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A facile one-step method for graphene oxide/natural rubber latex nanocomposite production for supercapacitor applications

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ABSTRACT

A new and facile one-step method to synthesise graphene oxide/natural rubber latex (GO/NRL) nanocomposite was achieved using an electrochemical exfoliation method. In this method, the fabrication of GO/NRL nanocomposite occurs concurrently with GO production that is intermixed with NRL. This approach is a simple and innovative method that succeeded in producing nanocomposite with better conductivity. The samples were characterized using FESEM, HRTEM, FT-IR, UV–vis, micro-Raman spectroscopy, XRD, TGA, *I*–*V* and *C*–*V* measurements. The *C*–*V* analysis showed that the specific capacitance of the samples prepared via the one-step method was 103.7 F g^{-1}, much better than those produced via a two-step method (32.6 F g^{-1}). These results were also consistent with the *I*–*V* analysis, in which a higher conductivity value was measured for the one-step method (7.12×10^{-5} S cm^{-1}) than for the two-step method (3.62×10^{-7} S cm^{-1}). In conclusion, the one-step method introduced for the fabrication of GO/NRL nanocomposite is a promising method for implementation in supercapacitor applications.

1. Introduction

Graphene oxide (GO), defined as sp^2-hybridised planar carbon sheets that are highly oxidised by oxygen functional groups, is widely used in electronics applications [1]. Various methods for GO production have been reported elsewhere [1]. Among them is Hummer's method, which has been widely used for GO production due to its easy scale-up. However, it involves strong acids and hazardous chemicals that would be detrimental to the environment if implemented industrially at a large scale. At present, the electrochemical exfoliation method is a greener, simpler and more convincing method for producing high-quality GO in large quantity. This is due to the lower chemical utilisation by this method and its ability to be easily carried out in a water-based medium. One possible route to exploiting graphene's properties is incorporating it into polymer composites as a nanofiller, with the potential of application as electrode materials.

Several approaches have been reported for the preparation of GO/natural rubber latex (NRL) nanocomposite, including latex technology [2], solution mixing [3], and a twin-roll milling process [4]. Generally, the conventional mixing method of GO/NRL nanocomposite involves a method of two steps, which are (1) producing GO and (2) mixing the GO with NRL to fabricate the nanocomposite. However, the complexity of the preparation makes these methods time-consuming and expensive. Moreover, the distribution of the GO sheets in the NRL polymer through the conventional two-roll mixing method, for example, is uneven [4]. Therefore, a simpler route for the production of GO/NRL nanocomposite needs to be developed, especially for the purpose of increasing the homogeneity of the fillers in the matrices.

The selection of NRL polymer, which is mostly applied in rubber-based industries, is beneficial as this natural polymer exhibits the highest tensile strength among synthetic rubbers [5]. It is cheap, easily accessible and exists in an aqueous form that is highly compatible with aqueous dispersions of GO. The NRL consists of cis-1,4-polyisoprene and non-rubber materials [6–7], which are believed to easily react with GO sheets to form stronger nanocomposite with improved electrical conductivity compared to conducting polymers such as polyaniline [8] and polypyrrole [9], which also need further modification before incorporation with the aqueous GO, or synthetic rubbers, which are difficult to process unless blended together with other curing agents and consume chemicals used as solvents. The addition of GO to NRL has been proven to enhance the mechanical, thermal and electrical

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properties of the material [10,11]. Nevertheless, there has been no report on the potential application of GO/NRL nanocomposite as electrodes in energy storage devices. Most studies have been limited to the mechanical, thermal and electrical enhancements of GO/NRL nanocomposite [10,11]. The study of the possible application of GO/NRL nanocomposite as a new electrode material is necessary to broaden its forthcoming applications.

In this work, we introduce a facile one-step method to produce GO/NRL nanocomposite using an electrochemical exfoliation method. In this method, the fabrication of GO/NRL nanocomposite occurs together with GO production, which is intermixed with NRL for nanocomposite of better homogeneity. The one-step method adopted in this study is a convenient approach for the fabrication of GO/NRL nanocomposite, and we also demonstrate its potential use as an electrode material for supercapacitor devices.

2. Materials and methods

GO was synthesised through an electrochemical exfoliation method assisted by a surfactant, SDS, in a concentration of 0.01 M. The one-step method to fabricate GO/NRL nanocomposite was achieved via intermixing GO into the NRL at a volume ratio of 1:1. The dispersions obtained were then subjected to mechanical stirring and bath sonication for 2 h. The dispersions were drop-casted into a $5 \times 5\ \text{cm}^2$ container and dried in an oven overnight. For comparison with the conventional (two-step) mixing method for nanocomposite production, the following procedures were followed: (i) production of GO in 0.01 M SDS and (ii) fabrication of 1:1 volume ratio GO/NRL nanocomposite via similar stirring and ultrasonication processes. The samples were characterized using FESEM, HRTEM, FT-IR, micro-Raman, XRD, TGA, UV–vis spectroscopy, four-point probe and cyclic voltammetry measurements (see Supplementary material).

3. Results and discussion

Before the mixing of the GO into the NRL, several initial characterizations were performed on the pristine GO. An FESEM image of the GO (Fig. 1(a)) shows rose-like structures with thin and almost transparent sheets. The oxidation process presumably caused the wavy structure of the GO obtained. The HRTEM results confirmed that the folded-up graphitic layers observed at the edges of the GO were oxidised (Fig. 1(b)). The oxidation process on the GO was further confirmed by the presence of oxygenous groups in FT-

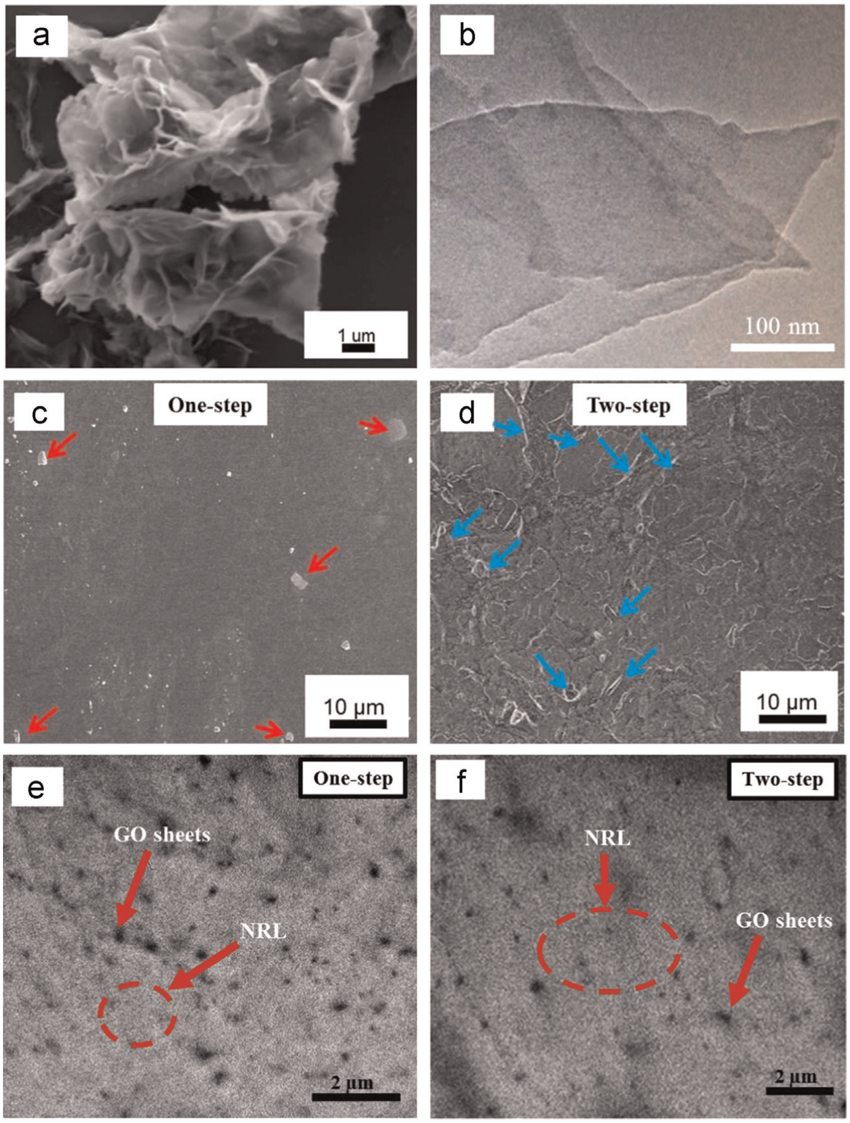

Fig. 1. (a) FESEM and (b) HRTEM images of pristine GO, (c,d) FESEM and (e,f) HRTEM images of GO/NRL nanocomposite.

IR and the absorption peak at 230 nm in the UV–vis spectrum, as presented in the Supplementary material.

After the one-step intermixing of the GO into the NRL, a fairly smooth surface with several agglomerations of GO was observed (Fig. 1(c)). The result obtained was due to the interfacial interaction between the GO and the NRL matrix (shown by →). This was further confirmed by FT-IR spectroscopy, where a lowered intensity of the hydroxyl groups was observed due to the interaction between the NRL and the oxygen functional groups of GO sheets. In contrast, a rough and fractured surface was observed in nanocomposite produced via the conventional mixing method (Fig. 1(d)). There are several parts showing the high degree of agglomerated GO surfaces, which is due to the inhomogeneous GO distribution in the matrix (shown by →). HRTEM micrographs also reveal that the nanocomposite sample produced via the one-step method (Fig. 1(e)) has a more uniform dispersion of the GO particles (indicated by →) compared to the sample prepared via the conventional mixing method (Fig. 1(f)).

The crystallinity of the samples was characterized using micro-Raman and XRD spectroscopy. A moderate I_D/I_G ratio of pristine GO of 1.04 was found from micro-Raman analysis. After the addition of NRL, the two-step method produces a higher I_D/I_G ratio (1.40) than the one-step method (1.36). The shifted peak of the GO in the XRD patterns of the nanocomposite samples further confirmed the interaction of GO with NRL. This was also supported by the TGA analysis, which found that only a small amount of decomposition was observed in the two-step method, which indicates that a minimal amount of GO was intercalated within the NRL. Further micro-Raman, XRD and TGA analyses are presented in the Supplementary material.

Fig. 2(a) and (b) shows the *C*–*V* curves of the nanocomposite electrodes. The leaf-like shape observed indicates the good capacitive behaviour of the redox reaction. The calculated specific capacitance of nanocomposite prepared via the one-step method was found to be 103.7 F g^{-1}, which is higher than that of the two-step method (32.6 F g^{-1}). The result obtained for the one-step method was comparable to that of a previous study [12]. These results were also consistent with the *I*–*V* analysis, in which a higher conductivity value was measured for the one-step method (7.12×10^{-5} S cm^{-1}) than for the two-step method (3.62×10^{-7} S cm^{-1}) (see Supplementary material). This result paves the way to the development of new supercapacitor applications based on GO/NRL nanocomposite.

The suggested mechanism for the fabrication of GO/NRL nanocomposite is illustrated in Fig. 3. The exfoliation process of GO can be described based on mechanisms proposed by Lu et al. [13]. The OH and O radicals derived from the anodic oxidation of H_2O opens up edge sheets in the oxidative cleavage reaction. This facilitates the non-covalent intercalation of the SDS surfactant of the hydrophobic tail group within the graphite layers. The weak bonding force between the graphite layers leads to exfoliation and precipitation as GO sheets (first figure in Fig. 3(a)). After the formation of the GO solution, the NRL was subsequently mixed, as is usually done in the two-step method (Fig. 3(a)). The hydrophilic headgroup of the SDS was forced to interact with the NRL particles that were covered by both positive and negative charges of protein and phospholipid molecules (second figure in Fig. 3(a)) [2,6,14,15]. The NRL was then directly linked and self-arranged along the surface of the surfactant tail coated GO (third figure in Fig. 3(a)). However, through this conventional mixing, only one tail group connected between the GO and NRL, demonstrating a 1:1 interaction ratio (shown by → in Fig. 3(a)). Compared to the one-step method, an increase in the electrical conductivity was contributed by the tail numbers that connect the GO and NRL (shown by → in Fig. 3(b)) [16]. This occurred due to the negatively charged hydrophilic headgroup that was initially directed towards the NRL, providing sufficient interactions between the GO and NRL before the surfactant tails were intercalated into the graphite layers (second figure in Fig. 3(b)) [2,6,7,16]. Through this approach, the interaction between the GO and NRL increased compared to the two-step method. The interaction of GO and NRL was most likely further enhanced by the 5 V supplied during the intermixing process. Hence, the GO/NRL nanocomposite prepared via this facile one-step method offer better electrical and capacitive performances than those produced by the two-step method.

4. Conclusion

A new and simple fabrication of GO/NRL nanocomposite via a one-step method was introduced and found to enhance the electrical properties of the nanocomposite. The higher specific capacitance of one-step GO/NRL nanocomposite was also measured (103.7 F g^{-1}) than that of the nanocomposite produced via a two-step method (32.6 F g^{-1}). Thus, the produced GO/NRL nanocomposites have potential applications in energy storage devices, such as supercapacitors.

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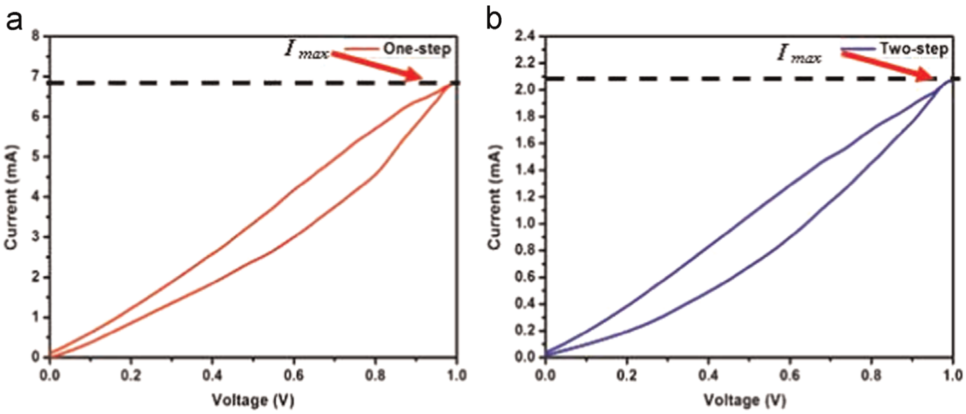

Fig. 2. (a) and (b) *C*–*V* characteristics of GO/NRL nanocomposite.

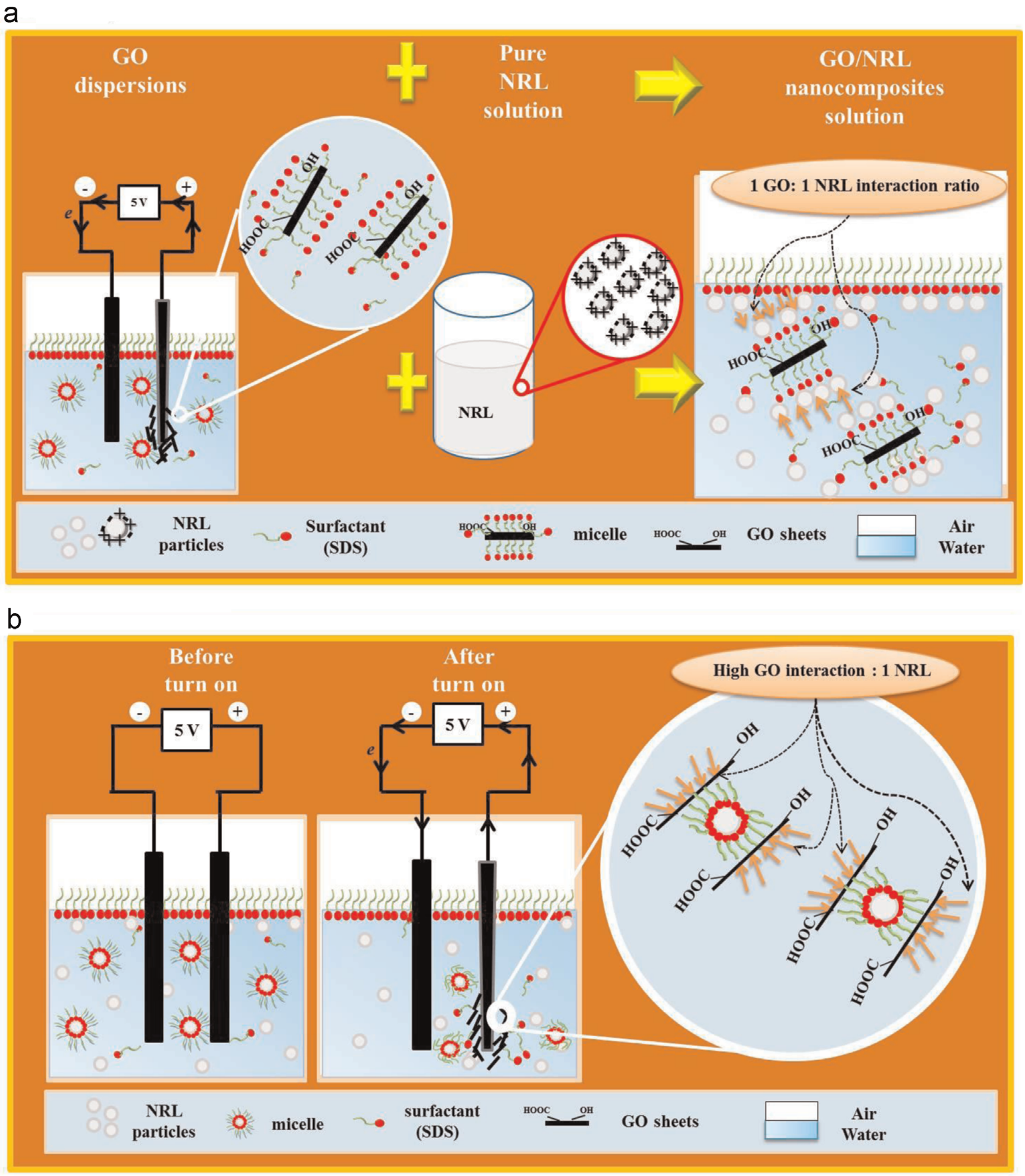

Fig. 3. Schematic growth mechanism of GO/NRL nanocomposite.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2015.09.050.

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