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Novel synthesis of self-assembled CNT microcapsules by O/W Pickering emulsions

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ABSTRACT

Novel carbon nanotube microcapsules were prepared by oil in water (O/W) Pickering emulsions without any surfactant used. The oxygen plasma treatment introduced several hydrophilic groups on carbon nanotubes resulting in the improved aqueous dispersion. The plasma-treated carbon nanotubes were self assembled at the interface between water and oil phases. Contact angle measurement and XPS analysis proved the hydrophilic formed on carbon nanotubes. The content of carbon nanotubes played an important role in determining both the morphology and size of microcapsules.

1. Introduction

Over the past decade, microcapsules have attracted considerable attention because they have not only unique properties such as low density [1], large surface area [2], and surface permeability [3] but also potential applications, such as microcapsules [4], pigments [5], catalyst loading [6], and drug delivery [7]. Among the many materials which were suitable to make microcapsules, carbon nanotubes (CNTs) have attracted tremendous interests because of their unique optical [8], mechanical [9], and electrical properties [10]. Therefore several approaches have been developed recently to fabricate CNT-based superstructures to utilize their properties [11]. However, the hydrophobic property of pristine CNTs made them difficult to control structures [12,13], which limited their applications. To overcome such difficulties, the chemical oxidation of CNTs was attempted to introduce the carboxylic groups on CNTs, which gave the feasibility to react with various materials [14,15]. However, some of CNTs were chopped inevitably during the oxidation process. Layer-by-layer assembly supplied a different way to create two or three-dimensional CNT architectures via very complex methods [16,17].

In this work, we demonstrated a simple and effective method for the fabrication of CNT microcapsules by O/W Pickering emulsions. Plasma treatment, which was non-polluting, less detrimental to CNTs, and time-saving [18–20], was chosen to introduce the hydrophilic groups on the surface of CNTs.

2. Experimental procedures

2.1. Materials

Multi-walled CNTs, which were 110–170 nm in diameter and 5–9 μm in length with purity over 90%, were purchased from Aldrich and used as received. Sudan III as the oil soluble dye was purchased from Sigma-Aldrich. Cyclohexane (anhydrous, 99.5%) was purchased from Aldrich. Deionized water was used as an aqueous phase.

2.2. Preparation procedures

CNTs were treated with oxygen plasma (radio frequency of 13.56 MHz, Model EPPs 2000, Plasmart Inc., Korea) at a power of 100 W and a pressure of 200 mTorr for several different periods. Oxygen was introduced to the plasma instrument with a flow rate of 10 ml/min. The oil phase, cyclohexane containing oil soluble dye Sudan III was sonicated for 10 min. The plasma-treated CNTs were sonicated in water for 30 min. The aqueous dispersion containing the plasma-treated CNTs was mixed with cyclohexane solution and sonicated for a given period to get the O/W Pickering emulsion. The emulsion was transferred to a glass flask equipped with a condenser and continuously stirred for 2 h at 85 °C. CNT microcapsules were fabricated successfully after cyclohexane was evaporated. After washing with ethanol and water several times, CNT microcapsules were isolated via filtration and subsequently dried in air. (Scheme 1).

2.3. Characterization

The purified CNT microcapsules were characterized by contact angle measurement (Krüss DSA 100 drop shape analyzer), scanning electron microscopy (SEM) (JEOL JSM-7000F microscope), X-ray

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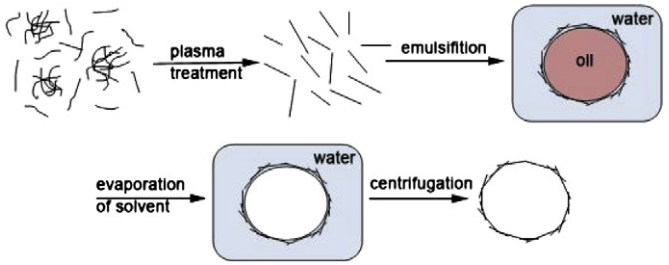

Scheme 1. Schematic illustration of the preparation of CNT hollow microspheres by O/W Pickering emulsions.

photoelectron spectroscopy (XPS) (MultiLab ESCA 2000 X-ray photoelectron spectra spectometer), and optical microscopy (Leica DM 2000 microscope equipped with Canon powershot A95 camera).

3. Results and discussion

For the studies on the wetting behavior of plasma-treated CNTs, the photographs of water droplets formed on CNT pellets were taken as shown in Fig. 1. The contact angle on the CNTs decreased from 115.2° to 79.3° by plasma treatment due to the more hydrophilic nature of CNTs which contained several hydrophilic functional groups, such as hydroxyl and carboxyl groups. The insets in the figure showed the improved dispersion stability of the plasma-treated CNTs. This phenomenon implied that the plasma-treated CNTs could work as an emulsifier suitable for making O/W Pickering emulsions.

XPS measurements were carried out to investigate the surface functional groups on both pristine CNTs and plasma-treated CNTs. As shown in Fig. 2, the obvious increase of the O1s peak was observed in the plasma-treated CNTs due to the oxygen group introduced during the plasma treatment. C1s peak of pristine CNTs indicated that they were mainly composed of the C–C C1s (284.5 eV) and the surface defects of CNTs as –C–OH C1s (285.8 eV). For the plasma-treated CNTs, the increase of –C–OH C1s (285.8 eV), –C = O C1s (287.5 eV), and –COOH C1s (289.0 eV) was clearly observed. These hydrophilic groups were introduced successfully by O_2 plasma, which played an important role in the dispersion stability of CNTs in water.

Optical photographs were taken to investigate the long-term stability of CNT Pickering emulsions. As shown in Fig. 3, almost all the emulsion droplets remained intact and no any noticeable coalescence was observed after staying for 2 weeks. Both the steric repulsion between CNT microcapsules and the robust self-assembly of CNTs on the surface of microcapsules were responsible to prevent the agglomeration and to fabricate the reproducible CNT microcapsules.

The effect of CNT content on the morphology and size of microcapsules was shown in Fig. 4. CNT microcapsules could not be fabricated when the content of CNTs was too low to cover the oil

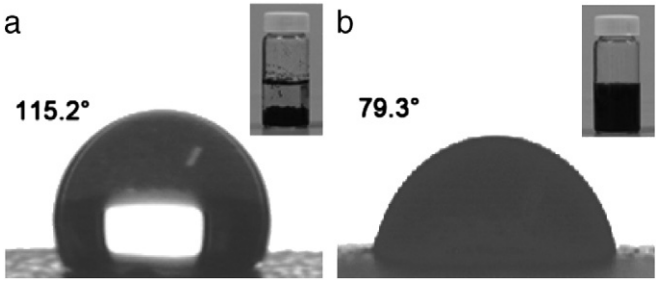

Fig. 1. Photographs of the water droplet placed on the surface of the CNT pellet: (a) pristine CNTs and (b) O_2 plasma-treated CNTs (plasma treatment: 20 min). (Insets: photographs of CNT dispersions (0.03 wt.%) in water after staying 48 h from preparation.)

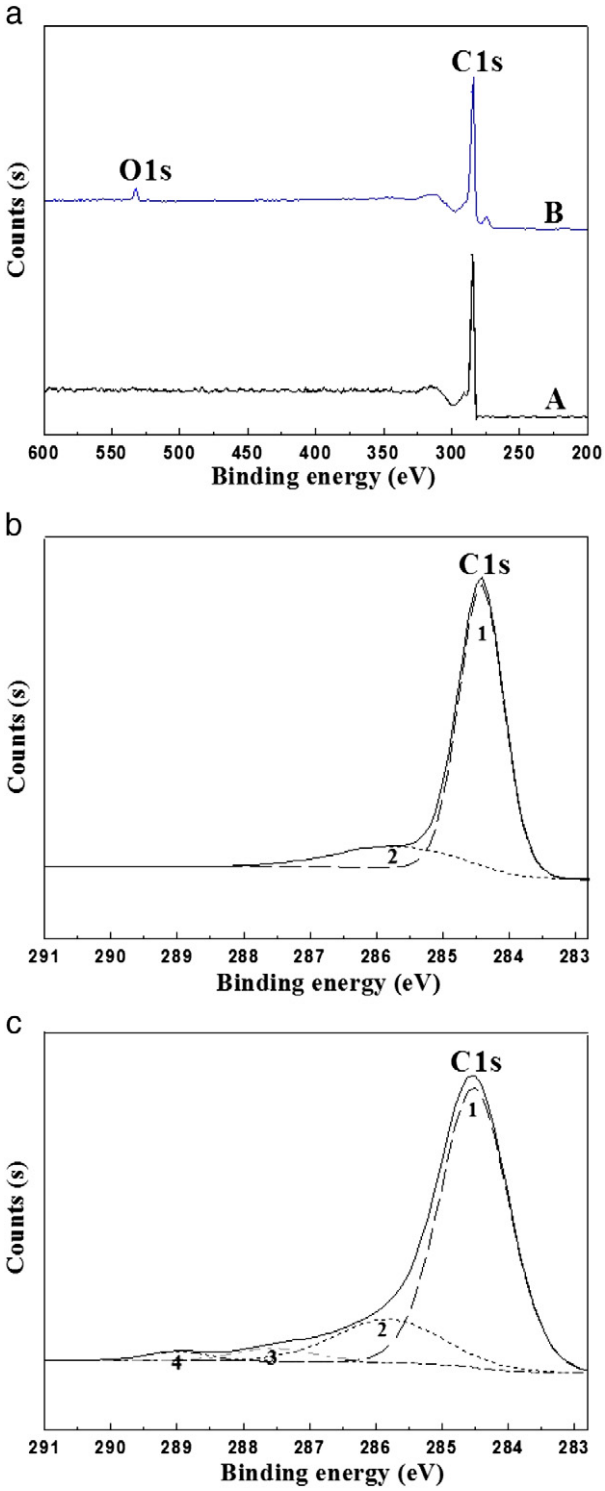

Fig. 2. XPS spectra of CNTs. (a) A: pristine CNTs, B: O_2 plasma-treated CNTs, (b) C1s spectra of pristine CNTs, and (c) C1s spectra of O_2 plasma-treated CNTs (plasma treatment time: 20 min).

droplets in O/W Pickering emulsions. With the increase of the CNT content, intact microcapsules were obtained even though some of them were broken. Further increase of the CNT content kept nearly all the CNT microcapsules undamaged with a more uniform size distribution, which was due to the decrease in the interfacial tension between oil and water phases. In addition, the broken microsphere that existed in Fig. 4d proved that hollow structure was successfully fabricated.