

Effect of Geometric Shape on Nano-Dispersion of Carbon Nanotubes and Layered Platelets

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INTRODUCTION

Carbon nanotubes (CNT) are expected to exhibit superior chemical and physical properties because of their high aspect-ratio dimension and the conjugated character of individual tube. However, the tube-shaped CNT tends to aggregate through its lengthy geometric shape and van der Waals force attraction, which may consequently hinder its practical applications. In literature, several approaches for rendering the CNT dispersion through its surface modifications have been developed: oxidation¹, atom transfer radical polymerization (ATRP)², acylation-mediated amidation³, and carbodiimide-activated coupling⁴. Nevertheless, most of these processes which are involved an organic covalent bonding reaction may be disadvantageous due to the inevitable destruction of the unique CNT properties. Alternative methods by using physical absorption and non-covalent bonding modification are desired. Suitable surfactants⁵, ionic liquids⁶ and polymers⁷ are commonly applied for the CNT surface interactions for the purpose of easy dispersion. However, in those cases, the contamination of the added surfactants or polymers may adversely affect the downstream applications. In this report, we observed a factor of geometric-shape difference which largely influences fine dispersion of CNT by using clay as an inorganic dispersants which can avoid the destruction of chemical modification and contamination of organic dispersants. Moreover, the clay-CNT hybrids have an dually irreversible dispersion in either water or toluene, depending on the exposing order.

EXPERIMENTAL

Materials and Preparation of Mica-CNT Hybrids. Multiple-wall carbon Nanotubes (CNT, code CN3004), was supplied by Seedchem Company Pty., Ltd. and prepared from chemical vapor deposition. The carbon nanotubes are 95% pure and 40–60 nm in diameter and 0.5–10 μm in length. The synthetic fluorinated mica (Mica, SOMASIF ME-100), with a chemical composition of Si (26.5%), Mg (15.6%), Al (0.2%), Na (4.1%), Fe (0.1%), and F (8.8%) was obtained from CO-OP Chemical Co. (Japan). Sodium montmorillonite (MMT) was supplied from Nanocor Co. The geometric structures of the pristine Mica and MMT are irregularly aggregated with the primary units consisting of silicate platelets in stacks. The unit platelets are irregularly shaped and ionic charges with $\equiv\text{SiO}^-\text{Na}^+$. Their average dimension was estimated to be $100 \times 100 \times 1 \text{ nm}^3$ for MMT and $300 \times 300 \times 1 \text{ nm}^3$ for Mica. Due to the presence of an intensive ionic charge character, these clays are capable of swelling in water and gelling at high concentration. Their interlayer space between neighboring platelets is commonly 1.2 nm d spacing. These silicate/aluminum oxide layers are filled with exchangeable cationic metal counter ions, titrated to be 1.2 mequiv/g for Mica, and 1.2 mequiv/g for MMT. With similar platelet structure but a different anionic character, the clay of $\text{AlMgO}_x^+\text{NO}_3^-$ (layered double hydroxide, LDH) was compared. The procedure of mixing Mica-CNT hybrid is exemplified below. CNT (1 mg) and Mica (1 mg) were ground adequately in an agate mortar and pestle. The sides of the mortar were occasionally scraped down with the pestle during grinding to ensure a thorough mixing. The mixture was washed from mortar and pestle using deionized water at concentration of 1 mg CNT/20 g water. The Mica-CNT hybrids were prepared at clay/CNT, or α , weight ratios of 0.33, 0.5, 1, 2 and 3.

Amphiphilic Dispersion of Mica-CNT Hybrids. Ternary mixtures of the Mica-CNT hybrid were examined for the dispersion ability in water and toluene in different orders of addition. In the first

example, the hybrid of Mica-CNT (3 mg at $\alpha=2$) was added to 7.5 g water first, thoroughly dispersed and then added to 7.5 g toluene. In the second example, the hybrid was dispersed in toluene, homogeneously mixed and then added to water. During the mixing, ultrasonication was applied for 2 min.

RESULTS and DISCUSSION

(1) Effect of Geometric Shape on CNT Dispersion. We reveal a convenient method without organic dispersants but to disperse CNT together with inorganic clays such as Mica. When CNT was properly ground with the plate-like Mica, the pulverized powders in a physical mixture became readily dispersible in water. Initially, it was found that the Mica-CNT mixture at 2:1 weight ratio, or $\alpha=2$ (defined as the weight ratio of clay to CNT), could be easily dispersed in water to generate a fine slurry. The fine dispersion can be differentiated by naked eyes as a black suspension from poor black solid precipitates (**Figure 1A**). The controlled experiments showed that the pristine CNT was not dispersible in water but forming severe aggregates. The efficacy for the CNT dispersion depends on the relative amount of the Mica presence. The black CNT was mostly precipitated at the bottom of water phase when using a lesser amount of Mica to CNT at $\alpha=1\sim 0.5$. It is visualized that the presence of Mica has largely mitigated the tendency of CNT aggregation.

In order to understand the nature of Mica-CNT interaction, two other clays including MMT and anionic type of LDH were further examined. The differences of these clays in geometric dimension, Mica ($300 \times 300 \times 1 \text{ nm}^3$), MMT ($100 \times 100 \times 1 \text{ nm}^3$) and LDH ($200 \times 200 \times 1 \text{ nm}^3$), allow the understandings of their size effect for the CNT dispersion in water. In **Figure 1B** and **1C**, the photographs illustrate the black CNT dispersion which is required the presence of MMT at $\alpha=6$ (6 times the clay weight to CNT). It appears that Mica is more effective than MMT under the agitating condition of mechanical stirring or shaking, and LDH at $\alpha=2$ under mechanical and ultrasonication. These results indicate that the difference in the platelet size may be the dominating factor for the fine dispersion. Beside the direct observation, the dispersion was further measured by analyzing the suspension using a UV-visible spectrometry. As shown in **Figure 2**, the absorption at 550 nm for the CNT becomes more intense with the increasing amount of added Mica, implying the increase of CNT concentration in water⁸. Experimentally, the comparison of dispersing ability by the UV-visible absorption is plausible since the absorption actually correlates well to the hybrid concentration by following the Lambert-Beer's law. According to the UV-vis analysis, the Mica is most effective for enhancing the CNT dispersion in water. The absorption reached to a maximum when the Mica-CNT weight ratio approached $\alpha=2\sim 3$, but required a higher α value of 6 for the comparative MMT. In considering their ionic charges, the LDH is anionic, with cationic charges on the platelet surface and nitrate anionic species as the counter ions. The ionic charge interaction between CNT and clay, through the clay surface anions ($\equiv\text{SiO}^-$) in MMT and Mica structures or cations in LDH, may be the second reason for affecting the CNT dispersion. The apparent dispersing experiments indicated that the LDH was also effective but requiring an additional ultrasonication during mixing as shown in **Figure 2A** (LDH-CNT).

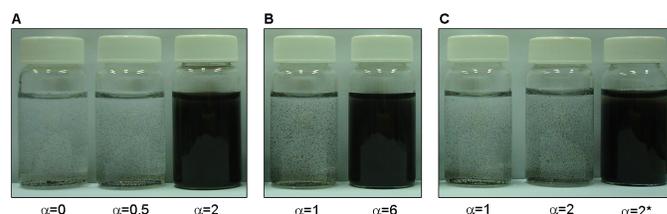


Figure 1. Visual observation of clay-CNT hybrid dispersion in water. (A) Mica-CNT, (B) MMT-CNT and (C) LDH-CNT. *: dispersed by mechanical stirring and ultrasonication.

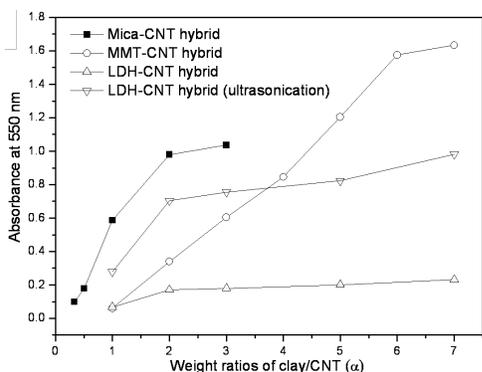


Figure 2. UV-vis adsorption of various clay-CNT hybrids in water.

(2) Dually Irreversible Dispersion. Being dispersible in both water and organic solvents, the Mica-CNT hybrid ($\alpha=2$) is considered to be amphiphilic in nature. Its dual dispersing behavior was further shown to be in an irreversible manner. Two different types of Mica-CNT dispersions are illustrated, but both are derived from the same batch of pulverized powder ($\alpha=2$). When the hybrid was dispersed in water first and then adding toluene, shaking and allowing settlement, the black Mica-CNT dispersion still remained in the water phase (**Figure 3A**). In contrast, if the hybrid was dispersed in toluene first, the same hybrid powder was then remained in toluene after the water layer was introduced and vigorously agitated (**Figure 3B**). The order of exposure to either water or toluene determined the hybrid dispersing behaviors in irreversible. The phenomenon is explainable by using the concept of stable “micelle-like” microstructures, the formations of water-in-oil (W/O) and oil-in-water (O/W) phases.

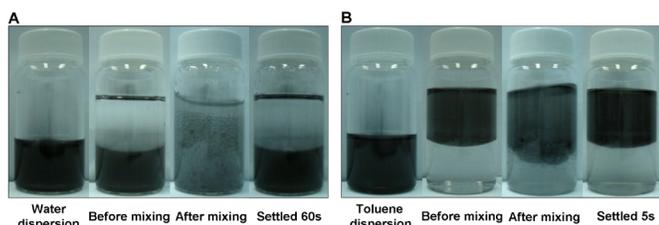


Figure 3. Irreversible dispersion of Mica-CNT hybrid ($\alpha=2$) in solvents. (A) The hybrid was dispersed in water first and then adding an equal amount of toluene. (B) The hybrid was dispersed in toluene first and then adding an equal amount of water.

Regarding the nature of “micelle-like” microstructures, both water and toluene suspensions were examined by TEM. Due to the experimental procedures of evaporation on copper grid, the microstructures may not be survived on the film. However, it is still differentiable and recorded the different morphologies for the hybrid being exposed with water or toluene first. With water as the continuous phase, the dried microstructure exhibits the separated CNT and visible Mica platelets in a range of 2~5 μm (**Figure 4A**). The enlarged TEM shows the appearance of platelet Mica and also the CNT aggregates in a network lump (**Figure 4B**). On the contrary, when the Mica-CNT hybrid was dispersed in toluene, the CNT aggregates appear to be the major component, perhaps the Mica platelets are buried by CNT (**Figure 4C**). The higher magnification of TEM micrograph allows the measurement of the CNT aggregates to be in a range of 1~3 μm (**Figure 4D**).

Therefore, we proposed a mechanism to account for the fine dispersion of CNT in various mediums and in an irreversible manner. As illustrated conceptually in **Figure 5**, the initial grinding of two distinctly different shapes of nanomaterials, fiber-like CNT and platelet-like Mica, redistributed the original CNT van der Waals bonds. Their CNT entanglement force may be mitigated or blocked by the neighboring Mica platelets. Furthermore, since Mica is hydrophilic and swells easily in water, the contact with water could render the hybrid to

form an O/W microstructure, consisting of CNT as the core and Mica as the surrounding corolla. Similarly, the opposite water-in-oil (W/O) microstructures is possibly generated while the first exposure of the Mica-CNT hybrid is toluene instead of water.

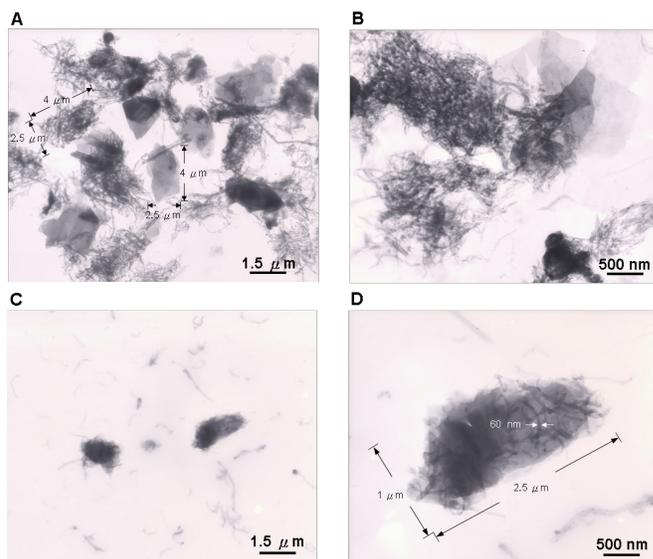


Figure 4. TEM images of the hybrids dispersed in water (**A** and **B**) and in toluene (**C** and **D**) dried on carbon-coated copper grids.

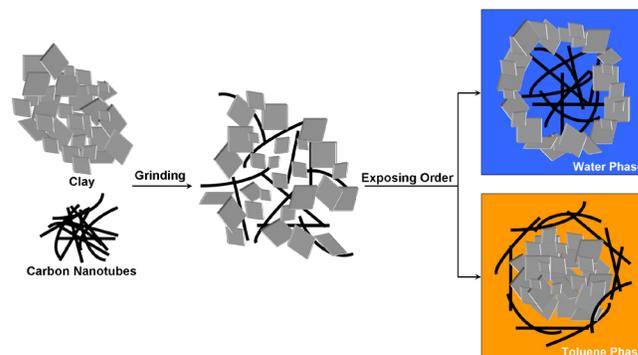


Figure 5. Conceptual presentation of oil-in-water type and water-in-oil type dispersion.

CONCLUSION

We discovered a convenient method for dispersing CNT in various organic mediums and also in water, by simply grinding CNT with clays into fine powder. The Mica-CNT hybrid exhibited a unique dispersible behavior in both of water and organic mediums. A mechanism of forming CNT-Mica and Mica-CNT core-shell microstructures, resembling the organic surfactants that have parallel structures of oil-in-water and water-in-oil micelles, is proposed. This new method for dispersing CNT in medium without using an organic dispersant may offer a significant advances for the CNT applications.

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