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

Zehang Zhou, Xinxing Zhang, Xiaodong Wu and Canhui Lu**

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

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

**Corresponding author: Xinxing Zhang and Canhui Lu*

E-mail address: xxzwwh@scu.edu.cn; canhuilu@scu.edu.cn

Tel: +86-28-85460607 Fax: +86-28-85402465

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.

Key words: Graphene; A. Polymer-matrix composites (PMCs); A. Nano composites; B. Electrical properties

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, 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 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 ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25-28%), toluene ($\geq 99.5\%$), xylene ($\geq 99.5\%$), 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 $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (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 $\text{NH}_3 \cdot \text{H}_2\text{O}$ 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 $\lambda = 514$ 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 scanning electron microscopy (SEM, JEOL JSM-5600, Japan). PANI@rGO/NR composite (3.89 vol% of rGO) was soaked in liquid nitrogen and fractured. Then the cryo-fractured PANI@rGO/NR composite was etched with toluene for 4 h (Soxhlet extraction). The sample was dried and then the fractured surface was sputter-coated with a thin layer of Au for observation. The cross-section of rGO/PANI/NR blend prepared in the same way was also observed by SEM for comparative study.

The electric conductivity of the samples were measured on undeformed samples by a two-point measurement with a resistance meter (UT61, Uni-Trend, China) for $R \leq 2 \times 10^8 \Omega$ or using ZC36 high resistance instrument for $R > 2 \times 10^8 \Omega$. A rectangle strip samples (40 mm×10 mm×1 mm) or square samples (100 mm×100 mm×1 mm) were used for electrical measurement. Five specimens were measured for each sample to achieve an average value. The measured volume resistance (Ω), R_v was converted to volume resistivity (ρ_v) according to ASTM D4496 and D257 using the formula

$$\rho_v = R_v \frac{A}{t}$$

Where A is effective area of the measuring electrode (m^2) and t is specimen thickness (m).

3. Results and discussions

3.1 Preparation and Characterization of self-stabilized PANI@rGO aqueous colloids.

Aniline has been proved as a promising reductant which could spontaneously reach stable aqueous dispersions [31]. Meanwhile, GO has been recognized as a feasible oxidizing agent [32].

These studies inspired the designed strategy for the preparation of the stable PANI@rGO nanohybrids aqueous suspension. The formation mechanism of the PANI@rGO aqueous suspension is schematically illustrated in Fig. 1.

Aniline monomer which contains benzene ring is dissolved in deionized water and homogenized with GO dispersion. It is expected to be preferentially adsorbed on the sites containing carboxylic and phenolic hydroxyl groups on the surface of GO sheets through hydrogen bonds or with van der Waals interactions [33]. With the increase of temperature and the addition of HCl, the reduction of GO is initiated accompanied by the oxidative polymerization of aniline. In this process, the adsorbed aniline monomers could act as the seeding dots to form PANI nanoparticles on the surface of GO nanosheets. After reaction, the pH of resulted suspension of PANI@rGO nanohybrids is adjusted to 9.0 by NH_4OH , resulting stable PANI@rGO aqueous suspension.

The obtained PANI@rGO nanohybrids are very stable in aqueous suspension. The digital camera pictures of PANI@rGO nanohybrids and the conventional mixed rGO/PANI blend aqueous suspension are shown in Fig. 2a to intuitively observe their dispersion stability. Both samples were homogenized with vigorous stirring and placed under same condition (0.15 mg/mL, 9.0 pH). The rGO/PANI blends were easily to agglomerate in aqueous phase, and began to sediment immediately after standing. All the rGO/PANI blends precipitated to the bottom after placing for only 20 min, leaving upper part almost transparent. To contrast, the aqueous suspension of PANI@rGO nanohybrids remained stable after standing for 30 days. The PANI@rGO nanohybrids aqueous suspension is demonstrated to be a lyophobic colloid which stabilized through the electrostatic repulsion as shown in the Supporting Information (Fig. S1). [The conclusion is further confirmed by studying the stability of PANI@rGO nanohybrids in neutral aqueous suspension \(Fig. S2\).](#)

ζ -Potential study was conducted to reach a semi-quantitative understanding of the stability of the composites. The ζ -Potential stands for the degree of electrostatic repulsion between charged particles in dispersion [34]. The PANI@rGO nanohybrids aqueous suspension was negatively charged and its ζ -Potential was measured to be -52.6 ± 1 mV. The high absolute value of ζ -Potential for this suspension indicates that the strong electrostatic repulsion between the PANI@rGO nanohybrids lead to the dispersion stable enough to resist the particle aggregation and precipitation [35]. The excellent dispersity of PANI@rGO nanohybrids aqueous suspension facilitates its construction of conductive network in NR matrix.

In order to study the structure of PANI@rGO nanohybrids and rGO/PANI blend, their morphologies were observed by TEM and high magnification optical microscopy. Fig. 2b reveals the morphology of PANI@rGO nanohybrids. During the polymerization process, aniline monomers were homogenized with GO nanosheets. The in situ synthesized PANI nanoparticles are uniformly located on the surface of the obtained rGO nanosheets, which also prevented rGO nanosheets from restacking due to the steric hindrance effect. For comparison, severe agglomeration is observed in the mixture of hydrazine hydrate reduced rGO and PANI nanoparticles. They are agglomerated into huge bulks in aqueous phase as shown in Fig. 2c.

In this study, PANI@rGO nanohybrids were in situ synthesized by the reduction of GO using aniline as reductant. The structure changes of GO before and after reduction is further investigated by FT-IR spectroscopy. As shown in Fig. 3a, characteristic bands of oxygen-containing groups are observed in the FTIR spectrum of GO. The bands at 3377 cm^{-1} , 1403 cm^{-1} , 1245 cm^{-1} and 1076 cm^{-1} are attributed to the vibration, deformation bands of O-H groups, C-O epoxy and C-O alkoxy stretches, respectively [36]. The 1734 cm^{-1} band is ascribed to the C=O stretching vibration of the

carboxy/carbonyl group [37]. After reduction, the bands of oxygen-containing functional groups are significantly decreased in the spectrum of rGO, which indicates that these groups were effectively removed during the process.

Raman spectroscopy is a feasible tool to study the microstructure information of carbon-based materials, especially graphene [38]. In order to further investigate the structure changes of GO before and after reduction, the Raman spectra of GO and rGO were recorded and shown in Fig. 3b. In the spectrum of GO, two main prominent peaks corresponding to D and G bands are observed at 1349 cm^{-1} and 1592 cm^{-1} , respectively. The D band corresponds to the defects and disorder activated Raman mode, while the G band is ascribed to the E_{2g} vibrational mode of sp^2 carbon atoms [39]. The D and G bands are also presented in the spectrum of rGO at 1367 cm^{-1} and 1617 cm^{-1} , respectively. It is noticeable that the D/G intensity ratio of rGO (1.09) shows an obviously increase comparing to that of GO (0.92) after reduction, which indicates that smaller in-plane sp^2 domains were formed during the reduction of GO [40]. The result corresponds well with the rGO reduced by other reducing agents, indicating the efficient deoxygenation ability of aniline towards GO during its polymerization [36].

The structure and chemical components of GO before and after reduction was further investigated by XPS. The core-level XPS signals of C 1s of GO and rGO are shown in Fig. 3c and Fig. 3d and the detailed XPS data are given in Table 1. The XPS spectrum of GO (Fig. 3c) presents two prominent peaks centered at 284.6 and 286.8 eV, which can be further divided into three Gaussian peaks with binding energy of 284.6 (C-C/C-H), 286.8 (C-O, hydroxyl and 1,2 epoxide functionalities) and 287.8 (C=O, carboxyl and ketone functionalities), respectively [41]. The peak area ratio of oxygen containing bonds is 46.5%. For comparison, only one prominent peak is

observed in the spectrum of rGO (Fig. 3d) at 284.6 eV, and the peak attributed to C=O vanished. Furthermore, the peak area ratio of oxygen-containing bonds decreased from 46.5% to 24.3% while the portion of sp^2 hybridized carbon species remarkably increased from 53.5% to 75.7%, indicating that most oxygen containing functional groups in GO were removed. The XPS spectra illustrate that the reducing efficiency of the reducing agents used in this study is valid for the reduction of GO. The electrical conductivity of GO before and after reduction was also investigated. The conductivity of GO was significantly improved after reduction by aniline as discussed in the Supporting Information, confirmed the successful reduction of GO during polymerization of PANI.

3.2 Construction of 3D conductive network in NR matrix.

The SEM microscopy was carried out to intuitively observe the conductive network in PANI@rGO/NR composite and rGO/PANI/NR blend. Fig. 4a presents that PANI@rGO nanohybrids are well dispersed in the NR matrix and organized into a 3D continuous network. After the NR matrix was extracted by toluene, this interconnected network almost maintained and acted as scaffold which prevented PANI@rGO nanohybrids from agglomeration. TEM observation (Fig. S3) indicates that NR latex microspheres are homogeneously encapsulated by the PANI@rGO nanohybrids, which is beneficial to the formation of continuous network. For comparison, rGO/PANI/NR blend was also extracted at the same condition to observe the morphology. rGO and PANI nanoparticles are seriously aggregated as pointed out in Fig. 4b. The blend is prone to collapse after extraction of NR matrix, which hindered the formation of 3D conductive network.

The strategy for the preparation of PANI@rGO/NR composite and rGO/PANI/NR blend is illustrated in Fig. 5. In the preparation of PANI@rGO/NR composite, PANI nanoparticles are located on the surface of rGO nanosheets and well dispersed in aqueous suspension under a pH of

9.0. This PANI@rGO nanohybrids suspension is homogeneously dispersed with NR latex. In the subsequent coagulation process, the NR latex microspheres would create an excluded volume and PANI@rGO nanohybrids are pushed into the interstitial space between them, organized into a continuous 3D hierarchical conductive network. The water in the interstitial space of NR latex microspheres coated by PANI@rGO nanohybrids was evaporated during drying process. The spherical NR particles transformed into multi-facets with PANI@rGO conductive layers sandwiched in the contacting interfaces and joints. As a result, the conductive network is well constructed in NR matrix.

For comparison, the rGO/PANI blends are prone to agglomerate in the suspension according to previous discussion, which makes them very difficult to uniformly disperse in NR latex. The randomly located aggregates of rGO, PANI and blends can hardly fabricate feasible conductive network.

3.3 Enhanced conductivity and chemical sensing properties.

The electrical conductivity of PANI@rGO/NR composite and rGO/PANI/NR blend are presented in Fig. 6 to study the effect of the elaborately constructed 3D conductive network on the electrical properties of CPCs. Considering aniline is initially added in the PANI@rGO nanohybrids as a reductant, the electrical conductivity of the samples is studied as a function of rGO volume fraction. The initial conductivity of neat NR is measured to be about 10^{-12} S/m. For both samples, the electrical conductivity increases with the increase of rGO content. With increasing content of conductive fillers, the conductivity of the composites will present a sharp increase at a certain amount of filler loading, which is known as the percolation threshold [42]. It indicates the construction of feasible conductive network. Typically, an extremely high filler loading is usually

required to reach satisfying electrical properties for most CPCs. Comparing to rGO/PANI/NR blend, PANI@rGO/NR composite with 3D hierarchical conductive network shows much higher conductivity and lower percolation threshold. The electrical conductivity of PANI@rGO/NR composite is about 5 orders of magnitude higher than that of the rGO/PANI/NR blend at the same rGO volume fraction (0.61 vol%, PANI@rGO vol% = 3.29%). The PANI@rGO/NR composite reaches the percolation threshold at an rGO volume fraction of 0.23 vol% (PANI@rGO vol% = 1.11%), while that of rGO/PANI/NR blend is 0.70 vol% (rGO/PANI vol% = 3.69%). The PANI@rGO/NR nanocomposites reduces electrical percolation threshold 3-fold. The results provide valid support for the conclusion that the construction of the assembled conductive network contributes to the highly improved electrical conductivity of CPCs. Besides, the as-prepared PANI@rGO/NR composites also show good mechanical properties (as discussed in Fig. S4).

The prepared PANI@rGO/NR composite possesses continuous hierarchical conductive network and low percolation threshold, which makes it attractive as sensing material. When they are exposed to organic solvent like toluene, the organic molecules will be absorbed by NR matrix and lead to its swelling. Thus, the continuous conductive network is disconnected and lead to the increase of electric resistance. In this study, its liquid sensing properties was determined by soaking in toluene and compared with PANI/rGO/NR blend with the same initial resistance. The volume fraction of rGO for PANI@rGO/NR composite is 1.04 vol% (PANI@rGO vol% = 5.63%) while that for rGO/PANI/NR blend is 2.19 vol% (rGO/PANI vol% = 12.89%). The sensing sensitivity of the samples is evaluated in terms of electrical resistance variation, which can be quantitatively expressed by $A_R = \Delta R / R_0$, where A_R is defined as the responsivity, R_0 is the initial resistance and ΔR is the resistance change from R_0 due to the explosion to toluene. The samples were immersed in

toluene and their resistances were measured by resistance meter. As shown in Fig. 5, both plots present ascending trend during the immersion due to the breakdown of conductive network. However, the A_R of PANI@rGO/NR composite starts to increase dramatically after immersing for over 6 min, and exceeds 952.5 after 12 min. To sharp contrast, the A_R of rGO/PANI/NR blend only reaches 34.2 during this period. Comparing to rGO/PANI/NR blend whose conductive network was built up by agglomerates of large content conductive fillers, the 3D hierarchical conductive network constructed by the assembled PANI@rGO nanohybrids was much more vulnerable to the absorption of toluene. Besides, the responsivity of PANI@rGO/NR composite is compared to the previous reported chemical sensing materials as shown in Supporting Information (Table S1), which further demonstrates its excellent sensing properties.

In order to gain intuitive understanding of the chemical sensing properties, the PANI@rGO/NR composite was connected to a blue LED light to monitor the illumination changes. As shown in the inset picture in Fig. 7, during the immersing in toluene, the LED light connected with PANI@rGO/NR composite gradually faded, indicating the increase of electrical resistivity. It went out after immersing for about 8 min. These results demonstrate that the prepared PANI@rGO/NR composite has great potential as a promising chemical sensing material.

4. Conclusions

In summary, we developed a simple and eco-friendly strategy to obtain self-stabilized PANI@rGO nanohybrids aqueous suspension by in situ reduction of GO using aniline as reductant. This effective method had no requirement for superfluous toxic reducing or stabilizing agents and it was unnecessary to remove residual reducing agents. It was demonstrated that the self-stabilized PANI@rGO nanohybrids had great dispersion stability in aqueous suspension and could be located

in the interstitial space between the NR latex microspheres and organized into a continuous 3D hierarchical network by latex assembly technique. The resulted CPCs presented enhanced electrical conductivity, low percolation threshold and excellent chemical sensing properties. These performances make it to have great potential in the application of flexible CPCs and chemical sensing materials.

Author information

Acknowledgements

The authors thank the National Science Foundation of China (51203105 and 51473100) and State Key Laboratory of Polymer Materials Engineering (Grant No. sklpme2015-3-04) for financial support.

References

- [1] Heeder N, Yussuf A, Chakraborty I, Godfrin MP, Shukla A, et al. Fixed-angle rotary shear as a new method for tailoring electro-mechanical properties of templated graphene–polymer composites. *Compos Sci Technol* 2014;100:70-75.
- [2] Novoselov KSA, Geim AK, Morozov SV, Jiang D, Katsnelson M, et al. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* 2005;438(7065):197-200.
- [3] Montes S, Carrasco P M, Ruiz V, Cabanero G, Grande HJ, et al. Synergistic reinforcement of poly (vinyl alcohol) nanocomposites with cellulose nanocrystal-stabilized graphene. *Compos Sci Technol* 2015;29(117):26-31.
- [4] Stankovich S, Dikin DA, Dommett GHB, Kohlhaas K, Zimney E, et al. Graphene-based composite materials. *Nature* 2006;442(7100):282-286.
- [5] Hazarika M, Jana T. Graphene nanosheets generated from sulfonated polystyrene/graphene nanocomposite. *Compos Sci Technol* 2013;87:94-102.
- [6] Kuilla T, Bhadra S, Yao D, Kim N, Bose S, et al. Recent advances in graphene based polymer composites. *Prog Polym Sci* 2010;35(11):1350-1375.

- [7] Deng H, Lin L, Ji M, Zhang S, Yang M, et al. Progress on the morphological control of conductive network in conductive polymer composites and the use as electroactive multifunctional materials. *Prog Polym Sci* 2014;39(4):627-655.
- [8] Tang Z, Kang H, Shen Z, Guo B, Zhang L, et al. Grafting of polyester onto graphene for electrically and thermally conductive composites. *Macromolecules* 2012;45:3444-3451.
- [9] Shi G, Meng Q, Zhao Z, Kuan H, Michelmore A, Ma J. Facile fabrication of graphene membranes with readily tunable structures. *ACS Appl Mater Interfaces* 2015;7:13745-13757.
- [10] Park S, An J, Jung I, Piner R, An S, et al. Colloidal suspensions of highly reduced graphene oxide in a wide variety of organic solvents. *Nano Lett* 2009;9:1593-1597.
- [11] Wang J, Li B, Ni T, Dai T, Lu Y. One-step synthesis of iodine doped polyaniline-reduced graphene oxide composite hydrogel with high capacitive properties. *Compos Sci Technol* 2015;109:12-17.
- [12] Goswami S, Paul S, Manna A. Highly reactive (< 1 min) ratiometric chemodosimeter for selective “naked eye” and fluorogenic detection of hydrazine. *RSC Adv* 2013;3:18872-18877.
- [13] Zhao G, Li J, Wang X. Kinetic and thermodynamic study of 1-naphthol adsorption from aqueous solution to sulfonated graphene nanosheets. *Chem Eng J* 2012;173:185-190.
- [14] Niyogi S, Bekyarova E, Itkis ME, McWilliams JL, Hamon M, et al. Solution properties of graphite and graphene. *J Am Chem Soc* 2006;128:7720-7721.
- [15] Si Y, Samulski ET. Synthesis of water soluble graphene. *Nano Lett* 2008;8:1679-1682.
- [16] Hao R, Qian W, Zhang L, Hou Y. Aqueous dispersions of TCNQ-anion-stabilized graphene sheets. *Chem Commun* 2008;6576-6578.
- [17] Liu S, Tian J, Wang L, Sun X. A method for the production of reduced graphene oxide using benzylamine as a reducing and stabilizing agent and its subsequent decoration with Ag nanoparticles for enzymeless hydrogen peroxide detection. *Carbon* 2011;49:3158-3164.
- [18] Li D, Mueller M, Gilje S, Kaner RB, Wallace G. Processable aqueous dispersions of graphene nanosheets. *Nat Nanotech* 2008;3:101-105.
- [19] Yan DX, Pang H, Li B, Vajtai R, Xu L, et al. Structured reduced graphene oxide/polymer composites for ultra-efficient electromagnetic interference shielding. *Adv Funct Mater* 2015;25:559-566.
- [20] Wu TM, Chen EC. Preparation and characterization of conductive carbon nanotube-polystyrene nanocomposites using latex technology. *Compos Sci Technol* 2008;68:2254-2259.
- [21] Zhan Y, Lavorgna M, Buonocore G, Xia H. Enhancing electrical conductivity of rubber composites by

- constructing interconnected network of self-assembled graphene with latex mixing. *J Mater Chem* 2012;22:10464-10468.
- [22] Rafiee MA, Rafiee J, Wang Z, Song H, Yu ZZ, et al. Enhanced mechanical properties of nanocomposites at low graphene content. *ACS Nano* 2009;3:3884-3890.
- [23] Yan N, Buonocore G, Lavorgna M, Kaciulis S, Balijepalli SK, et al. The role of reduced graphene oxide on chemical, mechanical and barrier properties of natural rubber composites. *Compos Sci Technol* 2014;102:74-81.
- [24] Zhan Y, Wu J, Xia H, Yan N, Fei G, et al. Dispersion and Exfoliation of Graphene in Rubber by an Ultrasonically-Assisted Latex Mixing and In situ Reduction Process. *Macromol Mater Eng* 2011;296:590-602.
- [25] Ge D, Yang L, Fan L, Zhang C, Xiao X, et al. Foldable supercapacitors from triple networks of macroporous cellulose fibers, single-walled carbon nanotubes and polyaniline nanoribbons. *Nano Energy* 2015;11:568-578.
- [26] Moussa M, Zhao Z, El-Kady M, Liu H, Michelmore A, Kawashima N, Majewski P, Ma J. Free-standing composite hydrogel film for superior volumetric capacitance. *J Mater Chem A* 2015;3:15668.
- [27] Wu X, Lu C, Zhang X, Zhou Z. Conductive natural rubber/carbon black nanocomposites via cellulose nanowhisker templated assembly: tailored hierarchical structure leading to synergistic property enhancements. *J Mater Chem A* 2015;3:13317-13323.
- [28] Zhang X, Wu X, Lu C, Zhou Z. Dialysis-free and in situ doping synthesis of polypyrrole@cellulose nanowhiskers nanohybrid for preparation of conductive nanocomposites with enhanced properties. *ACS Sustain Chem Eng* 2015;3:675-682.
- [29] Wu X, Lu C, Xu H, Zhang X, Zhou Z. Biotemplate synthesis of polyaniline@ cellulose nanowhiskers/natural rubber nanocomposites with 3D hierarchical multiscale structure and improved electrical conductivity. *ACS Appl Mater Inter* 2014;6:21078-21085.
- [30] Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, et al. Improved synthesis of graphene oxide. *ACS Nano* 2010;4:4806-4814.
- [31] Yang J, Yin H, Jia J, Wei Y. Facile synthesis of high-concentration, stable aqueous dispersions of uniform silver nanoparticles using aniline as a reductant. *Langmuir* 2011;27(8):5047-5053.
- [32] Boehm HP, Clauss A, Fischer G, Hofmann U. Fifth conference on Carbon, Pergamon Press, Oxford 1962, p. 73.
- [33] Yan X, Chen J, Yang J, Xu Q, Miele, P. Fabrication of free-standing, electrochemically active, and

- biocompatible graphene oxide-polyaniline and graphene-polyaniline hybrid papers. *ACS Appl Mater Inter* 2010;9:2521-2529.
- [34]Jiang L, Gao L, Sun J. Production of aqueous colloidal dispersions of carbon nanotubes. *J Colloid Interf Sci* 2003;260:89.
- [35]Wang Y, Guan XN, Wu CY, Chen MT, Hsieh HH, et al. Processable colloidal dispersions of polyaniline-based copolymers for transparent electrodes. *Polym Chem* 2013;4:4814-4820.
- [36]Zhang J, Yang H, Shen G, Cheng P, Zhang J, et al. Reduction of graphene oxide via L-ascorbic acid. *Chem Commun* 2010;46:1112-1114.
- [37]Luong ND, Pahimanolis N, Hippel U, Korhonen JT, Ruokolainen J, et al. Graphene/cellulose nanocomposite paper with high electrical and mechanical performances. *J Mater Chem* 2011;21:13991.
- [38]Zhan D, Ni Z, Chen W, Sun L, Luo Z, et al. Electronic structure of graphite oxide and thermally reduced graphite oxide. *Carbon* 2011;49:1362-1366.
- [39]Zhang Z, Xu F, Yang W, Guo M, Wang X, et al. A facile one-pot method to high-quality Ag-graphene composite nanosheets for efficient surface-enhanced Raman scattering. *Chem Commun* 2011;47:6440-6442.
- [40]He D, Cheng K, Peng T, Sun X, Pan M, et al. Bifunctional effect of reduced graphene oxides to support active metal nanoparticles for oxygen reduction reaction and stability. *J Mater Chem* 2012;22:21298.
- [41]Huang WS, Humphrey BD, MacDiarmid AG. Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 1986;82:2385-2400.
- [42]Yorifuji D, Ando S. Enhanced thermal conductivity over percolation threshold in polyimide blend films containing ZnO nano-pyramidal particles: advantage of vertical double percolation structure. *J Mater Chem* 2011;21:4402-4407.

Fig. 1. Schematically illustration of the formation mechanism of PANI@rGO aqueous colloids.

Fig. 2. The digital camera pictures of PANI@rGO nanohybrids and rGO/PANI blends aqueous suspension (0.15 mg/mL, 9.0 pH) before and after standing for 30 d (a); TEM image of PANI@rGO nanohybrids (b); High magnification optical microscope image of rGO/PANI blend with a scale bar of 100 μm (c).

Fig. 3. The FTIR spectra (a) and Raman spectra (b) of GO and rGO; The XPS spectra of GO (c) and rGO (d).

Fig. 4. SEM images of the cross-section of cryo-fractured PANI@rGO/NR composite (a) and rGO/PANI/NR blend (b).

Fig. 5. Schematically strategy of preparing PANI@rGO/NR composite and rGO/PANI/NR blend.

Fig. 6. Electrical conductivity of PANI@rGO/NR composite and rGO/PANI/NR blend as a function of rGO volume fraction.

Fig. 7. Plots of relative resistance change as a function of time and photographs of illumination changes during PANI@rGO/NR composite immersing in toluene (inset).

Table 1. Detailed XPS data of GO and rGO

		Peak Position (eV)	Peak Area Ratio (%)
GO:	C-C	284.6	53.5
	C-O	286.8	35.3
	C=O	287.8	11.2
rGO:	C-C	284.6	75.7
	C=O	286.8	24.3