Flow-Induced Enhancement of in Situ Thermal Reduction of Graphene Oxide during the Melt-Processing of Polymer Nanocomposites

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ABSTRACT: In situ thermal reduction (ISTR) of graphene oxide (GO) dispersed in a polymer matrix has attracted broad interest due to its great potential as an environmentally friendly and commercially viable process to prepare polymer/graphene nanocomposites (PGNs). In this work, the ISTR of GO in two dramatically different conditions, quiescent melt and sheared melt, was comparatively studied. Comprehensive characterization of the bulk composites and the extracted graphene-based powders from composites, as well as the results of an independent parallel plate experiment, revealed that the GO in the sheared melt has a higher reduction degree than that in the quiescent melt within identical processing temperatures and times. On the basis of our results, we hypothesize that the more intense reduction of GO in the sheared melts relative to the quiescent melts is associated with the enhanced π–π stacking and the possible radical reaction between polymers and GO sheets.

1. INTRODUCTION

Graphene is a fascinating new two-dimensional carbon material with a honeycomb lattice and shows excellent electrical, thermal, and mechanical properties, so there is increasing interest in using graphene as a promising nanofiller material for polymer nanocomposites.1−5 The incorporation of graphene sheets leads to significant enhancement in various physical properties of the polymer/graphene nanocomposites (PGNs) relative to neat polymers. Thanks to the advantages of low cost and large scalability of graphene oxide (GO), the precursor of graphene, together with its ability of being chemical modified, GO has been widely used as the starting material, in place of graphene, to produce PGNs.6 Hitherto, three strategies have been developed to prepare PGNs from GO: in situ polymerization, solvent blending, and melt-blending.7−9 Of all the strategies, a reduction process, that is generally chemical reduction for liquid-based strategies and thermal reduction for solvent-free melt-blending, needs to be carried out to transform GO into reduced GO (rGO). Recently, the so-called in situ thermal reduction (ISTR) of GO dispersed in polymer matrix has attracted considerable attention in both industrial and academic institutions due to no addition of surfactant and reduction reagents, and it holds great potential to be developed as an environmentally friendly and commercially viable process to produce PGNs.10−13 Yu et al. first found that the electrical conductivity of a polystyrene (PS)/modified GO composite increased after it was compression-molded at 210 °C, which indicates that the modified GO was further reduced under the thermal treatment.14 Sodano et al. creatively synthesized conductive polyvinylidene fluoride (PVDF)/graphene nano-

composites by simply hot-pressing the PVDF/GO nanocomposites at 200 °C.11 Tang et al. and She et al. independently fabricated PGNs with superior electrical conductivity by a two-step reduction technique consisting of a chemical reduction and a subsequent ISTR.12,13 Although the fact that the ISTR translates the GO dispersed in a polymer matrix to rGO has been recognized and widely applied to the preparation of PGNs, research on the factors influencing the ISTR of GO is surprisingly scarce. Until recently, a few dedicated research groups made continuous efforts to obtain deeper insights into this issue.15−18 By thermally annealing the poly(vinyl alcohol)/GO composites under different conditions, Fu et al. found that high temperature is more efficient for reducing the GO than low temperature, and the long annealing time could improve the reduction degree of GO to a certain level.19 Through differential scanning calorimetry (DSC) thermograms, Schniepp et al. found that the polymer chemistry significantly affects the reduction degree of GO; that is, poly(vinylpyrrolidone) inhibits, whereas poly(vinyl acetate) facilitates the ISTR of GO.16 By similar means, our own research demonstrated that the interactions between GO and polymers play a key role in decreasing the reduction temperature of GO.17 The polar polymers and aromatic polymers that show strong interactions with GO sheets cause a larger decrease in the reduction temperature than the nonpolar polymers that have weak interactions with GO sheets.
All of these studies lead to a better understanding of the influencing factors for ISTR, which is certainly helpful for us to unveil the mysterious veil of ISTR of GO.

Up to now, almost all the related research focuses on the ISTR of GO dispersed in polymer matrices under quiescent conditions, including hot-pressing or thermal annealing. However, for the preparation of polymer nanocomposites, the uniform dispersion of nanofillers in the polymer matrixes is the prerequisite for achieving the desired mechanical and physical characteristics. It is impossible for hot-pressing, just a basic molding technology, to reach the goal of mixing and dispersion. Instead, the fabrication of polymer nanocomposites with fine dispersion of nanofillers can be industrially achieved by melt-processing using an extruder, mill, and mixer, in which an external shear flow is exerted on the components in the composites. With the help of flow-induced stretching, arrangement, and entanglement of polymer chains occurring in the sheared melts, the different components are well blended with each other, producing various high-performance materials. Particularly, recent reports demonstrate that shear flow offers advantages in exfoliating the layered nanofillers, facilitating the dispersion of nanofillers in a matrix, and enhancing the interactions between nanofillers and polymers, which are certainly beneficial to the good performance of the resulting materials. Considering the great potential of melt-blending in fabricating PGNs, together with the unique feature of a sheared melt, investigating the influence of the shear flow on the reduction behavior of GO is of great importance.

In this work, the ISTR of GO dispersed in the quiescent PS melt under hot-pressing and the sheared melt under melt-blending was comparatively investigated. Both the PS/graphene nanocomposites (PSGNs) and the graphene-based powders extracted from PSGNs were systematically characterized by various physico-chemical techniques. The results indicate that the shear flow during melt-blending induces more intense reduction of GO as compared with the quiescent condition in hot-pressing. In the parallel plate experiment, the GO located in the high-flow rate zone shows more significant reduction than that located in the low-flow rate zone, which further confirms that the shear flow plays a key role in enhancing the ISTR of GO. On the basis of our results and previous studies, the enhanced $\pi-\pi$ stacking and possible radical reaction between PS and GO sheets in the sheared melt are speculated to be responsible for the flow-induced enhancement of the ISTR of GO. We believe that the results presented in this work will advance our understanding of the ISTR of GO and promote the commercialization of PGNs.

2. EXPERIMENTAL SECTION

2.1. Preparation of PSGNs. GO was prepared via a modified Hummers method and dried completely for subsequent use. First, the PS/GO nanocomposite containing 1.0 wt % GO was prepared by solution blending, which can ensure a fine dispersion of GO in the PS matrix. In a typical procedure, a desired amount of dried GO powder was dispersed in tetrahydrofuran (THF) with the aid of ultrasonication for 2 h at room temperature. Then, the preweighted PS ($M_w = 22,000$ g mol$^{-1}$, New Zhongmei Chemical Industries Co., Ltd.) was dissolved into the uniform GO suspension by vigorous stirring for 24 h. Before drying in a vacuum oven at 80 °C for 2 days to remove the residual THF, the evaporation of the continuously stirred PS/GO solutions was carried out in a fume cupboard for 7 days at room temperature. The dried PS/GO nanocomposite stored at room temperature was denoted as PSGN-RT. To realize the reduction of GO in the quiescent melt, the PSGN-RT was hot-pressed under 5 MPa using a QLB-D molding press at 180 °C for 10 min, and the resulting sample was denoted as PSGN-Q. The reduction of GO in the sheared melt was achieved by melt-blending the PSGN-RT in a Haake PolyLab OS mixer under identical 180 °C and 10 min at a rotating speed of 20 rpm, and the obtained sample was denoted as PSGN-S.

The parallel plate experiment was conducted by employing a Linkam CSS 450 stage equipped with two parallel plates. Typically, a piece of PSGN-RT was held between two quartz plates and sheared by rotation of the bottom plate with the top plate stationary. The gap was fixed at 300 μm, and the applied angular speed was kept constant at 50 rad s$^{-1}$. After shearing for 10 min at 180 °C, the resulting film was peeled from the parallel plates. The samples cut from two different locations of the above film, the central zone and the outer zone, along the radial direction, were denoted as PSGN-C and PSGN-O, respectively.

2.2. Extraction of Graphene-Based Powders from PSGNs. In order to indirectly determine the reduction of GO dispersed in the PS matrix, the graphene-based powders were isolated from the PSGNs by exhaustive extraction. Typically, a small amount of PSGNs was dissolved in THF under continuous stirring. Then, the dark suspensions were centrifuged at 10,000 rpm for 20 min, and the supernatants were decanted and used for the gel permeation chromatography (GPC) measurements. The operations including washing and centrifugation were conducted more than 10 times to remove the free PS as completely as possible. After that, the remaining precipitates were dried at 80 °C for 24 h under a vacuum. The extracted powders obtained from the original PSGN-RT, PSGN-Q, and PSGN-S were denoted as G-RT, G-Q, and G-S, respectively.

2.3. Characterization and Tests. DSC experiments were conducted on a Mettler Toledo DSC 821e in nitrogen with a heating rate of 5 °C min$^{-1}$ at the temperature range of 25–250 °C. Thermogravimetric analysis (TGA) experiments were carried out on a PerkinElmer Pyris 1 TGA with a heating rate of 20 °C min$^{-1}$ from 100 to 800 °C under a nitrogen atmosphere. Electrical conductivity was measured at room temperature by a ZC-90G resistivity meter from Shanghai Taiou Electronics. Fourier transform infrared (FTIR) spectra were recorded by a Nicolet 6700 FTIR spectrophotometer using the KBr method. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo ESCALAB 250Xi electron spectrometer with monochromatic 150 W Al Kα radiation. X-ray diffraction (XRD) patterns were collected using a PANalytical X’pert diffractometer with Cu Kα radiation. Raman spectra were recorded on a HORIBA Xplora Laser Raman spectrometer with 532 nm laser excitation. GPC of the eluted PS was conducted in THF using an Agilent-Wyatt GPC 1260 system. Dynamic mechanical analysis (DMA) of the PSGNs was conducted with a Mettler Toledo DMA/SDTA 861e machine in tensile mode with a frequency of 1 Hz and a heating rate of 3 °C min$^{-1}$ from room temperature to 120 °C. Transmission electron microscopy (TEM) images of the ultrathin sections of the PSGNs and the extracted powders were collected using a Tecnai G2 20 TWIN TEM operated at 200 kV.
3. RESULTS AND DISCUSSION

3.1. ISTR of GO in the Quiescent and Sheared Melts.
Before melting, the PSGN-RT is semitransparent and dark yellow in color. After hot-pressing or melt-blending at 180 °C, the resulting PSGNs become black in color and completely opaque (Supporting Information, Figure S1), indicating the reduction of GO. As an effective technique to evaluate the reduction behavior of GO dispersed in a polymer matrix,16,27,28 here, DSC was used to determine the reduction degree of GO in PSGNs, as shown in Figure 1. It can be seen that neat PS shows no apparent thermal signals within the investigated temperature range of 100–250 °C, so the single exothermic peak that appears in the DSC thermogram of the PSGNs can be certainly attributed to the reduction enthalpy of GO (inset of Figure 1). Since the exothermic signal is contributed by the reaction energy of the decomposition of oxygen functional groups on the GO surface,17 the reduction enthalpy revealed by DSC is inversely correlated with the reduction degree of GO. The DSC thermogram of PSGN-RT exhibits a strong exothermic peak at ∼208 °C with an enthalpy of 5.3 J g⁻¹. This value is decreased to be 1.8 J g⁻¹ for PSGN-Q, indicating that GO is partially reduced in the quiescent melt with a small number of oxygen-containing groups remaining. The reduction enthalpy is further decreased to be as small as about zero for PSGN-S, indicating that these oxygen functional groups that cannot be removed in the quiescent melt at relatively moderate temperature are almost eliminated completely in the sheared melt.

The decomposition of the oxygen-containing groups of the GO surface generally results in the restoration of the π-conjugation structure and the improvement of electrical conductivity of PGNs.29,30 As shown in Figure 2, the electrical conductivity of PSGN-RT is increased by ∼4 orders of magnitude after hot-pressing, correlating well with the findings of many previous reports.12,14,19 A continuing increase of the electrical conductivity (∼1 order of magnitude) is observed in the PSGN-S experiencing shear flow, which could be ascribed to the more significant reduction of GO achieved by melt-blending. Given that both PSGN-Q and PSGN-S were produced from the same PSGN-RT precursor, all of these results suggest that the GO in the sheared melt exhibits a higher reduction degree than that in the quiescent melt. On the basis of the feature of the sheared melt, we believe that the shear flow during melt-blending plays a crucial role in enhancing the ISTR of GO dispersed in the polymer melt.

To better prove the flow-induced enhancement of the ISTR of GO, an independent parallel plate experiment providing different flow conditions was conducted. Compared with the melt-blending in the internal mixer, the parallel plates equipped with a shearing hot-stage (Linkam CSS-450) can realize more precise control of flow conditions with tiny temperature fluctuations.31,32 As illustrated in the inset of Figure 3, the PSGN-RT was held between two quartz plates and sheared by rotation of the bottom plate with the top plate stationary. In the parallel plates, the flow rate (γ) increases linearly with the radius (r) in the torsional geometry according to the function, γ = Ω r/d, where Ω is the angular speed, and d is the shear gap.20 Therefore, the flow rate of the PS melt in the outer zone is higher than that in the central zone. The PSGN-C cut from the central zone and the PSGN-O cut from the outer zone of the sheared sample between parallel plates were characterized by DSC, which is shown in Figure 3. Obviously, PSGN-C exhibits a slightly larger reduction enthalpy (∼2.2 J g⁻¹) than PSGN-O (∼1.6 J g⁻¹), indicating that the GO under the high flow rate experiences a relatively heavier reduction than that under the low flow rate. Considering that the flow rate is the only variable in the parallel plate experiment, the above result provides
convincing evidence for the view that shear flow has an enhancement effect for the ISTR of GO dispersed in the PS melt.

3.2. Characterization of the Extracted Graphene-Based Powders. Apart from the characterization of the bulk PSGNs by DSC and electrical conductivity, structural and component analyses were also made for the extracted powders from the PSGNs. First, the eluted PS was collected and investigated by GPC (Supporting Information, Figure S2), which exhibits an extremely tiny change in the molecular weight, indicating that PS is thermally stable under hot-pressing and melt-blending at 180 °C.

The thermal stability of the extracted powders was investigated by TGA in nitrogen, as shown in Figure 4a. All the curves almost exhibit two major weight loss steps at about 200 and 400 °C, respectively. In the first step lying at the temperature range of 150–260 °C, the samples G-RT, G-Q, and G-S hold an approximate weight loss of 30, 20, and 4 wt %, respectively. Combined with the typical TGA curve of GO, the first weight loss step is thus presumably assigned to the pyrolysis of the oxygen-containing groups bonded to GO sheets in this narrow temperature range.13 Another obvious weight loss step occurs around 400 °C, which lies on the decomposition temperature of PS (the TGA curve of pure PS is shown in the inset of Figure 4a). The PS content in the extracted powders was determined to be 0, 20, and 41% for G-RT, G-Q, and G-S, respectively. Therefore, the true weight loss of the GO independent of PS (W_G) could be estimated according to the following function

\[ W_G = \frac{100\% - W_{PS}}{W_O} \]

where W_O represents the weight loss of oxygen-containing groups from 150 to 260 °C, and W_{PS} represents the weight loss of PS around 400 °C. The values of W_G are 30, 25, and 6.8 wt % for G-RT, G-Q, and G-S, respectively. The gradually decreased weight loss of GO directly indicates a more significant reduction of GO in sheared melts than in quiescent melts.

From the TGA curves, we notice that a fair amount of PS firmly adheres to the surface of graphene sheets that cannot be removed by repeated washing. To verify this, FTIR spectra of the extracted powders were also collected, as shown in Figure 4b. G-RT exhibits typical characteristic peaks of raw GO corresponding to the oxygen-containing groups. After melting processing in both quiescent and sheared conditions, the oxygen-containing peaks obviously weaken, while several new peaks occur in the FTIR spectra of the extracted G-Q and G-S. Four new peaks at 700, 742, 1453, and 1490 cm\(^{-1}\) correspond to the absorptions of the benzene ring of PS segments, while the peaks at 2912 and 3015 cm\(^{-1}\) arise from the attachment of additional methylene groups.23 These results confirm that PS chains adhere to the graphene surface after melt-processing. According to previous study,18,22 this part of adherent PS could originate from the physical adsorption through π−π stacking.
and covalent grafting by radical reaction during melt-blending. It was found that the FTIR signals corresponding to PS are relatively stronger in the spectrum of G-S than that of G-Q, signifying the more adherent PS on the G-S, which is in line with the TGA results. Possibly, the enhanced ISTR of GO in the sheared melt restores the larger π-conjugated region, which enhances the π−π interaction between PS and graphene sheets and thus leads to more adsorption of PS. The adherent PS was also confirmed by the TEM images of the extracted powders, in which some opaque PS patches bestrew the G-Q and G-S sheets (Supporting Information, Figure S3).

Subsequently, an XRD experiment was carried out to gain insight into the internal structure of the extracted powders (Figure 5a). A strong and sharp XRD peak appears at around 10.6° for G-RT, the typical diffraction peak of GO. This peak becomes slightly broader and weaker for the G-Q, corresponding to a minor reduction of GO. Compared with G-RT and G-Q, the typical peak around 10.6° of G-S shows a markedly reduced intensity and dramatically broadened width, indicating the removal of major oxygen-containing groups. A diffraction peak around 23° simultaneously occurs, which could be assigned to the 002 reflection of graphene, further indicative of developing graphitic structures of G-S. We also note that the diffraction peaks of all the extracted powders almost stay around the same position of 10.6°, suggesting no remarkable changes in the interlayer space of graphene sheets. On the one hand, the oxygen-containing groups of GO were removed during the melt-processing, as confirmed by the XPS data (Supporting Information, Figure S4) that the bands associated with the oxygenated groups in the spectra of G-S are much weaker than those of G-RT and G-Q. This theoretically decreases the interlayer space of graphene sheets. However, on the other hand, the adsorbing of the PS chains onto graphene sheets simultaneously happened, as presented above (Figure 4), which increases the interlayer space. Therefore, the final interlayer space of graphene sheets should be the result of the competition of the two effects.

Raman spectroscopy was also employed to study the transformation of GO in the polymer melts. As shown in Figure 5b, two strong Raman bands at 1338 cm⁻¹ (D band) and 1565 cm⁻¹ (G band) appear in G-RT, which are ascribed to structure defects and the in-plane bond stretching vibration of sp²-bonded carbon atoms in GO sheets, respectively. Notably, the location of the G band shifts to 1585 cm⁻¹ for G-Q and near 1590 cm⁻¹ for G-S, presumably stemming from the reduction of GO and the better exfoliation of the rGO sheets. The increased D/G intensity ratio of 0.99 for G-Q compared to 0.74 for G-RT also indicates the reduction of GO under the condition of quiescent melt. This value is further increased to 1.05 for G-S, which is attributed to the increase of the number of polyaromatic domains with a smaller overall size in the graphene sheets after a heavier reduction under the condition of sheared melt. The results of Raman, together with the information obtained from TGA, FTIR, XPS, and XRD, provide adequate evidence for the above-mentioned conclusion that flow in sheared melts induces more intense reduction of GO as compared to the reduction in the absence of shear flow.

### 3.3. Dynamic Mechanical Property of PSGNs with and without Shear Flow.

The reinforcement of PGNs is strongly dependent on the interactions between graphene sheets and polymers, which is generally related to the surface chemistry or reduction degree of GO. Therefore, the mechanical properties of PGNs can also indirectly reflect the reduction degree of GO in the polymer matrix. As shown in Figure 6, the dynamical mechanical property of neat PS, PSGN-Q, and PSGN-S was investigated. The storage modulus (′) of PSGN-S at 50 °C is 2.25 GPa and that of PSGN-S is 2.42 GPa, both of which exceed that (2.05 GPa) of neat PS (Figure 6a). Generally, the incorporation of graphene-based materials generates a great increase in the ′ of polymers, which is mainly attributed to the strong interfacial interaction between graphene sheets and the polymer matrix and the well dispersion of graphene sheets. As discussed before, the flow-induced enhancement of ISTR results in more adherent PS on the graphene surface through π−π stacking. Therefore, the G-S sheets exhibit enhanced compatibility and interfacial interaction with the PS matrix as compared to G-Q sheets, which leads to the improvement of ′. Additionally, the well dispersion of graphene sheets engendered by melt-blending also benefit the increase of ′ of PSGN-S. As shown by the TEM images (Supporting Information, Figure S5a,b), the aggregated G-Q sheets in the PS matrix are easily observed for PSGN-Q. The poor dispersion is due to the polarity mismatch between the polar low-reduction degree G-Q sheets and the nonpolar PS matrix. On the contrary, the G-S sheets were dispersed randomly in the PSGN-S matrix (Supporting Information, Figure SSc,d), which should be ascribed to the more matching polarity of the high-reduction degree G-S sheets with PS, as well as the mechanical exfoliation of graphene sheets under high shear force. In addition to the improvement of ′, the glass transition temperature (Tg) of PGNs will also be increased due to the interactions between polymer and graphene-based...
materials. As expected, the $T_g$ increases to 85 °C for PSGN-Q, and 93 °C for PSGN-S, while pure PS has a $T_g$ of 84 °C (Figure 6b). Above all, the dynamical mechanical property, in turn, is a good evidence to confirm the flow-induced enhancement of the ISTR of GO.

3.4. Speculation of the Mechanism for the Flow-Induced Enhancement of ISTR of GO. So far, the research relative to the ISTR of GO is still lacking. The mechanism for the flow-induced enhancement of the ISTR of GO in sheared melts is currently not known. Compared to the quiescent melts, the sheared melts are more complicated and interesting. Earlier in this article, we have confirmed that shear flow can lead to more $\pi-\pi$ stacking between graphene sheets and PS. Researchers have found that macromolecular radicals were produced during the melt-blending of polymers. We believe that the enhanced reduction degree of GO in sheared melts is, at least, concerned with these two aspects.

Our previous study found that the intercalation of polymer chains facilitates the ISTR of GO in the quiescent melt. For the sheared system, more PS chains could be strongly adsorbed on the graphene surface through $\pi-\pi$ stacking with the assistance of high shear force, which certainly favors the intercalation of PS chains into the interlayer space of GO. Furthermore, the PS chains are also stretched under shear flow, which may promote the stripping of oxide debris from graphene-like sheets further increasing the interlayer distance of GO sheets. As a result, the GO reduction could go to a relatively higher degree in the sheared melts than the quiescent melts at the same temperature.

Additionally, the possible radical reactions between graphene and PS should also be taken into account when considering the mechanism for the flow-induced enhanced ISTR of GO. Shear flow may cause a slight degradation of PS and GO fracture, which might lead to the formation of PS macromolecular radicals, graphene, and oxygen free radicals. These produced free radicals are considered to contribute to the thermal reduction of GO, resulting in a higher reduction degree of GO in the sheared melts. To our knowledge, no other research groups have suggested such a mechanism, but some evidence supporting this hypothesis can be seen in previous reports. For example, Zhang et al. have achieved the reduction of GO under mild conditions using phenyl free radicals based on the free-radical-promoted elimination of the oxygen-containing groups. Chabal et al. thought that, during the thermal reduction of GO, the produced oxygen free radicals propagate by reaction with the oxygen groups of GO or the carbon dangling bonds at defective sites. Work by Zhai et al. found that the radical reaction between PS and graphene sheets likely exists during melt-blending under high shear force and high temperature. However, it remains a difficult matter for us to understand the details of the free radical reaction. In the current stage of the research, it is impossible for us to put forward an exact mechanism for the flow-induced enhancement of the ISTR of GO. Considering the great importance of melt-blending for the preparation of PGNs, further research to more explicitly identify the mechanism of this system is needed.

4. CONCLUSIONS

In summary, we made a comparative study of the ISTR of GO dispersed in a quiescent melt and a sheared melt. The comprehensive physico-chemical characterization of the PSGNs and the extracted rGO indicates that the shear flow during melt-blending induces more intense reduction of GO as compared with the quiescent condition in hot-pressing at the identical temperature. An independent parallel plate experiment further confirms flow-induced enhancement of the ISTR. On the basis of the results and previous studies, we conjecture that the enhanced $\pi-\pi$ stacking and possible radical reaction between PS and GO sheets in the sheared melt may be responsible for the flow-induced enhancement of the ISTR of GO. Although the exact mechanism for the flow-induced enhancement of the ISTR of GO in polymer melts is still lacking, our results are doubtlessly beneficial to the further understanding of its potential influencing factors and can promote the development of the environmentally friendly and cost effective melt-processing manufacture technologies for high-quality PGNs.

ASSOCIATED CONTENT

\section*{Supporting Information}

Digital pictures of PSGN-RT, PSGN-Q, and PSGN-S; GPC curves of PS eluted from PSGN-RT, PSGN-Q, and PSGN-S; TEM images of G-RT, G-Q, and G-S; XPS spectra of G-RT, G-Q, and G-S; and TEM images of the ultrathin sections of PSGN-Q and PSGN-S. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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