Kabob-like Carbon Nanotube Hybrids

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Inspired by the formation of stalagmite in nature, calcium carbonate nanoparticles ($CaCO_3$) have been successfully generated along multiwalled carbon nanotubes (MWNTs) backbones periodically via a very simple wet chemical route, thus forming the kabob-like MWNTs–$CaCO_3$ hybrids. These MWNTs–$CaCO_3$ hybrids are expected to have many potential applications in biomaterials and polymer reinforcement.

The surface decoration of carbon nanotubes (CNTs) with other materials has been proposed and well investigated by many researchers.[1] There are two main aims for the decoration of carbon nanotubes. First, the surface decoration can improve the processibility and dispersibility of carbon nanotubes in various solvents or polymer matrixes, and thus facilitates the studies and applications of CNTs. Second, the surface decoration processes can realize the intimate combination of CNTs with other materials in nanorange, and thus creates new nanomaterials with combined properties. In our previous work, we reported the surface decoration of CNTs with polymers,[2] biomolecules,[3] metallic nanoparticles,[4] and inorganic oxides.[5] In this letter, we demonstrate the periodically decoration of CNTs with $CaCO_3$ nanoparticles using a simple wet-chemical route.

Nanomaterials are being developed for medical and biotechnological applications including gene delivery, drug delivery, enzyme immobilization, and biosensing.[6] The most commonly used materials are gold,[7] silica, and semiconducting materials.[8] Recently, calcium carbonate ($CaCO_3$) nanoparticles have been proposed as a new drug-releasing system for the delivery of hydrophilic drugs and bioactive proteins.[9] A key challenge in nanotechnology is the more precise control of nanoparticle assembly for the engineering of particles with the desired physical and chemical properties. Much research is currently focused on CNTs as a promising material for the assembly of nanodevices. CNTs have several unique properties, including physical strength, chemical stability, and electronic conductivity. The assembly of nanoparticles on carbon nanotubes may provide an ideal platform for the interaction between drugs (or proteins) and living cells, and thus facilitates the understanding of the interaction-mechanism between drugs (or proteins) and living cells. In addition, because both $CaCO_3$ nanoparticles[10] and carbon nanotubes[11] have been widely used as fillers for the reinforcement of polymer materials, this new type of CNTs–$CaCO_3$ nanomaterial would have potential applications in polymer reinforcement as well.

It is well known that calcium carbonate solids can be produced expediently by introducing carbon dioxide (CO_2) gas into aqueous calcium hydroxide $Ca(OH)_2$ solutions, which is considerably familiar to most chemists. This process occurs widely in nature, e.g., the formation of stalactites. Stalactites, the most familiar structures found hanging from the ceilings of limestone caves, are usually formed by the deposition of calcium carbonate ($CaCO_3$) and other minerals from mineralized water solutions. The corresponding formation on the floor underneath a stalactite is known as a stalagmite. Given enough time, these formations can meet, resulting in a formation known as a column or pillar. Inspired by the formation of stalagmite in nature, herein, we demonstrate the surface decoration of multi-walled CNTs with $CaCO_3$ nanoparticles via a very simple wet-chemical route, thus forming the kabob-like MWNTsCaCO$_3$ hybrid nanomaterials.

This CNTs–$CaCO_3$ can be fabricated by the controlled precipitation of $CaCO_3$ from aqueous $Ca(OH)_2$ solutions. The mechanism for the precipitation of calcium carbonate from aqueous $Ca(OH)_2$ solutions can be expressed as the following:

$$Ca^{2+} + CO_2 + 2OH^- \rightarrow CaCO_3\downarrow + H_2O. \qquad (1)$$

Multiwalled carbon nanotubes (MWNTs, from NTP, Shenzhen, China) synthesized by the catalytic chemical vapor deposition (CCVD) method were used as-received without further purification. In a typical procedure, 100 mg of CNTs was added to 100 mL of saturated aqueous $Ca(OH)_2$ solution under N_2, and then the blend was sonicated for 60 min to suspend CNTs in the aqueous $Ca(OH)_2$ solution. After the sonication treatment, a blend-gas (N_2:CO_2 = 19:1, volume ratio) was introduced into the solution immediately using a blowing pump. When the solution became turbid, the blowing pump was turned off, and then the solution was kept stirring for 2 h. The CNTs–$CaCO_3$ products were recovered by centrifugalization. The CNTs–$CaCO_3$ products were washed with water for several times and then dried at 60 °C for 2 h. The morphology of the pristine carbon nanotubes and CNTs–$CaCO_3$ products was analyzed using a field emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F) and transmission electron microscopy (TEM, JEOL JEM-2010).

With intrinsic van der Waals forces, nanotubes are typically held together as bundles and have very low dispersibility in most solvents. When mixed into a matrix, nanotubes tend to exit as entangled agglomerates and homogenous dispersions are not easily to be obtained. To well-dispersed CNTs in saturated $Ca(OH)_2$ solution, the MWNTs can be fisrtly suspended in aqueous surfactant solutions. With the aids of surfactants, CNTs can be individually suspended in aqueous media. Figure 1a presents the SEM image of the pristine MWNTs, indicating that the surface of the pristine MWNTs is smooth and the diameter of the pristine MWNTs is less than 100 nm. Figure 1b shows the TEM image of the pristine CNTs used in our research. Figures 1c, 1d, and 1e show the morphologies of the CNTs–$CaCO_3$ hybrids. Figure 1c shows the SEM image of a long MWNTs which has been periodically decorated with $CaCO_3$ nanoparticles. It reveals that $CaCO_3$ nanoparticles have been formed along the MWNTs backbone. The $CaCO_3$ nanoparticles and the CNTs backbone can be seen clearly, at the same time, dissociative $CaCO_3$ nanopartiles can also be observed. Figure 1d shows an enlarged section of the CNTs–$CaCO_3$ hybrids. It inidicates that these $CaCO_3$

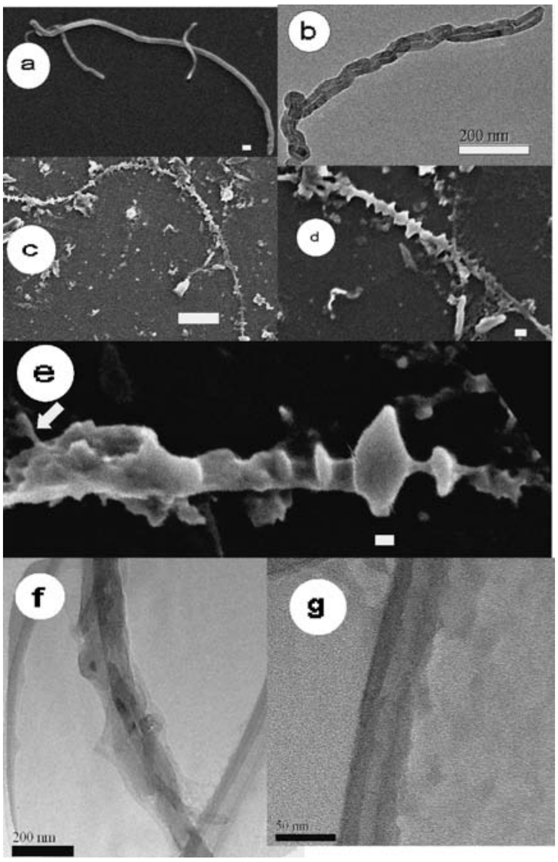

Figure 1. Microstructures of the pristine MWNTs (a, bar = 100 nm; b, bar = 200 nm) and the CNTs–$CaCO_3$ hybrids (c, bar = 1 μm; d and e, bar = 100 nm; f, bar = 200 nm; g, bar = 50 nm.).

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

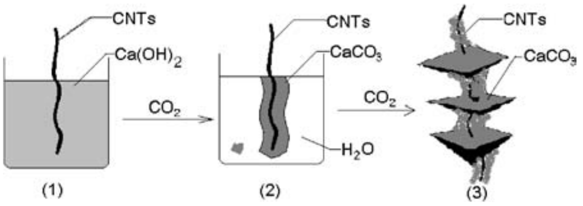

Figure 2. The formation of the kabob-like carbon nanotube hybrids: periodically decoration of CNTs with $CaCO_3$ nanoparticles.

nanoparticles have dentiform shapes with the diameters about 100 nm. Figure 1e shows the tip of a CNTs–$CaCO_3$ hybrid, indicating that CNTs were periodically enwrapped by the $CaCO_3$ coating and the tip of CNTs can be seen clearly (as marked in Figure 1e). Figure 1f shows a typical TEM image of the CNTs–$CaCO_3$ hybrid, indicating that the CNTs are coated by continuous $CaCO_3$ layers with in kabob-like structures. The profile of CNTs and the dentiform-shaped $CaCO_3$ surface coatings can be seen clearly. Figure 1g presents the section of a MWNTs whose $CaCO_3$ surface coatings have been eroded away by the superfluous aqueous CO_2 solution.

The schematic picture and equation presented in Figure 2 can explain the formation mechanism of the kabob-like carbon nanotube hybrids. When CNTs was introduced into aqueous $Ca(OH)_2$ solution, with the aid of surfactant or ultrasonic, CNTs can be well dispersed in aqueous $Ca(OH)_2$ solution. When CO_2 gas was introduced into the solution, water-soluble $Ca(OH)_2$ will react with CO_2 forming the water-insoluble $CaCO_3$ particles. Because of its porous nature, CNTs can adsorb Ca^{2+} onto its surface and thus $CaCO_3$ will form on the surface of CNTs. At the same time, some of the $CaCO_3$ particles suspended in the solution will also deposit on the surface of the CNTs, forming a layer of $CaCO_3$ coating on the CNTs (Figure 2 step 2). However, as suggested in Figure 1, the CNTs were not coated by a layer of continuous $CaCO_3$ coatings but decorated with periodically distributed $CaCO_3$ nanoparticles. This can be explained as the dissolution of $CaCO_3$ by aqueous CO_2 solutions (as shown by the equation in Figure 2). That is to say, the $CaCO_3$ coatings have been selecteroded away by the superfluous aqueous CO_2 solutions. This process resembles that of the formation of stalagmites in nature. The morphology of the CNTs–$CaCO_3$ hybrids can be controlled by adjusting the conditions of the fabrication process.

In summary, carbon nanotubes have been successfully decorated with $CaCO_3$ nanoparticles via a simple wet-chemical route. The significance of the present study is two-fold. First, carbon nanotubes are expediently functionalized by $CaCO_3$ nanoparticles. Because both $CaCO_3$ nanoparticles and carbon nanotubes have been widely used as fillers for the reinforcement of polymer materials, this new type of CNTs–$CaCO_3$ nanomaterial would have potential applications in polymer reinforcement as well. Afer periodically decorated with $CaCO_3$ nanoparticles, the specific surface area and the surface-roughness of the CNTs have been improved greatly, and thus increases the interfaces between the CNTs and polymer matrix. Second, $CaCO_3$ nanoparticles have been assembled (or immobilized) on carbon nanotubes whose chemical properties are considerable stable in living conditions. Calcium carbonate nanoparticles have been proposed as a new drug-releasing system for the delivery hydrophilic drugs and bioactive proteins. The assembly of $CaCO_3$ nanoparticles on carbon nanotubes may provide an ideal platform for the interaction of drugs (or proteins) and living cells, and thus facilitates the understanding of the interaction of drugs (or proteins) and living cells. The method and parameter developed in this research can be reasonably extended to other region for the surface decoration of nanomaterials with $CaCO_3$ nanoparticles.

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