Supporting Information

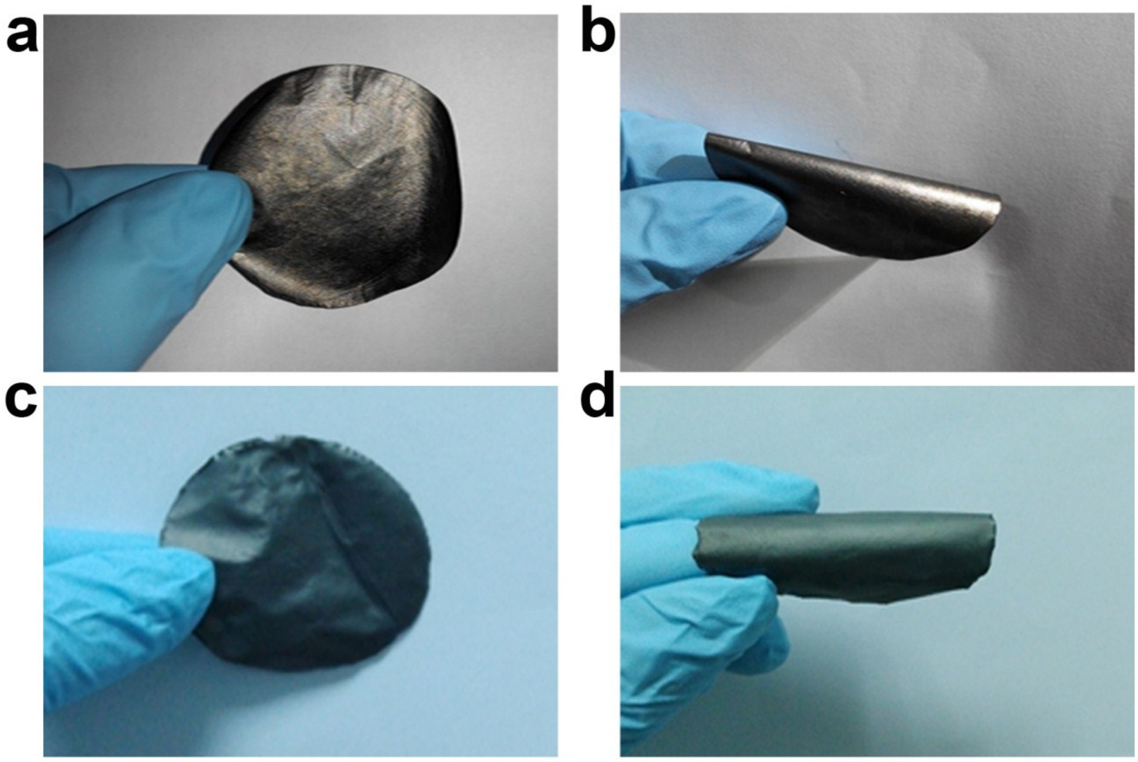
Synergistic Toughening of Bioinspired Artificial Nacre by Polystyrene Grafted Graphene Oxide

Yanhong Wu, Rui Cao, Liangliang Ji, Xiaoming Yang, and Yingfeng Tu**

Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China.

*: Corresponding-Author
* Xiaoming Yang, Yingfeng Tu
Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China.
Tel: +86 512 65882130; Fax: +86 512 65882130; E-mail: yangxiaoming@suda.edu.cn, tuyingfeng@suda.edu.cn.

It is important to impart electrical conductivity to these artificial nacre films to broaden the range of their application, such as in battery, supercapacitor and conductivity devices.[1] In this study, the GO and GO-PS films were reduced by HI because of its powerful reducing ability.[2]



Scheme S1. The photographs of rGO and rGO-PS paper.

Scheme S1 presents the appearances of rGO and rGO-PS films, from which we can see that after reduction all films remain flexible. The color of the GO film apparently changed from red-brownish to black after the reduction. For GO-PS, the films have a smooth metallic shiny surface after reduction.[3] The smooth surfaces also suggest the macroscopic uniformity of all films.

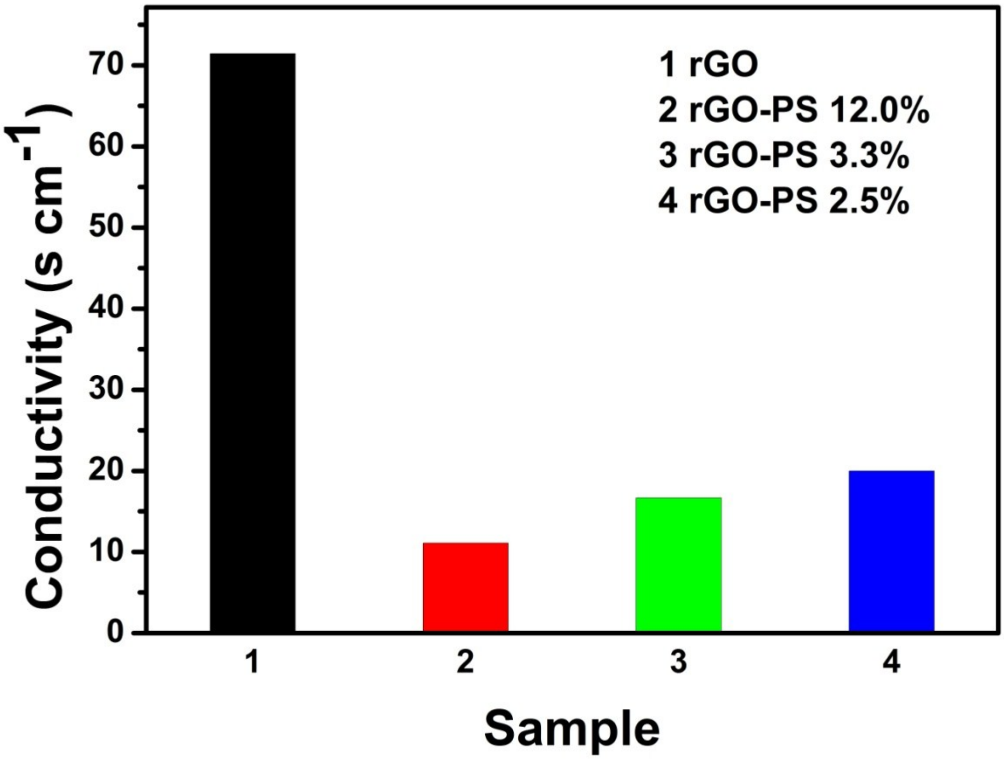


Figure S1. The conductivity of rGO and rGO-PS.

We measured the electrical properties of rGO and rGO-PS films, the results are presented in Figure S1. The conductivity of the rGO sample reaches 71.43 S/cm. The electrical conductivity reflects the reduction degree and defect repair degree. It can be concluded that all the electrical conductivity has been improved compared with GO after performing reduction. The conductivity of rGO-PS 12% is 16.67 S/cm. The decrease of the conductivity is due to the insulated PS chains. The conductivity is inferior to some rGO based materials,[4] which may be due to the decreased sp^2 area and discontinuous conjugated area of rGO sheets. In future work, improvement the sp^2 area or conjugated area of rGO sheets by increasing annealing time and temperature will be studied.

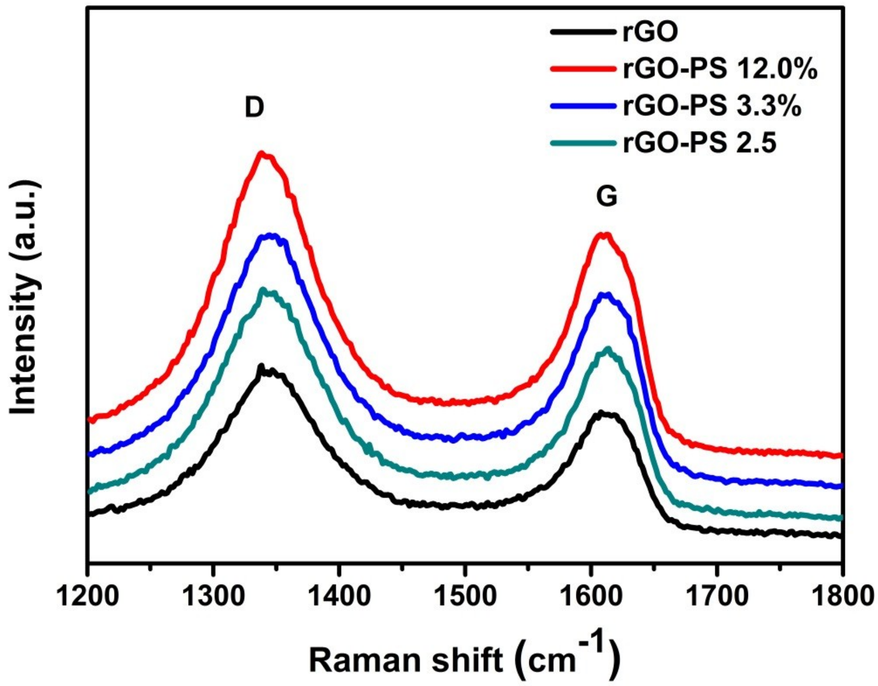


Figure S2 . Raman spectra of pure rGO, rGO-PS 12%, rGO-PS 3.3%, rGO-PS 2.5%.

Table S1 The comparison of peak intensity D band and G band

Sample	Pure rGO	rGO-PS 12%	rGO-PS 3.3%	rGO-PS 2.5%
I_D/I_G	1.34	1.35	1.31	1.38

The changes of GO and GO-PS films after reduction were explored by Raman spectroscopy. Figure S2 shows the results of the Raman characterization, from which we can see that rGO and rGO-PS also show a well-defined D band at 1341 cm^{-1} and G band at 1610 cm^{-1}. The intensity ratio of D band to G band (I_D/I_G) increases from 0.98 to 1.34 for pure rGO (Table S1). For rGO-PS 12%, the I_D/I_G also increases from 1.01 to 1.35. Stankovich et al. suggested that the removal of oxygen-containing groups of GO would increase the number the aromatic domains but decrease the average size of the sp^2 domains, which could lead to the increase of I_D/I_G ratio.[5] The increased I_D/I_G intensity ratios indicated higher reduction degree, but simultaneous higher defect degree. This phenomenon was also observed in other chemically reduced GO.[6,7] Therefore, the Raman results demonstrate that GO and GO-PS films have been reduced after treatment with HI acid and the average size of the sp^2 domains decreased.

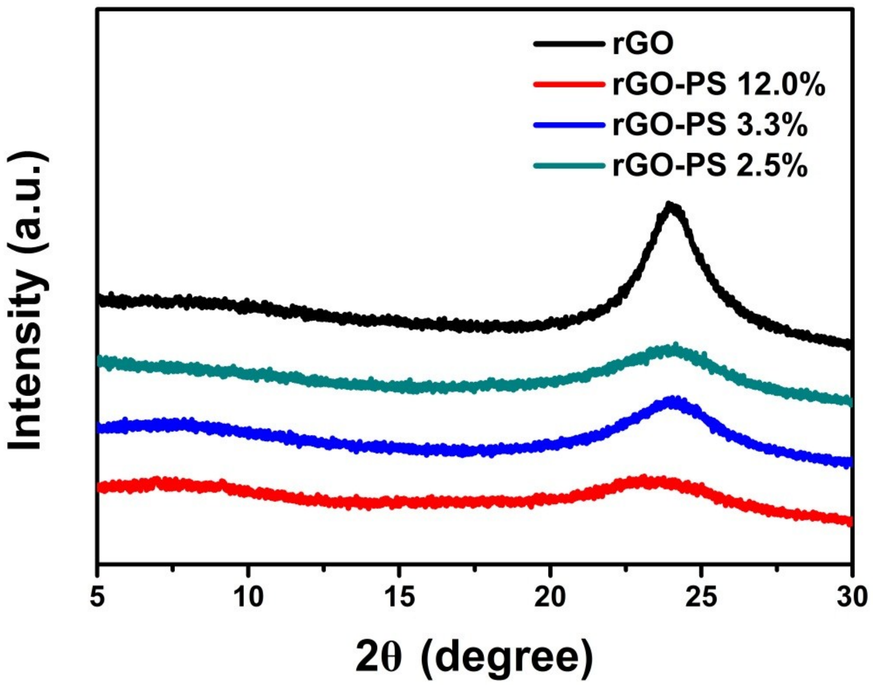


Figure S3 XRD curves of rGO and rGO-PS.

More information about the structure of rGO and rGO-PS films can be obtained by XRD measurement. After the removal of oxygen groups, the XRD patterns of rGO and rGO-PS composite paper are totally different from those of GO and GO-PS (Figure S3) The peaks at about 10° disappear, while a new peak appear at about 23-24° in the reduced sample, which are attributed to the stacking of rGO sheets. This result also suggest again the efficient reduction of GO. It is also noted that the peak at about 23-24° becomes broaden, suggesting preventing effect of the stacking of rGO sheets by PS chains.

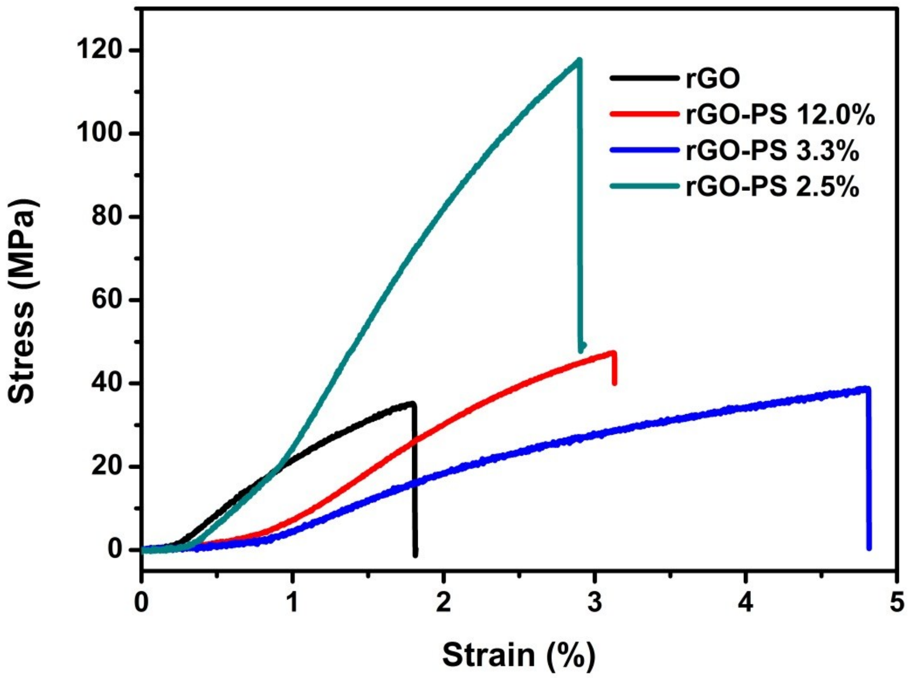


Figure S4. Typical stress-strain curves of tensile tests for rGO and rGO-PS films.

Table S2 Mechanical Properties of rGO and rGO-PS films with different of PS content[a]

Samples	Tensile strength (MPa)	Ultimate strain (%)	Young's modulus (GPa)	Toughness ($MJ\cdot m^{-3}$)
rGO	35.2	1.80	2.94	0.33
rGO-PS 12%	47.3	3.13	2.19	0.66
rGO-PS 3.3%	38.8	4.80	1.49	0.97
rGO-PS 2.5%	117	2.90	4.49	1.53

a: Values are averaged from ten artificial nacre samples

The mechanical properties of rGO and rGO-PS films were also evaluated (Figure S4). The mechanical properties of rGO film remained compared with GO film. The possible reason is that in the process of reduction, many oxygen-containing groups were removed from the surface of GO, and thus, the GO sheets were packed more compacted, as convinced by XRD results. At the same time, some defects formed in the process of reduction. The direct evidence is SEM image of the fractural cross-section of rGO film. Figure S4a shows the SEM image of cross-section of rGO film. It can be seen that rGO sheet can't form dense structure, macrocosmically. Another reason is that in the reduction process the oxygen-containing groups of GO decreased but he average size of the sp^2 domains decreased (confirmed by Raman results), which could attributed to the same mechanical properties. But, the mechanical properties of artificial nacre films were greatly improved by the glue effect of PS. The tensile strength, ultimate strain and toughness increased obviously as shown in Table S2. But the Young's modulus decreased for artificial nacre films with high PS content, while increase for films with low PS content.

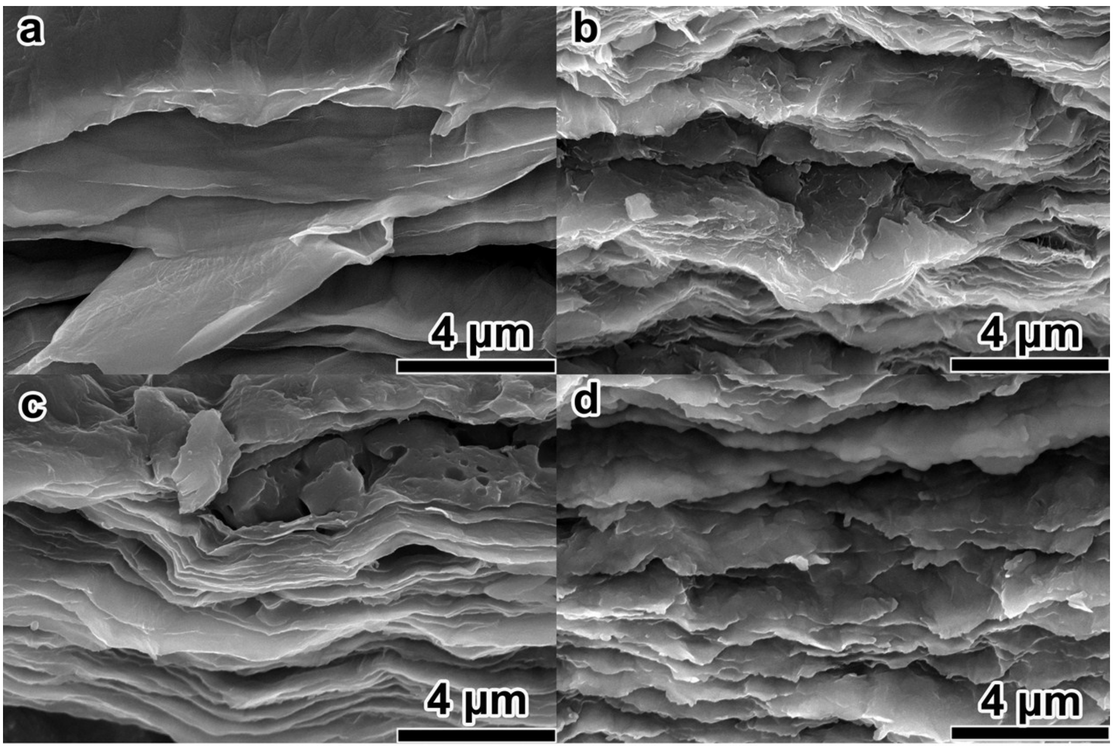


Figure S5 SEM images of the cross-section of (a): rGO; (b): rGO-PS 12%; (c): rGO-PS 3.3%; (d): rGO-PS 2.5%.

To explore the mechanism of the toughness and the morphological changes of the cross-section of the rGO and rGO-PS films, fracture morphology of the artificial nacre is carefully examined by SEM, as shown in Figure S5. The SEM images of rGO and rGO-PS films reveal that the 2D nanosheets are also assembled into layered microstructure. But at the macro level, rGO-PS cannot form densely structure. The possible reason is that PS chains prevent the stacking of rGO sheets. Figure S5 also shows that the rGO plate and rGO-PS platelets are pulled out. The feature of the fracture surface indicates that GO sheets sliding happen not only on the fracture surface but also in the interior of the composite, which may be responsible for the improved fracture energy of the composite.

References:

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