Preparation of graphene oxide coated polystyrene microspheres by Pickering emulsion polymerization

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Exfoliated graphene oxide (GO) nanosheets with hydrophilic oxygen-containing functional groups and hydrophobic residual conjugated structure are prepared by the oxidation of graphite powders. Polymerization of styrene stabilized by GO nanosheets is conducted at varied pH values. The morphology of the products is observed by field-emission scanning electron microscope (FE-SEM). It is found that GO coated polystyrene (PS) microspheres with narrow size distribution are obtained, although highly hydrophilic GO nanosheets cannot stabilize the monomer droplets in aqueous phase. Flocculation of polymer microspheres and GO nanosheets embedded in the PS matrix is induced by further decreasing the hydrophilicity of stabilizer. FT-IR, UV–vis spectra, XRD patterns and TGA results indicate the strong interaction between resulted PS chains and GO nanosheets during the initial stage of the polymerization. The amphiphilicity of GO nanosheets and the interaction between polymer and stabilizer are considered to be responsible for the fabrication of GO coated PS colloidal particles.

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1. Introduction

Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice [1]. It received tremendous interest since 2004 [2] for its prominent electrical, mechanical and thermal properties [3]. Therefore, it has many important potential applications, such as transistors [4], sensors [5], electrodes [6], batteries [7] and hydrogen storage [8]. Graphene has also been used as filler to fabricate functional graphene/polymer nanocomposites. Several kinds of polymers such as polyaniline [9], chitosan [10], poly(vinyl alcohol) [11] and nylon-6 [12] have been selected to fabricate the nanocomposites for their unique structure and properties.

Chemical oxidation–reduction method is considered to be one of the most valuable methods in preparing large amount of fully exfoliated graphene sheets [13]. In this method, graphene oxide (GO) is first obtained by intense oxidation of graphite [14,15] and can be subsequently reduced by hydrazine [16] to prepare graphene. The chemical structure of GO is varied according to the oxidation conditions [17]. Generally speaking, GO has several oxygen-containing functional groups such as hydroxyl, carbonyl, epoxy groups on the basal plane, as well as carboxylic groups mainly at the edges of the carbon layers [18]. These functional groups make it easy to modify GO with polymer chains. GO/polymer composites have attracted much attention in recent years. By using single electron transfer living radical polymerization (SET-LRP), thermal-responsive composites GO-poly(N-isopropylacrylamide) (GO-PNIPAM) [19,20] and GO-poly(N,N-diethylmethacrylamide) (GO-PDEMA) [21] are synthesized via grafting-from [19,21] or grafting-onto strategy [20]. The hydrophilic functional groups on the hydrophobic carbon layers also make GO become amphiphilic [22]. Thus GO nanosheets can assemble at the interface of emulsion droplets and hollow GO spheres are obtained [23]. Huang’s group utilized GO to achieve well-controlled 2D assemblies by using its amphiphilicity [22]. Furthermore, they found that the hydrophilicity of GO in water highly depended on pH value of the solution [24].

An emulsion stabilized by solid particles instead of organic surfactants is called Pickering emulsion [25]. The emulsion droplets of polymerizable monomers have also been stabilized by solid particles to fabricate supracolloid structure. Some inorganic particles such as clay [26–28], ZnO [29], TiO2 [30] and Fe3O4 [31] were employed as stabilizer to prepare polymer/inorganic nanocomposite microspheres based on Pickering emulsions. Very recently, adopting this method, Yang and Zhao reported the synthesis of polymer colloidal particles using GO as stabilizer [32]. In their preparation procedure, the stabilized emulsion droplets act as nanocontainers in which the polymerization takes place, resulting in composite polymer particles with a similar size as the initial droplets. Sharif has used the similar method to synthesize GO-PMMA composite [33]. It has also been found that the polymer nanocomposite particles were achieved even if the original solid particles did not have the capability to stabilize the monomer droplets [34–37]. The
formation of polymer microspheres is proven to be correlative with the interaction between the growing polymer chains and inorganic particles. We also reported the fabrication of PS/titania colloidal particles using highly hydrophilic titania as stabilizer [38,39]. The hydrophilicity of these titania nanoparticles was decreased to produce nuclei due to the photocatalytic polymerization of the monomer and providing hydrophobic patches on the surface of inorganic particles.

In this paper, the PS/GO nanocomposite particles with the size of submicrometer are fabricated by using hydrophilic GO nanosheets as stabilizer. The structure and morphology of the GO coated polymer microspheres are investigated extensively. We also clarify the effects of the interaction between polystyrene chains and GO nanosheets on the surface chemistry of GO and the emulsion polymerization. The mechanism of Pickering emulsion polymerization stabilized by GO is then proposed, which provides a method to control the structure of the polymer composite microspheres.

2. Materials and method

2.1. Materials

Graphite powder (99.9%), KMnO₄ (99%), H₂SO₄ (98.3%), styrene (99%), tetrahydrofuran (THF, 99%) and azo-bisobutyronitrile (AIBN, 99%) were all purchased from Shanghai Chemical Reagent Co. (China). Styrene was distilled under vacuum and AIBN was recrystallized prior to use. Other reagents were used as received. Deionized water was used throughout the experiments.

2.2. Preparation of GO water solution

GO was prepared using modified Hummer method [14]. The produced GO was dialyzed in deionized water for 1 week and then dried in vacuum at room temperature. Dried GO was dispersed in water and the mixture was sonicated for 1 h to form 0.25 mg/ml GO water solution.

2.3. Preparation of PS/GO composites

A typical polymerization procedure is described as follows (samples 1–6 in Table 1): the oil phase (styrene and 1.0 wt% AIBN) and GO water solution (0.25 mg/ml) were added into a 100 ml three-neck round bottom equipped with a nitrogen inlet and a reflux condenser with an outlet to a bubble counter. The mixture was deoxygenated by bubbling with nitrogen for 10 min without further treatment such as homogenization and sonication followed by the reaction at 65 °C for 10 h via magnetic stirring.

2.4. Characterization

Digital photographs were obtained by using Cannon 550D. All of the samples had been stored for 1 week.

Atomic force microscopy (AFM) studies were performed using a Multimode Nano 4 in the tapping mode. Before AFM observations, the GO dispersions (0.25 mg/ml) were treated with ultrasonication and then spin-coated onto a freshly cleaved mica surface.

The morphologies of the prepared PS/GO microspheres were characterized by a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM). The samples were dropped onto the copper mesh and sprayed by gold for 15 s before characterization.

The particle-size distribution of the polymer latex was determined by means of dynamic light scattering (DLS) using a Malvern Autosizer 4700 instrument.

Fourier-transform infrared (FT-IR) spectra were collected using a Nicolet Nexus–470 FT-IR spectrometer. The samples were dried at room temperature and then pressed into KBr pellets for FT-IR tests.

UV–vis spectra were measured on Perkin Elmer Lambda 35 instrument. The samples were directly obtained by diluting the products about 10 times.

XRD patterns were carried out using X’ Pert PRO (PANalytical) with Cu Kα radiation (λ = 0.15418 nm). The samples were dried at 50 °C for 24 h.

TGA curves were obtained using Perkin Elmer Pyris 1 at a heat rate of 20 °C/min under nitrogen atmosphere. Before TGA test, sample 6 was washed by THF using centrifugation–sonication cycle for five times to remove the free PS chains.

3. Result and discussion

It is well known that the epoxy, hydroxyl and carboxyl groups are introduced onto the surface of GO via oxidation process [18]. FT-IR spectrum of GO (Fig. 1) confirms the existence of these oxygen-containing functional groups. The broad band in the range of 3000–3600 cm⁻¹ is caused by the stretching of hydroxyl groups. The absorption at 1730 cm⁻¹ corresponds to C=O bonds. The peaks at 1405, 1240 and 1070 cm⁻¹ are due to the absorption of C–O bonds of carboxyl, epoxy and hydroxyl groups, respectively [40–42]. In addition, the strong peak at 1625 cm⁻¹ is ascribed to remaining C=C bonds in GO [41–43].

The presence of huge amount of oxygen-containing functional groups makes GO highly hydrophilic. Therefore, it is easy to fully exfoliate GO into monolayer nanosheets in water via sonication and the dispersion has good stability with golden color as shown in Fig. 2a. The morphology of GO nanosheets is observed by AFM (Fig. 2b). The crosssectional view of the AFM image shows these sheets with the height of about 1 nm (Fig. 2c and d), indicating that a fully exfoliation is achieved. The size of GO nanosheets is in the range of 400 nm to 1 μm. The pH value of water dispersion of GO is about 5.0.

<table>
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Fig. 1. FT-IR spectrum of GO.
Some reports have confirmed that GO nanosheets are capable to stabilize the oil droplets to produce o/w emulsions [24,32]. We also tried to stabilize the styrene droplets by GO via the treatment such as homogenization and sonication. However, the monomer phase and water separated quickly, indicating insufficient stabilization of the prepared GO nanosheets due to their hydrophilic surface nature [44]. Therefore, in the following experiments, only mild magnetic stirring was used during the reaction for the mass and heat transfer. From Fig. 3a, it is clearly found that gray latex (sample 1) is achieved after polymerization. These colloidal particles have good dispersion stability for more than 3 months, indicating the particles may have hydrophilic surface. FE-SEM image shows the morphology of the polymer microspheres (Fig. 3b). It illustrates that the size of PS microspheres is about 500 nm and the size distribution is narrow. Moreover, the surface of these polymer microspheres is coated by wrinkled GO monolayer nanosheets. Dynamic light scattering (DLS) test was carried out to investigate the dispersity of the GO coated PS nanocomposite microspheres in water as shown in Fig. 4. The result indicates that the hydrodynamic diameter of the colloidal particles is about 660 nm with size dispersity of 1.10, in good agreement with the observation in FE-SEM image.

As mentioned above, our prepared GO nanosheets cannot stabilize the Pickering emulsion efficiently due to their high hydrophilicity, although GO coated PS microspheres with the diameter of 500 nm is achieved. It has been proven that GO’s amphiphilicity can be tuned by pH because the degree of ionization of the edge—COOH groups is affected by pH [24]. In order to clarify the effect of GO’s hydrophilicity on the morphology of the resulted PS microspheres, the GO nanosheets are used as stabilizer during polymerization by changing pH value. It is clearly found that the product after polymerization becomes completely flocculated when the pH is tuned to 3.0 as shown in Fig. 5a. The flocculation shows a brown1 color after filter which may be caused by the GO nanosheets in it. FE-SEM image indicates that the flocculation does not display the sphere-like nature but irregular morphology (Fig. 5b). The wrinkled surface may be induced by the GO nanosheets embedded in the PS matrix. When the pH value of GO dispersion is raised to 4.0, the flocculation with brown color is also clearly seen after polymerization (Fig. 5c). However, the morphology of the flocculation revealed by FE-SEM is completely different

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1 For interpretation of color in Fig. 5, the reader is referred to the web version of this article.
the highly hydrophilic TiO₂ nanoparticles were used both as a photocatalyst and stabilizer to produce polymer microspheres. In our previous papers, the highly hydrophilic TiO₂ nanoparticles were used both as a photocatalyst and stabilizer to produce polymer microspheres. The attachment of polymer chains on the surface of TiO₂ nanoparticles induced by the surface-initiated polymerization makes the nucleation process become easier, leading to the formation of polymer microspheres with small size and narrow distribution [38,39].

In this paper, GO is also too hydrophilic to play as stabilizer of the monomer droplets, while PS microspheres stabilized by GO nanosheets are formed. As the decreased hydrophilicity of GO nanosheets before the polymerization by tuning the pH value is not beneficial in forming PS microspheres in our system (Fig. 5), it can be speculated that the surface nature of GO may change during the polymerization. FT-IR spectrum of sample 1 is investigated to reveal the change of GO’s surface structure after polymerization. However, the discrepancy can hardly be found between PS nanocomposite microspheres and pure PS microspheres synthesized by emulsifier-free emulsion polymerization. The extremely low content of GO in the polymer nanocomposite (about 1/400 estimated according to the recipe listed in Table 1) leads to the fact that most of PS chains are not on the surface of GO nanosheets. Consequently, the absorption peaks ascribed to the interaction between PS and GO cannot be distinguished from the FT-IR spectrum of sample 1. Based on above results, much less styrene is used in the polymerization to decrease the “bulk” PS chains which are not on the surface of GO nanosheets and the amount of monomer is 5, 10 and 20 times of the GO’s weight (samples 4–6 in Table 1). The FT-IR spectra of dried samples 5 and 6 are presented and the spectra of pure PS and GO are also provided as reference, as shown in Fig. 6.

The size of PS nanocomposite microspheres is about 200–300 nm. However, as shown in Fig. 3, GO coated PS colloidal particles are obtained at pH 5, while flocculation with spherical and irregular morphology is observed when GO’s hydrophilicity is decreased which is proven beneficial for the stabilization of emulsions. These results eliminate the possibility of the formation of an oil-in-water Pickering emulsion and the monomer droplets acting as the vessels for the following polymerization. This indicates that the mechanism in our experiments is obviously different from Yang and Zhao’s [32].

The preparation of polymer microspheres has been reported via Pickering emulsion polymerization using highly hydrophilic particles as stabilizer [35,45]. The decrease of the particles’ hydrophilicity caused by the adsorption of the hydrophobic oligomer at the initial stage of the polymerization process is regarded as crucial for the formation of the polymer microspheres. In our previous papers, the highly hydrophilic TiO₂ nanoparticles were used both as a photocatalyst and stabilizer to produce polymer microspheres. The attachment of polymer chains on the surface of TiO₂ nanoparticles induced by the surface-initiated polymerization makes the...
UV–vis spectra (Fig. 7) of GO and samples 4–6 are collected to further confirm the interaction between GO nanosheets and PS chains. The curve of GO dispersion (Fig. 7a) exhibits a peak at 231 nm and a tiny shoulder at ~300 nm, which are attributed to π–π* transitions of aromatic C=C bonds and n–π* transitions of C=O bonds [11]. PS particles in water normally have an absorption peak at about 280 nm. However, this peak cannot be found in samples 4–6, indicating the change of electronic structure of PS in our reaction system. This is probably due to the interaction between PS chains and GO sheets. It is also obviously found that the absorption peak at 231 nm for GO gradually shifts with the increasing amount of added styrene and the peaks are at 235, 237 and 241 nm for samples 4–6, respectively. That means the energy of π–π* transitions of aromatic C=C bonds in GO has changed significantly by the addition of PS, which is very likely caused by the π–π stacking between PS and GO.
XRD patterns (Fig. 8) of GO and sample 6 also show that efficient adsorption occurred between PS chains and GO sheets. The diffraction angle of GO nanosheets is about 4.84°, indicating that the layer spacing of GO (002) is about 0.91 nm. This is in accordance with the results in literatures [49,50]. The diffraction angle of sample 6 is detected to be about 3.88°, which means the layer spacing is about 1.14 nm. The increase of the layer spacing of about 0.2 nm is obviously due to the intercalation of single-atom-thick PS chains into GO nanosheets during the in situ polymerization. The peak at 4.84° cannot be found in sample 6, which means nearly all intervals between GO sheets are intercalated by PS chains. The XRD results indicate the existence of strong interaction between PS and GO and a considerable fraction of PS chains adsorbed on the surface of GO nanosheets.

TGA results of GO and the composite are shown in Fig. 9. Sample 6 has been washed by THF to completely remove the “bulk” (free) PS chains before TGA test. The mass fraction of the residue of GO after heating to 700°C in nitrogen is about 51.7 wt%, while that of sample 6 washed by THF is 41.3 wt%. This means about 20 wt% PS chains are still adsorbed on GO nanosheets even after the sample has been washed by THF intensively. It is also clearly seen from Fig. 9 that the thermal decomposition temperature of sample 6 is about 40°C higher than that of pure PS, indicating the tight attachment of polymer chains on the surface of GO nanosheets and good thermal stability of these chains.

All FT-IR, UV–vis, XRD and TGA results indicate the strong interaction between GO nanosheets and PS chains. Thus, the evolvement of the surface structure of GO nanosheets and the formation of GO coated PS microspheres can be speculated, as shown in Fig. 10. Highly hydrophilic GO nanosheets disperse in water and polymerization of styrene initiated by AIBN first takes place in oil phase. The PS oligomers precipitate from the monomer phase as chain growing due to their poor solubility. The adsorption of generated PS oligomers on the surface of GO is induced by their strong interaction with GO nanosheets. The adsorption of hydrophobic PS oligomers on the surface of GO nanosheets reduces dominantly after the attachment of hydrophobic PS chains. The improvement in hydrophobicity induces the aggregation of GO nanosheets to produce nuclei that can be quickly swollen by the monomer. With further polymerization, the nascent nuclei grow in size and the increasing interfacial area is stabilized by GO remaining in aqueous phase. Therefore, as speculated from the mechanism, the strong interaction between GO nanosheets and PS chains is very important for the preparation of GO coated PS nanocomposite microspheres. Furthermore, this mechanism can also well explain the effect of GO’s pH value on the morphology of the products. It has been proven that the hydrophilicity of GO nanosheets decreases with the decline of pH value [24], while the π–π interaction between GO and PS is almost pH-independent. When pH is 3.0, the GO nanosheets attached by PS chains are too hydrophobic to play as stabilizer and the composite is more prone to be embedded into PS matrix due to their good compatibility as shown in Fig. 5b. The adsorption of hydrophobic PS oligomers on the surface of highly hydrophilic GO nanosheets at pH 5.0 can produce GO coated PS microspheres with narrow size distribution because the composite has good stabilization during the polymerization. The remaining hydrophilicity of GO nanosheets is enough for the good water dispersion of PS microspheres (Fig. 3a). When pH is 4.0, the decreased hydrophilicity of GO nanosheets makes the nucleation easier in water, leading to a smaller size of microspheres (about 200–300 nm). However, the aggregation of PS composite microspheres is induced by the insufficient hydrophilicity of GO on the surface of polymer microspheres and macroscopic flocculation is observed in Fig. 5d. Compared with the GO nanosheets at pH 3, the more ionized —COOH groups improve the hydrophilicity of GO at pH 4 and thus the product with spherical morphology is obtained. Therefore, the pH-dependent amphiphilicity of GO nanosheets and strong interaction between GO and PS are responsible for the structure and morphology of the products.

4. Conclusion

The preparation of GO coated PS nanocomposite microspheres using GO as stabilizer is reported. Stable gray latex is obtained after polymerization of styrene stabilized by highly hydrophilic GO nanosheets. The adsorption of hydrophobic PS oligomers on the surface of GO nanosheets is induced by their strong interaction...
via the π–π stacking and π-bonding interaction. The improvement in hydrophobicity leads to the aggregation of GO nanosheets to produce nuclei that can be quickly swollen by the monomer. The nascent nuclei grow in size and the increasing interfacial area can be stabilized by GO remaining in aqueous phase with further polymerization. Furthermore, the pH-dependent amphiphilicity of GO nanosheets is observed to have a great effect on the morphology of the products.

References