Hybrids of CO₂-Responsive Water-Redispersible Single-Walled Carbon Nanotubes by a Surfactant Based on Natural Rosin

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ABSTRACT: A kind of polymerizable dispersant based on natural rosin was used to disperse single-walled carbon nanotubes (SWNTs) in aqueous solution followed by in situ free-radical polymerization to achieve a controllable SWNT dispersion, that not only can be controlled by CO₂/N₂, but can also be recycled and redispersed in CO₂-saturated water after drying without sonication.

INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have gained increasing interest because of their excellent thermal, electronic, and mechanical properties.¹ However, SWNTs tend to form aggregates because of their strong π–π stacking, resulting in their indispersibility in water and most conventional solvents,² and these aggregates are problematic for some practical applications where dispersed individual tubes are demanded.³ To solve this problem, covalent and noncovalent approaches have been developed to modify SWNTs. Noncovalent functionalization is superior to covalent functionalization because the latter generates unwanted functional groups, changing the intrinsic electronic properties of the SWNTs.⁴ In noncovalent functionalization, amphiphilic molecules have often been used to disperse SWNTs such as surfactants,⁵ DNA,⁶–⁹ ionic liquid,¹⁰ lipids,¹¹ and polymers.⁴,¹² However, once these isolated SWNTs were freeze-dried, they were difficult to redisperse in water again without sonication and instead formed aggregates.¹³

Although Kim¹⁶ reported a kind of water dispersible surfactant, maleopimamic acid glycidyl methacrylate ester 3-dimethylaminopropylamine imide (MPAGN), based on natural rosin. It was used to disperse SWNTs in aqueous solution followed by in situ free-radical polymerization to achieve a controllable SWNT dispersion. This SWNT dispersion modified by a noncovalent approach that not only can be controlled by CO₂/N₂, but can also be redispersed in CO₂-saturated water after drying without sonication just requiring mild shaking.
RESULTS AND DISCUSSION

The structures of the SWNT samples were characterized by IR, 1H NMR, as shown in Figures S1 and S2. The synthetic route and reversible transformation of P-MPAGN between its nonionic and cationic states are shown in Figure 1A and a schematic illustration of this dispersion is shown in Figure 1B.

At first, neutral MPAGN was protonated to form cationic MPAGNH⁺ by bubbling with CO₂ into solution to disperse SWNTs and then the cationic MPAGNH⁺ was polymerized on the surface of the SWNTs to obtain P-SWNTs dispersion; the zeta potential of the P-SWNTs dispersion was approximately +58 mV. The electrostatic repulsion among the charged nanotubes can prevent the bundling of debundled SWNTs.

After N₂ was bubbled through the dispersion at 60 °C, the cationic P-SWNT hybrids were deprotonated and the nonionic sample was formed leading to a decrease in the zeta potential of the dispersion to nearly 0 mV. The electrostatic repulsion disappeared among the nonionic P-SWNTs, and the P-SWNTs precipitated. The nonionic P-SWNTs were protonated and returned to cationic P-SWNTs by bubbling of the sample with CO₂ leading to a zeta potential of the dispersion returning to approximately +58 mV. This process can be reversed several times without an obvious change in the zeta potential of the dispersion as shown in Figure 2A. The transmittance of the dispersion at 600 nm was also measured to illustrate the responsiveness of the P-SWNTs to CO₂/N₂. A black powder...
composed of P-SWNTs settled out of solution by bubbling N₂ through the water solution at 60 °C with the transmittance at 600 nm of the supernatant increasing, and this powder can be redispersed into water easily by bubbling CO₂ through the solution. After precipitation by bubbling with N₂, the precipitate could be recovered and reused after drying. It can be redispersed in a CO₂-saturated water solution again with only mild shaking and no visible aggregates appeared over a long time. The zeta potential and transmittance of dispersed P-SWNTs after being dried were basically in line with that of U-SWNTs and P-SWNTs dispersion, and the cycle zeta potential, and transmittance of P-SWNTs dispersion after being dried was almost no different from that of the freshly prepared ones. It can be concluded that the drying operation has little influence on the responsiveness of P-SWNTs.

As shown in Figure 2C, the UV−vis−NIR spectra of the U-SWNTs and P-SWNTs dispersion showed van Hove transition peaks, which indicated the existence of individually isolated SWNTs in the U-SWNTs and P-SWNTs dispersion, and the UV−vis−NIR spectra of P-SWNTs was almost the same as that of U-SWNTs. It can be concluded that the optical properties of SWNTs were not destroyed after in situ polymerization. The UV−vis−NIR spectra of the redispersed P-SWNTs dispersion after responsiveness with N₂/CO₂ and that of dispersion after drying were basically in line with that of the as-prepared sample, which indicated the excellent responsiveness of the P-SWNTs to CO₂ and their excellent redispersibility after drying. The UV spectra of P-SWNTs prepared after 1 month was basically in line with that of the freshly prepared ones, which indicates the excellent durability of P-SWNTs dispersion, as shown in Figure S4.

Thermogravimetric analysis (TGA) was used to count the amount of MPAGN or P-MPAGN attached to the nanotubes. These dispersions were filtered through a membrane (0.22 μm) and dried before measurement. The pristine SWNTs had lost little weight, while the P-SWNTs had a 77.66% weight loss at 800 °C, as shown in Figure 2D. This discrepancy confirmed that the surfactant had been combined with SWNTs. In other words, the ratio of P-MPAGN to SWNTs in P-SWNTs was 3.48:1 by weight. However, U-SWNTs had a 53.9% weight loss at 800 °C, such that the ratio of MPAGN to SWNTs in U-SWNTs was 1.17:1 by weight. It can be concluded that the MPAGN in the U-SWNT sample was partially washed away with the filter liquor in the process of filtration because the intermolecular forces between MPAGN and SWNT were weak. The amount of residue MPAGN attached to the SWNTs in the U-SWNTs was insufficient to redisperse SWNTs in water. In addition, the intermolecular forces between MPAGN and the SWNTs in the U-SWNTs may be destroyed by harsh processing procedures, such as freeze-drying. Therefore, although a black powder consisting of U-SWNTs also settled out of solution after bubbling with either N₂ or air through the aqueous solution at 60 °C, it could not be redispersed in water after freeze-drying by bubbling CO₂ through the aqueous solution without sonication, rather appearing to visibly aggregate. However, the MPAGN monolayer on the SWNT surface was solidly locked in after the in situ free-radical polymerization of P-SWNTs, therefore, the P-SWNTs can be redispersed easily. The photographs of redispersion of U-SWNTs and P-SWNTs after drying are shown in Figure S5.

The SWNTs exhibited bundled and networked microstructures in water, as shown in Figure S6A. However, some well-dispersed and individualized nanotubes of U-SWNTs with diameters of 10−12 nm were observed from the transmission electron microscopy (TEM) image, as shown in Figure 3A, which were larger than those of the original SWNTs (approximately 2 nm). This could indicate that a thick MPAGNH⁺ layer was attached to the surface of the nanotubes effectively. After polymerization, the diameter of the individual tubes of the P-SWNTs shown in Figure 3B was larger than that of the U-SWNTs, from which it can be concluded that polymerization of MPAGNH⁺ has reacted on the surface of the nanotubes and the obtained polymer MPAGNH⁺ has been wrapped around the surface of the nanotubes and prevent the bundling of the SWNTs. The diameter of individualized nanotubes wrapped by MPAGN was much larger than that of the ones wrapped by surfactants based on long-chain alkane because of the steric hindrance of large rigid structures. After bubbling with N₂, the P-SWNTs precipitated from the aqueous solution, and its TEM image is shown in Figure 3C. When CO₂ was bubbled through the solution again, the P-SWNT hybrid suspension became homogeneous without the need for sonication, and the polymer was still wrapped around the surface of the SWNTs, based on their diameters, as shown in Figure 3D. The same was seen for the dispersion after drying, as shown in Figure S6B. Therefore, P-SWNT could be redispersed in CO₂-saturated water without sonication, requiring only mild shaking.

To clarify the influence of the dispersion treatment on the intrinsic properties of SWNTs, Raman spectrometry was carried out because it was sensitive to the change in both the electronic and optical properties of SWNTs. If there was
charge transfer or the optical property change of SWNTs, the shift and peak shape change of the G band and radial breathing mode (RBM) would be observed. The tangential (G) band at 1589.7 cm\(^{-1}\) and the represent active second disordered band (D) at 2678.3 cm\(^{-1}\) were revealed from the Raman spectrometry of SWNTs, respectively. RBM of the nanotubes was found at 100–200 cm\(^{-1}\). However, the Raman spectra of U-SWNTs and P-SWNTs were almost the same as that of raw SWNTs as shown in Figure 4. It can be concluded that there was no charge transfer between the surfactant and SWNTs and the intrinsic optical properties and electronic properties of SWNTs were still reserved.

## CONCLUSIONS

In summary, SWNTs were modified by a CO\(_2\)-switchable polymerizable dispersant based on natural rosin in water followed by in situ free-radical polymerization, and the tubes were wrapped by the obtained polymer. The dispersion and precipitation in an aqueous solution can be controlled reversibly by bubbling with CO\(_2\) or N\(_2\). After precipitation, the polymer surfactant-fabricated SWNTs could be redispersed in water after drying without the need for sonication, requiring only mild shaking because the polymer was still solidly attached to the surface of the SWNTs after either bubbling with N\(_2\) or drying, while the MPAGN-fabricated SWNTs without polymerization could not.

## EXPERIMENTAL SECTION

MPAGN was synthesized following our previous report.\(^{32}\) A mixture of MPAGN (8 mg) and SWNTs (0.8 mg) in water (24 mL) bubbled with CO\(_2\) was treated by sonication for 20 min. The dispersion was filtered through membranes (0.22 \(\mu\)m) to remove the unreacted monomer and poly-MPAGN that was not wrapped around the SWNTs (P-MPAGN).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b03027.

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