



Strings of polymer microspheres stabilized by oxidized carbon nanotubes



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ABSTRACT

Oxidized carbon nanotubes (CNTOs) with hydrophilic oxygen-containing functional groups and hydrophobic conjugated structure are prepared by the oxidation of carbon nanotubes (CNTs). After the polymerization of styrene with CNTOs dispersed in aqueous phase, polystyrene (PS) microspheres with string-like structure are obtained. Thermogravimetric analysis (TGA), differential scanning calorimeter (DSC) and Raman results indicate the strong interaction between the separated PS chains from the oil phase and CNTOs during the initial stage of the polymerization. These adsorbed PS chains on the surface of CNTOs are quickly swollen by the monomer and they grow in size during the further polymerization. The pH value and the ion strength of aqueous phase obviously affect the stability of PS microspheres. The particle size of microspheres is also determined by the pH. We demonstrate that the one-dimensional structure of CNTOs is responsible for the formation of polymer microspheres with special architecture.

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1. Introduction

Carbon nanotubes (CNTs) are one kind of admiring 1D material due to their prominent electrical [1], mechanical [2] and thermal [3] properties. In order to prepare functional polymer composites using CNTs as the filler, a high degree of exfoliation of these nanotubes is necessary [4]. It has been proven that the surface treatment of CNTs can improve their dispersion in polymers [5–7], although CNTs cannot bring into play their desired physical characteristic in the final polymer composites [8]. In recent years, the inherent amphiphilicity of CNTs and the oxidized CNTs (CNTOs) has been proposed, which makes them have the ability to assemble at oil/water interface as the stabilizer of Pickering emulsions [9,10]. Porous polymers with the improved mechanical and electrical properties were fabricated via Pickering-stabilized emulsion templates using CNTs as the stabilizer [11]. CNTs can also be trapped at the interface of an immiscible blend of polymers and act as a mechanical barrier against coalescence of colliding droplets due to their amphiphilicity [12,13].

Polymer/inorganic composite microspheres are popular in recent years for the particular applications in coating [14], drug delivery [15,16] and E-ink [17,18]. Two efficient methods have been reported to prepare composite microspheres [19]. One is the hetero-flocculation. Amine-functionalized carbon nanotubes

were deposited on the surface of sulfonated PS microspheres to form the core-shell structure [20]. The other is to directly use nanoparticles as the stabilizer to fabricate composite microspheres. If the polymerization occurred, it can be called Pickering polymerization [21–27]. Microspheres with different morphologies such as supracolloid [28,29] and raspberry-like structures [30] have been achieved by this strategy. Because of its distinctive geometric shape, the 1D nanoparticles have great potential in fabricating nanocomposites with special structures and unique functionalities. For example, the “hairy” colloidosomes have been successfully fabricated by using polymeric microrods as the stabilizer [31]. The amphiphilicity of the CNTs (or CNTOs) shows that it is possible to use them as the sole 1D stabilizer. Combined with its excellent mechanical and electrical properties, it has a high possibility that composite microspheres with peculiar nature will be obtained by using CNTs (or CNTOs) as the stabilizer. For example, CNT-armored polymer microspheres have been successfully prepared by polymerizing the Pickering emulsion stabilized by CNTs, which have potential applications as microelectronic and microoptical components [32].

In this paper, PS composite microspheres with novel string-like morphology are fabricated by using CNTOs and CNTs as the stabilizer. This special architecture seems to relate more or less with the 1D structure of CNTOs (CNTs). Obviously, this kind of polymer microspheres cannot be obtained via conventional Pickering polymerization because nanotubes are not located on the surface, and thus the formation mechanism is studied. As reported in our

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previous paper [33], there is strong interaction between PS chains and carbon materials. The adsorbed PS chains on the surface of CNTOs become the loci for the further polymerization. The morphology of PS microspheres is affected by the pH value and the ion strength of aqueous phase. The stabilization of CNTOs for the growing microspheres is proved and the effect of one-dimensional nanotubes on the morphology of the products is determined. This paper provides a new facile method to prepare polymer/CNT composite microspheres with special architecture.

2. Materials and methods

2.1. Materials

Multi-walled CNTs (20–30 nm in diameter and 1–2 μm in length) were purchased from Shenzhen Nanometer Gang Co., Ltd. KMnO_4 (99%), H_2SO_4 (98.3%), styrene (99%), tetrahydrofuran (THF, 99%), potassium persulfate (KPS, 99.5%) and azo-bisobutyronitrile (AIBN, 99%) were all supplied by Shanghai Chemical Reagent Co. (China). Styrene was distilled under vacuum and AIBN and KPS were recrystallized prior to use. Other reagents were used as received. Deionized water was used throughout the experiments.

2.2. Preparation of CNTOs

CNTOs were prepared using the same way as the modified Hummers method [34]. The produced CNTOs were dialyzed in deionized water for one week and then dried in vacuum at room temperature. Dried CNTOs were dispersed in water and the mixture was sonicated for one hour.

2.3. Preparation of PS microspheres

A typical polymerization procedure is described as follows (Entry 1–10 in Table 1): the oil phase (styrene and 1.0 wt% AIBN) and CNTOs water solution (15 g) were added into 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 treatments such as homogenization and sonication followed by the reaction at 65 $^\circ\text{C}$ for 10 h via magnetic stirring. As a control, AIBN was replaced by KPS before the polymerization and the other components were the same as sample 1.

2.4. Characterization

Digital photographs were taken with the Cannon 550D. The morphology of the prepared PS microspheres was characterized by the TESCAN 5136MM scanning electron microscopy (SEM) and the 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 the observation. Raman spectra were recorded using Dilor LABRAM 1B multi-channel confocal microscope. The wavelength of the excitation light is 631 nm. The thermal decomposition of the samples was measured by thermogravimetric analysis (TGA) using a Perkin Elmer Pyris 1 thermogravimetric analyzer at a heat rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Before TGA test, sample 3 was washed by THF using centrifugation–sonication cycles for five times to remove the free PS chains. Differential scanning calorimetry (DSC) was carried out under a nitrogen flow (40 ml/min) using a PerkinElmer DSC-7 apparatus at a heating rate of 10 $^\circ\text{C}/\text{min}$ to measure the glass transition temperature (T_g). The samples were heated from 50 to 180 $^\circ\text{C}$ and then cooled from 180 to 50 $^\circ\text{C}$ with the rate of 10 $^\circ\text{C}/\text{min}$ to eliminate the thermal history before the test.

3. Results and discussion

3.1. Oxidation of CNTs

The functional groups such as carbonyl, hydroxyl and epoxy are produced after the extensive oxidation of CNTs and these groups make the obtained CNTOs hydrophilic [35]. The digital photographs of CNTs and CNTOs dispersed in water after 2 months are shown in Fig. 1. The aggregates of CNTs in water are clearly found due to their hydrophobicity. The dispersion stability of CNTOs is good even after 2 months because of hydrophilic groups on the surface. The pH value of CNTOs solution is detected to be about 4.4.

Raman spectrum was employed to reveal the structure evolution of CNTs after the oxidation (Fig. 2). For pristine CNTs, tangential mode band is exhibited at 1570 cm^{-1} as G band and another D band at 1328 cm^{-1} [36]. The D band is ascribed to the defect sites in the hexagonal framework of carbon nanotube walls and its intensity will be increased by the modification [37]. The intensity ratio of peak G and D, $I(G)/I(D)$ for CNTs is about 5.40, while it dramatically decreases to 0.55 for CNTOs. The significant decrease in $I(G)/I(D)$ caused by the oxidation means the incremental proportion of sp^3 C in CNTOs.

The morphology of CNTOs is similar to CNTs, as shown in Fig. 3, indicating that the oxidization mainly occurs on the surface of CNTs. The diameter of CNTOs is 20–50 nm and the length is about several hundred nanometers to several microns.

3.2. Preparation of PS/CNTO nanocomposite microspheres

As reported in some papers, the oxidized CNTs are amphiphilic, and thus CNTOs can be used as stabilizer of Pickering emulsions [10]. In our experiments, the oil phase (including styrene and AIBN) is simply added into water without any further treatments such as ultrasound or homogenization and only mild magnetic stirring is used during the reaction for the mass and heat transfer. It is

Table 1
Formulation in 15 g CNTO solutions for the preparation of PS microspheres.

Entry	Oil phase (g)	CNTO solution (wt.%)	pH value	Ion strength (M)	Agents ^a
1	1.5	0.01	4.4	–	–
2	1.5	0.10	4.4	–	–
3	1.5	0.05	4.4	–	–
4	1.5	0.025	4.4	–	–
5	1.5	0.05	4.4	0.0017	NaCl
6	1.5	0.05	4.4	0.017	NaCl
7	1.5	0.05	3.0	–	HCl
8	1.5	0.05	2.0	–	HCl
9	1.5	0.05	5.0	0.07	NaH_2PO_4
10	1.5	0.05	7.2	0.07	$\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$

^a The agents were used to adjust the pH value and/or the ion strength of aqueous phase containing CNTOs.

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