

Facile and Controllable Assembly of Multiwalled Carbon Nanotubes on Polystyrene Microspheres^{*}

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Abstract Herein a facile and controllable heterocoagulation between polystyrene (PS) microspheres and multiwalled carbon nanotubes (MWCNTs) is introduced based on colloid thermodynamics. The MWCNTs play the role of steric stabilizer for stabilizing the metastable PS microspheres and thus immobilize spontaneously on the surface of PS microspheres. The synthesized MWCNTs-coated PS composite particles have been extensively characterized by scanning electron microscopy, transmission electron microscopy, thermogravimetry and Raman spectroscopy. The results indicate that the structure and morphology of the resultant MWCNTs-coated PS composite particles are significantly affected by the weight ratio of PS and MWCNTs and the amount of poly(vinylpyrrolidone) that is injected into PS dispersion before they are mixed with MWCNTs. Therefore, these composite particles have the potential to produce MWCNTs-based composite materials with controllable mass loading and dispersity of MWCNTs.

Keywords: Multiwalled carbon nanotube; Polystyrene microsphere; Heterocoagulation; Structural control; Colloid thermodynamics.

INTRODUCTION

In recent years, carbon nanotubes (CNTs) have attracted tremendous attention owing to their exceptional optical, mechanical, thermal and electrical properties. These intriguing salient features lead to a variety of applications in the field of electronics, optics, medical chemistry and so on^[1–10]. However, due to the strong van der Waals attraction and hydrophobicity, pristine CNTs cannot be dispersed and manipulated in most solvents^[11–13]. Thus, applying the CNTs in an effective way and taking advantage of their prominent functions to the full still remain a scientific challenge, even if low-cost and large-scale production of CNTs is achieved. One possible route would be the preparation of CNTs-based composite materials, and naturally, the performance of the resultant composites is determined by both the size of CNTs and their homogeneous distribution in matrices. In principle, the problem of uniform dispersion of CNTs in composites can be effectively resolved by preparing colloidal composite particles^[14]. On the basis of this strategy, the spatial distribution and mass loading of CNTs within the final composite materials are highly controllable.

So far, a series of methods has been developed to assemble CNTs onto various types of colloidal particles

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and the driving forces mainly involve electrostatic interaction, van der Waals attraction, hydrogen bond attraction and *etc.*^[15–25] Among them, the layer-by-layer (LbL) assembly is a well-known method for coating the colloidal substrates with CNTs. For example, Correa-Duarte *et al.* reported that the dense mono- and multi-layers of multiwalled carbon nanotubes (MWCNTs) were successfully deposited on the surface of silica, PS and melamine particulate colloids using the LbL technique^[2, 15]. Similarly, Qin and co-workers realized the assembly of MWCNTs onto the surface of PS microspheres based on the same technique^[24, 25]. Besides the LbL method, CNTs-based composite particles could also be prepared by simply blending the CNTs with substrate microspheres. Nevertheless, it usually relies on engineering the surface of substrate microspheres or CNTs in order to enhance physicochemical or chemical interaction between them. For example, Liu's group prepared the MWCNTs-coated PS composite particles by simply blending the aqueous dispersions of poly(*N*-vinylpyrrolidone)-grafted MWCNTs with acid functionalized PS nanoparticles^[19]. Moreover, as an alternative method, *in situ* polymerization can be utilized to prepare CNTs-coated polymer composite particles^[20].

Recently, we reported that a series of functional materials were coated on PS microspheres based on colloid thermodynamics^[26–29]. As a significant idea, the thermodynamic effect, a very ordinary but probably disregarded one was purposively utilized to drive and govern the coating of PS microspheres with various functional materials. Thus, in sharp contrast to traditional synthetic protocols, the prominent advantage of this strategy is that the complicated surface pretreatments of PS microspheres or functional materials, involving functionalizations and modifications, are not necessary at all.

In this work, we present a comprehensive investigation of the synthesis and characterization of the MWCNTs-coated PS composite particles based on colloid thermodynamics. The MWCNTs mass loading of the resultant composite particles was controllable by simply changing the weight ratio of MWCNTs/PS and PS/PVP, respectively, and the techniques such as SEM, TEM, Raman spectroscopy and TGA were used to characterize the resultant MWCNTs-coated PS composite particles.

EXPERIMENTAL

Materials

Styrene (AR) obtained from Shanghai Chemical Reagent Co., was purified by distillation under reduced pressure. Multiwalled carbon nanotubes (MWCNTs) were provided by Shenzhen Nanotech Port Co. Azodiisobutyronitrile (AIBN) of chemical reagent grade (Shanghai Chemical Reagent Co.) was purified by recrystallization in 95% ethanol. Poly(vinylpyrrolidone) with an average molar mass of 58 kg/mol (PVP K-30) was purchased from Acros Organics. Nitric acid, absolute ethanol, 95% ethanol, and 2-propanol were purchased from Nanjing Chemical Reagent Co. and used as received. Deionized water (18.2 MΩ·cm) was prepared in a Sartorius Arium 611 system and used throughout the experiment (unless otherwise specified).

Synthesis of Polystyrene (PS) Microspheres

For the synthesis of PS microspheres, the PVP stabilizer (2.8 g) was dissolved in 2-propanol (160 mL) within a four-necked round-bottom flask and heated to 70 °C. It was purged with nitrogen to eliminate the inhibiting effect of oxygen. A solution of AIBN initiator (0.2 g) predissolved in styrene monomer (20 g) was injected into the reaction vessel under vigorous mechanical stirring. The polymerization was allowed to proceed for 24 h before cooling to ambient temperature. Subsequently, the PS microspheres were transferred from 2-propanol to deionized water by repeated centrifugation and redispersion process, and finally diluted with deionized water to 10 wt% solid content before use.

Acid Treatment of the Raw Multiwalled Carbon Nanotubes (MWCNTs)

Pristine MWCNTs (5 g) and nitric acid (500 mL, 69%) were first added to a 1 L three-necked round flask. The mixture was sonicated for 30 min and then refluxed for 30 h at 120 °C. After cooling to room temperature, the mixture was diluted with 5 L deionized water and filtered with a 0.8 μm PC membrane. The redispersion and filtration steps were repeated until the pH value of filtrate became neutral. The final black solid was dispersed in deionized water.

Preparation of MWCNTs-coated PS Composite Particles

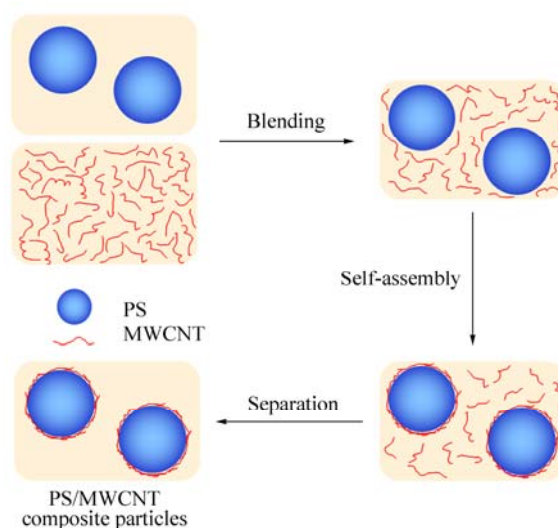
The heterocoagulation process of the preformed aqueous dispersions of PS microspheres and MWCNTs was summarized as follows. The appropriate amount of PS dispersion (0.2 g) was injected into various amount of acid-treated MWCNTs aqueous dispersion mentioned above. Otherwise, different amount of PVP was added to the PS dispersion prior to the heterocoagulation. These mixtures were homogenized *via* ultrasonic treatment for 1 min and then allowed to stir at 300 r/min using a magnetic stirrer for 1 h at room temperature. The resulting MWCNTs-coated PS composite particles were collected by centrifugation/wash/redispersion cycle to remove the free MWCNTs.

Characterization

The morphology of MWCNTs-coated PS composite particles was observed by transmission electron microscopy (TEM) using a JEM-100 CX (JEOL Co., Japan) microscope and scanning electron microscopy (SEM) using an S-4800 instrument (Hitachi Co., Japan). Raman spectra were measured by virtue of the MultiRam spectrometer (Bruker Co., Germany). Thermogravimetric analysis (TGA) was conducted with a Pyris 1 TGA instrument (Perkin Elmer Co., USA) at a heating rate of 20 K/min in N₂ from room temperature up to 700 °C.

RESULTS AND DISCUSSION

The whole preparation process of MWCNTs-coated PS composite particles is represented in Scheme 1. The PS microspheres employed in our system are prepared by dispersion polymerization using AIBN and PVP as initiator and stabilizer, respectively. Therefore, the resultant PS microspheres have no chemically bound ionic groups, which are solely stabilized by the amphiphilic and nonionic PVP. Subsequently, the PS microspheres are transferred from isopropanol to deionized water by repeated centrifugation and redispersion process. During this procedure, the adsorption of PVP on the surface of PS microspheres is minimized, although the PVP cannot be completely removed. Thus, the PS microspheres become metastable since the interfacial tension against the aqueous medium is enhanced, owing to the elimination of most of the PVP. With respect to MWCNTs, an acid pretreatment is carried out for the formation of hydrophilic groups at both the tips and sidewalls, which are responsible for obtaining a stable aqueous dispersion of MWCNTs^[19, 30]. Finally, following a simple blending, the MWCNTs adsorb and assemble spontaneously at the PS/water interface, as this is energetically more favorable based on colloid thermodynamics. The adsorbed MWCNTs stabilize the PS microspheres and then the MWCNTs-coated PS composite particles are formed.



Scheme 1 Schematic illustration of the preparation of MWCNTs-coated PS composite particles by the proposed heterocoagulation strategy

Figure 1 illustrates the scanning electron microscopy (SEM) images of MWCNTs-coated PS composite particles, which were prepared by different weight ratios of PS microspheres and MWCNTs. The adsorption of MWCNTs on the surface of PS microspheres can be directly confirmed by these SEM images. It is evident that the chemically pretreated MWCNTs lie along the spherical surface of PS microspheres, behave like water-soluble, long and flexible polymer chains in stabilizing the unstable PS microspheres, and the uncovered region on the surface of PS microspheres is smooth. With the increase of the weight ratio of MWCNTs/PS, more and more MWCNTs attach densely and wrap tightly on the surface of PS microspheres due to their flexibility, making the surface of PS microspheres increasingly rough. Moreover, some MWCNTs also serve as joints between neighboring PS microspheres. When the weight ratio of MWCNTs/PS is higher than 1:4, the MWCNTs either connect to one another or nest one on top of another to form an interdigitated overlayer. On the other hand, transmission electron microscopy (TEM) was also used to investigate the formation of MWCNTs-coated PS composite particles and the variation of surface morphology of MWCNTs-coated PS composite particles with different mass loadings of MWCNTs. As illustrated in Fig. 2, the MWCNTs can be hardly distinguished on the surface of PS microspheres as the weight ratio of MWCNTs/PS is lower than 1:10. With the increase of the initial amount of MWCNTs, the presence of MWCNTs on the surface of PS microspheres is readily observed and the amount of adsorbed MWCNTs increases.

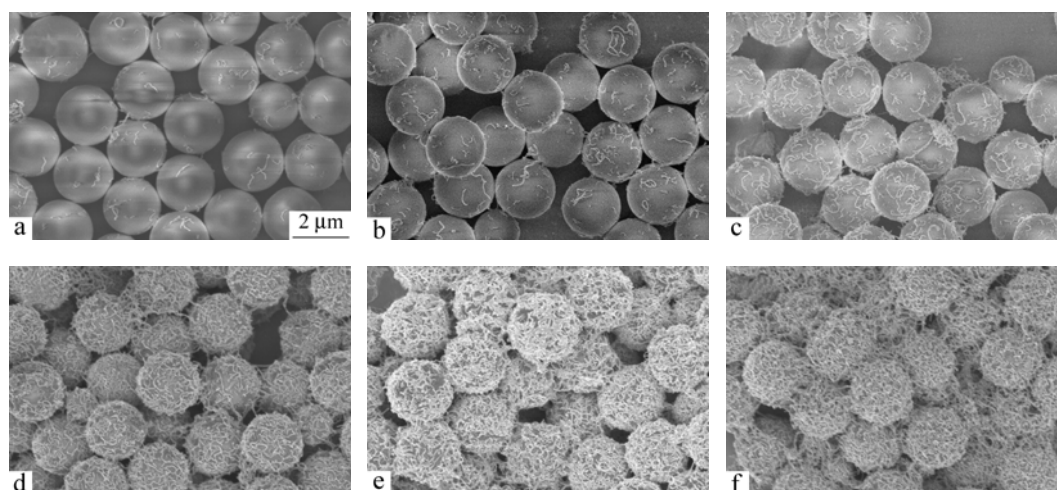


Fig. 1 SEM images of MWCNTs-coated PS composite particles prepared by different weight ratios of MWCNTs/PS, 1:100 (a), 1:25 (b), 1:10 (c), 1:4 (d), 1:2 (e) and 1:1 (f) (The scale bar corresponds to all SEM images.)



Fig. 2 TEM images of MWCNTs-coated PS composite particles prepared by different weight ratios of MWCNTs/PS, 1:25 (a), 1:10 (b) and 1:2 (c) (The scale bar corresponds to all TEM images)

In fact, the successful heterocoagulation between PS microspheres and MWCNTs can also be demonstrated by thermogravimetric analysis (TGA). Figure 3 represents the TGA results of the PS microspheres and MWCNTs-coated PS composite particles with different MWCNTs/PS weight ratios mentioned in Fig. 1. As seen

from curves (b) to (f), the residual weight percentage indicates the existence of MWCNTs in composite particles since the PS has been completely decomposed below 475 °C. The more amount of the MWCNTs was added initially, the higher mass loading of the MWCNTs was obtained in the composite particles. Concretely, the mass loading of MWCNTs derived from Fig. 3 is about 1.84 wt%, 6.21 wt%, 11.27 wt%, 24.78 wt% and 48.21 wt%, respectively. This variation tendency of mass loading of MWCNTs is corresponding to the SEM observation in Fig. 1, and thus allows us to conclude that the increase of the mass loading of MWCNTs in composite particles can be conveniently achieved by changing the initial amount of MWCNTs. In addition, with respect to curves (d) to (f), the entire degradation of PS component is remarkably shifted to the higher temperature derived from the formation of MWCNTs overlayer on the surface of PS microspheres, which is illustrated in Fig. 1. This phenomenon can be attributed to the enhancement of the thermal stability of PS component owing to the presence of the MWCNTs overlayer, which acts as the thermal barrier to shield the PS component from the heat source^[31].

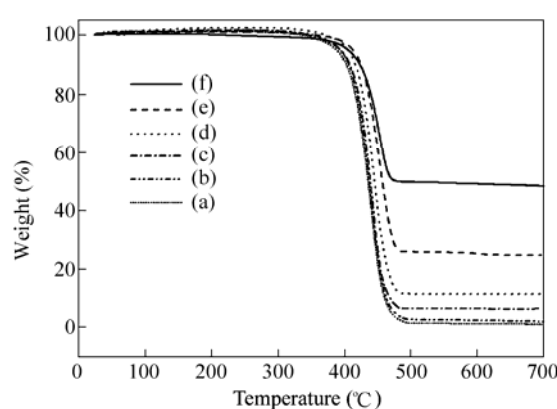


Fig. 3 TGA curves of PS microspheres (a) and MWCNTs-coated PS composite particles prepared by different weight ratios of MWCNTs/PS, 1:25 (b), 1:10 (c), 1:4 (d), 1:2 (e) and 1:1 (f)

As a powerful nondestructive tool extensively used to characterize carbon-based materials, Raman spectroscopy was adopted to determine the existence of MWCNTs in the resultant composite particles herein^[4, 30, 32, 33]. Raman spectra of PS microspheres and MWCNTs-coated PS composite particles with different mass loadings of MWCNT are depicted in Fig. 4. As in the case of Raman spectrum of PS microspheres, there is a very strong signal at about 1003 cm^{-1} , which can be ascribed to ν_1 ring-breathing mode of PS^[34]. In contrast, for the MWCNTs-coated PS composite particles prepared by different weight ratios of MWCNTs and PS, the G peak and D peak of MWCNTs at about 1600 cm^{-1} and 1287 cm^{-1} , respectively, are displayed obviously^[30, 33]. Moreover, the characteristic signal of PS became weak but not completely disappeared with the increase of weight ratio of MWCNTs/PS. On the one hand, this phenomenon can be regarded as a powerful evidence for the formation of MWCNTs-coated PS composite particles, because the Raman signal belonging to PS microspheres could be attenuated or absorbed when the MWCNTs overlayer is formed. On the other hand, because the MWCNTs form an interactive net structure on the surface of PS microspheres rather than an intact overlayer, the characteristic signal of PS still can be detected.

According to our established mechanism, if the PVP was added to the dispersion of PS microspheres before blending them with MWCNTs, it would have negative influence on the adsorption of MWCNTs on the surface of PS microspheres^[26]. Figure 5 displays the SEM images of the MWCNTs-coated PS composite particles prepared by blending different amount of PVP with PS dispersion beforehand. Obviously, the amount of MWCNTs adsorbed on the surface of PS microspheres decreases as the amount of PVP is increased. Furthermore, if the PVP is added enough, few of MWCNTs are attached onto the surface of PS microspheres. In the system, the MWCNTs and PVP both played the role of stabilizer for metastable PS microspheres, however,

the PVP was preferred, and namely, the flexible polymer was more powerful and efficient than the nano-size object as stabilizer. Heterocoagulation only occurred and maintained when the PVP was insufficient. As enough PVP was added before blending the PS dispersion with MWCNTs, there was obviously no need for the adsorption of extra MWCNTs onto the surface of PS microspheres. Hence, we could conclude that this synthetic strategy distinctly has the flexibility and controllability based on colloid thermodynamics.

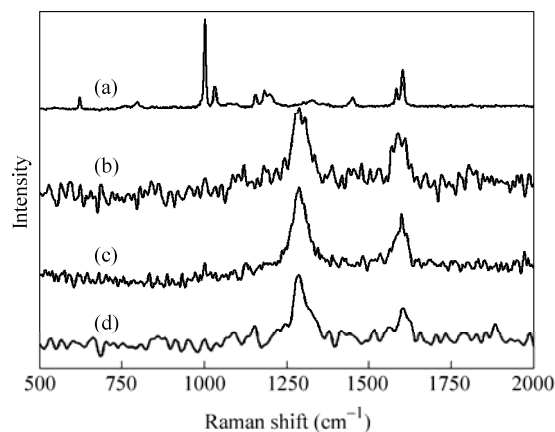


Fig. 4 Raman spectra of PS microspheres (a) and MWCNTs-coated PS composite particles prepared by different weight ratios of MWCNTs/PS, 1:25 (b), 1:10 (c) and 1:2 (d)

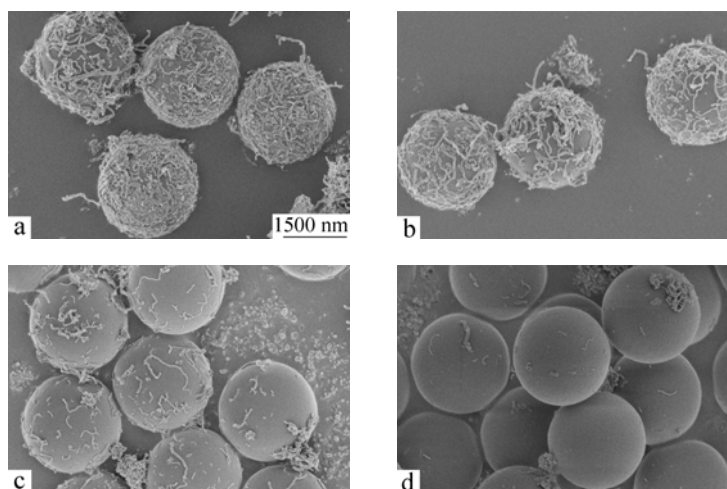


Fig. 5 SEM images of the resultant MWCNTs-coated PS composite particles prepared by blending PS dispersion with PVP and MWCNTs in turn and weight percent of PVP to PS as 0.4 wt% (a), 0.8 wt% (b), 2 wt% (c) and 5 wt% (d) (The scale bar corresponds to all SEM images.)

CONCLUSIONS

In summary, it has shown that PS microspheres can be readily coated with MWCNTs based on colloid thermodynamics. This method is advanced because the complicated surface pretreatments of substrate microspheres or MWCNTs are avoidable. The adsorption amount of MWCNTs on the surface of PS microspheres was significantly influenced by the initial weight ratio of MWCNTs/PS and the concentration of PVP, added before mixing PS microspheres with MWCNTs. Gradual increase of the initial proportion of MWCNTs to PS microspheres resulted in a corresponding increase in the adsorption of MWCNTs on the surface of PS microspheres. In contrast, the more PVP was involved beforehand in the aqueous dispersion of PS

microspheres, the less MWCNTs were observed on the surface of PS microspheres. Therefore, this work should afford a potential of fabricating the MWCNTs-based composite materials with highly ordered structure and controllable mass loading of MWCNTs, which are of importance in various promising applications, and detailed research activities are underway.

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