixed with NR latex and processed according to the aforementioned procedure and marked as rGO/PANI/NR blend.

2.4. Characterization

Transmission electron microscopy (TEM) was performed to observe the morphology of PANI@rGO nanohybrids and PANI@rGO/NR composite using a transmission electron microscope (JEOL JEM-100CX, Japan). Diluted PANI@rGO nanohybrids aqueous suspension (0.05 mg/mL) was directly dropped on a copper grid for observation. PANI@rGO/NR composite dispersion (NR concentration = 1 mg/mL) was homogenized by stirring before test. High magnification optical microscope was used to investigate the dispersion state and microstructures of rGO/PANI blend. The mixture of rGO/PANI blend was casted on a glass slide and covered with a coverslip. Then the samples were dried and observed using a microscope (UB 200i, Chongqing UOP Photoelectric Technology Co., Ltd., China) with a digital camera.

Zeta potential (ζ potential, ZP) of the PANI@rGO nanocomposites aqueous suspension (0.15 mg/mL) was measured using Zetasizer nano-ZS (Malvern, UK) under a pH value of 9.0.

In order to evaluate the reduction efficiency of GO, PANI was extracted from PANI@rGO nanohybrids by Soxhlet extraction with dimethyl formamide (DMF). Fourier transform infrared (FTIR) spectroscopy was recorded on a Nicolet 560 spectrophotometer to investigate the structure of GO and rGO. Raman spectroscopy was carried out using a Horiba LabRAM HR apparatus (Horiba Co., France) with an excitation laser λ = 514 nm. Elemental composition analysis of GO and rGO was carried out via X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos Inc., Britain). The obtained XPS spectra were analyzed using XPSpeak4.1 software and Shirley was used as background when fitting the peaks.

The 3D hierarchical conductive network fabricated with PANI@rGO nanohybrids in NR matrix was intuitively observed by