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Aqueous Dispersions of Carbon Nanotubes with Self-assembled Micelles of Photosensitive Amphiphilic Random Copolymer Containing Coumarin

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A general approach toward dispersing carbon nanotubes (CNTs) in aqueous solution was reported by using photosensitive micelles as dispersant. Micelles are made from a novel photo-crosslinkable amphiphilic random copolymer P(St/VM-*co*-MA), which first self-assembled around carbon nanotubes in selective solvent (DMF/H_2O) and then underwent photo-crosslinking to generate micelle-encapsulated carbon nanotubes. It was found that the photo-crosslinked micelle-encapsulated carbon nanotubes could form a very stable suspension in aqueous solution, indicating the micelles are effective for dispersing carbon nanotubes.

Since carbon nanotubes (CNTs) were discovered,[1] they have exhibited exciting potential applications in sensors, nanocomposites, molecular devices, and advanced materials with electronic and optical properties owing to their remarkable thermal, mechanical, and electrical properties.[2] However, dispersion of CNTs in solvents and polymer matrices is an obstacle for their further applications due to the poor solubility and processability. In this respect, much effort has been made on the surface modification of CNTs to enhance their solubility and processability.[3] Among them, covalent modifications with small organic molecules or macromolecules utilizing defect chemistry of oxidized CNTs through amidation and esterification are commonly applied methodology. Using the covalent modification approach, the electronic conjugation will be disrupted by introducing new covalent bonds to the graphene sheet, resulting in the inevitable alteration of CNTs properties.[4] The modification of CNTs can also be preformed through the noncovalent interaction between CNTs and the functional group comprising the polymer.

Noncovalent surface modifications provide a simple and nondestructive way for dispersion of CNTs through the relatively weak interaction between CNTs and the modifiers.[5] Molecules of high molecular weight that could wrap themselves around the surfaces of nanotubes disrupt the van der Waals interactions that cause CNTs to aggregate into bundles, leading to an individually dispersed nanotube in solution. Several studies have reported on noncovalent adsorption of amphiphilic copolymers and hydrophilic polymers on CNTs.[6] Kang et al.[7] have recently demonstrated that the encapsulation of SWCNTs with crosslinkable, amphiphilic block copolymer enhanced the dispersion of nanotubes in a variety of polar solvents and polymer matrix. Kim et al.[8] describe a noncovalent process for surface functionalization of SWCNTs using amphiphilic diblock copolymer (PEtOz-PCL), to exhibit remarkably enhanced solubility particularly in aqueous media. Although big progress in noncovalent modification of CNTs using amphiphilic block copolymers has been achieved in the last few years, there still exist some challenges and problems in this field: the preparation of block copolymers is normally complex, many of them used strict and harsh experimental conditions, and the productivity of block copolymers is relatively low, which makes it unsuitable for large-scale production. Amphiphilic random copolymer could also self-assemble into micelles similar to block copolymer,[9] but it has the advantages of low cost, easy synthesis, and good yield, which is very suitable for scaling up. Thus, it is quite attractive to employ random copolymer as dispersant to noncovalently modify CNTs. Furthermore, because the copolymer is photo-crosslinkable, it has good and fast film-forming properties, which can expand its scope of application.

Here we report a simple and fast nondestructive approach for the modification of CNTs-OH, by encapsulating carbon nanotubes into a novel photo-crosslinked amphiphilic random copolymer micelle P(St/VM-*co*-MA). The resulting P(St/VM-*co*-MA) micelle encapsulated carbon nanotubes were highly dispersible in aqueous solution and form a very stable suspension of carbon nanotubes. This approach provides an economical solution for dispersing carbon nanotubes suitable for large-scale production.

Photosensitive copolymer P(St/VM-*co*-MA) was synthesized through free-radical copolymerization (Figure 1). The photo-crosslinking mechanism of copolymer P(St/VM-*co*-MA) is illustrated in Figure 1 which involved photodimerization of coumarin moieties. Photodimerization of coumarin group led to the formation of polymer network in a few minutes under irradiation with UV light.[10] Based on the calibration curve according to the Lambert–Beer law equation, the concentration of the VM in the copolymer is 9.4 wt % (Figures S1 and S2 in Support Information; SI[14]).

The strategy for wrapping the photosensitive copolymer P(St/VM-*co*-MA) around CNTs-OH (Figure 2) is similar to that reported by Kang and Taton.[7] A small amount of SWCNTs-OH or MWCNTs-OH (<2.5 mg) was suspended in 1 mL of P(St/

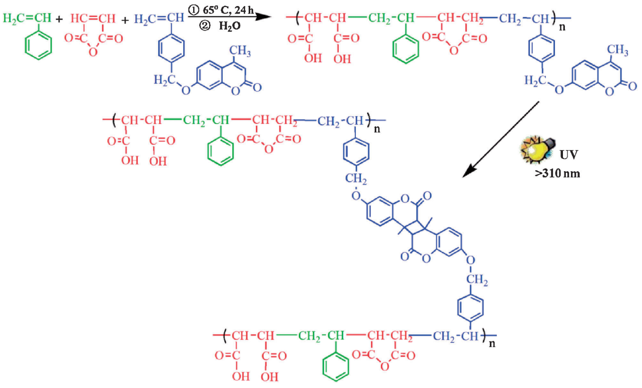

Figure 1. Synthesis and photodimerization of copolymer P(St/VM-*co*-MA).

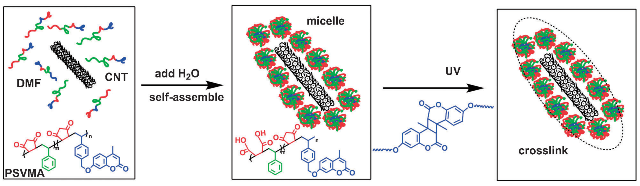

Figure 2. Scheme for the formation of micelle-encapsulated CNTs-OH (e-CNTs).

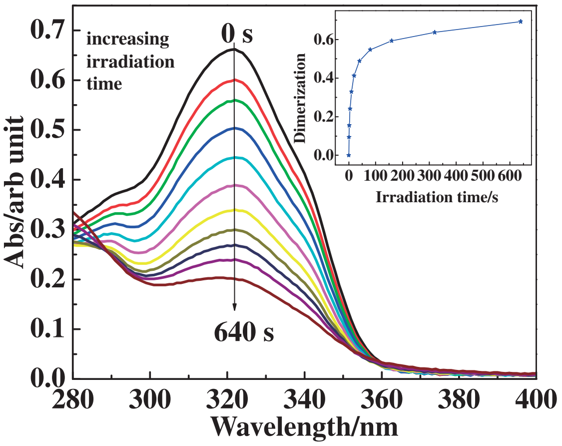

Figure 3. UV–vis spectra of P(St/VM-*co*-MA) micelle with various irradiation time. Inset: The dimerization of P(St/VM-*co*-MA) micelle versus irradiation time. The concentration of micellar solution is 0.1 mg mL^{-1}.

VM-*co*-MA) solution (2.5–5.0 mg mL^{-1}) in DMF, and the suspension was sonicated using a water bath sonicator for 1 h. Then, 0.1 mL of deionized water was added to induce the formation of micelles around the nanotubes. After sonication for 1 h, an extra amount of deionized water was added till the DMF/H_2O ratio reached 1:9 (wt %) under sonication. The copolymer P(St/VM-*co*-MA) underwent partial hydrolysis in water during this process and produced a large amount of carboxy groups which have noncovalent reaction with CNTs-OH. Partial hydrolysis of the copolymer can be evidenced by ^{1}H NMR and FTIR characterizations of P(St/VM-*co*-MA) (Figures S1 and S2 in SI[14]). The homogeneous nanocomposite was crosslinked under irradiation of UV light (without the crosslinker and the initiator, $\lambda > 310$ nm). Finally, the resultant suspension was filtered through cotton to remove the undispersed materials, yielding micelle-encapsulated CNTs-OH (e-CNTs).

The photosensitivity of P(St/VM-*co*-MA) micelle was investigated by UV–vis spectroscopy. As shown in Figure 3, before photoirradiation, P(St/VM-*co*-MA) micelle exhibits a main absorption peak at 320 nm from the maximum absorption of coumarin moieties. Its absorbance at 320 nm (A_{320}) significantly deceases with prolonging the irradiation time, resulting from the dimerization of the coumarin groups. The coumarin chromophore is known to undergo only [2 + 2] photodimerization because of its fused-ring structure. As the coumarin dimerizes, the level of unsaturation decreases due to the formation of crosslinks of the coumarin side groups via [2 + 2] photodimerization.[11] Therefore, the decrease in A_{320} can be primarily attributed to the loss of coumarin chromophores as a result of UV-light-induced photodimerization. The inset of Figure 3 depicts the dependence of the crosslinking degree of P(St/VM-*co*-MA) micelle on UV irradiation time. It is noted that the crosslinking degree is leveled off after irradiation for 600 s, indicating the saturation point is reached. Thus in the following experiment, the time for crosslinking is set to 10 min.

Figure 4. Aqueous dispersions of 0.5 wt % SWCNT-OH (A) without any dispersants (B) with P(St/VM-*co*-MA), and of 0.5 wt % MCWNT-OH (C) without any dispersants (D) with P(St/VM-*co*-MA). CNT:P(St/VM-*co*-MA) = 1:1 (weight ratio). The images were taken after 3 months storage.

Figure 4 presents the dispersion behaviors of P(St/VM-*co*-MA) micelle-encapsulated CNTs-OH in water. The black-colored solution of micelle-encapsulated CNTs-OH is visually nonscattering, and no precipitation was observed after 3 months standing. In contrast, the same amount of CNTs-OH dispersed in water without the block copolymer began to precipitate immediately after sonication and completely settled within 0.5 h as shown in Figures 4A and 4C. The excellent stability of the micelle-encapsulated CNTs-OH in our present study can be reasoned as follows: There is a definite hydrogen-bonding interaction between the hydroxy groups (–OH) on the CNTs-OH and carbonyl groups on P(St/VM-*co*-MA) copolymers, the aromatic rings along the polymer chain also have great affinity for the carbon nanotubes surface via π–π interaction,[12] and thus P(St/VM-*co*-MA) chains are strongly attached to and non-covalently functionalize the CNTs surfaces. In addition, the photo-crosslinking of the P(St/VM-*co*-MA) around the CNTs could encapsulate carbon nanotubes and further stabilize the noncovalent functionalization. On the other hand, the carboxy groups along the P(St/VM-*co*-MA) make the polymer chain negatively charged in neutral media, and thus the anionic P(St/VM-*co*-MA) layers confer to the carbon nanotubes both steric and electrostatic repulsions, resulting in the stable aqueous dispersion of carbon nanotubes. The combination of these three attributes together with the multipoint attachment of the P(St/VM-*co*-MA) micelle contributes to the micelle-encapsulated CNTs-OH with remarkable colloidal stability.

The typical nanostructure of CNTs-OH encapsulated in P(St/VM-*co*-MA) micelles is shown in Figure 5. From the images shown in Figure 5A (SWCNTs-OH) and Figure 5C (MWCNTs-OH), it can be obviously seen that the nanotubes without dispersant are characterized by regions of thick, aggregated CNTs-OH ropes caused by the large van der Waals

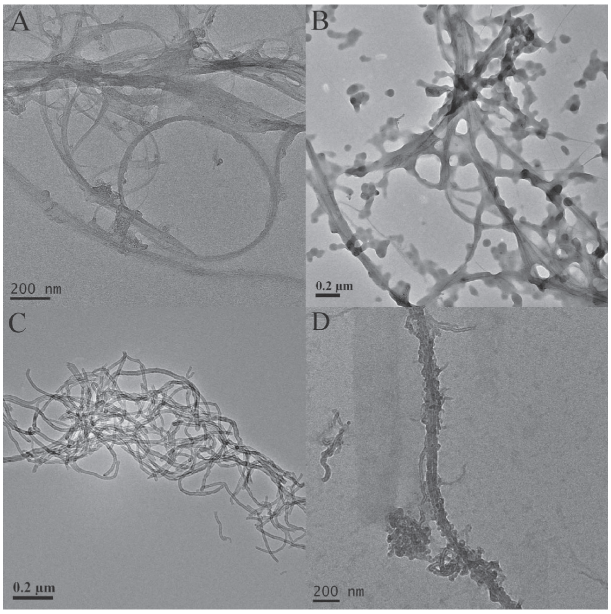

Figure 5. TEM images of SWCNT-OH (A) without any dispersants (B) with P(St/VM-*co*-MA), and MCWNTs-OH (C) without any dispersants (D) with P(St/VM-*co*-MA). CNT:P(St/VM-*co*-MA) = 1:1 (weight ratio).

forces. The surface coverage of the CNTs-OH was inhomogeneous on the grid, with tubes localized only at isolated regions of the grid.[13] In contrast, well-separated nanotubes are observed with the crosslinked micelles wrapping uniformly around the nanotubes, as shown in Figure 5B (SWCNTs-OH) and Figure 5D (MWCNTs-OH). The surface coverage of the CNTs-OH on the grid becomes highly uniform, which can be attributed to the micelles breaking up the bundles into suspension of smaller bundles. The addition of P(St/VM-*co*-MA) enhances the suspension stability with the micelles overcoming the van der Waals force through steric hindrance. The TEM images also demonstrate that the two kinds of P(St/VM-*co*-MA) micelle-encapsulated CNTs-OH can all be dispersed individually in water solution, well indicating the efficacy and the applicability of this approach.

Figure 6 shows SEM surface morphologies of CNTs-OH and micelle-encapsulated CNTs-OH. It is observed that the pristine CNTs-OH showed a clustered or bundled surface morphology like a reptile chain (Figures 6A and 6C). The micelle-encapsulated CNTs-OH was tightly covered by a thick layer of P(St/VM-*co*-MA) micelles (Figures 6B and 6D). The SEM analysis shows that the CNTs-OH was well wrapped by the P(St/VM-*co*-MA) micelles primarily through noncovalent interactions.

In conclusion, we presented a facile and efficient approach to disperse carbon nanotubes in water, by using a novel photosensitive amphiphilic random copolymer micelle which could encapsulate and stabilize CNTs-OH. The resulting micelle-encapsulated carbon nanotube was well-dispersed in water phase and forms a very stable suspension of carbon nanotubes. The good dispersing behavior with the added advantages of easy synthesis and low cost makes the random copolymer micelle an attractive dispersant for carbon nanotubes.

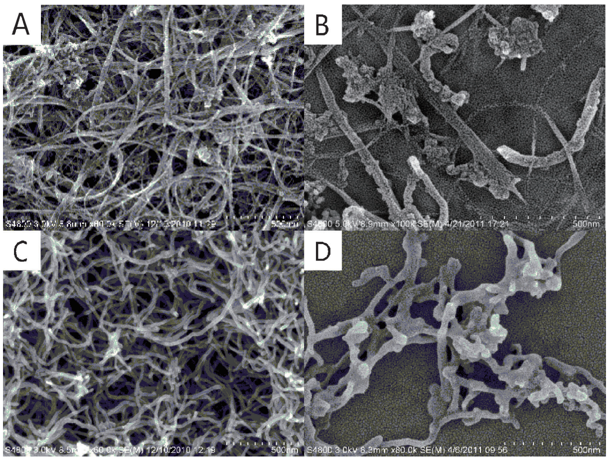

Figure 6. SEM images of SWCNT-OH (A) without any dispersants (B) with P(St/VM-*co*-MA), and MCWNTs-OH (C) without any dispersants (D) with P(St/VM-*co*-MA). CNT:P(St/VM-*co*-MA) = 1:1 (weight ratio).

In addition, since the random copolymer has good and fast film-forming properties, the micelle-encapsulated carbon nanotubes could be used as nanotube composites alone or as starting materials for various applications.

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