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## COMMUNICATION

## Efficient coating of polystyrene microspheres with graphene nanosheets†

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Herein, we propose a facile and efficient method to obtain the polystyrene/graphene nanosheets (PS/GNSs) nanocomposite particles. As far as we know, it is the first example that GNSs are attached onto the surface of PS microspheres, with such smooth morphology, and without relying on any surface pretreatments of substrate microspheres.

In recent years, graphene has attracted tremendous attention owing to its unique combination of electrical, thermal, mechanical, and chemical properties, based on a two-dimensional monolayer carbon nanostructure, which holds great promise for potential applications in many technological fields such as batteries, sensors, supercapacitors, energy storage devices, nanocomposites, and so on.<sup>1–12</sup>

Applying the graphene nanosheets (GNSs) in an effective way and taking advantage of their potential functions to the full still remain a scientific challenge, even if a low-cost, large-scale production of GNSs is achieved.<sup>13–15</sup> One possible route would be the preparation of GNSs-based composite materials, and naturally, the performance of the resultant composites is determined by both the size of GNSs and their homogeneous distribution in substrates.<sup>11,16</sup> Until now, the most common method to obtain such composites is a random liquid-phase blend by simply adding GNSs suspension into polymer solutions.<sup>11,12,17–21</sup> Recently, latex technology, blending polymer emulsion and GNSs suspension, has also been applied for the incorporation of GNSs into a polymer substrate.<sup>22</sup> Nevertheless, it is still a simple and random blend in essence, and the variation is just that polymer solution is replaced by polymer emulsion. In general, surface pretreatment of GNSs is inevitable in order to improve their homogeneity of dispersion in media. Moreover, to avoid reaggregation or restacking of GNSs during removal of the organic or aqueous media, some particular treatments, such as rapid precipitation in a non-solvent<sup>11,12</sup> or freeze-drying,<sup>22</sup> are also necessary and crucial to fixing the previously established uniform distribution of GNSs in polymer substrates.

In principle, the problem of non-uniform dispersion of GNSs in composites can be effectively overcome by preparing colloidal nanocomposite particles.<sup>23</sup> On the basis of this strategy, the spatial distribution of GNSs within the final composite materials is highly controllable. As far as we know, few papers have been reported on the preparation of GNSs-based nanocomposite particles.<sup>24,25</sup> Herein, we propose a facile and effective method to attach GNSs onto the surface of polystyrene (PS) microspheres, and ultimately to obtain the PS/GNSs nanocomposite particles having smooth morphology.

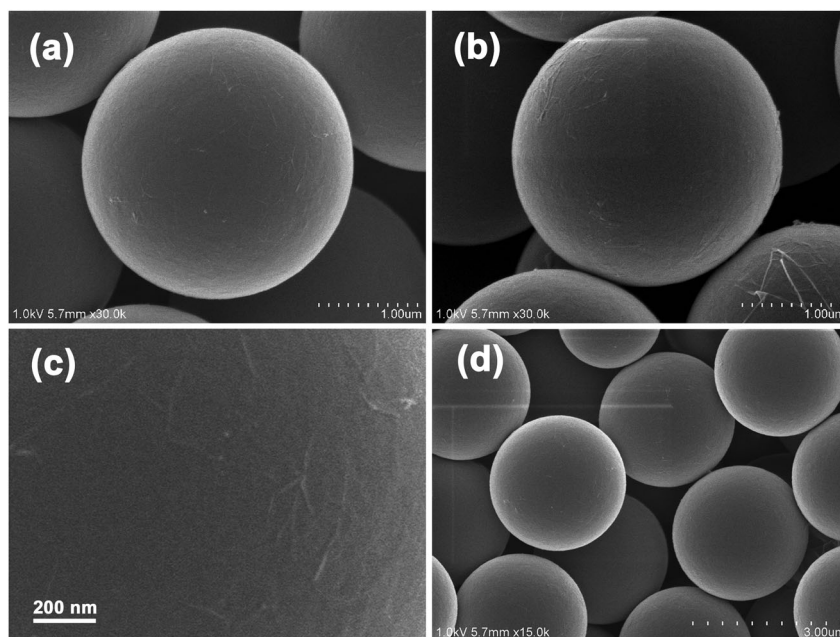
Fig. 1 shows scanning electron microscopy (SEM) images of PS/GNSs nanocomposite particles. In Fig. 1a and b, many fine wrinkles irregularly distributed on the surface of microspheres prepared with graphite oxide (GO)/PS weight ratios of 1 : 100 and 1 : 50, respectively, are observed. Especially, under a much higher magnification (Fig. 1c) for the sample shown in Fig. 1a, it is found that they are obviously due to slight creases of flexible and ultrathin nanosheets, looking like a creased aluminium foil. This provides direct visual evidence for the presence of GNSs. The smoothly spherical outline of the PS/GNSs nanocomposite particles, as shown in Fig. 1a, b and d, suggests that the GNSs were wrapped closely around the PS microspheres, though there were slight wrinkles. Upon reducing the weight ratio of GO/PS to 1 : 200, the coating of PS microspheres with GNSs is hard to distinguish clearly by SEM observation (Fig. S1, ESI†). Nevertheless, the presence of GNSs in the resultant nanocomposite particles can be confirmed by using Raman spectroscopy, a powerful nondestructive tool extensively used to characterize graphene.<sup>26,27</sup>

Fig. 2 shows Raman spectra of GO, PS microspheres and PS/GNSs nanocomposite particles prepared with different weight ratios of GO/PS. As in the case of our Raman spectrum of PS microspheres, there is a very strong signal at about 1002 cm<sup>−1</sup>, which can be assigned to  $\nu_1$  ring-breathing mode of PS.<sup>28</sup> In contrast, for the PS/GNSs nanocomposite particles prepared by using GO/PS weight ratio of 1 : 200 (curves b), the G peak and D peak of GNSs at about 1580 cm<sup>−1</sup> and 1360 cm<sup>−1</sup>, respectively, are displayed obviously.<sup>29</sup> The characteristic signal of PS gradually becomes weak with an increased weight ratio of GO/PS (e.g., 1 : 100) as shown in curve c, and at last, it completely disappears at the GO/PS weight ratio of 1 : 50 (curve d). This phenomenon can be regarded as a powerful evidence for PS/GNSs core/shell morphology, because the Raman signal belonging to PS core could be attenuated or absorbed when the intact GNSs layer is formed. In addition,

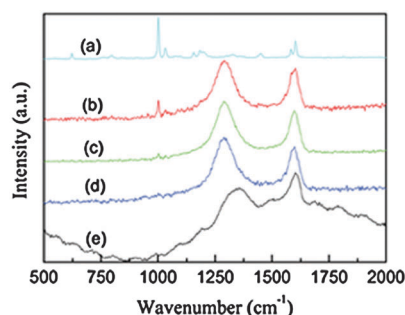
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**Fig. 1** SEM images of PS/GNSs nanocomposite particles prepared by using different weight ratios of GO/PS, 1 : 100 (a, c and d), 1 : 50 (b).



**Fig. 2** Raman spectra of PS microspheres (a), PS/GNSs nanocomposite particles prepared by using different weight ratios of GO/PS, 1 : 200 (b), 1 : 100 (c), 1 : 50 (d), and GO (e).

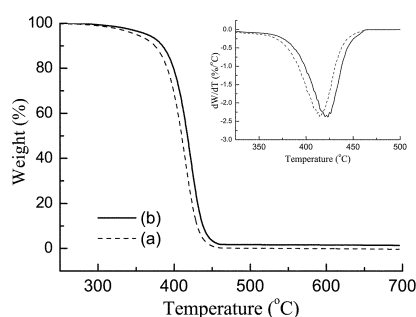
an increased D/G intensity ratio of nanocomposite particles compared to that of GO (curve e) indicates the successful reduction of GO according to previous works.<sup>26,29</sup>

To further validate the existence of GNSs on the surface of PS microspheres, we used XPS to characterize a series of PS/GNSs nanocomposite particles. As shown in Fig. S2 (ESI<sup>†</sup>), an obvious peak is observed at 286.7 eV, and it can be assigned to the C in C–O bonds. This phenomenon proves the presence of GNSs on the surface of PS microspheres, even at a very low weight ratio of GO/PS of 1 : 200, because the graphene oxide cannot be completely reduced and the obtained GNSs usually have the C–O bonds, as reported in previous works.<sup>29</sup> A peak at about 287.8 eV corresponding to C in C=O bonds can also be found, but in view of the residual PVP, it cannot be entirely assigned to GNSs. However, the intensity of the two peaks (C in C–O and C=O) is much weaker than those in graphite oxide reported by others, suggesting considerable de-oxygenation by the reduction process.

We propose the hydrophobic interaction to understand the formation of PS/GNSs nanocomposite particles. As the reduction of graphene oxide nanosheets (GONSs) proceeded,

the resultant GNSs became less hydrophilic as a result of oxygen removal. The PS microspheres employed in our system were prepared by dispersion polymerization using azobisisobutyronitrile (AIBN) as the initiator. It means that the PS microspheres bear no chemically bound ionic groups and have a hydrophobic surface. The adhesion of the GNSs to the surface of PS microspheres was thus believed to be dependent on the hydrophobic interaction. In nature, this interaction has been used to explain the phenomenon that GNSs can adhere to the surface of a Teflon-coated stir bar during the reduction of aqueous dispersion of the GONSs.<sup>29</sup> As soon as the GNSs clung to the surface of PS microspheres at a fairly close distance, strong  $\pi$  electrons interaction began to take effect, which was derived from aromatic organic molecules and the basal plane of graphite.<sup>30</sup> With the aid of this synergistic interaction, GNSs could tightly and conformally coat the PS microspheres, and thus the nanocomposite particles possessed such excellent morphology.

The presence of GNSs on the surface of PS microspheres was quantitatively confirmed by thermogravimetric analysis (TGA) of PS microspheres and PS/GNSs nanocomposite particles prepared using a weight ratio of GO/PS of 1 : 50, as shown in Fig. 3. In curve b, the residual weight percentage of about 1.6 wt% indicates the presence of GNSs in nanocomposite particles since PS has been completely decomposed below 475 °C. Upon comparing this residual weight percentage of GNSs with the original GO/PS weight ratio (2.0 wt%), the difference can be attributed to the removal of oxygen functional groups of GO by chemical reduction and the free GNSs left in the medium. The inset in Fig. 3 shows the differential thermogravimetric analysis (DTG) curves and the peak temperature ( $T_p$ ) corresponds to the maximum weight loss rate. The  $T_p$  of nanocomposite particles is increased by about 10 °C, as compared to original PS microspheres. This indicates that the thermal stability was improved by incorporating the PS

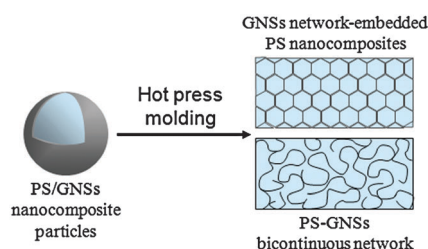


**Fig. 3** TGA and corresponding DTG (inset) of PS microspheres (a) and PS/GNSs nanocomposite particles prepared by using a weight ratio of GO/PS of 1 : 50 (b).

with GNSs and on the other hand, it suggests the efficient coating of PS microspheres with GNSs.

Adopting the PS/GNSs nanocomposite particles with strongly controlled structure and morphology, large-scale, three-dimensional ordered GNSs-based nanocomposite materials should be facily constructed through a simple molding method such as hot press molding, not merely to effectively solve the problem of non-uniform dispersion of GNSs in nanocomposites. As shown in Scheme 1, they could be designed to be either GNSs network-embedded polymer nanocomposites or GNSs–polymer bicontinuous nanocomposites. More significantly, no organic solvents must be used throughout the preparation of the PS/GNSs composite particles and construction of the highly ordered nanocomposite materials. The research activities are underway to explore their various properties and wide applications.

In summary, the present communication demonstrates that PS/GNSs nanocomposite particles can be prepared by a facile and effective method. The efficient coating of PS microspheres with GNSs was easily governed based on hydrophobic interaction. With the well-defined PS/GNSs nanocomposite particles, highly ordered GNSs-based nanocomposite materials should be prepared with a facile, efficient and environmentally friendly method. We anticipate that this strategy would provide a platform for the synthesis of functional GNSs-based composite materials having various potential applications and correlative research activities are underway.



**Scheme 1** Schematic illustration of the structure of PS-GNSs nanocomposites fabricated by hot press molding.

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