

Attachment of inorganic nanoparticles onto carbon nanotubes

Jing Sun · Lian Gao

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Abstract Carbon nanotubes have been the focus of intensive study due to their unique structure-dependent electronic and mechanical properties. They are thought to have potential applications as catalyst supports in heterogeneous catalysis, high engineering reinforcements, and molecular wires for the next generation of electronic devices. Good dispersion of carbon nanotubes in a matrix of composite materials, especially in inorganic materials, indeed is a significant problem due to the strong Van der Waals force between CNTs and the poor compatibility between the two phases. It is the intention of our research work to overcome the difficulties regarding incorporation of carbon nanotubes in structural and functional ceramics. The initial step toward this goal involves coating CNTs with materials that will eliminate the undesirable attractive interactions between the nanotubes and facilitate their incorporation into composites. In the present study, two new and simple methods named as heterogeneous coagulation and direct hydrolysis have been developed to attach various inorganic nanoparticles such as alumina, zirconia and titania to the surface of carbon nanotubes. These functionalization methods might be new strategies to altering the electronic properties of nanotubes. We expected that the attachment of metal oxides to nanotube surfaces will promote better ceramic or other inorganic matrix-CNT adhesion and may lead to the development of homogeneous composites, thereafter improving mechanical and/or electrical properties.

Keywords Carbon nanotube · Attachment · Inorganic nanoparticles

J. Sun (✉) · L. Gao
State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China
e-mail: jingsun@mail.sic.ac.cn

Introduction

Since its discovery in 1991 [1], carbon nanotubes are undoubtedly one of the most attractive materials discovered near two decades. Their electronic properties have already had a significant impact on field emission applications in various electronic devices, while their high mechanical strength offers a new and exciting means as reinforcement in various materials ranged from polymer to ceramics. However, the inertia of the C–C bonds limits their binding with host matrices, and the surface modification of carbon nanotubes is usually necessary before its evolution. Presently, two methods are commonly used to incorporate nanotubes into ceramics. Ma et al. [2] formed CNTs/SiC composites by mixing nanoparticles of SiC with 10 wt% carbon nanotubes and hot pressing. They reported a 10% improvement in the strength and fracture toughness as compared to the monolithic ceramics. Other researchers [3–5] have developed techniques to synthesize carbon nanotubes *in situ* to form carbon nanotube/metal-oxide composite powders. These powders were then hot pressed to form macroscopic composites. The incorporation of the long nanotube bundles grown *in situ*, however, did not provide the expected improvement in mechanical properties. Hence techniques to modify and characterize the surface chemical properties of carbon nanotubes become more and more important.

It is the intention of our research work to overcome the difficulties regarding incorporation of carbon nanotubes in structural and functional ceramics. The initial step toward this goal involves coating CNTs with materials that will eliminate the undesirable attractive interactions between the nanotubes and facilitate their incorporation into composites. In the present study, two new and simple methods named as heterogeneous coagulation and direct hydrolysis have been developed to attach various inorganic nanoparticles such as

alumina, zirconia and titania to the surface of carbon nanotubes. The surface properties were characterized by zeta potential measurement. The morphologies of the coated CNTs with oxide nanoparticles were observed by TEM. These methods might be new strategies to altering the electronic properties of nanotubes, and provide new way to disperse the CNTs homogeneously in matrix and improve the binding between interfaces.

Experimental procedure

SWNTs and MWNTs prepared by the catalytic decomposition of CH_4 were kindly provided by Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences.

- (1) *Heterogeneous coagulation*: Carbon nanotubes were treated in NH_3 at 600°C for three hours to change their surface properties [6]. 20 mg treated MWNTs were put into 100 ml solution containing a dispersant of 300 mg/L Polyethylene imine (PEI, BDH Laboratory Supplies). Commercially available $\alpha\text{-Al}_2\text{O}_3$ (from Taimei Chemical Co., Ltd., Japan) and 3Y-TZP (from Tosoh Corporation) were dispersed into poly (acrylic acid) (PAA, from Polymer Sciences, PA) solutions. The concentrations of $\alpha\text{-Al}_2\text{O}_3$ and 3Y-TZP were 0.04 wt% and that of PAA is 300 mg/L. Diluted alumina and zirconia suspensions were added dropwise into the vigorously stirred as-prepared carbon nanotube suspension with PEI. After mixing, the surfaces of MWNTs were coated by alumina or zirconia particles due to the heterogeneous coagulation reaction. The coated carbon nanotubes collected from above mixed suspension were filtered for TEM observation.
- (2) *Direct hydrolysis*: 1 ml 3 M TiCl_4 was added into 29 ml of distilled water in a glass flask, and then 0.15 ml solution of 50 ppm polyethylene imine was added into

the flask. The mixture was covered by aluminum film and put into oven where the temperature was kept at 70°C . The white precipitate began to appear after 40 min, and the suspension of SWNTs solution (10 mg SWNTs) was added into the suspension and mixed with magnetic stirrer. The mixture was stirred and refluxed at 70°C for another two hours. Then, the suspensions were centrifuged, washed with distilled water and ethanol for several times. The product was characterized by TEM (JEOL 200CX), high resolution TEM (HRTEM, JEOL 2010F), XRD (RAX-10) and energy dispersive X-ray spectroscopy (EDS).

Results and discussion

Zeta potentials of pristine Al_2O_3 , ZrO_2 and CNTs treated in NH_3 for 3 h were measured with Zeta Plus as a function of pH in 1mM NaCl solutions. The results are shown in Fig. 1(A). The pH_{iep} of alumina, zirconia and CNTs were located at 7.5, 8.5 and 9.8, respectively. Two dispersants PEI and PAA were used to alter the inherent surface potentials of CNTs and inorganic particles. The treated CNTs have positive surface charge in wide pH range. Addition of a small amount of PEI not only moves pH_{iep} to a little higher pH value, but also promotes a good dispersion after the ultrasonication.

After the addition of PAA, pH_{iep} of alumina and zirconia moved to pH2, they had negative surface potential from pH2 to pH 11. It is well known that when two sols of opposite electric charge are mixed, mutual coagulation may occur. If the proper pH range is selected, ceramic particles will be adsorbed onto CNTs by electrostatic attractive forces. Before performing the coating procedure, dilute suspension of treated CNTs with PEI is adjusted to pH8 with zeta potential value about 40 mV, while the diluted suspension of alumina or zirconia in presence of PAA is adjust to pH9.5 with zeta potential value about -40 mV. Once these two

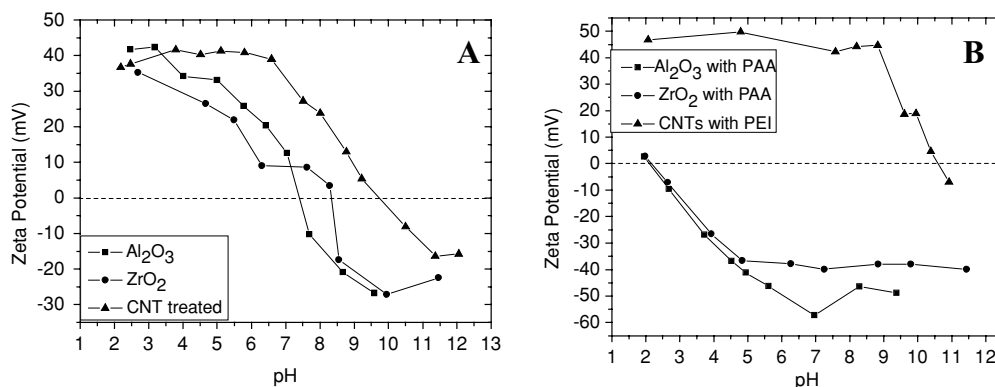


Fig. 1 Zeta potential values changed with pH: (A) pure alumina, zirconia and CNTs treated in NH_3 for 3 h. (B) Zeta potential values of CNTs in the presence of PEI, alumina and zirconia in the presence of PAA

Fig. 2 TEM micrographs of CNTs in coating states with alumina (a) and zirconia (b)

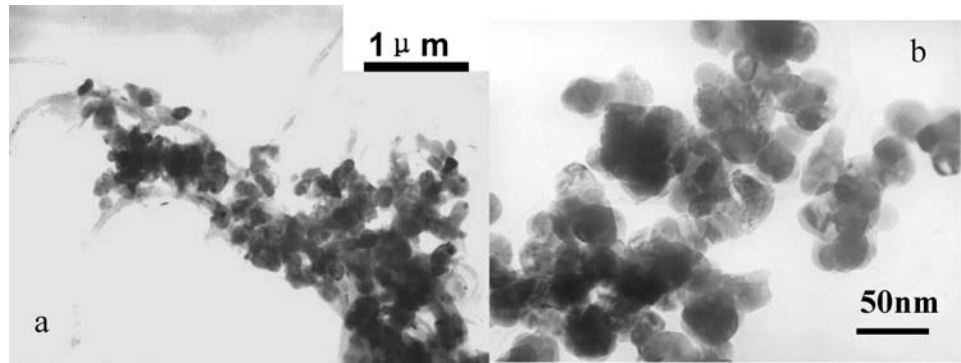
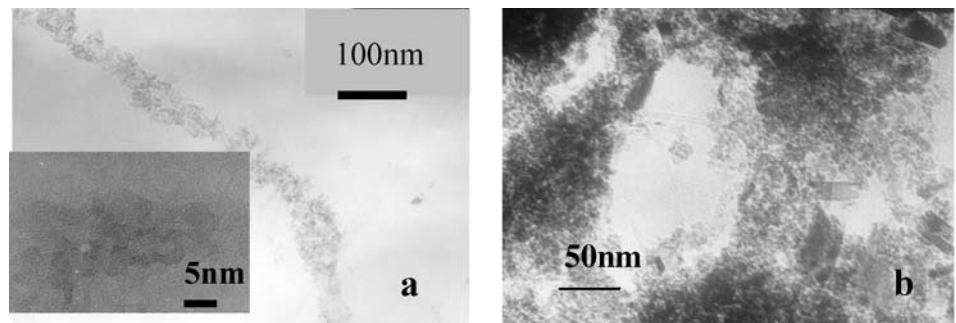


Fig. 3 (a) TEM and HRTEM micrographs of SWNTs coated with TiO₂ nanoparticles with PEI (b) TEM images of composite powder in the absence of PEI



suspensions encountered, particles of alumina or zirconia will bind onto CNTs due to strong electrostatic attractive force between them. CNTs were observed to be fully coated by alumina or zirconia particles as shown in Fig. 2.

The preparation of TiO₂ nanoparticles by the hydrolysis of TiCl₄ solution is an economical route. Pure anatase or rutile and mixed-phases titania could be obtained by controlling the temperature [7]. The hydrolysis process can be described as follows:

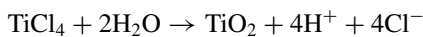


Figure 3(a) shows a typical TEM image of the composite powders. The SWNTs have been nearly fully coated with TiO₂. The thickness of the coating varied from the den-

sity of titania particles. The coating layer is composed of TiO₂ nanoparticles with sizes less than 5 nm and they are well attached onto the surface of SWNTs. Figure 3(b) shows that SWNTs was covered by the aggregated titania particles non homogeneously in the absence of PEI. We think the addition of PEI to TiCl₄ solution has two effects: they combined with hydrogen ion and promote the hydrolysis of TiCl₄ to TiO₂; protonized PEI attached onto titania particles, made them positively charged and stabilized TiO₂ electrostatically. When negatively charged SWNTs were added into, titania particles bound with SWNTs either by amide linkage or through electrostatic attraction.

XRD pattern of the composite powder is shown in Fig. 4. From the XRD peaks, it can be seen that anatase and rutile phases coexisted in the composite powders. Chemical anal-

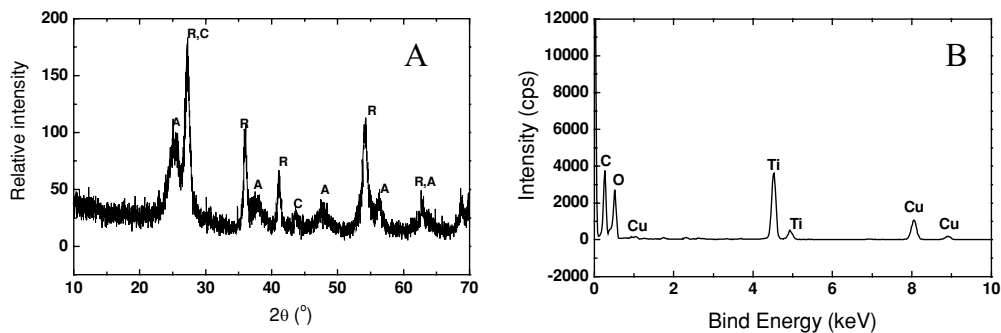


Fig. 4 (A) XRD pattern of SWNTs coated with TiO₂, A, R, C stand for anatase, rutile and SWNTs (B) EDS spectrum of the CNTs/TiO₂ composite powder

ysis using EDS (not shown here) indicates the presence of Ti, O and C in the coated SWNTs. For the majority of the coated nanotubes, the atomic ratio of O to Ti is close to 2.

Conclusions

This investigation has shown that alumina, zirconia and titania powders can be coated onto carbon nanotubes by a simple heterogeneous coagulation or direct hydrolysis method. Poly (ethylene imine) was identified to be effective for imparting a positive charge to the surface of CNTs. The versatility of this simple approach can be extended to other ceramic powders by varying pH and type of dispersant. The results obtained pave the way for the formation of coated carbon nanotubes

for the development of composites with a homogenous microstructure and improved performance.

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