Facile fabrication of highly conductive polystyrene/nanocarbon composites with robust interconnected network via electrostatic attraction strategy†

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An electrostatic attraction strategy was employed for the preparation of highly conductive composites using commercialized graphene or multi-walled carbon nanotubes (MWCNTs) as conductive fillers and polystyrene (PS) microspheres as the resin matrix. The PS microspheres were first sulfonated to endow them with a highly negatively charged surface while the nanocarbons were positively charged in water using an amino-functionalized perylene bisimide as a stabilizer. Direct mixing of the sulfonated PS microsphere and the aqueous nanocarbon dispersion produced agglomerates with PS–nanocarbon core–shell structure due to electrostatic attraction interaction. An interconnected conductive network was formed after hot-pressing the agglomerates. Because of the strong electrostatic attraction and the high \( T_g \) temperature of the sulfonated layer, the interconnected conductive network was well-preserved even at a low filler content or a high hot-pressing temperature, resulting in an ultralow percolation threshold of the composites (\(<0.047\) vol\%) and conductivity up to 104 S m\(^{-1}\) at a graphene content of 4.51 vol\%, and to 391 S m\(^{-1}\) at a MWCNTs content of 3.20 vol\%. The above approach is time-saving and applicable to the manufacture of other conductive polymer-based composites.

1. Introduction

Conductive polymer composites (CPCs) are strongly desired in many fields, such as electrostatic dissipation, electromagnetic interference (EMI) shielding, sensors, and biomedical applications.\(^1-5\) Although some intrinsic conducting polymers have been developed,\(^6-7\) most of the CPCs are still achieved by simply blending the commonly used polymer matrix with conductive fillers due to their low cost and easy processibility.\(^5\) Among the conductive fillers, graphene and carbon nanotubes (CNTs) have frequently been involved in the fabrication of CPCs in recent years\(^4-13\) because they have high electrical conductivity, high aspect ratio and low density. However, the strong van der Waals forces and \( \pi-\pi \) interactions between the nanocarbons prevent them from being uniformly distributed in the polymer matrix,\(^14\) and the randomly dispersed fillers hardly form a conductive network at a low content. Although a high load of conductive fillers can enhance the electrical conductivity, it will deteriorate the mechanical properties of the CPCs as well as remarkably increase the cost. Therefore, CPCs with low electrical percolation threshold (EPT) and high electrical conductivity are urgently expected.

Many efforts have been made to obtain CPCs with a low EPT. One of the strategies is to make nanocarbons as homogeneously distributed in the polymer matrix as they possibly can be.\(^15-18\) With this strategy, graphene oxide (GO) is frequently adopted as the starting material because GO is more easily dispersed relative to graphene. For example, Gao et al. mixed a GO/dimethylformamide dispersion with an acrylonitrile-butadiene-styrene resin (ABS) solution and subsequently reduced it with \( \text{N}_2\text{H}_4/\text{H}_2\text{O} \). ABS/graphene nanocomposites were obtained by further coagulation and compression molding. The nanocomposites exhibited an EPT of 0.13 vol\% and a conductivity of 0.1 S m\(^{-1}\) at 2.33 vol\%.\(^15\) Nassira et al. mixed GO with gelatin solution and the GO was reduced \textit{in situ} to graphene by the synergistic action of gelatin and ascorbic acid. The obtained gelatin/graphene nanocomposite has an ultralow EPT of 0.033 vol\% and a conductivity of 5 S m\(^{-1}\) at 5 vol\% graphene content.\(^16\) Homogeneous distribution of MWCNTs in polymer matrix was also reported to give low EPT of CPCs.\(^17,18\) Yuan et al. adopted poly(amic acid) as both the dispersant of MWCNTs and the precursor of the polymer matrix to produce a polyimide/MWCNTs composite with an EPT of 0.48 wt\%.\(^17\) Pedroni et al. deagglomerated MWCNTs in xylene with the aid of a polyurethane derivative and then blended with styrene-butadiene-styrene block copolymer. The obtained...
composite has an EPT of 0.25 wt% and a conductivity of 0.01 S m\(^{-1}\) at 1 wt% MWCNTs content.\(^{18}\) Selective location of nanocarbons in one continuous phase of the immiscible polymer blend is another well-adopted strategy to fabricate CPCs with low EPT.\(^{12,19,20}\) For instance, octadecylamine-functionalized graphene could be selectively located and percolated in the continuous PS phase of a poly(methylmethacrylate) (PMMA)/PS blend, leading to an EPT of 0.5 wt%.\(^{15}\) In the continuous polystyrene (12)/polypropylene blend, MWCNTs can be confined to form a percolated network at the polystyrene/polypropylene interface with the help of pyridine-modified poly(ethylene-co-methacrylic acid).\(^{29}\) Generally, both homogeneous distribution and selective location strategy cannot assure that all nanocarbons participate in the formation of the conductive network. Moreover, the highest electrical conductivities of CPCs reported based on the above two strategies are much lower than those of their conductive constituent, nanocarbons, and cannot meet extensive applications.

The third segregated structure strategy was hence proposed to produce CPCs with low EPT and high electrical conductivity.\(^{21–23}\) Namely, nanocarbons were first mixed with polymer particles and subsequently hot-pressed to construct an interconnected conductive network. This strategy has demonstrated superiority over homogeneous distribution strategy.\(^{24}\) The mixing process is generally carried out with their aqueous dispersions, leading to two basic forms: (i) homogeneous dispersion if the two components possess the same electric charges and no other interactions,\(^{25,26}\) and (ii) coagulation if electrostatic attraction interaction or hydrogen bonding exists between the two components.\(^{27–29}\) For the first case, apart from some polymers with low glass-transition temperature\( (T_g)\) that can form a coherent film after a significant amount of water has evaporated,\(^{30,31}\) freeze-drying is always an imperative process to get a homogeneous solid mixture.\(^{23,26,32,33}\) It is both an energy- and time-consuming process, making it not suitable for mass production. In contrast, it is much easier to collect the final mixture in the second case because the components coagulate after blending.

To the best of our knowledge, the electrostatic attraction strategy has not been reported for the preparation of CNT-based CPCs, but it has been frequently employed for the fabrication of graphene-based CPCs. However, GO is commonly used as the starting material because GO disperses well in water and its plentiful hydrophilic groups can interact with polymer particles through electrostatic interaction or hydrogen bonds.\(^{27–29,34–36}\) For example, Pham et al.\(^{27}\) prepared CPCs with an EPT of 0.16 vol% and an electrical conductivity of 64 S m\(^{-1}\) at 2.7 vol% based on GO and positively charged PMMA, while Wu et al.\(^{28}\) fabricated CPCs from GO and positively charged PS latex, of which the EPT is 0.15 vol% and the conductivity can be as high as 1083 S m\(^{-1}\) at 4.8 vol% graphene content. Tang et al.\(^{34}\) incorporated GO-stabilized CNTs into a PS matrix to construct CPCs through hydrogen bonding between PS microspheres and GO sheets; the composite has an EPT of 0.03 vol% and a conductivity of 153 S m\(^{-1}\) at 4 vol% nanocarbon content. Yan et al.\(^{35}\) produced a high-performance EMI shielding composite with an EPT of 0.14 vol% based on PS microspheres and GO dispersion. Although an interconnected network of GO can be formed in the polymer matrix, a reduction process for GO is indispensable for recovering its electrical conductivity. The final performance is thus greatly influenced by the reduction process. For example, the conductivity of the GO-based composite reduced by hydrazine is considerably different from that reduced by hydrazine.\(^{28}\) In addition, the reduction process has ultralow efficiency from the viewpoint of industry. Therefore, it is optimal to use graphene rather than GO as the starting material to construct CPCs. Nevertheless, there are no reports on direct coagulation of graphene or CNTs with polymer particles to fabricate CPCs via electrostatic attraction strategy.

Herein, we employed the electrostatic attraction strategy to prepare highly conductive nanocarbon-based composites with an interconnected network structure directly using commercialized graphene or MWCNTs. The nanocarbons were first homogeneously dispersed in water aided by an amino-functionalized perylene bisimide (PBI) derivative that was recently developed in our lab.\(^{37}\) The amino-functionalized PBI could endow nanocarbons with a positively charged surface. The nanocarbon dispersions were mixed with negatively charged sulfonated PS microspheres to form uniform sulfonated PS–nanocarbon core–shell particles by the strong electrostatic attraction interaction. A well-interconnected network was further constructed via a hot-pressing process in a wide operating temperature range even at quite a low filler content, resulting in the obtained composites with ultralow EPT (<0.047 vol%) and high electrical conductivity (104 S m\(^{-1}\) at a graphene content of 4.51 vol%, and 391 S m\(^{-1}\) at a MWCNTs content of 3.20 vol%). Careful inspection suggests that both the electrostatic attraction interaction and the high \(T_g\) of sulfonated PS are responsible for the robust interconnected network structure and thus superior conductivity.

2. Experimental section

2.1 Materials

Styrene (99.5%), 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%), polyvinylpyrrolidone (PVP-K30, average \(M_W\) 40 000), ethanol (99.7%), sulfuric acid (98%), toluene (99.5%), formic acid (HCOOH, 88%), and potassium hydroxide (KOH, 97%) were all purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, 98%) and triethylentetramine (TETA, 70%) were purchased from Aladdin Chemical Reagent Co., Ltd (Shanghai, China). Graphene powders (XF001W, thermally reduced method, lateral size of 0.5–5 microns, average surface area of 700–800 m\(^2\) g\(^{-1}\), 7.0–7.5 at% oxygen and 500–700 S m\(^{-1}\) conductivity) were purchased from Nanjing XFNANO Materials Co., Ltd (Nanjing, China). MWCNTs (NMC3, 95 wt%, CVD method, diameter of 10–20 nm, length of 10–30 μm, specific surface area of 200 m\(^2\) g\(^{-1}\), true density of 2.1 g cm\(^{-3}\) and conductivity of 10 000 S m\(^{-1}\)) were purchased from Beijing Boyu Gaoke New Materials Technology Co., Ltd (Beijing, China).

2.2 Preparation of sulfonated PS microspheres

PS microspheres with an average diameter of 2 μm were first prepared by dispersion polymerization according to the ref. 38.
Typically, PVP-K30 (4.80 g) was dissolved in ethanol (200 mL) in a 500 mL four-neck flask as stabilizer, then styrene (40.00 g) solution with AIBN (0.60 g) dissolved was added. The mixture was stirred at a constant speed of 200 rpm under a nitrogen atmosphere at room temperature for 30 minutes. Then the reaction was kept at 70 °C for 12 h. PS microspheres were obtained by centrifugation at 4000 rpm for 5 min, and subsequently rinsed with ethanol (200 mL) four times.

The sulfonation process was conducted as follows: the obtained PS microspheres (30 g) were re-dispersed in sulfuric acid (240 mL) at room temperature under magnetic stirring. Then the dispersion kept stirring (300 rpm) in a water bath heated at 40 °C for 24 h. After that, the microspheres were separated by centrifugation at 10 000 rpm for 5 min and repeatedly washed with ethanol four times. Finally, the obtained sulfonated PS microspheres were re-dispersed in water under sonication for later use.

2.3 Synthesis of protonated triethylenetetramine-functionalized perylene bisimide (HTAPBI)

The HTAPBI with molecular structure as shown in Scheme 1 was synthesized according to our previous report.37 That is, the HTAPBI with molecular structure as shown in Scheme 1 functionalized perylene bisimide (HTAPBI) 2.3 Synthesis of protonated triethylenetetramine-

2.4 Preparation of PS–nanocarbon composites

First, positively charged aqueous dispersions of graphene and MWCNTs were prepared using HTAPBI as a dispersant. Nanocarbons were added into HTAPBI solution at a weight ratio of 1:3 (nanocarbons : HTAPBI), and tip-sonicated for 1 h in an ice bath (cycle: 3 s on and 3 s off, power: 350 W, manufacturer: Shanghai Precision Instrument Co., Ltd JYD-650L). Second, the sulfonated PS microspheres dispersion (40.0 g, 2.0 wt%) was added into the graphene or MWCNTs dispersion (0.2 mg mL−1) under vigorous stirring, and then tip-sonicated for 30 min. The sulfonated PS microspheres wrapped by graphene (sulfonated PS/graphene) or MWCNTs (sulfonated PS/MWCNTs) were collected by vacuum filtration of the mixture through a polypropylene membrane with pore size of 0.43 μm and dried in a vacuum oven at 80 °C for 24 h. Third, the obtained solids were preheated at 120 °C in a mold for 10 min and subsequently pressed under 10 MPa for another 10 min to obtain the PS–nanocarbon composite sheets.

The mass fraction of nanocarbon content was converted to a volume fraction (φ) by the following equation:34

\[ \phi = \frac{\omega_r \rho_p}{1 + \omega_r \rho_r} \]

where \( \omega_r \) and \( \rho_r \) are the mass fractions of carbon nanofillers and PS matrix, respectively, and \( \rho_r \) and \( \rho_p \) are the corresponding densities, which can be taken as 2.2 g cm\(^{-3}\) for the graphene,22,27,34 2.1 g cm\(^{-3}\) for the MWCNTs (data provided by supplier) and 1.05 g cm\(^{-3}\) for the PS matrix.

2.5 Characterization

The morphology of the samples was characterized by scanning electron microscope (SEM, VEGA 3 XMU, TESCAN, Czech Republic). Transmission electron microscope (TEM) images were obtained using a Tecnai G2 20 TWIN instrument (Hillsboro, OR, USA) operated at an accelerated voltage of 200 kV. Zeta-potential measurements were conducted on a Zetasizer Nano ZS90 instrument (Malvern, UK). The \( T_g \) temperature was measured using a TA DSC Q2000 differential scanning calorimeter (DSC, New Castle, DE, USA) with a heating rate of 10 °C min\(^{-1}\) from 40 to 200 °C under nitrogen atmosphere. The electrical conductivity of the composites was measured with an RTS-9 four-point probe meter (Guangzhou, China).

3. Results and discussion

3.1 Formation of sulfonated PS–nanocarbon core–shell microspheres

PS microspheres were prepared by dispersion polymerization using PVP as a stabilizer. After centrifugation and thoroughly rinsing with ethanol several times, pure PS microspheres with an average diameter of 2 μm were obtained, as revealed from its SEM and TEM images (Fig. 1a). They were subsequently treated with sulfuric acid for 24 h to produce sulfonated PS microspheres. Because the reaction only proceeded on the surface, no obvious diameter or morphology changes appeared after sulfonation (Fig. 1b). Nevertheless, the zeta-potential of PS microspheres increased from −6.3 mV to −43.5 mV. The sulfuric acid groups (−SO₃H) on the surface played a key role in increasing the charge density. It not only enabled the sulfonated PS microspheres to be homogeneously dispersed in water but also provided a strong interaction with the carbon nanofiller additives.

The aqueous nanocarbon dispersion with a positively charged surface was prepared using HTAPBI as a dispersant. HTAPBI has a conjugated perylene core and six ammonium cations on its two sides (Scheme 1), demonstrating high ability to stabilize graphene and CNTs in water. In order to reduce its impact on the electrical conductivity of the nanocarbons, a minimum amount of HTAPBI at a weight ratio of 1:3 to nanocarbons was used. The ammonium cations in HTAPBI molecules not only guaranteed nanocarbons to be dispersed stably in water but also provided sufficient positive charges, i.e., zeta-potential of +29.4 mV and +30.5 mV for graphene and MWCNTs, respectively. When the

![Scheme 1](image-url)  
**Scheme 1** Molecular structure of HTAPBI.
highly negatively charged sulfonated PS microspheres were added into the nanocarbon dispersions, coagulation immediately appeared owing to the strong electrostatic attraction interaction. The mixture was subsequently tip-sonicated for 30 minutes to ensure the nanocarbons were uniformly wrapped on the microspheres’ surface. As a typical example, the photos of the mixed sulfonated PS/graphene dispersion are given in Fig. 2. When the quantity of nanocarbons is low in the dispersion, sulfonated PS/graphene microspheres can be re-dispersed again in water after sonication (Fig. 2a) because there are still enough negative charges left on the surface of the sulfonated PS microspheres. However, the dispersion is actually metastable; the sulfonated PS/graphene microspheres were settled down with a dark gray color after storage for 12 h (Fig. 2b). The colorless supernatant indicated that the graphene was all absorbed to the microspheres. When the graphene content is 0.47 vol% of the total solid, the flocculation cannot be re-dispersed even with longer sonication time because more charges were neutralized. All sulfonated PS microspheres were thoroughly coagulated with graphene (Fig. 2c). The formation of the uniform sulfonated PS/graphene and sulfonated PS/MWCNTs microspheres mainly originated from the inverse surface charge between sulfonated PS microspheres and nanocarbons.

3.2 Construction of interconnected conductive networks

PS–nanocarbon composites were prepared by hot-pressing the sulfonated PS–nanocarbon powders at 120 °C (beyond the T_g temperature of sulfonated PS spheres, 112.2 °C, as shown in Fig. S1, ESI†) at 10 MPa. The final products are in the form of discs with a diameter of 25 mm and thickness of 1 mm, as typically shown in Fig. 4. The discs were smashed into pieces to observe their internal structures. Fig. 5 displays the cross-sectional SEM images of PS composites with different nanocarbon contents. Except for the samples with 0.047 and 0.24 vol% MWCNTs, integrated segregated structures can be clearly seen.
even for the sample with as low as 0.047 vol% graphene. The fillers are all located at the interfaces of the cellular units, which should be attributed to the core–shell structure of sulfonated PS–nanocarbon microspheres. In comparison with PS/graphene composites, integrated network structures were observed at relatively high loads of MWCNTs (0.47 and 0.94 vol%) because the one-dimensional tube structure of MWCNTs means that the spheres' surface cannot be fully covered at a low content. In addition, Fig. 5 clearly indicates that a more dense nanocarbon network was formed at higher filler load, whether the composites were based on graphene or MWCNTs.

In addition, the sulfonated PS–nanocarbon powders were further hot-pressed at 150 °C and 180 °C; the distinct interconnected networks were still well-preserved, as seen from the
cross-sectional SEM images in Fig. S2 (ESI†). It suggests that the interconnected network structure is rather robust. This fact will be favorable for enlarging the operating temperature range and making it more applicable in practical processibility. The robust interconnected network structure should be attributed to the robust core–shell structure formed by the strong electrostatic attraction interaction. The higher $T_g$ temperature ($>112.2$ °C) of the outside layer of the sulfonated PS microsphere is another important factor for the robustness of the segregated structure. Because of the existence of hydrogen bonding between –SO$_3$H groups, the motion of surface segments is not as active as that of the interior chains, benefitting the stability of the network structure at high temperature.

Based on the above facts, the formation of PS–nanocarbon conductive composites with interconnected network could be schematically illustrated as shown in Fig. 6. That is, during the mixing of sulfonated PS microspheres and nanocarbon, sulfonated PS–nanocarbon microspheres and their agglomerates were simultaneously formed due to the strong electrostatic attraction interaction. When the agglomerates were compressed at a temperature above the $T_g$ of PS ($T_g$ temperature of 104.7 °C for PS as shown in Fig. S1, ESI†), the sulfonated PS–nanocarbon microspheres first deformed to fill most of the voids between the composite spheres. The outermost sulfonated PS layer strongly adsorbed with nanocarbons would not be destroyed but slightly deformed along the compression direction due to the high $T_g$ of sulfonated PS chains. However, the interior PS chains are able to move more freely at 120 °C, and some PS chains can extrude out through the gaps between surface-sulfonated PS chains. These chains further fill the residual voids between nanocarbon fillers and, meanwhile, establish a tightly connected structure with the adjacent PS microspheres. As a result, integrated conductive composites with good mechanical performance are formed.

3.3 Electrical properties of PS–nanocarbon composites

Fig. 7a shows the electrical conductivity of PS composites with different contents of graphene and MWCNTs. The polymer sheet prepared from sulfonated PS spheres has a conductivity of $1.92 \times 10^{-4}$ S m$^{-1}$, about eleven orders of magnitude higher than that of PS sheet ($1.10 \times 10^{-15}$ S m$^{-1}$). This conductivity must result from the proton conductivity of the –SO$_3$H groups dissociated by the trace amounts of water.$^{40}$ The slightly conductive fact together with its morphology (Fig. S3, ESI†) indicated

![Fig. 6](image)

The formation of PS–nanocarbon composite with an interconnected network.

![Fig. 7](image)

(a) Electrical conductivity of the composites with different contents of graphene or MWCNTs, and (b) a light bulb connected with the PS/MWCNTs composite (3.20 vol% MWCNTs).
that the sulfonated surface layer formed a connected network after the sulfonated PS spheres were hot-pressed at 120 °C. The composite containing 0.047 vol% graphene has a conductivity of 5.0 × 10⁻⁸ S m⁻¹, an order of magnitude higher than that of the sulfonated PS matrix. We thus reasonably infer that the EPT is lower than this value. This EPT is lower than most of the reported values. At a graphene content of 1.86 vol%, the conductivity is 16.6 S m⁻¹, and it increases to 104 S m⁻¹ when the graphene content reaches 4.51 vol%. This value is already in the same order of magnitude as the conductivity of the pure graphene film (500 S m⁻¹) prepared by vacuum filtration of the dispersion, meeting the demand for many electrical applications. The conductivity of PS/MWCNTs composite is 2.1 × 10⁻³ S m⁻¹ at a filler content of 0.047 vol%, indicating that the EPT is also below 0.047 vol%. Upon increasing the MWCNTs content to 0.94 vol%, an electrical conductivity of 14.2 S m⁻¹ was obtained. This conductivity is relatively high at such a low filler content, which has seldom been reported previously. When the MWCNTs content reaches 3.20 vol%, the conductivity reaches 391 S m⁻¹, which is sufficiently high as a connected part to light up a small light bulb (3.8 V, 0.3 A) using a 9 V battery, as shown in Fig. 7b. Since the pristine MWCNTs have higher conductivity than graphene (a pure MWCNTs film prepared by vacuum filtration is 2800 S m⁻¹), the conductivity of PS/MWCNTs composites is always higher than PS/graphene composites at the same nanocarbon content if the value is beyond 0.24 vol%. This result indicates that the electrical conductivity of the composites prepared with electrostatic attraction strategy is only dependent on the intrinsic properties of the nanocarbon fillers and has nothing to do with other additional processing, like the indispensable reduction procedure when using GO as the starting filler.

The electrical properties of the PS–nanocarbon composites were compared with other relevant works, as summarized in Table 1. The composites presented herein have much lower EPT and higher conductivity relative to most of the reported polymer/graphene or polymer/CNT composites, despite these composites also having a segregated structure. In our case, the strong electrostatic attraction, as well as the existence of –SO₃H groups on spheres’ surface, benefits the formation of an intact interconnected conducted network after hot-pressing even at low nanocarbon content, hence demonstrating the superior electric properties.

4. Conclusions

Highly conductive PS/graphene and PS/MWCNTs composites with an interconnected network were prepared using surface-sulfonated PS microspheres and HTAPBI-stabilized nanocarbon. First, the nanocarbon fillers were uniformly wrapped on the sulfonated PS microspheres, forming the sulfonated PS/graphene or sulfonated PS/MWCNTs core–shell structure due to the strong electrostatic attraction interaction. After subsequent hot-pressing at 120 °C, carbon nanofillers were connected together to create a conductive network. Because of the high Tg temperature of the sulfonated layer, the conductive network was not destroyed even at a hot-pressing temperature far above the Tg of PS. The interconnected network results in ultralow EPT (< 0.047 vol%) for both PS/graphene and PS/MWCNTs composites, and high conductivities of 104 S m⁻¹ for graphene at 4.51 vol% and 391 S m⁻¹ for MWCNTs at 3.20 vol%. This approach is time-saving and does not require further processing, so it is applicable to the manufacturing of highly conductive composites on large-scale.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Key Research and Development Program of China (2017YFA0204600), and the National Natural Science Foundation of China (51673047).

References
