

# Ultratough Artificial Nacre Based on Conjugated Cross-linked Graphene Oxide

Qunfeng Cheng\*, Mengxi Wu and Lei Jiang

\*School of Chemistry and Environment, BeiHang University, China, cheng@buaa.edu.cn

## ABSTRACT

Inspired by the natural nacre, we developed a novel strategy for fabricating the integration of supertough and high strength artificial nacre based on GO sheets via conjugated cross-linking. Highly  $\pi$ -conjugated long chain molecules of 10,12-pentacosadiyn-1-ol (PCDO) are cross-linked with GO sheets only with content of 6.5 wt%, resulting in huge displacement when loading and adsorption of much more fracture energy. The toughness is two times higher than that of natural nacre. Furthermore, the  $\pi$ -conjugated polymers could add additional benefit to the high electrical conductivity of the chemically reduced GO (rGO). This study opens the door toward biomimetic production of GO- or rGO-based composites with supertough and highly conductive properties, which will have great promising applications in many fields like aerospace, flexible supercapacitor electrodes, artificial muscle, and tissue engineering.

**Keywords:** bio-inspired; artificial nacre; graphene oxide; mechanical properties

## 1 INTRODUCTION

Natural nacre, consisted of almost 95 vol.% inorganic content (calcium carbonate) and 5 vol.% elastic biopolymers, possesses a unique combination of remarkable strength and toughness,<sup>[1]</sup> which is attributed to its hierarchical nano-/micro-scale structure and precisely designed inorganic-organic interface.<sup>[2]</sup> Inspired by the intrinsic relationship between the structures and the mechanical properties lying in the natural nacre, different types of nacre-like layered nanocomposites have been fabricated with two dimensional (2D) inorganic additives including glass flake,<sup>[3]</sup> alumina flake,<sup>[4]</sup> graphene oxide,<sup>[5]</sup> layered double hydroxides,<sup>[6]</sup> nanoclay,<sup>[7]</sup> and flattened double-walled carbon nanotube.<sup>[8]</sup> Although great progresses have been achieved in tensile mechanical properties,<sup>[7-9]</sup> only very rare cases of the artificial layered composites with excellent toughness are obtained.<sup>[6, 10]</sup> One of the most important causes is the relatively low interfacial strength between interlayers of the artificial nacre. Recently, 2D graphene attracts a lot of research interest due to their outstanding electrical, thermal and mechanical properties,<sup>[11]</sup> and many graphene-based devices have been fabricated, e.g. bulk composites,<sup>[12]</sup> one-dimensional fibers,<sup>[13]</sup> supercapacitors,<sup>[14]</sup> etc. As the water-soluble derivative of graphene, graphene oxide (GO) with the rich functional groups on the surface is one of the best

candidates for fabricating the artificial nacre, because functional surface groups allow for chemical cross-linking to improve the interfacial strength of the adjacent GO layers. Until now, several methods have been developed to functionalize the individual GO sheets and enhance the resultant mechanical properties, including divalent ion ( $Mg^{2+}$ ,  $Ca^{2+}$ ) modification,<sup>[15]</sup> polyallylamine<sup>[16]</sup> or alkylamines<sup>[17]</sup> functionalization, borate cross-linking,<sup>[18]</sup> glutaraldehyde (GA) treatment,<sup>[19]</sup>  $\pi$ - $\pi$  interaction<sup>[20]</sup> and hydrogen bonding.<sup>[21]</sup> Although the obtained strength and stiffness are significantly enhanced, the modified materials always accompany a reduced ductility or toughness.<sup>[18]</sup> In a brief, it still remains a great challenge to obtain the supertough artificial nacre based on the 2D GO sheets.

Herein, inspired by the relationship of excellent toughness and hierarchical nano-/micro-scale structure of the natural nacre, we developed a novel strategy for fabricating the supertough artificial nacre based on the 2D GO sheets via conjugated cross-linking. Highly  $\pi$ -conjugated long chain polymers made of 10,12-pentacosadiyn-1-ol (PCDO) monomers<sup>[22]</sup> are cross-linked with the GO sheets, resulting in a huge displacement when loading and adsorption of much more fracture energy. The toughness is two times higher than that of the natural nacre. Furthermore, the  $\pi$ -conjugated polymers could add additional benefit to the high electrical conductivity of the chemically reduced GO (rGO). It can be highly expected that this novel type of the supertough and conductive artificial nacre has great potential in aerospace,<sup>[23]</sup> flexible supercapacitors electrodes,<sup>[14]</sup> artificial muscle,<sup>[24]</sup> and tissue engineering.<sup>[25]</sup>

## 2 EXPERIMENTAL SECTION

### 2.1 Materials

GO was purchased from XianFeng NANO Co., Ltd. 10,12-pentacosadiyn-1-ol (PCDO) was purchased from Tokyo Chemical Industry Co., Ltd. 57 wt.% HI acid was purchased from Sigma-Aldrich.

### 2.2 Preparation of Artificial Nacre

GO was dispersed in deionized water. Exfoliation was performed by sonicating an aqueous suspension of GO for 1 h. Un-exfoliated aggregates were removed from the solution via centrifugation, and the supernatant solution was collected. The GO films were assembled by vacuum-assisted filtration, followed by air drying and peeling from the filter. The GO films were immersed in a PCDO solution.

Subsequently, the PCDO-grafted GO films were treated under UV irradiation at a wavelength of 365 nm. The final GO-PCDO composites were rinsed. The resultant GO-PCDO composites were reduced by HI solution. Finally, the artificial nacre of rGO-PCDO composites were obtained after washing and drying.

### 2.3 Measurements

Mechanical properties were evaluated using a Shimadzu AGS-X Tester. Scanning electron microscopy (SEM) images were obtained by the HITACHI S-4800. All X-ray photoelectron spectroscopy (XPS) measurements were taken in an ESCALab220i-XL (Thermo Scientific) using a monochromatic Al-K $\alpha$  X-ray source. Raman spectroscopy measurements were taken using a LabRAM HR800 (Horiba Jobin Yvon) with the excitation energy of 2.54 eV (488 nm). X-ray diffraction (XRD) experiments were carried out with a D/max-2500 (Rigaku) instrument using Cu-K $\alpha$  radiation. FTIR spectra were collected using a Thermo Nicolet nexus-470 FTIR instrument.

## 3 RESULTS AND DISCUSSION

The GO dispersion was infiltrated with vacuum assistance and assembled into the layered GO films as shown in step 1 in Figure 1a. The PCDO was then introduced into the pre-built GO films by soaking the GO films in a pre-mixed tetrahydrofuran and PCDO solution. After several hours, the esterification reaction between alkanol at one end of the PCDO molecules and carboxylic acids on the surface of the GO sheets was finished, and the PCDO monomers were grafted on the surface of the GO sheets (step 2 in Figure 1a). To improve the interfacial strength and conductivity of the resultant composites, the PCDO molecules were cross-linked via 1,4-addition polymerization of their diacetylenic units under UV irradiation (step 3 in Figure 1a). Thermogravimetric analysis reveals that the weight loading of the PCDO in the composites is about 6.5 wt.%, comparable to the natural nacre. X-ray diffraction (XRD) results showed that the interlayer distance of the GO-PCDO composites increased, suggesting that the PCDO was successfully embedded into the GO films. Finally, the GO-PCDO composites were reduced by hydroiodic acid (HI) solution (step 4 in Figure 1a).

The successful introduction of the PCDO into the rGO films is also proved by FTIR. After esterification, the carboxylic acid peak at 1730  $\text{cm}^{-1}$  is weakened, accompanying with appearance of strong peaks at 1100–1250  $\text{cm}^{-1}$  corresponding to the stretching vibration of the –C–O–C moiety in ester groups and at 1770  $\text{cm}^{-1}$  corresponding to the stretching vibration of the C=O moiety in ester groups. The XPS and Raman results highlight that the cross-linking bonds with the PCDO would simultaneously provide the strong interface strength and the electron-transfer path between the GO sheets.

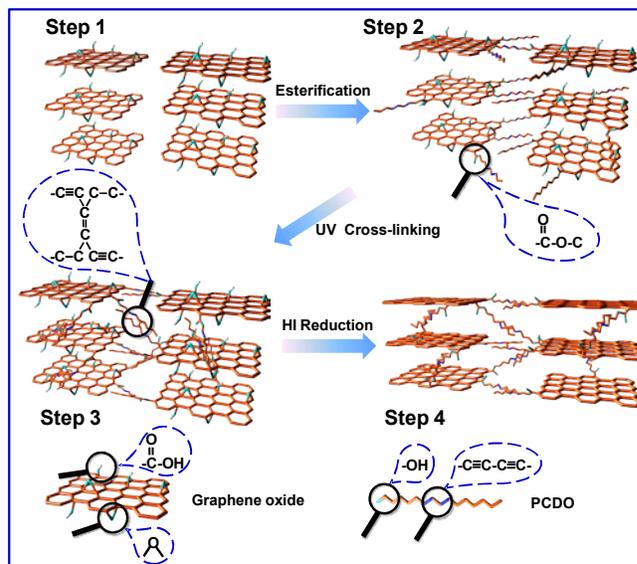


Fig. 1 Scheme of the fabrication procedure of the ultratough and conductive artificial nacre based on GO and PCDO.

The typical stress-strain curves of the prepared samples are shown in Figure 2. The tensile strength and toughness of the pure GO films are  $95.4 \pm 3.9$  MPa and  $0.37 \pm 0.06$   $\text{MJm}^{-3}$ , respectively, similar to the previous report.<sup>[26]</sup> When the PCDO molecules are grafted on the GO sheets and cross-linked together, the tensile strength is increased to  $106.6 \pm 17.1$  MPa, comparable to that of the natural nacre, while the toughness is dramatically raised to  $2.52 \pm 0.59$   $\text{MJm}^{-3}$ , which is about 40% higher than that of the natural nacre. In this study, HI is used to reduce the GO sheets.<sup>[27]</sup> As for the artificial nacre of the rGO-PCDO composites, the average tensile strength is increased to  $129.6 \pm 18.5$  MPa, and the maximum value can reach 156.8 MPa, higher than that of the natural nacre. More remarkably, the toughness of the rGO-PCDO composites is up to  $3.91 \pm 0.03$   $\text{MJm}^{-3}$ , which is two times higher than that of the natural nacre. The excellent mechanical properties of the rGO-PCDO composites are attributed to the layered hierarchical nano-/micro-scale structure and the unique chemical cross-linking with the PCDO polymers.

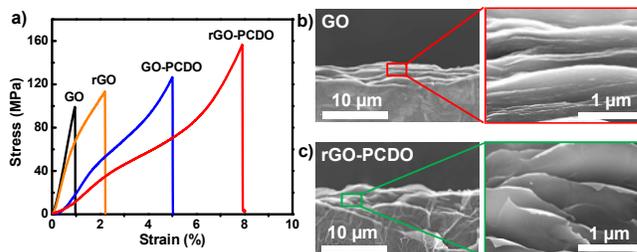


Fig. 2 Mechanical properties of GO film and rGO-PCDO composites. a) Stress-strain curves of GO films, rGO films, GO-PCDO composites and rGO-PCDO composites. b) and c) SEM images of pure GO films, and rGO-PCDO composites, respectively.

Detailed structural analysis is performed to understand the intrinsic factors to improve the mechanic strength. The

pure GO films show a typical brittle fracture morphology without any pulling out of the GO sheets (Figure 2b), which is similar to the previous report.<sup>[26]</sup> After cross-linking with the PCDO, many GO sheets are observed to be pulled out due to the strong interactions between the adjacent GO sheets (Figure 2c). Especially, one can see that the edges of the GO sheets are curved rather than flattened, indicating that breakage of the covalent bonds between the PCDO and the GO brings about obvious deformation of the GO sheets and would cost more energy (magnified image in Figure 2c). In the layered structure of the rGO-PCDO composites, the organic PCDO molecules are grafted on the 2D inorganic rGO sheets through the covalent ester bonds, while the PCDO molecules form intercross-linked networks through conjugation of ene-yne backbones and adopt a randomly coiled conformation. When loading, the rGO sheets extensively slide against each other. The weak hydrogen bonds between the rGO sheets are firstly ruptured, followed by stretching of the coiled PCDO long chains along the sliding direction, resulting in dissipation of a large amount of energy. When loading is further increased, the chemical bonds between the PCDO and the rGO sheets, as well as the ene-yne backbones in the conjugated PCDO, are broken, simultaneously resulting in curving of the rGO sheets. There are both similarity and difference in the fracture morphologies between the GO-PCDO composites and the natural nacre. In both samples, 2D platelets are irregularly pulled out. However, the GO sheets have the curved morphology due to their flexibility and the CaCO<sub>3</sub> platelets keep flattened due to their brittleness. The novel fracture morphology of the GO sheets demonstrates that although the artificial nacre based on the GO sheets exhibits high strength and toughness, the full potential of the GO sheets' mechanical properties has not yet to be exploited considering their superhigh mechanical properties. Further improvements in the interfacial bonding and load transfer could be expected to offer much higher mechanical performance

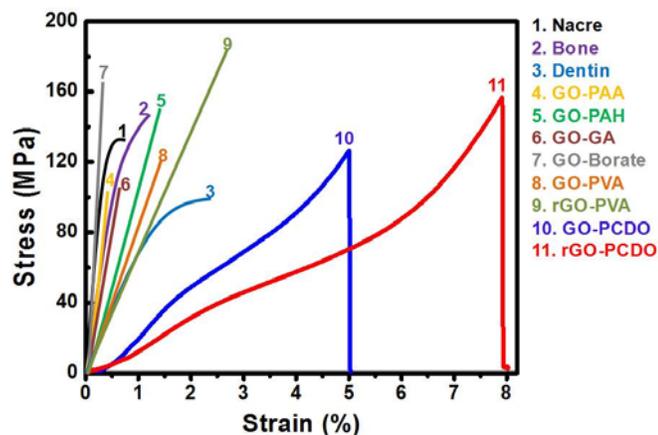


Fig. 3 Comparison of stress-strain curves of our artificial nacre of GO-PCDO and rGO-PCDO composites with the natural nacre, bone, dentin and other GO or rGO films with different cross-linking strategies.

Figure 3 compares the mechanical performances of the GO-PCDO and rGO-PCDO composites with those of the natural materials including nacre, bone and dentin, as well as different GO- or rGO-based composites. Impressively, the artificial nacre shows much higher mechanical properties. The maximum tensile strength of the rGO-PCDO composites can reach 156.8 MPa, higher than that of the natural nacre (tensile strength of 80-135 MPa),<sup>[28]</sup> bone (tensile strength of 150 MPa),<sup>[29]</sup> and dentin (tensile strength of 105.5±16.4 MPa).<sup>[30]</sup> The toughness of the rGO-PCDO composites is up to 3.91 ± 0.03 MJm<sup>-3</sup>, which is two times higher than that of the natural nacre (1.8 MJ m<sup>-3</sup>),<sup>[28]</sup> three times higher than that of bone (1.2 MJ m<sup>-3</sup>),<sup>[29]</sup> and 1.9 times higher than that of dentin (2.0 MJ m<sup>-3</sup>).<sup>[30]</sup> On the other hand, our strategy to fabricate the GO-based composites is also superior to other approaches of different cross-linking agents, such as divalent ion (Mg<sup>2+</sup>, Ca<sup>2+</sup>) modification,<sup>[15]</sup> borate cross-linking,<sup>[18]</sup> glutaraldehyde (GA) treated,<sup>[19]</sup> hydrogen bonding,<sup>[21]</sup> and nacre-like composites based on GO and poly(acrylic acid) (PAA),<sup>[16]</sup> poly(allylamine hydrochloride) (PAH),<sup>[31]</sup> poly(vinyl alcohol) (PVA)<sup>[32]</sup> and poly(methyl methacrylate) (PMMA).<sup>[32]</sup> The currently used cross-linking strategies are mostly responsible for improving the tensile strength instead of the toughness of the GO-based materials. As comparison, thanks to the coiled feature of the long chain of the PCDO, the rGO-PCDO composites have much higher strength and toughness. For example, the appropriate hydrogen bonding (H-bond) interactions between the adjacent GO sheets by incorporating water molecules<sup>[21]</sup> can only achieve less than 10% improvement in stiffness and 1% improvement in tensile strength since the H-bond interaction energy is relatively weak.<sup>[33]</sup> The effective borate cross-linking inspired by *Triticum aestivum* plants can make the improvements of 255% in stiffness and 25% in strength with addition of 0.94 wt.% boron.<sup>[18]</sup> However, the failure strain is dramatically decreased to only 0.15% and the corresponding toughness is only 0.14 MJ m<sup>-3</sup>.

## 4 CONCLUSIONS

In conclusion, we successfully fabricated the GO-based composites inspired by the natural nacre. In comparison with previous preparation methods, this novel cross-linking strategy demonstrates the following crucial advantages: i) It dramatically decreases the content of organic polymers in the resultant composites, which is comparable to the natural nacre; ii) It produces the distinct inorganic-organic layered hierarchical nano-/micro-structures; iii) It realizes integration of the high tensile strength and excellent toughness; iv) It creates highly conductive composites based on GO and conjugated molecules. This study opens the door toward biomimetic production of the GO- or rGO-based composites of superior toughness and high conductivity, which will have great promising applications in many fields like aerospace, flexible supercapacitor electrodes, artificial muscle and tissue engineering.

## REFERENCES

- [1] X. Li, Z.-H. Xu, R. Wang, *Nano Lett.* 6, 2301, 2006.
- [2] H.-B. Yao, H.-Y. Fang, X.-H. Wang, S.-H. Yu, *Chem. Soc. Rev.* 40, 3764, 2011.
- [3] H. Kakisawa, T. Sumitomo, R. Inoue, Y. Kagawa, *Compos. Sci. Technol.* 70, 161, 2010.
- [4] L. J. Bonderer, K. Feldman, L. J. Gauckler, *Compos. Sci. Technol.* 70, 1958, 2010.
- [5] Y.-Q. Li, T. Yu, T.-Y. Yang, L.-X. Zheng, K. Liao, *Adv. Mater.* 24, 3426, 2012.
- [6] H.-B. Yao, H.-Y. Fang, Z.-H. Tan, L.-H. Wu, S.-H. Yu, *Angew. Chem., Int. Ed.* 49, 2140, 2010.
- [7] Z. Tang, N. A. Kotov, S. Magonov, B. Ozturk, *Nat. Mater.* 2, 413, 2003.
- [8] Q. Cheng, M. Li, L. Jiang, Z. Tang, *Adv. Mater.* 24, 1838, 2012.
- [9] A. Walther, I. Bjurhager, J. M. Malho, J. Ruokolainen, L. Berglund, O. Ikkala, *Angew. Chem., Int. Ed.* 49, 6448, 2010.
- [10] E. Munch, M. E. Launey, D. H. Alsem, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Science* 322, 1516, 2008.
- [11] D. Li, R. B. Kaner, *Science* 320, 1170, 2008.
- [12] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* 442, 282, 2006.
- [13] Z. Xu, H. Sun, X. Zhao, C. Gao, *Adv. Mater.* 25, 188, 2013.
- [14] X. Huang, Z. Zeng, Z. Fan, J. Liu, H. Zhang, *Adv. Mater.* 24, 5979, 2012.
- [15] S. Park, K. S. Lee, G. Bozoklu, W. Cai, S. T. Nguyen, R. S. Ruoff, *ACS Nano* 2, 572, 2008.
- [16] S. Park, D. A. Dikin, S. T. Nguyen, R. S. Ruoff, *J. Phys. Chem. C* 113, 15801, 2009.
- [17] N. V. Medhekar, A. Ramasubramaniam, R. S. Ruoff, V. B. Shenoy, *ACS Nano* 4, 2300, 2010.
- [18] Z. An, O. C. Compton, K. W. Putz, L. C. Brinson, S. T. Nguyen, *Adv. Mater.* 23, 3842, 2011.
- [19] Y. Gao, L.-Q. Liu, S.-Z. Zu, K. Peng, D. Zhou, B.-H. Han, Z. Zhang, *ACS Nano* 5, 2134, 2011.
- [20] X. Qi, K.-Y. Pu, H. Li, X. Zhou, S. Wu, Q.-L. Fan, B. Liu, F. Boey, W. Huang, H. Zhang, *Angew. Chem., Int. Ed.* 49, 9426, 2010.
- [21] O. C. Compton, S. W. Cranford, K. W. Putz, Z. An, L. C. Brinson, M. J. Buehler, S. T. Nguyen, *ACS Nano* 6, 2008, 2012.
- [22] I.-W. P. Chen, R. Liang, H. Zhao, B. Wang, C. Zhang, *Nanotechnology* 22, 485708, 2011.
- [23] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, S. Seal, *Prog. Mater. Sci.* 56, 1178, 2011.
- [24] J. Liang, L. Huang, N. Li, Y. Huang, Y. Wu, S. Fang, J. Oh, M. Kozlov, Y. Ma, F. Li, R. Baughman, Y. Chen, *ACS Nano* 6, 4508, 2012.
- [25] H. Fan, L. Wang, K. Zhao, N. Li, Z. Shi, Z. Ge, Z. Jin, *Biomacromolecules* 11, 2345, 2010.
- [26] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* 448, 457, 2007.
- [27] S. Pei, J. Zhao, J. Du, W. Ren, H.-M. Cheng, *Carbon* 48, 4466, 2010.
- [28] R. Z. Wang, Z. Suo, A. G. Evans, N. Yao, I. A. Aksay, *J. Mater. Res.* 16, 2485, 2001.
- [29] W. J. Landis, J. J. Librizzi, M. G. Dunn, F. H. Silver, *J. Bone Miner. Res.* 10, 859, 1995.
- [30] H. Sano, B. Ciucchi, W. G. Matthews, D. H. Pashley, *J. Dent. Res.* 73, 1205, 1994.
- [31] A. Satti, P. Larpent, Y. Gun'ko, *Carbon* 48, 3376, 2010.
- [32] K. W. Putz, O. C. Compton, M. J. Palmeri, S. T. Nguyen, L. C. Brinson, *Adv. Funct. Mater.* 20, 3322, 2010.
- [33] H. Lu, Z. Chen, C. Ma, *J. Mater. Chem.* 22, 16182, 2012.