

Facile Synthesis of Soluble Graphene via a Green Reduction of Graphene Oxide in Tea Solution and Its Biocomposites

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S Supporting Information

ABSTRACT: The chemical reduction of graphene oxide (GO) typically involves highly toxic reducing agents that are harmful to human health and environment, and complicated surface modification is often needed to avoid aggregation of the reduced GO during reduction process. In this paper, a green and facile strategy is reported for the fabrication of soluble reduced GO. The proposed method is based on the reduction of exfoliated GO in green tea solution by making use of the reducing capability and the aromatic rings of tea polyphenol (TP) that contained in tea solution. The measurements of the resultant graphene confirm the efficient removal of the oxygen-containing groups in GO. The strong interactions between the reduced graphene and the aromatic TPs guarantee the good dispersion of the reduced graphene in both aqueous and a variety of organic solvents. These features endow this green approach with great potential in constructing of various graphene-based materials, especially for high-performance biorelated materials as demonstrated in this study of chitosan/graphene composites.



KEYWORDS: graphene oxide, green reduction, tea polyphenol, functionalization, composites

1. INTRODUCTION

The synthesis of graphene has been one of the hottest topics in scientific community in recent years^{1–4} because of the remarkable physical and chemical properties of graphene^{5–7} and its great promise application in devices or composites.^{8–10} During the past years, diverse procedures have been established for producing graphene, such as mechanical or ultrasonic exfoliation,^{1,2} chemical vapor deposition,³ epitaxial growth⁴ and chemical route via reduction of graphene oxide (GO). Among the currently existing methods, solution-based chemical reduction of GO offers the greatest ease for functionalization and potential for producing graphene on industrial scale.^{11–17} The solution-processable graphene was also more suitable for many applications such as transparent conductive thin films, paperlike materials, and polymer composites.^{18–21}

Despite the distinctive advantages of the wet chemical method, the most widely used reducing agents, such as hydrazine, dimethylhydrazine, and NaBH₄, are highly toxic; trace amount of the poisonous agents could have detrimental effect, especially for biorelated applications. Moreover, the handle of the hazardous waste generated by the reduction reaction may significantly increase the cost on industrial scale.^{22,23} Another obstacle in practical applications of chemical reduced graphene oxide (rGO) is the poor processability, because the rGO tends to form irreversible aggregation, which results from strong van der Waals attractive forces between the graphene planes, unless a modification step (both covalent and noncovalent) is included in the process.^{16,17,24} Nevertheless, the surface-modification process usually suffers from limited scalability, time-consuming and environmental problems. Very recently, solvothermal reduction in some high-boiling-point solvents has emerged as alternative for one-pot

reduction and functionalization of GO;^{22,25–27} however, refluxing at such high temperature could lead to the decomposition of the solvent molecules and release poisonous gases and wastes.^{25,26}

From last year, efforts have been made toward addressing the above-mentioned problems by using natural product instead of toxic reducing agents. For example, Vitamin C^{28–32} performs well in reduction of GO; however, in most cases, the product exhibited a highly agglomerated morphology without an external stabilizer.^{28–30} Reducing sugar³³ and protein bovine serum albumin³⁴ has also been employed in reducing GO, although the resultant rGO formed stable aqueous solution, an alkali is needed as a coreductant because of their weak reducing capability. Therefore, an effective, low-cost, and green reducing agent for chemical synthesis of soluble graphene in bulk quantity is still highly desirable.²³

Green tea is one of the most popular beverages worldwide and rich in polyphenolic compounds, whose content is about 10–15% in green tea leaves.³⁵ The tea polyphenols (TPs) are biocompatible and biodegradable, and mainly consisted of epicatechin (EC), epicatechin gallate (ECG), epigallocatechin (EGC) and epigallocatechin gallate (EGCG), in which the EGCG makes up about 50–60% of the total TPs,³⁶ the structures of these compounds are shown in Figure 1A.³⁷ The multiple pyrogallol and catechol groups make TPs highly water-soluble and excellent antioxidant agents because they can readily react with reactive oxygen species. Upon oxidation, the phenol groups were converted to their corresponding quinone forms.³⁸ Although TP has been used as antioxidant agent in foods or drugs for a long time,

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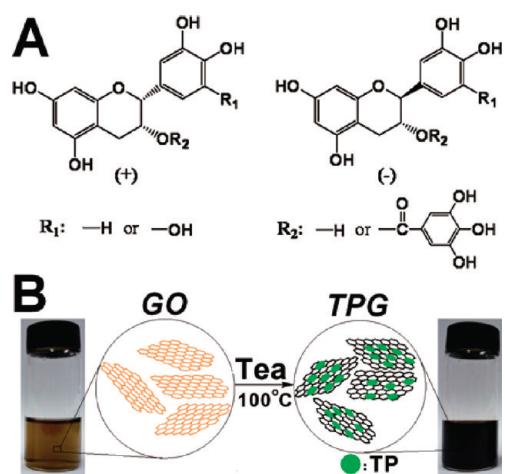


Figure 1. (A) Chemical structure of tea polyphenols (TPs). (B) Schematic illustration of the preparation of TP reduced graphene.

it is not until very recently does TP show its potential in the preparation of nanomaterials and nanocomposites. For instance, gold, silver, palladium, and iron nanoparticles have been synthesized and stabilized in tea solution thanks to the reductive property of TP.^{39–41} It is also demonstrated that carbon nanotube (CNT) and boron nitride nanotube (BNNT) could readily disperse in water in the present of TP due to the π - π interactions between tube-walls and aromatic rings of TP.^{42,43} The TP-functionalized BNNTs showed improved thermal conductivity enhancement efficiency over pristine ones in polymer composites.⁴³ By summarizing the recent advancement of tea chemistry in the field of nanotechnology and nanomaterials, it is anticipated that one-pot reduction and functionalization of GO could be achieved in tea solution.

Herein, we present a novel green and facile strategy to produce soluble graphene by reducing the GO in green tea solution. Our approach exhibits several distinctive features over the previously reported strategies, which makes it rather attractive for large-scale fabrication of soluble graphene for practical applications: (1) It is environmentally friendly, no synthetic chemical is used in the whole reduction process. (2) It is very cheap and safe and does not need a complex procedure. (3) No hazardous waste was generated in this method. (4) The reduction of GO and surface functionalization were achieved simultaneously; as a result, the obtained products could disperse in different solvents. (5) The biocompatible TPs make the soluble TP reduced graphene (TPG) a promising candidate in biorelated materials. For example, it can be used as an effective nanofiller in biomaterial without the risk of introducing detrimental effects, while homogeneous distributed in the matrix and greatly improve the properties of matrix as demonstrated in this study of Chitosan/TPG composites.

2. EXPERIMENTAL SECTION

2.1. Materials. Graphite powder (–100 mesh, 99.9995%) was obtained from Alfa-aesar Co Ltd. Concentrated sulfuric acid (95–98%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2 , 30%), concentrated hydrochloric acid and all organic solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC) and used as received. Chitosan with deacetylation degree $\geq 90\%$ and viscosity of 50.0–800.0 mPa/s was also supplied by SCRC. Green tea powder is

obtained in the local market. Pure tea polyphenol (99%) was purchased from Hangzhou Gosun Biotechnologies Co., Ltd.

2.2. Synthesis of Tea Polyphenol Reduced Graphene Oxide (TPG). GO was prepared by oxidizing the graphite powder in a mixture of concentrated sulfuric acid and $KMnO_4$ based on a modified Hummers method.^{44,45} For the tea solution, 2 g of green tea powder was added in 100 mL of deionized water and boiled at 100 °C for 20 min, and then filtered through a 0.44 μm cellulose membrane. 50 mg GO was added in the tea solution and sonicated for 30 min, the colloid was then refluxed at 90 °C in a nitrogen atmosphere. After that, the resultant TPG was collected by filtration and washed with deionized water five times to remove the excess TPs.

2.3. Preparation of Chitosan/TPG Composites. Required amount of TPG was first dissolved in 20 mL of water and treated with sonication for 30 min. In parallel, 1 g chitosan was dissolved in 80 mL 1 wt % aqueous acetic acid. Then, the aqueous solution of TPG was poured into the chitosan solution, and stirred overnight. After that, the homogeneous mixture was poured into a plastic dish and dried at 50 °C until the weight became equilibrate. The composite films were uniform with an average thickness of 0.07 mm.

2.4. Characterization. UV–vis spectra were recorded by a Shimadzu 2550 UV–vis spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer. The samples were prepared as KBr disk. Raman spectra were taken with Jobin Yvon Micro-Raman Spectroscopy (RamLab-010), equipped with a holographic grating of 1800 lines/mm and a He–Ne laser (632.8 nm) as excitation source. X-ray photoelectron (XPS) spectra were recorded on an ESCA LAB 250 spectrometer (VG Scientific) with an Al K α radiation (1486.6 eV). Thermogravimetric analysis (TGA) was performed in nitrogen with a Perkin-Elmer TGA 2050 instrument at a heating rate of 10 °C/min. X-ray powder diffraction (XRD) spectra were recorded on a D/max-2200/PC (Japan Rigaku Corporation) using Cu K α radiation. Atomic force microscopy (AFM) images were obtained using a digital Nanoscope IIIa Atomic Force Microscope in tapping mode. Transmission electron microscopy (TEM) images were obtained using JEOL2100F. The tensile fracture surfaces of composites were obtained using a scanning electron microscope (SEM) (JSM-7401F). The tensile property of composite films was measured with an Instron 4465 instrument at 23 °C with a humidity of about 50% at a crosshead speed of 2 mm/min and an initial gauge length = 30 mm, samples were cut into strips of ~ 60 mm \times 4 mm \times 0.07 mm using a razor blade, four strips were measured for each sample.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Tea Polyphenol Reduced Graphene Oxide (TPG). The procedure for making soluble graphene is illustrated in Figure 1B, as shown, after reaction, the color of the GO solution changed from brownish-yellow to black, suggesting the restoration of electronic conjugation. The reaction was monitored by recording the UV–vis absorption spectra of TPG as a function of time. The samples for characterization were prepared by extracting a portion of reaction solution in regular interval, filtering and washing for five times, then dispersing in water to form a dilute solution. As shown in Figure 2A, GO shows a peak at 228 nm and a shoulder at 300 nm. As the reaction processed, a characterized peak gradually established and red-shift to 271 nm, indicating the electronic conjugation is restored. It is noteworthy that the strong absorption peak at around 200 nm that belong to TP occurred in all TPG samples even after five runs washing, indicating the strong adsorption between aromatic TP and graphene. We also note that the TP shows a small peak centered at 273 nm, however,

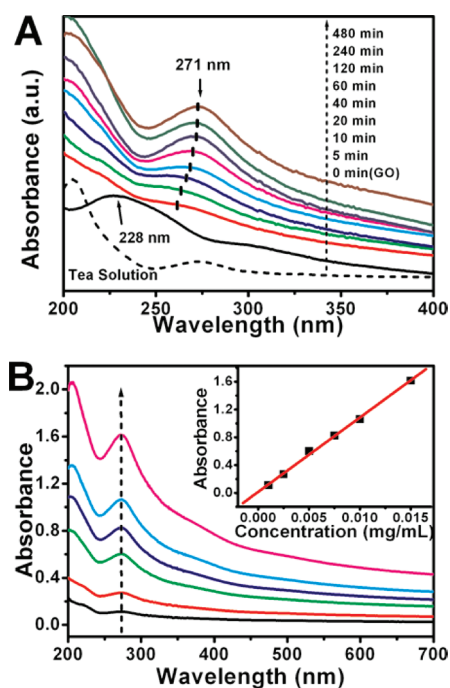


Figure 2. (A) UV-vis spectra of the GO aqueous dispersion as a function of reaction time (solid lines) and the spectrum of the tea solution (dash line). (B) UV-vis absorption spectra of the TPG aqueous dispersion. (Inset: correlation of absorbance at 271 nm against concentration.)

careful comparison of the intensity at this peak position of the series TPG leads us to conclude that the intense peak at 271 nm was mainly due to the restored sp^2 network of graphene. In a comparative study for evaluating the efficiency of various reducing agents, Merino et al. suggested that the maximum red-shift value can be used as a yardstick to estimate the performance of the reducing agent.³² In this regard, our TPG showed a similar final absorption peak position to the hydrazine¹⁴ and phenylhydrazine reduced graphene (270 nm),⁴⁶ and is higher than that of other “green” reduced GO,³³ which may suggest the efficient reduction of GO by TP. From Figure 2A, we also conclude that the reduction can be completed within 2 h because the peak was shifted no more when prolonged the reaction time. We have also investigated the influence of temperature on the reduction process, it is found that when the reaction was conducted at lower temperatures, the reducing effect was weakened (see Figure S1 in the Supporting Information), which was consistent with the literature.⁴⁷

The UV-vis spectrometer was also used to verify the formation of stable TPG suspension, because the absorbance at the characteristic peak was in a linear relationship with the concentration on the basis of Beer's law, if a homogeneous solution was formed.⁴⁸ The inset of Figure 2B shows that there is a good linear relationship (with $R = 0.9991$) between absorbance at 271 nm and the concentration of TPG, thus evidenced the good dispersibility of TPG in water. It is also noted that the concentration of TPG in water can be easily reached up to 2 mg/mL.

The removal of the oxygen-containing groups of GO is clearly reflected by the FT-IR spectra. As shown in Figure 3A, the GO shows multiple peaks in the range of 900 to 1500 cm^{-1} , which can be assigned to various functional groups, such as hydroxyl (1061 and 1393 cm^{-1}) and epoxy groups (1233 cm^{-1}).⁴⁹ The

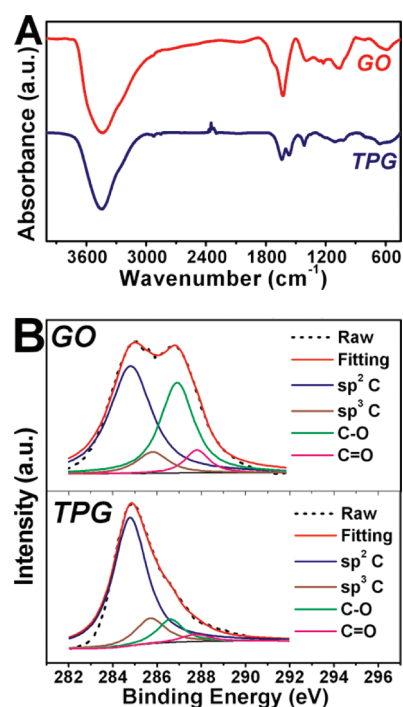


Figure 3. (A) FT-IR spectra of GO and TPG. (B) XPS survey scans of the C1s region of GO and TPG.

carboxyl group can also be found at 1724 cm^{-1} . After the reduction, the peak belonged to carboxyl group disappeared, and the peak intensity between 900 and 1500 cm^{-1} was decreased significantly. High-resolution C1s spectrum of GO (Figure 3B) shows that four different types of carbon components are existed: the sp^2 carbon (284.8 eV), the sp^3 C (285.7 eV), the carbon of C–O (286.8 eV) and the carbon of C=O (287.8 eV).^{8,49,50} In the C1s spectrum of TPG, although there are still some oxygen groups, the peak intensity of the oxygen-containing groups is much smaller than that in GO. Note that the adsorbed TPs may also contribute to the oxygen groups. The carbon content from sp^2 C–C makes up about 74.0% of the total carbon in TPG, which is much higher than that of 58.9% in GO, and this value was even similar to the graphene obtained by pyrene derivatives assistant liquid-phase exfoliation in water (76%).⁵¹

The thermal stability of TPG was examined by TGA and compared with that of GO (Figure 4A). Our GO shows no significant weight loss below 100 $^{\circ}C$, because we have completely dried the sample before testing to eliminate the influence of water on the test results. The DTG curve shows that the temperature of maximum weight loss of GO was 198.5 $^{\circ}C$, and a mass loss of 40 wt % is observed below 250 $^{\circ}C$, which could be attributed to the burning of labile oxygen-containing groups. In contrast, the maximum weight loss of TPG occurs at 283.4 $^{\circ}C$, an almost 85 $^{\circ}C$ increase. The mass loss in this range was attributed to the decomposition of the adsorbed TP, it is also deduced from the TGA and DTG curves that there were approximately 20 wt % TP remained in the TPG. The TPG exhibits only a 6.7 wt % loss at 250 $^{\circ}C$, which was much lower than that of the GO, indicating a significantly decreased amount of oxygenated functional groups.

Figure 4B shows the powder XRD features of graphite, GO, and TPG. The raw graphite shows a single peak at 26.6 $^{\circ}$, corresponding to an interlayer d -spacing of 0.338 nm. The characterized peak of GO appears at 9.6 $^{\circ}$, corresponding to a

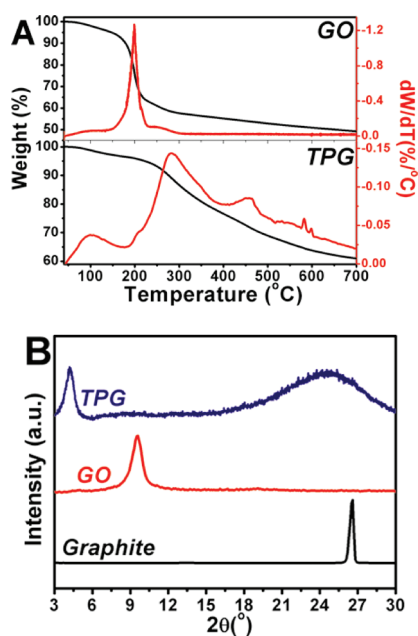


Figure 4. (A) TGA and DTG curves of GO and TPG. (B) XRD patterns of GO, TPG, and raw graphite.

d-spacing of 0.92 nm. In contrast to GO, the TPG shows two dominant peaks, one peak appears at 4.2° , corresponding to *d*-spacing of 2.1 nm, this enlarged *d*-spacing might be due to the TP that attached to the graphene layers. Therefore, the interlayer spacing between two adjacent TPG sheets is about 1.05 nm. Another broad peak is centered at 24.6° , corresponding to a *d*-spacing of 0.36 nm, which may be resulted from some restacked graphene layers, note that this spacing is very close to the pristine graphite, indicating the functional groups of GO have been efficiently removed.

The GO and TPG was also characterized by AFM, which was usually employed to determine the thickness and lateral size of graphene. Images A and B in Figure 5 are the typical AFM images and height profiles of GO and TPG. The average thickness of GO was found to be about 1 nm, consistent with previously reported thickness of single-layered GO.¹⁸ In contrast, the TPG shows an average thickness of about 2 nm. Considering the single-layered graphene has a thickness of 1 nm and the TP molecules were adsorbed on both sides of the graphene, it is rational that the resultant TPG has thickness up to 2 nm.^{28,33} This reveals that the interlayer distance between two adjacent TPG layers is about 1 nm, which is in good agreement with the value (~ 1.05 nm) obtained by XRD study. Both GO and TPG has polydisperse lateral sizes ranging from hundred nanometers to several micrometers. TEM images (Figure 5C, D) indicate that there is no significant difference in morphology between GO and TPG, both display silklike appearances.

The efficient reduction of GO in tea solution has thus been demonstrated, then, what are the active compounds in tea solution to reduce GO? As we mentioned in the previous sections, it is proposed that the TPs are responsible for the reduction of GO. Therefore, we tested the ability of pure TPs to reduce GO. The reduction process was identical to that in tea solution. As expected, the yellow colored GO solution changed into black after reduction (see Figure S2 in the Supporting Information). The UV–vis spectrum of the reduced GO showed a characterized

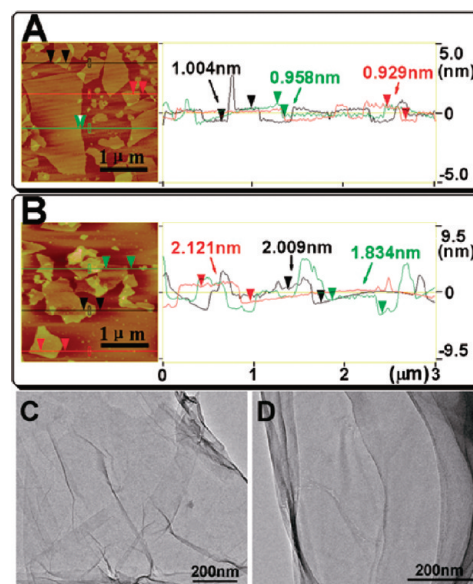


Figure 5. Typical AFM and TEM images of (A,C) GO and (B,D) TPG.

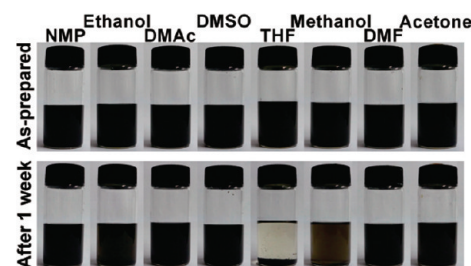


Figure 6. As-prepared dispersions of TPG (0.2 mg/mL) in various organic solvents and their dispersion state after 1 week.

peak at 271 nm (see Figure S3 in the Supporting Information), indicated the restoration of electronic conjugation of GO. The FT-IR spectrum of reduced GO became almost featureless (see Figure S4 in the Supporting Information), suggested the oxygen-containing groups in GO has been significantly removed. Thus far, it is evidenced that TPs contributed mainly to the reduction of GO in tea solution.

Besides water, the dispersions of TPG in different organic solvents were also considered. It must be pointed out that all solutions were prepared by modestly dried TPG, because we found that a completely dried sample could not be readily re-dispersed in nearly all solvents, which may be due to the re-established π – π interaction between adjacent layers. It is found that the TPG could be dispersed in all the polar solvents that used in this study after sonication, as shown in Figure 6. After one week, most of the solutions were remained stable with negligible sediment settled, excepted for methanol and tetrahydrofuran (THF), in which the TPG were precipitated out to a relatively large extent or completely. Of particular importance is the good dispersibility of TPG in ethanol and acetone, because the dispersion of graphene in solvents with low boiling point should largely facilitate the fabrication of composites or devices.⁵²

To examine the electrical property of the TPG, we have made a paper by filtering the aqueous solution of TPG through a filtration membrane, as shown in Figure 7A. The TPG paper shows a smooth

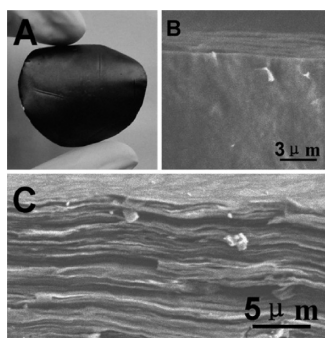


Figure 7. (A) Photograph of the as-prepared TPG paper. (B, C) SEM image of the surface and the cross-section of the TPG paper.

surface and well stacked layered structure as evidenced by SEM images (Figure 7B,C), which further confirmed the good dispersion state of TPG. A four-point probe measurement was carried out on the TPG paper. It is found that the average conductivity of the TPG is about 53 S m^{-1} . For the purpose of comparing the performance of TP with other reducing agents in reduction of GO, we have summarized the conductivity of some recent reported chemical reduced GO, as listed in Table S1 in the Supporting Information. Although the conductivity of TPG paper is lower than the paper made from nonmodified graphene reducing by hydrazine or vitamin C,^{14,31,32} it is comparable with that made from functionalized rGO.^{15,28} Note that the TP molecules that heavily adsorbed on the graphene surface may have a negative effect on the conductivity of TPG paper. Therefore, it is demonstrated that the electronic conjugation of graphene was indeed re-established by this green method, and confirmed the good reducing ability of TP toward reducing GO.

3.2. Preparation, Characterization, and Properties of Chitosan/TPG Composites. Graphene has been recognized as an ideal nanofiller for reinforcement of a polymer matrix, the reinforcement effect of which was thought to be rival or even better than CNT.^{10,18} Among the various processing technique that been developed to prepare graphene-based polymer composites, the chemical reduction of GO followed by solution-mixing procedure was the most effective method to incorporate well-dispersed graphene into a polymer matrix.^{18,53} However, when this protocol was applied to biocompatible composites for bioapplications, such as food package, tissue engineering, and drug delivery, care must be taken extremely because some reducing agents are difficult to completely remove, trace amount of the residual agent may have bad influence on human body. By contrast, if a “green” graphene was used as the fillers as in our case, the possible detrimental effect could be eliminated, because the TP is biocompatible and biodegradable. Therefore, it is assumed that our TPG might be a better choice for reinforcement of biopolymer for bioapplications. In a preliminary study, we have investigated the influence of the TPG on the properties of a most studied biocompatible polymer—chitosan.

The chitosan/TPG composites were fabricated by a simple solution-casting method. As the TPG can be dispersed very well in water because of the adsorbed hydrophilic TP, it is assumed that the TPG can be well dispersed in the chitosan matrix as well, because the amino and hydroxyl groups in the units of chitosan should cause strong interactions with the hydroxyl groups in TPG via hydrogen bonds or electrostatic attractions. SEM images were taken of the tensile fracture surface of the composite films to

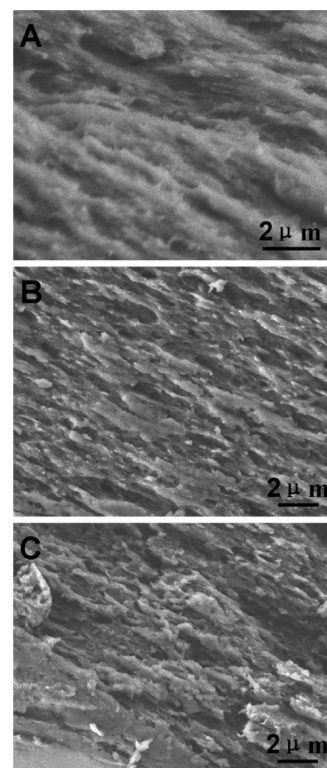


Figure 8. SEM images of the tensile-fracture surface of chitosan/TPG composites with (A) 0, (B) 0.2, and (C) 1 wt % TPG.

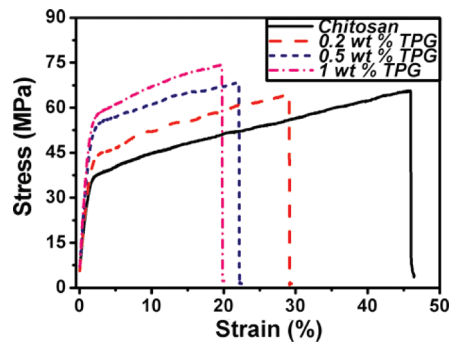


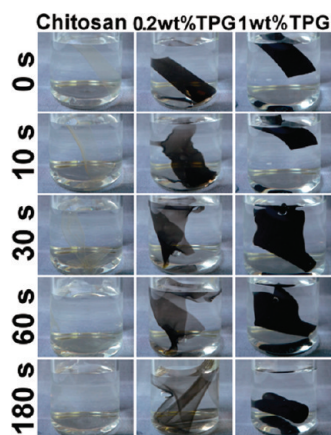
Figure 9. Typical stress–strain curves of the chitosan/TPG composites.

confirm our assumption, as shown in Figure 8. As compared to pure chitosan (Figure 8A), protruded TPG edges are clearly seen in the composite film that contained 0.2 wt % TPG (Figure 8B), and these TPGs are well-distributed across the film surface. The dispersion state remained well in composite with high concentration of TPG (Figure 8C), no cluster was seen from the SEM images.

As the good dispersion of TPG in the matrix and strong interactions between them, good reinforcement can be envisaged. To demonstrate this, tensile test were performed on the composite films. The typical stress–strain curves are shown in Figure 9, and their mechanical properties are compared in Table 1. The results indicate that the chitosan was strengthened by TPG. The modulus of chitosan gradually increases with an increasing amount of TPG from 2.6 to 4.2 GPa in the composite contained 1 wt % TPG, corresponding to a 62% increase, which is comparable to the

Table 1. Physical properties of Chitosan/TPG composites

TPG content (wt %)	Young's modulus (GPa)	max stress (MPa)	max strain (%)	conductivity ($S m^{-1}$)
0	2.6 ± 0.2	63.5 ± 1.8	45.0 ± 4.4	
0.2	2.8 ± 0.1	64.2 ± 1.6	32.6 ± 3.0	
0.5	3.8 ± 0.2	73.7 ± 4.7	22.9 ± 1.3	1.13×10^{-3}
1	4.2 ± 0.2	76.6 ± 1.0	20.1 ± 3.0	9.56×10^{-3}

**Figure 10.** Appearance of chitosan and chitosan/TPG composites immersed in 0.1 wt % aqueous acetic acid for different times.

value of GO⁵⁴ or CNT⁵⁵ reinforced chitosan. The strength of composite with 1 wt % TPG is 76.6 MPa, which is about an increase of 21% in comparison of that of pure chitosan. As an additional effect of the incorporation of TPG, we have also observed an improved electrical conductivity in the composites (Table 1). The conductivities of composites with 0.5 and 1 wt % TPG are in the order of $1 \times 10^{-3} S m^{-1}$, which is already satisfied the antistatic criterion ($1 \times 10^{-6} S m^{-1}$) for thin films.⁵⁶

Because water can be easily adsorbed on the chitosan, resulting in a lower mechanical property or even a structural destruction of chitosan films, we thus designed a simple experiment to investigate the effect of TPG on structural stability of the composites. We immersed composite films with different content of TPG into a 0.1 wt % aqueous acetic acid, as shown in Figure 10, pure chitosan and composite with 0.2 wt % TPG deformed after 10 s, while the 1 wt % composite still maintained its original shape. With prolonged exposure time to the acid water, both films were swelled. However, the extent of deformation in composite was clearly suppressed by the addition of TPG. After 180 s, although the pure chitosan was nearly dissolved and the 0.2 wt % composite was swelled to a large extent, the 1 wt % composite showed a much slower swelling rate with a curly appearance. Hence, the enhancement of structural stability of chitosan was evidenced, and the reason for such enhancement was attributed to the TPG in the composites, which could act as physical cross-linking point of polymer chains.

4. CONCLUSIONS

We have presented a green method for synthesis of graphene via chemical reduction of GO in green tea solution. The merit of this method lies in its low-cost, non use of toxic agent, no hazardous waste, high-efficient removal of functional groups in

GO and easily scalable. It is also found that the TP in the tea solution acts as both reducing agent and stabilizer, thus enable the resultant graphene good solubility in both aqueous and a variety of organic solvents. This simple approach should find practical applications in large-scale production of widely soluble graphene. As the TP molecules that adsorbed on the graphene are nontoxic and biocompatible, therefore bioapplications using the present soluble graphene might be of interesting. As an example, we have used the TPG as nanofillers for fabrication of a biocomposite with chitosan, the significantly improved physical properties, including mechanical property, electrical conductivity, and structural stability, are demonstrated.

■ ASSOCIATED CONTENT

S Supporting Information. Absorption spectra of GO reduced at various temperatures, photographs of aqueous dispersions of GO and reduced GO, UV–visible, and FTIR absorption spectra of pure TP reduced GO (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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