

DISPERSION OF CARBON NANOTUBES IN ORGANIC SOLVENTS

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Introduction

Carbon nanotubes (CNTs) have drawn intense attention due to their unique properties and exciting application potential [Iijima, Ebbesen, Balasubramanian]. The applications of nanomaterial depend on its compatibility with another material; therefore it is extremely important to be able to control the dispersion properties and to understand the dispersion mechanisms of nanomaterials in a second phase. Recently, the multi-walled nanotubes (MWNTs) have reached the commercial production scale; however, the MWNTs produced by the large-scale catalytic CVD method show highly entangled aggregates [Wang], which make the dispersion controlling more difficult. Previously, we have reported a novel acid-exclusive method for dispersing MWNT in aqueous suspensions, in which MWNTs was treated with H₂O₂ followed by dispersing with a polyelectrolyte dispersant [Li]. In this study, an organic modification of MWNTs was achieved by grafting oleic acid group on the H₂O₂-treated MWNT. This modification has greatly improved the dispersibility of MWNTs in some organic solvents.

Experimental

The MWNTs employed in this study were purchased from CNT Co., Ltd (Incheon, Korea). The purity was 95 wt%, and the impurities were iron, aluminum, cobalt, nickel and amorphous carbon. The average outer diameter and length were 10-50 nm and 5-20 μ m, respectively. The dispersants used was sodium oleate (SOA) which was prepared by mixing oleic acid (Showa Chemical Co., Japan) with equimolar of NaOH_(aq). The oxidative reagent used was hydrogen peroxide (H₂O₂) (35%, Showa Denko, Japan). Organic solvents of N-methylpyrrolidone (NMP), dimethylacetamide (DMAC), acetone and n-octane and de-ionized water were used as the dispersion medium in this study.

The chemical modification of MWNTs was carried out by a two-step process. First, MWNTs were treated by refluxing in H₂O₂ for 2 hrs. The H₂O₂-treated MWNTs were repeatedly washed by water and were added into 50 wt% SOA aqueous solution. Then the mixture was heated with vigorous stirring at 90°C for an hour. After reaction, the aqueous suspension was neutralized with 1 N HCl_(aq) followed by filtration. The filtered precipitate was washed with deionized water and absolute ethanol in sequence. The as-prepared SOA-modified MWNTs were kept in a vacuum desiccator at least for a day. Finally, 1-5 wt% of the dried powder was suspended into organic solvents and de-agglomerated via a high-energy ultrasonic horn (450D, Branson, CT).

The microstructures of SOA-modified MWNTs were analyzed by TEM (JEM-2100F, Jeol, Japan). The surface chemistry was characterized by X-ray photon spectroscopy (XPS) (PHI Quantera SXM, ULVAC-PHI, Inc., Japan), the technique known as the Electroacoustic method (ZetaProbe, Colloidal Dynamics Inc., USA), and FT-IR (DA8.3, Bomem, Canada). The dispersion stabilities of 1-5 wt% organic MWNTs suspensions were observed via sedimentation experiments, i.e. the suspensions were left in the graduates for different time periods to record the final sedimentation heights after one week.

Results and discussion

Nanotube morphology

Figure 1 shows the TEM micrographs of untreated MWNTs, H₂O₂-treated MWNT and SOA-modified MWNT. The as received MWNTs with diameter around 15nm composed of an inner graphitic layers and an outer amorphous layer (Fig 1(a)). After H₂O₂ treatment, the amorphous layer diminished but the graphitic layer was not much affected (Fig 1(b)). On the other hand, the SOA-modified MWNT has shown an amorphous shell of about 10 nm thick which indicates the wrapping of oleic acid group.

Surface characterization

In order to clarify the effect of SOA modification on the surface chemistry of the MWNTs, the (a) as-received MWNTs, (b) H₂O₂-treated MWNTs and (c) SOA-modified MWNTs were characterized by ESCA and FTIR. Table 1 lists the elemental analysis of the above three samples by ESCA. The as-received MWNTs contain 3.47 atom% of oxygen, which should be due to the environmental contamination or the defect sites on MWNTs. When the MWNTs were treated with H₂O₂, an obvious increase in oxygen content was observed from 3.47 to 9.13 atom%. This result demonstrates that there should be some

oxygen-containing functional groups derived on the surface of H₂O₂-treated MWNTs. According to the good wettability of H₂O₂-treated MWNTs in water, the oxygen-containing groups may be some polar functional groups, such as hydroxyl (–OH), carboxyl (–COOH) or carbonyl (–C(=O)) groups. From our previous work, the new derived group has been confirmed as the –OH group due to the milder oxidation of MWNTs by H₂O₂ [5]. As the H₂O₂-treated MWNTs were further modified with SOA, the oxygen content slightly decreased again, from 9.13 to 5.94 atom%. This result indicates that some of the –OH derived on the MWNTs have been reacted with the SOA.

From the FTIR spectra (Fig 2), the peak at 1430cm⁻¹, which was assigned to be the O-H bending deformation of phenolic group, was observed on both H₂O₂-treated MWNTs and SOA-modified MWNTs, but the intensity of the later sample was less intense. An additional peak at 1721cm⁻¹ observed on the SOA-modified MWNTs was attributed to the C=O from the oleic acid group. The zeta potential measurement results also demonstrated the grafting of oleic acid on MWNTs. After the H₂O₂ treatment, the CNT surface was negatively charged with increasing voltage from pH 2 to 12. However, the SOA-modified MWNTs show less potential and exhibit an IEP at pH=4. The surface potential was increased only after the pH value achieved 11.36.

Dispersion property

Figure 4 shows the sedimentation pictures of as received MWNTs and SOA-modified MWNTs suspensions (all 2wt%). The pictures were taken after one week of settling. The polarity of the solvents follows Di-water > NMP > DMAC > Acetone > THF > n-octane. MWNTs without any modification were poorly dispersed in all solvent systems as noticeable aggregates can be observed from the droplets from each suspension. With the SOA modification, the dispersion stability was greatly enhanced in the solvents with higher polarity (i.e. H₂O, NMP and DMAC). The rheology analysis of the suspensions was also consistent with the sedimentation experiments. All suspensions of as received MWNTs showed shear-thinning behavior, i.e., the decrease in viscosity with increasing shear rate; while improved rheology and viscosity were observed with SOA-modified MWNTs.

Oleic acid is an interesting molecular because it has dual functionality; one is hydrophilic (the carboxylic side) and one is hydrophobic (the long chain C=C side). At this moment, we can not clarify how the SOA reacted with MWNTs. It seems that the SOA-modified MWNTs show both hydrophilic and hydrophobic properties since they can be well dispersed in water and in organic solvents like NMP and DMAC. It is possible that some of the SOA was grafted on the MWNT by the esterification reaction with –OH group on H₂O₂-treated MWNTs and some by chemical adsorption. The improved dispersion may be due to the steric effect and the functionality of the grafted oleic acid group.

Conclusion

Combining functionalization with hydrogen peroxide and then modification with sodium oleate, the dispersibility of multi-walled carbon nanotubes was increased in water and in organic solvents such as NMP and DMAC. The grafting of SOA was confirmed by the TEM micrograph and FTIR. The SOA-modified MWNTs has less negative charge than H₂O₂-treated MWNTs, indicating the reaction of –OH group with SOA. The improved dispersion in the different solvent systems may be due to the steric hindrance of the grafted/adsorbed SOA and the oleic acid functional group.

Table 1. Elemental analysis from ESCA

Sample Description	C (1S)	O (1S)
As received MWNT	96.5%	3.5%
H ₂ O ₂ -treated MWNT	90.0%	9.1%
SOA-treated MWNT	94.1%	5.9%

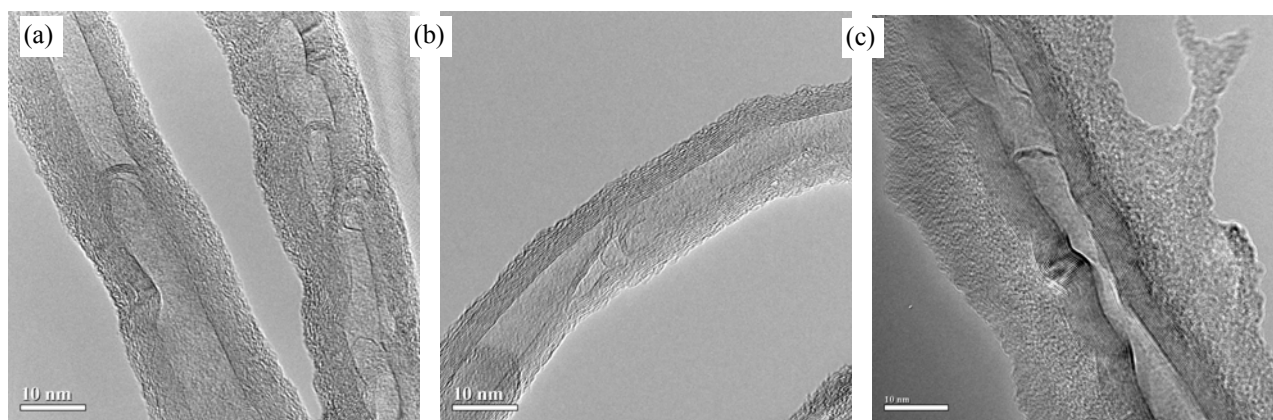


Figure 1. TEM of (a) as-received MWNT; (b) H₂O₂-treated MWNT; (c) SOA-modified MWNT

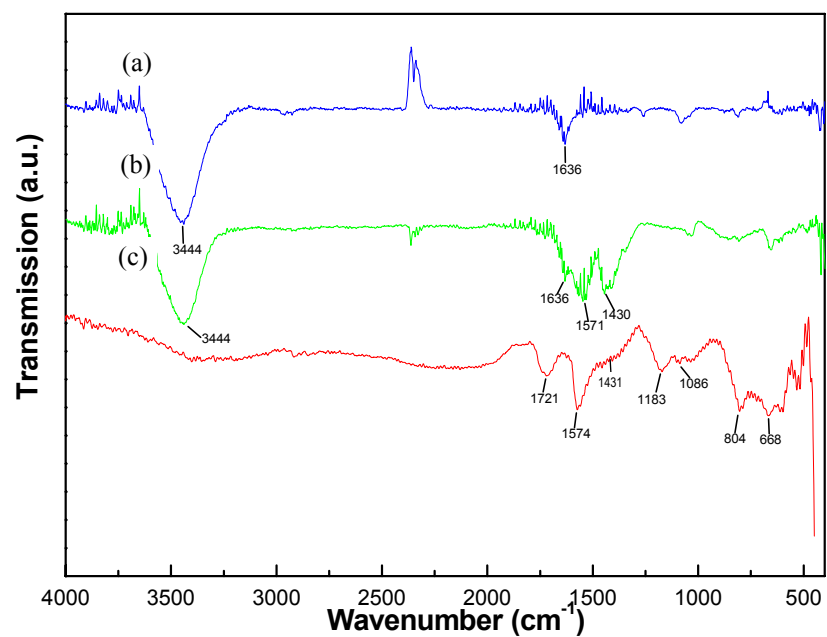


Figure 2. FTIR spectra of (a) as-received MWNT; (b) H₂O₂-treated MWNT; (c) SOA-modified MWNT

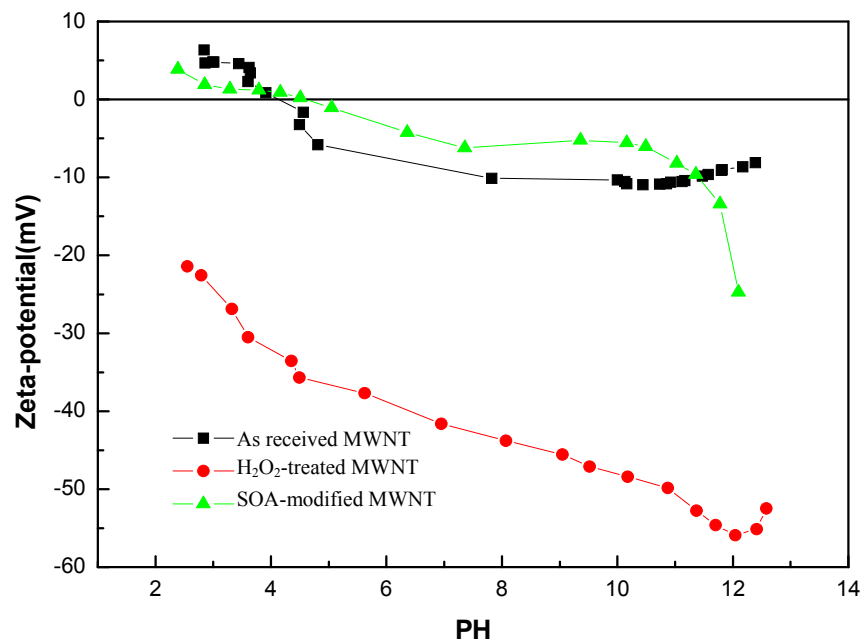


Figure 3. Zeta potential of MWNTs, H₂O₂-treated MWNTs and SOA-modified MWNTs

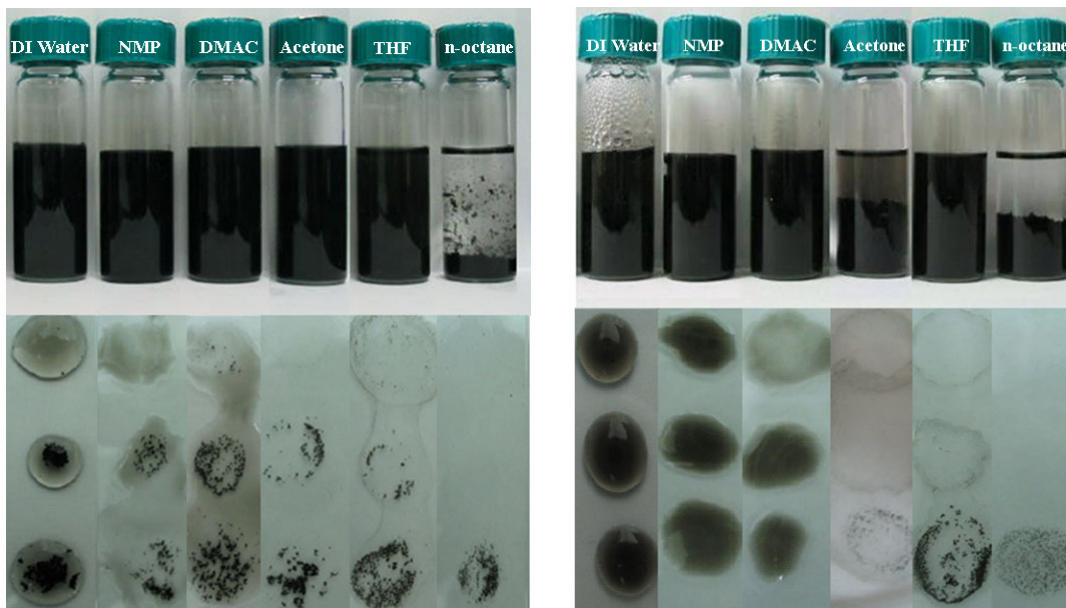


Figure4. Dispersion of MWNTs (left) and SOA-modified MWNTs (right) after one week of sedimentation in different solvents

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