Cellulose nanocrystals mediated assembly of graphene in rubber composites for chemical sensing applications

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Abstract

In this study, we report a green assembled approach to prepare natural rubber (NR) composites with 3D interconnected graphene-based conductive networks. Taking advantage of the water-dispersity and amphiphilicity of cellulose nanocrystals (CNC), well suspended graphene@CNC aqueous colloids could be prepared by the CNC-mediated reduction of graphene oxide. When homogenized with NR latex under ultrasonication and subsequently co-coagulation, the graphene@CNC nanohybrids selectively located in the interstitial space between the NR latex microspheres and constructed an ordered 3D conductive structure. This unique 3D conductive network endowed the NR composites with remarkably enhanced electric conductivity (the percolation threshold is 2-fold lower than that of the conventional NR/graphene composites), mechanical properties and more importantly resistivity response to organic liquids. Our strategy offered a novel, simple and eco-friendly route for the fabrication of liquid sensors capable of sensing and discriminating various solvent leakage in chemical industry as well as environmental monitoring.

Key words: cellulose nanocrystals; latex assembly; graphene; 3D conductive network; liquid sensors

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1. Introduction

Graphene, a new two-dimensional carbon nanostructure, has attracted tremendous attention due to its extraordinary electronic properties, thermal conductivity, large surface area, high strength and Young's modulus (Geim & Novoselov, 2007; Naeimi & Golestanzadeh, 2014; Lee, Wei, & Kysar, 2008). Graphene-filled conductive polymer composites (CPCs) have potential application in many areas such as stretchable conductors, antistatic sealing rings, electromagnetic shielding devices, etc. However, graphene has a pronounced tendency to form irreversible aggregation in water or organic solutions due to the intermolecular π - π stacking attraction forces and Van der Waals interactions (Li et al., 2008). The poor dispersion of graphene is always detrimental to achieve desired effects of graphene-based CPCs. Therefore, well dispersed graphene suspension is the prerequisite for the fabrication of high performance graphene-based CPCs. Covalent (Worsley et al., 2007; Niyogi et al., 2006) and non-covalent (Bai et al., 2009; Salavagione, Gomez, & Martinez, 2009; Stankovich et al., 2006) methods have been widely explored to enhance the dispersity of graphene. Niyogi et al. (Niyogi et al., 2006) modified the surface of the graphene via amide coupling reaction between the carboxyl acid groups of graphene oxide (GO) and octadecylamine; Zhang et al. (Tang, Lei, Guo, & Zhang, 2012) used cationic dye rhodamine B or surfactant like sodium deoxycholate to achieve homogeneous dispersion of graphene. However, the aforementioned studies require expensive chemicals and large amount of solvents, which is not environmentally sustainable. Moreover, the covalent strategy will damage the structure of graphitic lattice, and deteriorate the inherent properties of graphene (Hsiao et al., 2010; Kuila et al., 2011). As the emphasis of science and technology is shifting more towards environmentally friendly and sustainable resources and processes (Zhang, Zhang, Ma, & Guan, 2015; Rezayat et al., 2014; Qiu et al., 2014), it is necessary to develop a green approach to mediate graphene dispersion in aqueous media in order to fabricate graphene-based CPCs with great conductivity and mechanical properties.

Cellulose is a renewable and biodegradable natural polymer, which can be obtained from higher plants, tunicates, bacteria and alga (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose nanocrystals (CNC), a derivative of cellulose, are water-dispersible renewable materials through controlled acid hydrolysis (Xiong et al., 2013; Danial et al., 2015). CNC have been used as effective reinforcing fillers on several kinds of polymers including poly(butylene succinate) (Hu, Lin, Chang, & Huang, 2015), poly(lactic acid) (Lizundia et al., 2015; Kamal & Khoshkava, 2015), and elastomers (Chen et al., 2015; Ning et al., 2015). Recently, Kalashnikova et al. have reported that CNC can be irreversibly anchored at the oil-water interface to form the so-called Pickering emulsions (Kalashnikova & Kalashnikova, 2011, 2012). This is due to the colloidal-size structure of CNC as well as its unique amphiphilic character. The amphiphilicity of CNC comes from the rich hydroxyl groups on their surface and hydrophobic surface of some crystalline planes respectively. The tendency of CNC to migrate to interfaces is attributed to the 200 β /(220) α hydrophobic crystalline edge (glucopyranose) that orients towards the oil phase (Salas et al., 2014). According to the colloidal stability theory and Pickering emulsion model, the amphiphilic CNC can assemble or adsorb at the oil-water interface of graphene aqueous dispersions to improve its stability.

Recently, latex assembly technique has been widely reported as an emerging approach to prepare high performance CPCs (Yoonessi et al., 2010; Potts et al., 2012; Scherillo et al., 2014; Yan et al., 2015; Tian et al., 2014). During this process, polymer latex particles took effect of an excluded volume and pushed the conductive nanofillers into the interstitial space between them to form a 3D conductive network. However, most of these studies directly dispersed GO into polymer latex and then in situ reduced GO sheets by hydrazine hydrate under ultrasonic irradiation to obtain conductive reduced graphene oxide (RGO)/polymer composites. The reduction efficiency of GO was suppressed during this process due to the high viscosity of polymer latex, which would further affect the properties of the composites (e.g. electric conductivity). Furthermore, it is difficult to remove the toxic and explosive residue reducing agents from the viscous compound, resulting in an environmental-unfriendly process.

Our previous work (Wu et al., 2014; Zhang, Wu, Lu, & Zhou, 2015; Wu et al., 2013) demonstrated that CNC, with high aspect ratio and nanometric dispersity, could self-assemble and coat on the surface of natural rubber (NR) latex microspheres, forming a 3D network structure with several hundred nanometers to a few micrometers. This 3D network skeleton could provide a template/support for conductive fillers (e.g. polyaniline, polypyrrol and carbon black) to form an assembled network. Herein, we report an environmentally friendly approach to mediate graphene dispersion in aqueous media and its assembled morphology in NR matrix by the cheap, renewable and biodegradable CNC. In this proposed strategy, the amphipathic CNC were hybridized with graphene during reduction of GO, serving as a stabilizer or supporting agent. The obtained CNC-supported RGO had excellent aqueous suspension stability, which significantly facilitated its dispersion in NR latex. During the subsequent coagulation, the RGO@CNC nanohybrids selectively located in the interfaces between NR microspheres and assemble into a 3D hierarchical conductive network structure (Tian et al., 2014). This facile approach not only avoided the use of chemical modification agents but also improved the conductivity and mechanical properties of the graphene-based composites compared to RGO/NR composites with randomly dispersed RGO prepared by conventional processing method. Furthermore, the prepared RGO@CNC/NR nanocomposites with 3D conductive network showed high resistance sensitivity and good reproducibility under the stimuli of chemical solvents, which could be ascribed to the low percolation threshold and relatively “fragile” conductive networks. These properties made it highly attractive for the application in chemical sensors and “electronic noses” which capable of sensing, quantifying and discriminating various solvents or vapors in chemical industry, environmental monitoring and food industry, etc. To the best of our knowledge, this is the first demonstration that highly flexible, stretchable, sensitive, and reversible chemical solvent sensors can be fabricated from the conductive RGO/NR composites with this 3D hierarchical network structures tailored by CNC assisted latex assembly.

2. Materials and Methods

2.1. Materials

Phosphoric acid, potassium permanganate, sulfuric acid, hydrogen peroxide, toluene, chloroform, acetone, dimethyl formamide, stearic acid, OP emulsifier-10 and zinc oxide were all purchased from Chengdu Kelong Chemical Reagent Company

(China). Graphite powder was purchased from Sigma-Aldrich, Inc. The NR latex (solid content: 58 wt%) was provided by Chengdu Xinyuanding Co., Ltd (China). Medical purified cotton was obtained from Xuzhou Health Factory Co., Ltd (China). Vulcanization agent sulfur and accelerator N-cyclohexyl-2-benzothiazolesulfenamide (CBS) were purchased from Weihai Tianyu New Mstar Technology Co., Ltd (China).

2.2. Preparation of CNC

Cellulose nanocrystals (CNC) were prepared by controlled acid hydrolysis of cotton fibers based on our previous studies (Wu et al., 2014). Medical purified cotton (20 g) and sulfuric acid solution (350 mL, 64 wt%) were mixed at 45 °C for 45 min with magnetic stirring. The suspension was diluted 6 times to stop the hydrolysis immediately. Then, the suspension was dialyzed to remove residual acid and hydrolysate of cellulose in the suspension. The result was monitored by checking the neutrality of the dialyzate. Finally, the suspension was sonicated for 30 min at room temperature to disperse the aggregation. The solid content of the CNC suspension was measured 5 times and the mean value was calculated to be 0.63±0.02 wt%.

2.3. Preparation of GO nanosheets

GO was prepared according to the modified Hummers method (Hummers Jr & Offeman, 1958; Marcano & Kosynkin, 2010) with the oxidization of graphite powder by H₃PO₄, H₂SO₄, and KMnO₄ in an ice bath. The prepared GO nanosheets were purified by dialysis in deionized water. The solid content of the GO suspension was measured 5 times and the mean value was 0.79±0.02 wt%.

2.4. Preparation of RGO@CNC nanohybrids and neat RGO

For RGO@CNC nanohybrids, GO suspensions (12.72 g, 0.79 wt%), deionized water (80 mL) and CNC suspensions (10.65 g, 0.63 wt%) were added into a 500 mL round flask. Then, the suspension was reduced by hydrazine hydrate (0.1 g, the mass ratio of hydrazine hydrate and GO was 1:1) at 95 °C for 3 h with magnetic stirring (Ren et al., 2011). The resultant RGO@CNC nanohybrids were purified by centrifugation and redispersion cycles, washing with deionized water at 10000 r/min for 10 min until the hydrazine hydrate was completely removed. The preparation of RGO suspension was consistent with the methods above.

In order to determine the proper mass of GO used to achieve a desired loading of RGO in the nanocomposites, it was necessary to quantify the mass loss generated from reduction. In this case, an RGO aqueous dispersion produced from GO was centrifuged, dried, and weighed. This procedure was performed twice, giving a yield of GO to RGO of 65.8 wt%.

2.5. Preparation of RGO@CNC/NR and RGO/NR nanocomposites

For RGO@CNC/NR nanocomposites, a latex assembly approach was used to produce the nanocomposites. NR latex was weighed in calculated amounts to produce nanocomposites at specific loading intervals corresponding to 1, 2, 3, 4 and 5 phr of RGO. The RGO@CNC nanohybrids suspensions and NR latex were added to a beaker and stirred vigorously for 5 min until the mixture appeared homogeneous. Co-coagulation was induced by rapid addition of H₂SO₄ (1 mol/L) solution. The solid formed

upon coagulation was isolated by vacuum filtration and dried. The RGO/NR nanocomposites were prepared following the same procedure mentioned above.

2.6. Extraction of RGO@CNC and RGO skeleton

To intuitively observe and evaluate the 3D conductive network constructed with RGO@CNC skeleton in NR matrix, the unvulcanized RGO@CNC/NR nanocomposites were molded at 150 °C and 10 MPa for 5 min. Then, the RGO@CNC/NR nanocomposites were etched with toluene to remove the NR matrix. The RGO@CNC/NR sample (10/10/100 wt/wt/wt, prepared without vulcanization) was extracted (Soxhlet extraction) by toluene for 4 h. Then the extracted RGO@CNC nanohybrids skeleton was dried in drying oven at 60 °C for 12 h. The RGO skeleton was prepared following the same procedure above.

2.7. Characterization

2.7.1. TEM studies

Transmission electron microscopy (TEM) was performed using a transmission electron microscope (JEOL JEM-100CX, Japan). The diluted dispersions of CNC and RGO@CNC and RGO@CNC/NR latex were cast on copper grids for observation.

2.7.2. Zeta potential

The Zeta potential measurement was carried out using Zetasizer Nano ZS90 (Malvern Instruments Co., Britain) under room temperature. The sample was tested under a pH of 7.0.

2.7.3. Optical microscopy

Optical microscopy was used to investigate the dispersion state and microstructure of neat RGO using a microscope (UB200i, Chongqing UOP Photo electric Technology Co., Ltd., China) with a digital camera.

2.7.4. SEM studies

The morphology of the prepared materials was observed by scanning electron microscopy (SEM). The morphology of RGO@CNC/NR composites and RGO/NR composites was studied on a scanning electron microscope (Jed JSM-590LV, JEOL Inc., Japan).

2.7.5. Raman spectroscopy

Raman spectroscopy was carried out using a Horiba LabRAM HR apparatus (Horiba Co., France) with an excitation laser $\lambda=532$ nm.

2.7.6. XPS analysis

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.

2.7.7. XRD analysis

X-ray diffraction (XRD) patterns were collected on a Philips Analytical X'Pert X-diffractometer (Philips Co., Netherlands), using Cu-K radiation ($k = 0.1540 \text{ nm}$) at an accelerating voltage of 40 kV and the current of 40 mA. The data were collected from $2\theta = 5\text{--}60^\circ$ with a step interval of 0.03° . The degree of crystallinity could be relatively expressed by the percentage crystallinity index (% CrI). (Habibi, Chanzy, & Vignon, 2006) The equation used to calculate the CrI was described by Segal et al. (Segal, Creely, Martin, & Comrad, 1959) as follows:

$$CrI(\%) = [(I_{002} - I_{am})/I_{002}] \times 100 \quad (1)$$

where I_{002} is the counter reading at peak intensity at a 2θ angle close to 22° representing the crystalline part and I_{am} is the counter reading at peak intensity at 2θ close to 18° representing the amorphous part in cellulose.

2.7.8. The electric conductivity test

The electric conductivity of the samples was measured 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 (45 mm $\times$ 10 mm $\times$ 1 mm) or circular samples (100 mm in diameter, 1 mm thick) were used for electrical measurement. The measured volume resistance (Ω), R_v was converted to volume resistivity, ρ_v according to ASTM D4496 and D257 using the formula (2):

$$\rho_v = R_v A / t \quad (2)$$

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

2.7.9. Mechanical properties test

Mechanical properties measurement was conducted on a versatile testing machine (Instron-5560 electronic universal material testing machine, USA) at room temperature according to ASTM standards D412. The vulcanized rectangle specimens (45 mm $\times$ 10 mm $\times$ 1 mm) were stretched at a crosshead rate of 100 mm/min. The experimental vulcanization formula is given in Table S1.

2.7.10. Solvent sensing test

A resistance meter (UT61, Uni-Trend, China) was used to monitor the electrical resistance change of the rectangle samples (20 mm $\times$ 10 mm $\times$ 1 mm). The resistance values were real time recorded. The relative change of electrical resistance (R_{rel}) was evaluated by means of eqn (3):

$$R_{rel} = (R_t - R_0) / R_0 \times 100\% \quad (3)$$

Where R_0 is the initial resistance and R_t the resistance at time t .

A measurement cycle consisted of an immersion and drying step. The immersion was carried out under room temperatures. For the drying step, the samples were lifted up and remaining solvent drops were wiped off at drying oven and 60°C for 30 min. The samples were tested in toluene, chloroform, dimethyl formamide and acetone, respectively.

3. Results and discussion

3.1. Preparation and characterization of RGO@CNC/NR nanocomposites with 3D conductive network

In order to better understand the formation mechanism of RGO@CNC/NR nanocomposites with 3D conductive network, the entire experimental process is schematically illustrated in Fig. 1. CNC were derived from cellulose by the controlled acid hydrolysis of cotton fibers. When GO was added into the CNC suspensions under magnetic stirring, amphiphilic CNC could self-assemble on the surface of GO nanosheets due to the interfacial interaction between hydroxyl groups of CNC and oxygen-containing groups of GO. After the reduction of GO, CNC could facilitate the stable dispersion of RGO in aqueous media due to the stereo-hindrance effect according to the colloidal stability theory and Pickering emulsion model (Kalashnikova & Kalashnikova, 2011, 2012). Fig. S1 and S2 show that hydrazine hydrate was a very effective reductant for GO. Then, the well suspended RGO@CNC nanohybrids could be easily dispersed into the NR latex by magnetic stirring. During the subsequent coagulation process, the CNC were able to induce RGO to locate in the interstitial spaces between the NR latex microspheres. After vacuum filtration, washing and drying, the solid NR microspheres created an excluded volume and essentially pushed the RGO@CNC nanohybrids into the interstitial spaces between them to form a continuous 3D conductive network in the NR matrix.

Fig. 2 illustrates the microstructures of pristine CNC, neat RGO nanosheets and RGO@CNC nanohybrids. As shown in Fig. 2a, needle-like CNC with 10-20 nm in diameter and 100-300 nm in length can be clearly observed. The crystalline structure of CNC was characterized also by XRD analysis as shown in Fig. S3. Aggregated RGO suspensions are observed in Fig. 2b using optical microscopy. Large-scale aggregates of RGO nanosheets with a diameter of dozens to hundreds of microns can be clearly observed, indicating the poor dispersity of neat RGO suspensions. Fig. 2c and 2d illustrate that the added CNC self-assembled on the RGO single layers and formed veined RGO@CNC structure. These results demonstrate that the CNC are able to mediate the dispersion of RGO nanosheets and prevent aggregation between the graphene layers, and obtain well dispersed RGO@CNC suspensions which is beneficial to forming 3D continuous conductive networks.

The Zeta potential (ZP, ξ potential) is a crucial parameter to evaluate suspension stability. It is necessary for a stable suspension solely stabilized by electrostatic repulsion to have a ξ potential absolute value higher than 30 mV (Cabuk et al., 2014). The ξ potential values as well as the suspension performance of CNC and RGO@CNC nanohybrids were evaluated in a neutral environment. The ξ potential of the CNC was -32.1 mV, which demonstrated the excellent suspension property of CNC. This might be attributed to the sulfate ester groups on the CNC which could electrostatically stabilize the CNC. For the RGO@CNC nanohybrids, the ξ potential was measured to be -30.9 mV, which was slightly lower than that of CNC as a result of the hybridization of CNC with RGO. Nevertheless, the ξ potential of neat RGO (-2.2 mV) was much lower than that of the RGO@CNC nanohybrids. For comparison, as shown in Fig. 3a and 3b, the RGO@CNC nanohybrids suspension remained stable after standing for 24 h, while the neat RGO suspension showed complete sedimentation within several minutes. These results indicate that the CNC could serve as a stabilizer and enhance the suspension stability of neat RGO, which facilitates the

fabrication of a RGO-based 3D conductive structure in a NR matrix. In addition, the excellent suspension stability of RGO@CNC nanohybrids in water might have potential applications in waterborne inks, water-based antistatic coatings and so on.

To evaluate the feasibility of the RGO@CNC nanohybrids in the construction of 3D conductive network, we prepared RGO@CNC/NR nanocomposites by an eco-friendly latex assembly approach according to our previous studies (Wu, Lu, Zhou, & Zhang, 2015; Wu et al., 2014). The morphology of the blended suspension of RGO@CNC nanohybrids and NR latex was characterized by TEM observation as shown in Fig. S4. The RGO@CNC nanohybrids partly wrap on the NR latex microspheres, which is the prototype of the 3D conductive network. Because graphene nanosheets are ultrathin, flexible and difficult to keep their spatial conformation, RGO@CNC nanohybrids are apt to locate in the interstitial spaces between the NR latex microspheres and construct a 3D conductive network (Yang et al., 2014).

To intuitively observe and evaluate the 3D conductive structure fabricated with the RGO@CNC nanohybrids in the NR matrix, the unvulcanized NR nanocomposite was etched with toluene to remove the NR matrix. The residual RGO@CNC nanohybrid skeleton was characterized by SEM. As shown in Fig. 4a and 4b, uniformly porous network of the RGO@CNC nanohybrids is observed clearly, suggesting the existence of the designed 3D network structure in the NR matrix. For comparison, the morphology of the extracted RGO skeleton prepared by traditional method is shown in Fig. 4c and d. Aggregated RGO nanosheets are observed clearly. The size of these RGO nanosheets is larger than 20 μm , which is consistent with the optical microscope observation (Fig. 2b). The results show that the uniform porous network was benefited from the excellent dispersion of RGO@CNC nanohybrids and its selective location in the interstitial space between the NR microspheres, which was attributed to the mediating and templating effects of the CNC. This ordered 3D network structure is expected to realize the enhancement of electrical conductivity as well as the mechanical properties of the RGO@CNC/NR nanocomposites.

3.2. Enhancement of electric conductivity and mechanical properties of RGO@CNC/NR nanocomposites

Differences in nanocomposites morphology may have a significant impact on the electrical conductivity and mechanical properties. The highly ordered 3D RGO@CNC network structure undoubtedly can make a great contribution to the enhancement of materials properties. Fig. 5 shows the conductivity variation of the RGO@CNC/NR nanocomposites as a function of RGO volume fraction. The CNC mediated RGO nanocomposites show a much lower electrical conductivity percolation threshold and higher electrical conductivity values than that of the RGO/NR nanocomposites without CNC. The critical amount of conductive filler required to cause the insulator-to-conductor transition is known as the percolation threshold. The percolation threshold of RGO@CNC/NR nanocomposites is only 0.66 vol%, much lower than that of the RGO/NR nanocomposites without a RGO network (1.17 vol%). Moreover, the conductivity of RGO@CNC/NR nanocomposites with a RGO loading of 0.83 vol% is $3.98 \times 10^{-4} \text{ S/m}$, which is more than 10 orders of magnitude higher than that of the RGO/NR nanocomposites ($8.84 \times 10^{-15} \text{ S/m}$) at the same loading (Potschke et al., 2010).

The outstanding conductivity is absolutely benefited from the unique 3D network structure of RGO in the nanocomposites. The renewable **CNC** can mediate and induce the RGO filler to form an intact connected path through the insulating NR matrix with its content as low as possible, and hence, it can be regarded as an attractive electrical percolation material for resistivity-response applications.

The morphology, dispersity and the size of conductive filler have significant effects on mechanical properties. Fig. 6 shows the representative stress-strain curves of neat NR, RGO/NR, RGO@**CNC**/NR nanocomposites. Composites reinforced with RGO and RGO@**CNC** nanohybrids present better tensile strength and higher Young's modulus than the neat NR, indicating the reinforcement effect of these fillers. Compared with neat NR, the tensile strength of RGO@**CNC**/NR-2.08% is increased by 646.2%, while the tensile strength of RGO/NR-2.08% is increased by 196.1%. Meanwhile, the Young's modulus of RGO@**CNC**/NR-2.08% is 4.6 times of the neat NR. The results indicate that RGO@**CNC** nanohybrid is more efficient for reinforcing NR due to the high aspect ratio and crystallinity of **CNC**. On the other hand, the improved dispersity of RGO@**CNC** with the introduction of **CNC**, might play an important role in the enhancement of mechanical properties of the NR-based composites (Xu, Liu, Jiang, & Zhu, 2013; Yao et al., 2014). The results demonstrate that the combination of **CNC**-stabilizing effect and latex assembly method can improve the electrical conductivity as well as mechanical performance of NR-based composites simultaneously.

3.3. Resistivity-response of RGO@**CNC**/NR nanocomposites stimulated by organic solvent

The 3D RGO@**CNC**/NR nanocomposites can be further used to efficiently detect organic liquids, because they have high electrical conductivities, large liquid sensing capacities and good reproducibility due to the well-constructed 3D structure and low percolation threshold. In order to describe the liquid sensitivity of these RGO@**CNC**/NR nanocomposites with 3D conductive network, the R_{rel} of the samples with RGO loading of 2.08 vol% immersing in different organic solvents (toluene, chloroform, acetone and dimethyl formamide) as a function of time was recorded. Fig. 7a shows the typical resistivity response of RGO@**CNC**/NR nanocomposites to toluene. Clearly, the R_{rel} increases slowly in the first 120 s, and then, increases rapidly and reaches a very high value of 2.05×10^4 %. This fast response indicates that the RGO@**CNC**/NR nanocomposites are very sensitive to toluene. After immersion, the sample was dried in drying oven at 60 °C. In this case, the R_{rel} drops fast at the beginning and then gradually into balance. Fig. 7b shows the repeatability of liquid sensitivity behavior of the 3D network structured composites when the composites are immersed into toluene. Toluene is detected reproducibly with a short response time during the five immersion-drying cycles, which indicates the easy disconnection and recovery of the conducting paths in the 3D conductive network structure, indicating the high potential of these composites for the fabrication of high performance liquid sensing materials. Fig. 7c shows the resistivity responses of RGO@**CNC**/NR nanocomposites under the stimuli of different organic solvents. The R_{rel} values for chloroform, dimethyl formamide and acetone are 2.05×10^4 %, 50% and 220%, respectively. This result suggests that the RGO@**CNC**/NR nanocomposites have remarkable liquid response sensitivity for toluene and chloroform.

Meanwhile, the solvent response time for chloroform is much longer than that of toluene. The resistivity changes are attributed to the different solubility parameter between the NR and the used organic solvents. The solubility parameter of NR, toluene, chloroform, dimethyl formamide and acetone are 8.5, 8.9, 9.6, 9.9 and 12.1, respectively. Because of the similarity of toluene with that of NR, toluene can swell the RGO@CNC network and easily disconnect the RGO conductive paths. Thus, toluene showed the greatest liquid sensing behavior (Pang et al., 2013).

The superior liquid sensing performance combined with the balanced electrical conductivity and good reproducibility at a low RGO loading can be well understood by considering the microstructural developments in the 3D conductive network composites during the liquid sensing tests. The original samples show a perfect 3D conductive network of RGO with high electrical conductivity at a low RGO loading. Nevertheless, the samples swell when exposed to a volatile organic solvent, causing the disconnection of the RGO network, and thus leading to a decrease of conductivity. During the immersing-drying process, the desorption of the solvents resulted in the reestablishment of the RGO network (Qi, Mäder, & Liu, 2013; Fan, Qin, & Villmow, 2011; Potschke et al., 2010).

4. Conclusions

We demonstrated a simple, eco-friendly and scalable approach to prepare NR composites with 3D conductive network via the renewable CNC-mediated assembly of graphene nanosheets in NR latex. The assembled conductive structure played a key role to improve electric conductivity and mechanical properties of NR/graphene composites. Furthermore, the unique “fragile” but effective conductive network with low percolation threshold facilitated the disconnection and reestablishment of conductive paths under the stimulation of organic solvents, exhibited high resistivity responses and good reproducibility. This work offers not only a feasible approach to enhance electric conductivity and mechanical properties of conductive NR composites but also an extremely simple model system for high performance sensing materials with superior resistivity responses for organic liquids.

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References

Bai, H., Xu, Y. X., Zhao, L., Li, C., & Shi, G. Q. (2009). Non-covalent functionalization of graphene sheets by sulfonated polyaniline. *Chemical Communications*, 13, 1667-1669.

294 Cabuk, M., Alan, Y., Yavuz, M., & Unal, H. I. (2014). Synthesis, characterization and antimicrobial activity of biodegradable
 295 conducting polypyrrole-graft-chitosan copolymer. *Applied Surface Science*, 318, 168-175.

296 Salas, C., NypelÖ, T., Rodriguez-Abreu, C., Carrillo, C., Rojas, O. J. (2014). Nanocellulose properties and applications in
 297 colloids and interfaces. *Current Opinion in Colloid & Interface Science*, 19, 383-396.

298 Chen, Y. K., Zhang, Y. B., Xu, C. H., & Cao, X. D. (2015). Cellulose nanocrystals reinforced foamed nitrile rubber
 299 nanocomposites. *Carbohydrate Polymers*, 130, 149-154.

300 Danial, W. H., Majid, Z. A., Muhid, M. N. M., Triwahyono, S., Bakar, M. B., & Ramli, Z. (2015). The reuse of wastepaper for
 301 the extraction of cellulose nanocrystals. *Carbohydrate Polymers*, 118, 165-169.

302 Fan, Q. Q., Qin, Z. Y., & Villmow, T. (2011). Vapor sensing properties of thermoplastic polyurethane multifilament covered
 303 with carbon nanotube networks. *Sensors and Actuators B-Chemical*, 156, 63-70.

304 Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene. *Nature Materials*, 6, 183-191.

305 Habibi, Y., Chanzy, H., & Vignon, M. R. (2006). TEMPO-mediated surface oxidation of cellulose whiskers. *Cellulose*, 13, 679–
 306 687.

307 Hsiao, M. C., Liao, S. H., Yen, M. Y., Liu, P. L., Pu, N. W., Wang, C. A., & M. Ma, C. C. (2010). Preparation of covalently
 308 functionalized graphene using residual oxygen-containing functional groups. *ACS Applied Materials & Interfaces*, 2, 3092-
 309 3099.

310 Hummers Jr, W. S., & Offeman, R. E. (1958). Preparation of graphitic oxide. *Journal of the American Chemical Society*, 80,
 311 1339.

312 Hu, F., Lin, N., Chang, P. R., & Huang, J. (2015). Reinforcement and nucleation of acetylated cellulose nanocrystals in foamed
 313 polyester composites. *Carbohydrate Polymers*, 129, 208-215.

314 Kalashnikova, I., Bizot, H., Cathala, B., & Capron, I. (2011). Modulation of cellulose nanocrystals amphiphilic properties to
 315 stabilize oil/water interface. *Biomacromolecules*, 13, 267-275.

316 Kalashnikova, I., Bizot, H., Cathala, B., & Capron, I. (2012). New Pickering emulsions stabilized by bacterial cellulose
 317 nanocrystals. *Langmuir*, 27, 7471-7479.

318 Kamal, M. R., & Khoshkava, V. (2015). Effect of cellulose nanocrystals (CNC) on rheological and mechanical properties and
 319 crystallization behavior of PLA/CNC nanocomposites. *Carbohydrate Polymers*, 123, 105-114.

320 Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: fascinating biopolymer and sustainable raw material.
321 *Angewandte Chemie-International Edition*, 44, 3358-3393.

322 Kuila, T., Khanra, P., Bose, S., Kim, N. H., Ku, B. C., Moon, B., & Lee, J. H. (2011). Preparation of water-dispersible graphene
323 by facile surface modification of graphite oxide. *Nanotechnology*, 22, 305710.

324 Lee, C. G., Wei, X. D., Kysar, J. W., & Hone, J. (2008). Measurement of the elastic properties and intrinsic strength of
325 monolayer graphene. *Science*, 321, 385-388.

326 Li, D., Muller, M. B., Gilje, S., Kaner, R. B., & Wallace, G. G. (2008). Processable aqueous dispersions of graphene nanosheets.
327 *Nature Nanotechnology*, 3, 101-105.

328 Lizundia, E., Vilas, J. L., & León, L. M. (2015). Crystallization, structural relaxation and thermal degradation in Poly(L-
329 lactide)/cellulose nanocrystal renewable nanocomposites. *Carbohydrate Polymers*, 123, 256-265.

330 Marcano, D. C., & Kosynkin, D. V. (2010). Improved synthesis of graphene oxide. *ACS Nano*, 4, 4806-4814.

331 Naeimi, H., & Golestanzadeh, M. (2014). Highly sulfonated graphene and graphene oxide nanosheets as heterogeneous
332 nanocatalysts in green synthesis of bisphenolic antioxidants under solvent free conditions. *RSC Advances*, 4, 56475-56488.

333 Ning, N. Y., Wang, Z. F., Yao, Y., Zhang, L. Q., & Tian, M. (2015). Enhanced electromechanical performance of bio-based
334 gelatin/glycerin dielectric elastomer by cellulose nanocrystals. *Carbohydrate Polymers*, 130, 262-267.

335 Niyogi, S., Bekyarova, E., Itkis, M. E., McWilliams, J. L., Hamon, M. A., & Haddon, R. C. (2006). Solution properties of
336 graphite and graphene. *Journal of the American Chemical Society*, 128, 7720-7721.

337 Pang, H., Bao, Y., Xu, L., & Li, Z. M. (2013). Double-segregated carbon nanotube-polymer conductive composites as candidates
338 for liquid sensing materials. *Journal of Materials Chemistry A*, 1, 4177-4181.

339 Potschke, P., Andres, T., Villmow, T., & Pegel, S. (2010). Liquid sensing properties of fibres prepared by melt spinning from
340 poly(lactic acid) containing multi-walled carbon nanotubes. *Composites Science and Technology*, 70, 343-349.

341 Potts, J. R., Shankar, O., Du, L., & Ruoff, R. S. (2012). Processing-morphology-property relationships and composite theory
342 analysis of reduced graphene oxide/natural rubber nanocomposites. *Macromolecules*, 45, 6045-6055.

343 Qi, H. S., Mäder, E., & Liu, J. W. (2013). Unique water sensors based on carbon nanotube-cellulose composites. *Sensors and*
344 *Actuators B-Chemical*, 185, 225-230.

345 Qiu, B., Xu, C. X., Sun, D. Z., Yi, H., & Wei, S. Y. (2014). Polyaniline coated ethyl cellulose with improved hexavalent
346 chromium removal. *ACS Sustainable Chemistry & Engineering*, 2, 2070-2080.

347 Ren, P. G., Yan, D. Y., Ji, X., Chen, T., & Li, Z. M. (2011). Temperature dependence of graphene oxide reduced by hydrazine
348 hydrate. *Nanotechnology*, 22, 5.

349 Rezayat, M., Blundell, R. K., Camp, J. E., Walsh, D. A., & Thielemans, W. (2014). Green one-step synthesis of catalytically
350 active palladium nanoparticles supported on cellulose nanocrystals. *ACS Sustainable Chemistry & Engineering*, 2, 1241-1250.

351 Salavagione, H. J., Gomez, M. A., & Martinez, G. (2009). Polymeric modification of graphene through esterification of graphite
352 oxide and poly(vinylalcohol). *Macromolecules*, 42, 6331-6334.

353 Scherillo, G., Lavorgna, M., Buonocore, G. G., Zhan, Y. H., Xia, H. S., Mensitieri, G., & Ambrosio, L. (2014). Tailoring
354 assembly of reduced graphene oxide nanosheets to control gas barrier properties of natural rubber nanocomposites. *ACS*
355 *Applied Materials & Interfaces*, 6, 2230-2034.

356 Segal, L., Creely, J. J., Martin, A. E., Jr., & Comrad, C. M. (1959). An empirical method for estimating the degree of crystallinity
357 of native cellulose using the X-ray diffractometer. *Textile Research Journal*, 29, 786-794.

358 Stankovich, S., Piner, R. D., Chen, X., Wu, N., Nguyen, S. T., & Ruoff, R. S. (2006). Stable aqueous dispersions of graphitic
359 nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate). *Journal of*
360 *Materials Chemistry*, 16, 155-158.

361 Tang, Z. H., Lei, Y. D., Guo, B. C., & Zhang, L. Q. (2012). The use of rhodamine B-decorated graphene as a reinforcement in
362 polyvinyl alcohol composites. *Polymer*, 53, 673-680.

363 Tian, M., Ma, Q., Li, X. L., Zhang, L. Q., Nishi, T., & Ning, N. Y. (2014). High performance dielectric composites by latex
364 compounding of graphene oxide-encapsulated carbon nanosphere hybrids with XNBR. *Journal of Materials Chemistry A*, 2,
365 11144-11154.

366 Worsley, K. A., Ramesh, P., Mandal, S. K., Niyogi, S., Itkis, M. E., & Haddon, R. C. (2007). Soluble graphene derived from
367 graphite fluoride. *Chemical Physics Letters*, 445, 51-56.

368 Wu, X. D., Lu, C. H., Xu, H. Y., Zhang, X. X., & Zhou, Z. H. (2014). Biotemplate synthesis of polyaniline@cellulose
369 nanocrystals/natural rubber nanocomposites with 3D hierarchical multiscale structure and improved electrical conductivity.
370 *ACS Applied Materials & Interfaces*, 6, 21078-21085.

371 Wu, X. D., Lu, C. H., Zhang, W., Yuan, G. P., Xiong, R., & Zhang, X. X. (2013). A novel reagentless approach for synthesizing
372 cellulose nanocrystal-supported palladium nanoparticles with enhanced catalytic performance. *Journal of Materials Chemistry*
373 *A, 1*, 8645-8652.

374 Wu, X. D., Lu, C. H., Zhou, Z. H., & Zhang X. X. (2015). Conductive natural rubber/carbon black nanocomposites via cellulose
375 nanowhisker templated assembly: tailored hierarchical structure leading to synergistic property enhancements. *Journal of*
376 *Materials Chemistry A, 3*, 13317-13323.

377 Wu, X., Lu, C., Zhou, Z., Yuan, G., Xiong, R., & Zhang X. (2014). Green synthesis and formation mechanism of cellulose
378 nanocrystal-supported gold nanoparticles with enhanced catalytic performance. *Environmental Science-Nano, 1*, 71-79.

379 Xiong, R., Lu, C. H., Zhang, W., Zhou, Z. H., & Zhang, X. X. (2013). Facile synthesis of tunable silver nanostructures for
380 antibacterial application using cellulose nanocrystals. *Carbohydrate Polymers, 95*, 214-219.

381 Xu, X. Z., Liu, F., Jiang, L., Zhu, J. Y., Haagenson, D., & Wiesenborn, D. P. (2013). Cellulose nanocrystals vs. cellulose
382 nanofibrils: a comparative study on their microstructures and effects as polymer reinforcing agents. *ACS Applied Materials &*
383 *Interfaces, 5*, 2999-3009.

384 Yan, D. X., Pang, H., Li, B., Vajtai, R., Xu, L., Ren, P. G., Wang, J. H., & Li, Z. M. (2015). Structured reduced graphene
385 oxide/polymer composites for ultra-efficient electromagnetic interference shielding. *Advanced Functional Materials, 25*, 559-
386 566.

387 Yang, L., Wang, Z. Q., Ji, X. C., Wang, J. L., & Xue, G. (2014). Highly ordered 3D graphene-based polymer composite materials
388 fabricated by "particle-constructing" method and their outstanding conductivity. *Macromolecules, 47*, 1749-1756.

389 Yao, X. L., Qi, X. D., He, Y. L., Tan, D. S., Chen, F., & Fu, Q. (2014). Simultaneous reinforcing and toughening of polyurethane
390 via grafting on the surface of microfibrillated cellulose. *ACS Applied Materials & Interfaces, 6*, 2497-2507.

391 Yoonessi, M., & Gaier, J. R. (2010). Highly conductive multifunctional graphene polycarbonate nanocomposites. *ACS Nano, 4*,
392 7211-7220.

393 Zhang, C., Zhang, R. Z., Ma, Y. Q., & Guan, W. B. (2015). Preparation of cellulose/graphene composite and its applications for
394 triazine pesticides adsorption from water. *ACS Sustainable Chemistry & Engineering, 3*, 396-405.

395 Zhang, X. X., Wu, X. D., Lu, C. H., & Zhou, Z. H. (2015). Dialysis-free and in situ doping synthesis of polypyrrole@cellulose
396 nanocrystals nanohybrid for preparation of conductive nanocomposites with enhanced properties. *ACS Sustainable Chemistry*
397 *& Engineering*, 3, 675-682.

Figure Captions

Fig. 1 Schematic illustration of RGO@CNC/NR nanocomposites with 3D conductive network.

Fig. 2 TEM image of CNC (a), optical microscope image of neat RGO nanosheets (b), TEM image of RGO@CNC nanohybrids (c, d).

Fig. 3 Digital pictures of RGO and RGO@CNC nanohybrids aqueous dispersions before (a) and after (b) standing for 24 h.

Fig. 4 SEM images of the extracted RGO@CNC nanohybrids skeleton from RGO@CNC/NR nanocomposites (a, b) and RGO skeleton from RGO/NR nanocomposites (c, d) by toluene.

Fig. 5 Electrical conductivity of RGO/NR and RGO@CNC/NR nanocomposites as a function of RGO content.

Fig. 6 Stress-strain curves of neat NR (a), RGO/NR (1.25 vol% of RGO) (b), RGO@CNC/NR (1.25 vol% of RGO) (c), RGO@CNC/NR (2.08 vol% of RGO) (d) and RGO@CNC (2.08 vol% of RGO) (e) nanocomposites.

Fig. 7 Responsivity-time relationship for the RGO@CNC/NR nanocomposites filled with 2.08 vol% RGO when exposed to toluene at first time (a) and during five immersion-drying runs (b), as well as when exposed to different solvents (c).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7