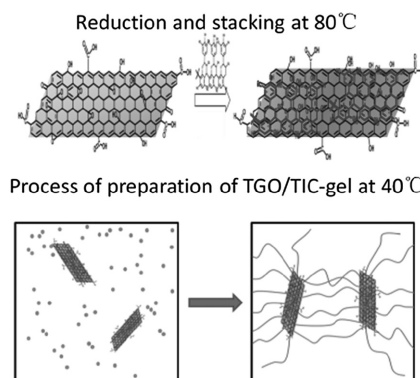


Fabrication of Super Extensible and Highly Tough Graphene Composite Hydrogels by Thermal Treatment Strategy for the Mixture of Tannin and Graphene Oxide

Qihua Guo, Zixing Shi,* Hongjie Xu, Xiaodong Ma, Jie Yin, Ming Tian

Inspired by using the condensed tannins as coinitiator and crosslinker to prepare stretchable hydrogel (TIC-gel) and by tannins' ability to prepare tannins-reduced graphene oxide (TGO) at 80 °C, this paper designs a simple and effective method with a thermal treatment process for the mixture of tannin and graphene oxide (GO) to prepare super extensible TGO composite TIC-gel (TGO-gel). After the thermal treatment process, graphene oxide is reduced by tannin and its surface becomes orderly which leads to strong π - π stacking interaction between tannins and graphene sheets. By this way, the interaction between graphene sheets and polymer chains is improved. As a result, these composite hydrogels have high tensile strength (0.5–1.2 MPa) and extremely high elongations (3100–4800%) which are much higher than those of GO composites TIC-gel (TA/GO-gel) without thermal-treated process and those of normal graphene composite hydrogel.



1. Introduction

Hydrogels are aggregations of crosslinked polymer networks and water. In the last three decades, polymeric hydrogels have attracted lots of scientific interest due to their potential applications in drug delivery,^[1,2] sensing,^[3] actuation,^[4] scaffolds for tissue engineering,^[5] etc. However, the conventional chemically crosslinked hydrogels

exhibit brittle, low-stretchable, and poor mechanical properties which limited its extensively practical application. Many works have been done focusing on preparing hydrogels with high toughness.^[6–17] According to the theory of dissipation-induced toughening,^[18–20] it is believed that preparing nanocomposite hydrogel (NC gels) is one of the simple ways to build tough hydrogels.^[21] Graphene and graphene oxide sheets are usually used to fabricate graphene-based polymer nanocomposites due to its brilliant properties.^[22–31] However, as reviewed by Macosko and co-workers, the improvements are always inefficient which is mainly due to the weak interactions between polymer chains and graphene oxide (GO) sheets.^[32] The improvement of GO/polymer composites are usually less than 80%.^[33,34] Some works improved the interactions between polymer chains and GO sheets by introduction of strong covalent bonds through grafting. The “grafting-to” approach utilizes the reactions between the reactive ends of a preformed polymer with the functional groups

Q. Guo, Prof. Z. Shi, Prof. H. Xu, X. Ma, Prof. J. Yin
School of Chemistry & Chemical Engineering
Shanghai Key Lab of Electrical Insulation and Thermal Ageing
State Key Laboratory for Metal Matrix Composite Materials
Shanghai Jiao Tong University
Shanghai 200240, P. R. China
E-mail: zxshi@sjtu.edu.cn
Prof. M. Tian
State Key Lab of Organic-Inorganic Composites
Beijing University of Chemical Technology
Beijing 100029, China

on GO.^[35] But it is low-efficiency and has difficulty in obtaining a high grafting density. The “grafting-from” process used the graphene peroxide (GPO) as polyfunctional initiating and crosslinking centers and had prepared brilliant nanocomposite hydrogels.^[29] But the preparation of GPO may be demanding.

In this paper, we designed a simple method—thermal treatment strategy for the mixture of tannin and graphene oxide—to prepare super extensible and highly tough graphene composite hydrogels by improving the interaction between GO sheets and polymer chains with the assistance of a kind of natural extracts from bark-condensed tannins (TA). According to our study, we know that condensed tannin could act as co-initiator and crosslinker to prepare tough and highly stretchable hydrogels (TIC-gels) due to the graft polymerization of acrylamide (AAM) onto tannins,^[36] as shown in Schemes S1 and S2 and Figures S1–S3 (Supporting Information). Based on our further study, we found that TA solution could reduce GO at 80 °C and disperse graphene in water very well. After GO was reduced by TA with the thermal treatment (TGO), its surface became orderly and TA would adsorb on the graphene sheets due to the strong π - π stacking interactions. For comparison, GO (0.5 mg mL⁻¹) composites TIC-gels (TA/GO-gels) were prepared, the elongation and tensile strength only increased from 2184% and 160 kPa to 3297% and 297 kPa. Impressively, when we heated the mixture of TA and GO (to get TGO) before adding it into the polymerization system, the mechanical property of TGO-gels had prominent improvement with a brilliant elongation of 4811% and tensile strength of 836 kPa (with a maximum toughness about 17 MJ m⁻³). It is the second highest elongation in the graphene hydrogel composites that ever reported. The highest is 5300% (with a rupture strength about 400 kPa) by the GPO gel with 1 mg mL⁻¹ GPO reported by Wang and co-workers.^[29] More important, we provided a simple way to prepare graphene-based polymer composites which have strong interactions between graphene sheets and polymer chains based on radical polymerization.

2. Experimental Section

2.1. Extraction of Tannin from *Myrica Esculenta* Bark

The myrica esculenta bark was smashed and then immersed the bark with acetone–water system. This mixture was filtered, kept the liquid, and washed the solution with petroleum ether, ether, and ethyl acetate sequentially. The solution was dried to get the extracts. Major components of extracts from myrica esculenta bark were partially galloylated polymeric prodelphinidins—myrica condensed tannins (TA). TA was directly used after drying. The structure of TA is shown in Figure S1 (Supporting Information).

2.2. Synthesis of GO and TGO

GO was prepared from pristine graphite by the modified Hummers method (see the Supporting Information). TGO was prepared as follows. The suspension of GO was prepared by dispersing GO into water via sonication. Tannin (400 wt% relative to GO) was added into the GO dispersion and a sonication process was followed for 30 min. The reduction process was performed for 4 h at 80 °C. The mixture was washed as follows: the mixture was centrifuged at 10 000 rpm for 30 min and the liquid was removed. The TGO was redispersed in deionized water and was washed for seven times. The TGO dispersion was used directly after washed.

2.3. Preparation of Hydrogel Composites

All the gels mentioned in this article were prepared at AAM concentrations 30 wt%. A one-pot method was used to synthesize TGO nanocomposite hydrogels (TGO hydrogel). To exemplify the progress, a 0.1 wt% (mass ratio to the monomer) ammonium persulfate (APS) and 0.1 mg mL⁻¹ TGO nanocomposites hydrogel were prepared as follows: 23.5 mL 0.1 mg mL⁻¹ TGO water dispersion liquid was treated with sonication for 2 h. After that, 10 g of AAM was added to it. The mixture solution was stirred for 2 h. Then the mixture was deaired for 20 min with nitrogen gas. After that, 0.01 g APS was added into the solution. The system was stirred for 10 min to yield a homogeneous dispersion and a reduced pressure process was followed to remove the excess gas. The resulting solution was transferred to glass molds made by placing a silicone spacer with a height of 2 mm between two flat glass plates. The samples were placed in oven at 40 °C for 24 h to form TGO gel. Samples were cut by a 4 × 50 dumbbell cutter (overall length: 50 mm, inner width 4 mm, gauge length: 16 mm) according to GB/T528. Gels were also prepared with higher or lower levels of composites, as indicated in the text. For comparison, GO-gel was also made. The synthetic process was same to the procedures as illustrated before.

3. Results and Discussion

3.1. Synthesis and Characterization of GO

Details on the synthesis and characterization of GO can be found in the Supporting Information.

3.2. Synthesis and Characterization of TGO

According to our previous study, tea solution could reduce graphene oxide at 80 °C and disperse graphene well in water.^[37] Condensed tannins have same functional group with the tea solution. Maybe the TA solution could reduce GO too. So we heated the mixture of TA and GO for 4 h at 80 °C in nitrogen atmosphere, and monitored the thermal treatment process by UV and characterized the product by X-Ray powder diffraction (XRD). The results were in Figure S8 (Supporting Information). According to the previous work^[38–40] and our analysis (see Figures S9–S12,

Supporting Information), the TA indeed could reduce GO and there was strong interaction between TA (stabilizers) and graphene which is proposed to mainly be π - π interaction.^[41–43]

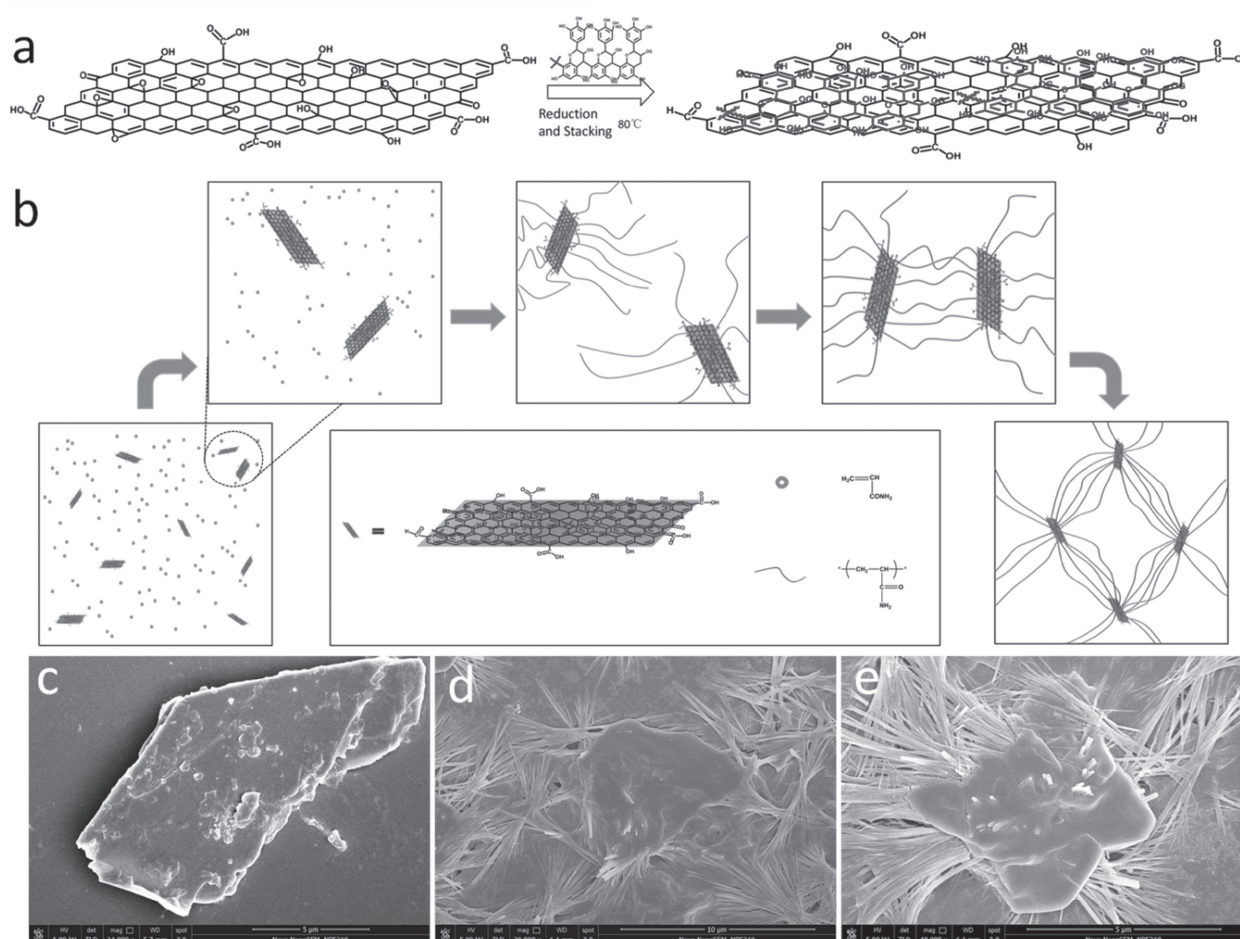
Atomic force microscopy (AFM) was also measured to characterize the TGO. Images in Figure S13 (Supporting Information) are the typical AFM images and height profiles of TGO, we can see that the average thickness is about 1.8 nm. Considering that TA molecules adsorbed on the surface of graphene, we believed that most of TGO exist in the form of single layer and there is TA on their surface because of the π - π stacking interaction.

3.3. Preparation of Hydrogel Composites and Measurements

Based on all these research, we designed a simple method—thermal treatment strategy for the mixture of tannin and graphene oxide—to prepare super extensible and highly

tough graphene composite by improving the interaction between the GO sheets and polymer matrix. TA gradually reduced the GO during the thermal treatment process and then stacked on the graphene due to π - π stacking interactions. So TGO could act as coinitiator and crosslinker due to the TA on their surface, and the interaction between polymer chains and graphene sheets became stronger. The whole process for radical polymerization with the presence of TGO is illustrated in Scheme 1. Scanning electron microscope (SEM) investigations of the reaction mixture after short reaction time (20 min) shows that there are fibers on the surface of TGO sheets which also confirmed our assumption about the role of TGO in the polymerization process.

For comparison, we prepared TA/GO-gel (brown) and TGO-gel (black) as shown in Figure 1a. Compared with TIC-gel, the tensile strength and strain of TA/GO-gel had some improvements. However, the mechanical properties of TGO-gel improved prominently. As shown in Figure 1b, TIC-gel prepared by 0.1 wt% APS and 0.04 wt% TA could



Scheme 1. a) Schematic model of GO and TGO. b) Schematic model for the formation of a TGO hydrogel. The blue sheets are the TGO, the green points are the monomers, and the green lines are the polymer chains. c) Typical SEM of TGO. d, e) SEM graphs showing the formation process of a TGO hydrogel when the reaction time is 20 min. Preparation process: 0.06 g TGO, 0.1 g AAM, 0.001 g APS, 10 mL H₂O, at 40 °C for 20 min, then it was diluted with 100 times deionized water.

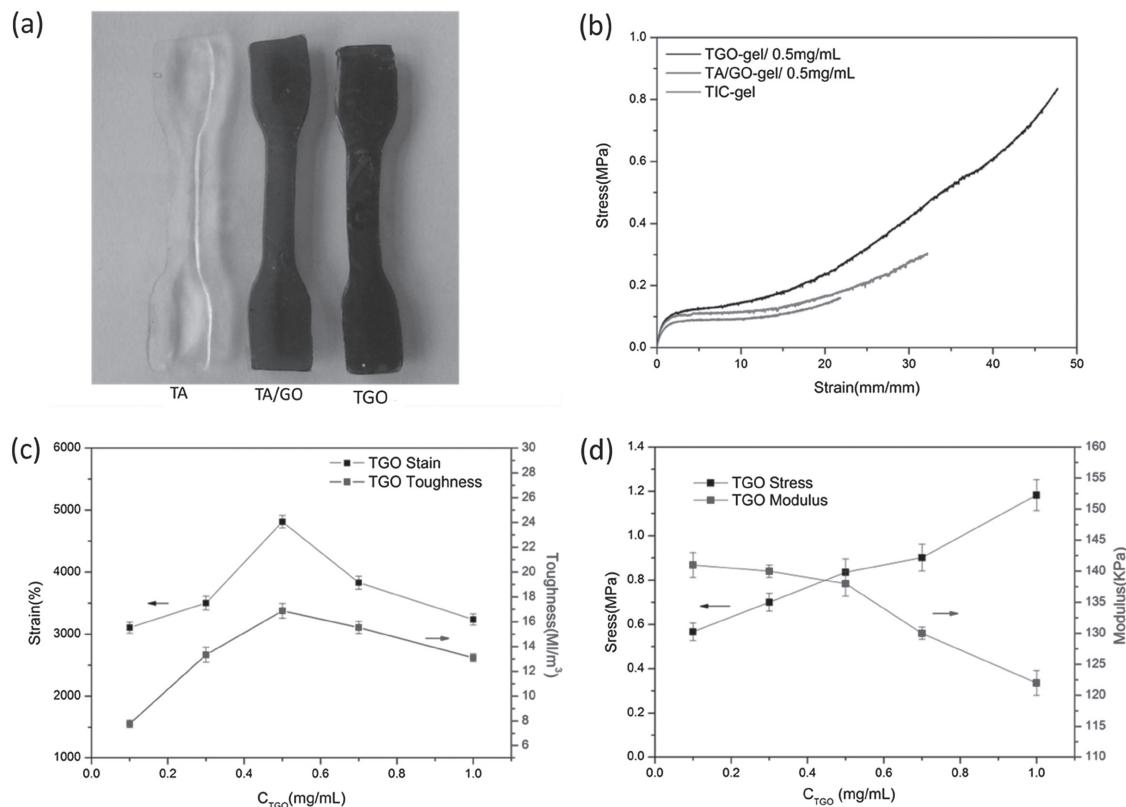


Figure 1. a) Picture of TIC-gel, TA/GO-gel, and TGO-gel. b) Stress–strain curves of TIC-gel, TA/GO-gel, and TGO-gel (concentration of graphene sheets: 0.5 mg mL⁻¹). c) Fracture strain and toughness of TGO-gel. d) Fracture stress and modulus of TGO-gel.

be stretched up to 2184% with a tensile strength 160 kPa. TA/GO-gel could be stretched up to 3297% with a tensile strength 297 kPa. The improvement in tensile strength was only about 85%. However, the mechanical property of TGO-gel had prominent improvement with a brilliant elongation of 4811% and tensile strength of 836 kPa. The improvement in tensile strength was almost 423% which was much higher than the value of TA/GO-gel (85%). More important, we prepared super extensible and highly tough graphene composite hydrogels by a simple thermal treatment strategy for the mixture of TA and GO.

A series of TGO-gels were prepared by using TGO aqueous dispersions with different TGO concentrations and measured by the tensile test. The solid content in all these hydrogels was 30 wt%. In order to ensure the homogeneous dispersion of TGO, the highest concentration of TGO was selected as 1 mg mL⁻¹. When the TGO (0.1–1 mg mL⁻¹) was incorporated into the gel, we obtained TGO-gels exhibiting excellent mechanical properties which had very high tensile strength (0.5–1.2 MPa) and extremely high elongations (3100–4800%). For example, when the concentration of TGO is 0.1 mg mL⁻¹, its elongation was 3106% and toughness was 7.77 MJ m⁻³ (Figure 1c,d). As its concentration increased to 0.5 mg mL⁻¹, its elongation increased to 4811% with a toughness of

16.88 MJ m⁻³. Further increasing concentration of TGO to 1 mg mL⁻¹ would decrease its elongation and toughness to 3237% and 13.10 MJ m⁻³, respectively. The tensile strength of these gels gradually increased from 567 to 1183 kPa with the concentration of TGO increasing from 0.1 to 1 mg mL⁻¹ with their modulus shifting around 130 kPa. As we have illustrated, our TGO composite hydrogels exhibit excellent mechanical properties. Compared with most of tough double-network^[6,7] and nanocomposite^[8,9] gels, the extensibility of TGO-gels (3000–4800%) is higher than most other double-network gels (1000–3000%). The extensibility of 4800% exhibited by our TGO-gel is the second-highest ever reported. Some data of reported tough hydrogels are listed in Table S1 (Supporting Information). Increasing the concentration of TGO has three effects on the structure of TGO composite hydrogel. First, more crosslinking structure will be formed in the system. Second, the increase of graphene content will enhance the mechanical property of TGO composite hydrogel. Third, when the content of TGO is high, it may cause some heterogeneous dispersion of TGO in the system. A combination of all these effects resulted in the performance of strain, toughness, stress, and modulus as we illustrated.

Moreover, the TGO-gels also exhibit good elastic recovery. Cyclic tensile tests were carried out on the

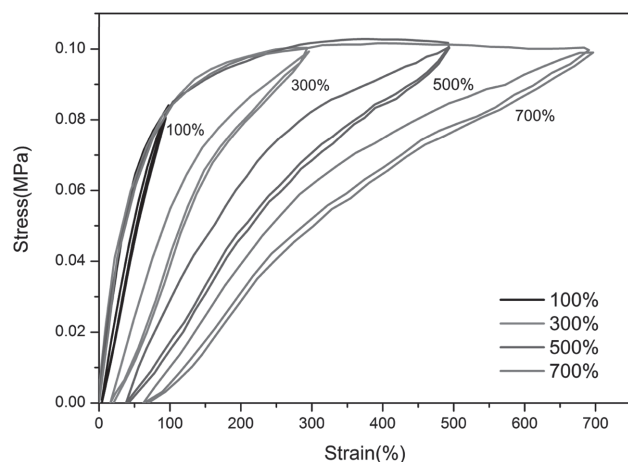


Figure 2. Cyclic tensile loading–unloading curves of the TGO-gels to the strain of 100, 300, 500, and 700% for 2 cycles. Conditions: 0.1 mg mL⁻¹ TGO concentration.

hydrogels (Figure 2). A hysteresis loop could be found in the first loading–unloading cycle, and it became much smaller in the following cycle. When the tensile strain was 100%, it showed high elastic recovery, up to 96% in the first cycle. When the tensile strains were increased to 300, 500, and 700%, their elastic recovery ratios changed to 94.7, 92.4, and 91.2%, respectively. It had little residual deformation even when it fractured (Figure S14, Supporting Information). The hydrogen bond ruptures and the disentanglements of polyacrylamide chains may contribute to the hysteresis loops. The fracture of covalent bonds in the network and the pullout of graphene from polymer may cause permanent damage.

We also turned to dynamic rheology measurement to further investigate the property of TGO composite hydrogel. As shown in Figure 3, the elastic modulus (G') of the TGO-gel is always much higher than the viscous

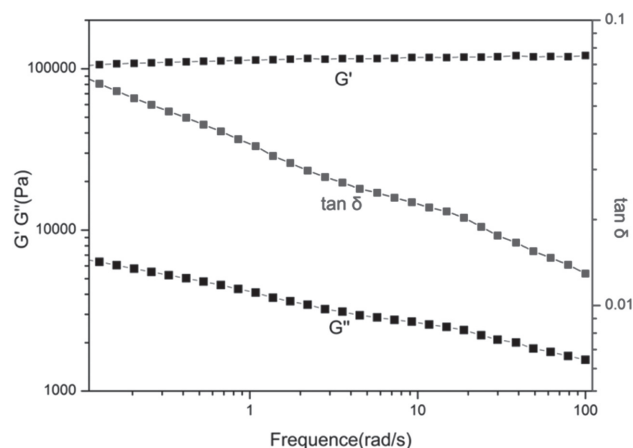


Figure 3. Storage modulus (G'), loss modulus (G''), and loss factor ($\tan \delta$) of TGO-gel as a function of frequency. TGO gel: 0.3 mg mL⁻¹ TGO, 0.1 wt% APS, 70 wt% water content.

modulus (G'') over the tested range from 0.1 to 100 rad s⁻¹. However, at lower frequency, its $\tan \delta$ was much larger than that at higher frequency, and $\tan \delta$ showed some dependence on the frequency. This phenomenon indicated that there also exist some hydrogen-bond interactions between tannin and polyacrylamide. Such specific rheology may contribute to the super extensibility and high toughness of the TGO composite gels.

4. Conclusions

In summary, we have designed a simple and effective method to prepare super extensible TGO-gels. Specifically, by heating the mixture of TA and GO, we can prepare TGO where tannin could attach on the surface of graphene via the strong π - π interaction. By this way, TGO could act as the coinitiator, crosslinker and nanofiller to prepare composite hydrogels with high tensile strength and elongation. The mechanical properties of the TGO-gels are pretty good even compared with those of some soft tissues.^[44,45] So they may have many applications in biomedical fields and may be helpful for the design of biomaterial. This paper provides a novel and simple way to prepare stretchable graphene-based polymer composites based on radical polymerization with strong interactions between graphene and polymer chains. So we believe more types of graphene polymer composite could be prepared by this method.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: The authors thank the National Nature Science Foundation of China (No. 51473091, No. 51641304), the Natural Science Foundation of Shanghai (16ZR1416600), and the National Science Fund for Distinguished Young Scholars of China (Grant No. 51525301) for financial support.

Received: November 22, 2016; Published online: ; DOI: 10.1002/macp.201600549

Keywords: graphene-based composites; mechanical property; super extensible

- [1] D. S. Kohane, R. Langer, *Chem. Sci.* **2010**, *1*, 441.
- [2] T. R. Hoare, D. S. Kohane, *Polymer* **2008**, *49*, 1993.
- [3] J. D. Ehrick, S. Stokes, S. B. Daunert, E. A. Moschou, S. K. Deo, L. G. Bachas, S. Daunert, *Adv. Mater.* **2007**, *19*, 4024.
- [4] M. K. Shin, G. M. Spinks, S. R. Shin, S. I. Kim, S. J. Kim, *Adv. Mater.* **2009**, *21*, 1712.
- [5] K. Y. Lee, D. J. Mooney, *Chem. Rev.* **2001**, *101*, 1869.
- [6] J. F. Wang, L. Lin, Q. F. Cheng, L. Jiang, *Angew. Chem., Int. Ed.* **2012**, *51*, 4676.

- [7] K. Haraguchi, T. Takehisa, *Adv. Mater.* **2007**, *14*, 1120.
- [8] Z. Q. Hu, G. M. Chen, *Adv. Mater.* **2014**, *26*, 5950.
- [9] P. Lin, S. H. Ma, X. L. Wang, F. Zhou, *Adv. Mater.* **2015**, *27*, 2054.
- [10] T. Huang, H. G. Xu, K. X. Jiao, L. P. Zhu, H. R. Brown, H. L. Wang, *Adv. Mater.* **2007**, *19*, 1622.
- [11] G. X. Sun, Z. J. Li, R. Liang, L. T. Weng, L. N. Zhang, *Nat. Commun.* **2016**, *7*, 12095.
- [12] J. Chen, Y. Y. Ao, T. R. Lin, X. Yang, J. Peng, W. Huang, J. Q. Li, M. L. Zhai, *Polymer* **2016**, *87*, 73.
- [13] Y. Zhai, X. Meng, H. D. Duan, Z. Y. Ding, Y. Liu, L. Lucia, *Macromol. Chem. Phys.* **2016**, *217*, 32.
- [14] J. L. Wang, J. H. Wei, S. H. Su, J. J. Qiu, S. R. Wang, *J. Mater. Sci.* **2015**, *50*, 5458.
- [15] Y. N. Sun, S. Liu, G. L. Du, G. R. Gao, J. Fu, *Chem. Commun.* **2015**, *51*, 8512.
- [16] Y. Hu, Z. Du, X. Deng, T. Wang, Z. Yang, W. Zhou, C. Wang, *Macromolecules* **2016**, *49*, 5660.
- [17] M. Zhu, Y. Liu, B. Sun, W. Zhang, X. Liu, H. Yu, Y. Zhang, D. Kuckling, H.-J. P. Adler, *Macromol. Rapid Commun.* **2006**, *27*, 1023.
- [18] R. M. McMeeking, A. G. Evans, *J. Am. Ceram. Soc.* **1982**, *65*, 242.
- [19] H. R. Brown, *Macromolecules* **2007**, *40*, 3815.
- [20] Y. Tanaka, *Europhys. Lett.* **2007**, *78*, 56005.
- [21] X. H. Zhao, *Soft Matter* **2014**, *10*, 672.
- [22] A. K. Geim, *Science* **2009**, *324*, 1530.
- [23] C. Lee, X. D. Wei, J. W. Kysar, J. Hone, *Science* **2008**, *321*, 385.
- [24] J. W. Suk, R. D. Piner, J. H. An, R. S. Ruoff, *ACS Nano* **2010**, *4*, 6557.
- [25] J. H. Seol, I. Jo, A. L. Moore, L. Lindsay, Z. H. Aitken, M. T. Pettes, X. S. Li, Z. Yao, R. Huang, D. Broido, *Science* **2010**, *328*, 213.
- [26] J. F. Shen, B. Yan, T. Li, Y. Long, Na Li, M. X. Ye, *Soft Matter* **2012**, *8*, 1831.
- [27] Z. C. Zhu, Y. Li, H. Xu, X. Peng, Y. N. Chen, C. Shang, Q. Zhang, J. Q. Liu, H. L. Wang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 15637.
- [28] Z. Y. Xiong, X. W. Yun, B. Tang, X. G. Wang, *Carbon* **2016**, *107*, 548.
- [29] J. Q. Liu, C. F. Chen, C. C. He, J. Zhao, X. J. Yang, H. L. Wang, *ACS Nano* **2012**, *6*, 8194.
- [30] S. Das, F. Irin, L. Ma, S. K. Bhattacharia, R. C. Hedden, M. J. Green, *ACS Appl. Mater. Interfaces* **2013**, *5*, 8633.
- [31] R. Liu, S. Liang, X. Tang, D. Yan, X. Li, Z. Yu, *J. Mater. Chem.* **2012**, *22*, 14160.
- [32] H. Kim, A. A. Abdala, C. W. Macosko, *Macromolecules* **2010**, *43*, 6515.
- [33] X. Zhao, Q. Zhang, D. Chen, P. Lu, *Macromolecules* **2010**, *43*, 2357.
- [34] J. Shen, B. Yan, T. Li, Y. Long, N. Li, M. Ye, *Soft Matter* **2012**, *8*, 1831.
- [35] S. Mohamadi, N. Sharifi-Sanjani, H. Mahdavi, *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2011**, *48*, 577.
- [36] R. Vasantha, K. P. Rao, K. T. Joseph, *J. Appl. Polym. Sci.* **1987**, *33*, 2271.
- [37] Y. Wang, Z. X. Shi, J. Yin, *Appl. Mater. Interfaces* **2011**, *3*, 1127.
- [38] D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.* **2008**, *3*, 101.
- [39] M. J. Fernandez-Merino, L. Guardia, J. I. Paredes, S. Villar-Rodil, P. Solis-Fernandez, A. Martínez-Alonso, J. M. D. Tascón, *J. Phys. Chem. C* **2010**, *114*, 6426.
- [40] V. H. Pham, T. V. Cuong, T. D. N. Phan, H. D. Pham, E. J. Kim, S. H. Hur, E. W. Shin, S. Kim, J. S. Chung, *Chem. Commun.* **2010**, *46*, 4375.
- [41] X. Yang, X. Zhang, Z. Liu, Y. Ma, Y. Huang, Y. Chen, *J. Phys. Chem. C* **2008**, *112*, 17554.
- [42] A. J. Patil, J. L. Vickery, T. B. Scott, S. Mann, *Adv. Mater.* **2009**, *21*, 3159.
- [43] F. H. Li, Y. Bao, J. Chai, Q. X. Zhang, D. X. Han, L. Niu, *Langmuir* **2010**, *26*, 12314.
- [44] N. S. Khan, A. Ahmad, S. M. Hadi, *Chem.-Biol. Interact.* **2000**, *125*, 177.
- [45] N. Sahiner, S. Sagbas, N. Aktas, C. Silan, *Colloids Surf., B* **2016**, *142*, 334.