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Dispersion of carbon nanocapsules by using highly aspect-ratio clays

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The poor solubility of zero-dimensional nanomaterials can be greatly improved by using two-dimensional nanomaterials as a dispersant. The solubility of nano-spherical carbon nanocapsules (CNCs) was improved by using platelet-like clays. Three clays including synthetic fluorinated mica (Mica), sodium montmorillonite, and synthetic smectite were selected for assist CNCs to disperse in several solvents. The aspect ratios of clays were calculated by dimension over thickness, and the results revealed that the aspect ratio is the dominated factor to control the dispersion of CNCs in solvents. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3702783]

Carbon nanocapsules (CNCs) are the common nanomaterials and generally prepared from carbon sources. Because CNCs had the advantage in nano-spherical shape and sp^2 orbital structures, the diversified practical applications were reported such as oil lubrication,[1] electromagnetic interference,[2] fuel cell,[3] thermal dissipation,[4] and carbon nanocomposites of rubber,[5,6] epoxy resin,[7,8] poly(lactic acid),[9] polypropylene,[10] poly(vinyl chloride),[11] poly(vinyl alcohol),[12] and poly(vinyl pyrrolidone).[13]

However, the applications of CNCs were obstructed by the poor dispersion of CNCs. Nowadays the finely dispersing CNCs can be obtained by covalent-bonding modification. The surface graft of polymers onto CNCs provided functional carbon materials. The grafting polymer methods were achieved by grafting onto process,[14–20] grafting from process,[21–24] polymer reaction process,[25] stepwise growth by dendrimeric synthesis,[26] etc.[27–29] The alternated approaches of noncovalent bonding interactions were used to improve the solubility of carbon nanoparticles.[30–41] Compared to the covalent-bonding approaches, the noncovalent-bonding methods are more convenient and easy to improve solubility of carbon nanoparticles. Recently, the concept of nanoshaped-exclusion effect was reported and applied in dispersed nanomaterials including carbon nanotubes (CNTs),[42] carbon blacks (CBs),[43] silver nanoparticles (AgNPs),[44] iron nanoparticles (FeNPs),[45] and hydrophobic conjugated polymers (CPs).[46,47]

Herein, we reported the influence of aspect ratio on improved the solubility of nanomaterials. Carbon nanocapsules (CNCs) were supplied by Industrial Technology Research Institute of Taiwan (ITRI). The CNCs are 70% pure (30% impurity of tubular nanocarbon and amorphous carbon) and have diameter in ca. 10–50 nm. The CNCs are polyhedral nanoparticles that consist of a concentric graphene-layered structure with a cavity in the center. CNCs have poor solubility in organic solvents or water because of the seriously aggregated CNCs. The serious aggregations of CNCs are mainly caused by strong van der Waals force attraction. However, according to the concept of nanoshaped-exclusion effect, the hydrophobic CNCs can be easily dispersed in hydrophilic water (Fig. 1(a)). Initially,

CNCs were homogeneously mixed with the platelet-like synthetic fluorinated mica (Mica). Mica has trade name as SOMASIF ME-100 and received from CO-OP Chemical Co., Japan. The anionic clays are irregularly aggregates from their primary units consisting of silicate platelets in stacks.[48] Mica has average dimension of $300 \times 300 \, nm^2$ in square and 1 nm in thickness. Initially, CNCs (1 mg) and clay (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 nanomaterial in 5 g water. The CNC-clay powders were prepared at weight ratios of
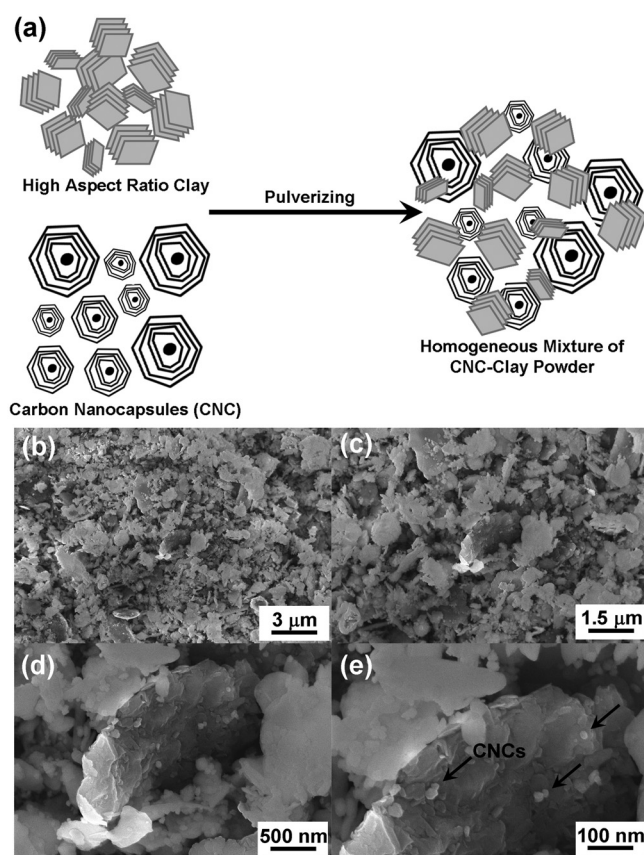

FIG. 1. (a) Conceptual Diagram of dispersing carbon nanocapsules by nanoshaped exclusion. (b)–(e) FE-SEM of CNC-Mica mixture after pulverized.

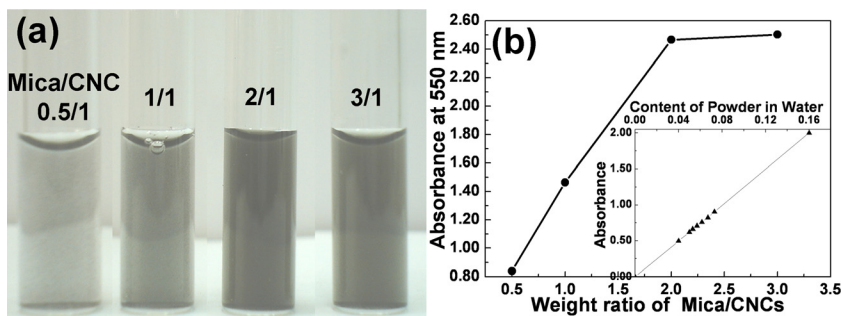[a]Author to whom correspondence should be addressed. E-mail: d95549006@ntu.edu.tw.

FIG. 2. (a) Visual observation of CNC-Mica poder dispersed in water. (b) UV-vis absorbance of CNC-Mica powder in water and their standard curve of absorbance against concentration (inset).

Mica/CNCs = 0.5/1, 1/1, 2/1, and 3/1. The mixing procedure can be monitored by the field emission-scanning electron microscope (FE-SEM, JOEL JSM-6700F SEM system). As shown in Figs. 1(b) and 1(c), the CNC-Mica powder revealed homogeneous powder after mixing. The CNC nanoparticle can individually exist on the platelet-like Mica (Figs. 1(d) and 1(e)).

The mixed powders of CNC-Mica became readily dispersible in water, and the result is shown in Fig. 2(a). The photos showed that CNC-Mica dispersions were greatly influenced by the amount of Mica. Initially, the solutions revealed light-grey at weight ratio of Mica/CNCs = 0.5/1 and 1/1. After increased the weight ratio up to Mica/CNCs = 1/1 and 2/1, CNCs-Mica powders rendered easily dispersible in water and generate a deep-color solution. The differences of color indicated the degree of dispersion: deep-color solution means homogeneous dispersion and light-grey means partial dispersion.[42]

The CNC-Mica solutions were further investigated by ultraviolet-visible (UV-vis) spectrophotometer at 550 nm (Perkin-Elmer Lambda 20) and transmission electron microscopy (TEM, Zeiss EM 902 A at 120 kV). The UV-vis result revealed enhancing absorbance with increasing Mica amount. The increase of absorbance at 550 nm has no correlation with the amount of Mica.[46] Optimal weight ratio of Mica/CNCs was found at Mica/CNCs = 2/1 (Fig. 2(b)). The optimal weight ratio of CNC-Mica powder was explained by the seriously aggregated CNCs required twice amount of platelet-like Mica to reduce or redistribute the van der Waal attraction within CNCs. Experimentally, the UV-vis result is based on the Lambert-Beer's law, and the absorbance has positively correlated to the content of CNC-Mica powder in the water (Fig. 2(b) inset). In the TEM observation, the CNC-Mica powder (weight ratio of Mica/CNCs = 2/1) has random distribution, and individual CNCs can be observed

(Fig. 3(a)). The morphology also showed the tubular nanocarbon due to the 30% impurity. On the contrary, the pristine CNCs revealed severe aggregation in the water, and other carbon materials can be observed (Fig. 3(b)).

The solubility of CNC-Mica powder was summarized in Table I. Mica could generally improve the CNCs to disperse in organic mediums. For example, the pulverized powder at weight ratio of Mica/CNC = 2/1 became dispersible in organic solvents such as isopropanol, methyl ethyl ketone, N,N-dimethyl formaldehyde, propylene glycol monomethyl ether, and toluene.

In order to understand the influence of aspect-ratio effect on dispersion of CNCs, the other clays including sodium montmorillonite (MMT, received from Nanocor Co.) and synthetic smectite (SWN, trade name as Lucentite[TM] SWN, received from CO-OP Chemical Co.) were used for this study. MMT has average dimension of $100 \times 100 \, nm^2$ in square and 1 nm in thickness. SWN has average dimension of $50 \times 50 \, nm^2$ in square and 1 nm in thickness. The aspect ratios of the clay were calculated by dimension over thickness. Mica has largest aspect ratio of 9×10^4, MMT is 1×10^4, and SWN is 2.5×10^3. Fig. 4(a) showed the dispersion of CNCs by platelet-like clay; both CNC-Mica and CNC-MMT revealed well dispersed and deep-color solutions. However, the CNC-SWN powder and pristine CNCs rendered large aggregation in solution and precipitated on the bottom. Considered to the aspect-ratio effect, the UV-vis absorbance of solutions has positive correlation with the aspect ratios of clay (Fig. 4(b)). These results indicated that highly aspect-ratio clay can effectively disperse CNCs in solvents. We think highly aspect-ratio clay has large-dimension area to reduce and block the aggregated CNCs in an effective way. In other words, the solubility of zero-dimensional nanomaterials can be improved by using highly aspect ratio of two-dimensional nanomaterials.
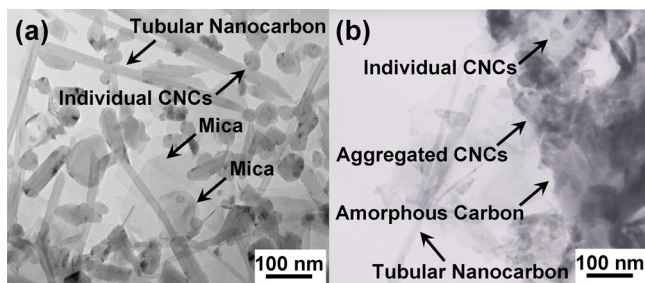

FIG. 3. TEM morphology of CNC-Mica powder dispersed in water (a) and pristine CNCs dispersed in water (b).

TABLE I. Dispersion of pristine CNCs and CNC-Mica powder in various solvents. +: Dispersed well by shaking only. −: Poor dispersion or sedimentation after ultrasonic agitation (1 mg CNCs/5 g solvent).

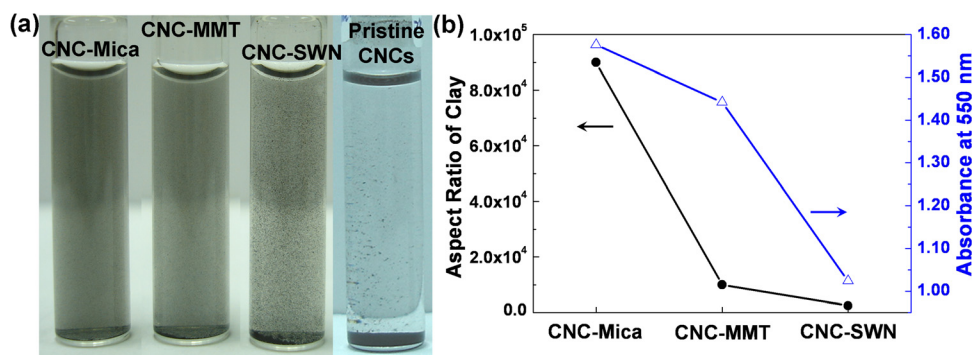| Solvents	Pristine CNCs	CNC-Mica powder
H₂O	−	+
Isopropanol (IPA)	−	+
Methyl ethyl ketone (MEK)	−	+
N,N-dimethyl formaldehyde (DMF)	−	+
Propylene glycol monomethyl ether acetate (PGMEA)	−	+
Toluene	−	+

FIG. 4. (a) Visual observation of dispersing CNCs by different clays. (b) Plot of UV-vis absorbance against with aspect ratio of clay.

The pristine CNCs were dispersed in solvents by using platelet-like clay. Three clays were selected to understand the influence of aspect ratio on dispersion of CNCs. As a result, the highly aspect-ratio clay is the key-point to control the dispersion. The highly aspect ratio of two-dimensional nanomaterials revealed powerful ability to redistribute or block the aggregated zero-dimensional nanomaterials and improved the solubility of nanomaterials. This finding for dispersing nanomaterials will broaden their applications in the future.

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