Functional Boron Nitride Nanotubes

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Abstract- we describe synthesis, property investigations and composite applications of multi-walled boron nitride nanotubes.

I. INTRODUCTION

Nanotubes have attracted significant attention over the last decades since identification of carbon nanotubes (CNTs) [1]. BN nanotubes (BNNTs) are structural analogs of CNTs where C atoms are substituted by alternating B and N atoms. Different from helicity dependent band structures of CNTs, BNNTs have a constant band gap of ~5.5 eV [2], which results in truly insulating properties. Due to effective phonon heat transfer, BNNTs are good thermal conductors as revealed by theoretical and experimental studies [3]. They are regarded as prospective nanofillers for insulating composite materials which may lead to high thermal conductivities while preserving the insulation. Moreover, BNNTs possess other excellent properties, e.g. high elastic modulus, superb structural stability, anti-oxidation ability, chemical inertness and surface polarization [3]. These open various routes for numerous BNNTs' applications.

II. SYNTHESIS OF BNNTS

Large yields of BNNTs are required for application studies. However, synthesis of pure BNNTs is difficult due to high crystallization temperature, toxic gas precursors etc. We developed an effective chemical vapor deposition method using a boron powder and a metal oxide as precursors [4]. The design of an induction furnace was optimized to separate a solid B precursor (boron+metal oxide) from as-grown BNNTs, that guarantees high BNNT purity. Grams level of pure multi-walled BNNTs is now routinely achievable in every experimental run. Figure 1(a) shows 2 grams of white-colored BNNTs. Figures 1(b) and 1(c) are scanning electron (SEM) and transmission electron microscopy (TEM) images of purified BNNTs. A tubular structure is seen. The nanotubes have diameters of ~50 nm, and their length can reach tens of micrometers. The periodic black dots visible in tube TEM images are due to a specific double-helical structure. It was proposed that B can be oxidized by a metal oxide to form B_2O_2 species (as B source) and a metal oxide is reduced to metal, which then serves as a catalyst for the formation of tubes.

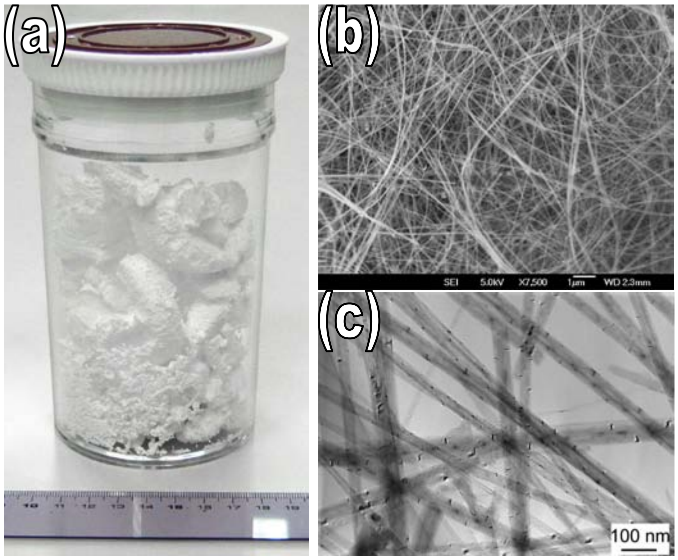

Fig. 1. (a) An image of 2 grams of BNNTs; (b) SEM image of purified BNNTs; (c) low-magnification TEM image of multi-walled BNNTs.

III. PROPERTY INVESTIGATIONS

Based on high-quality BNNTs synthesized, we have investigated their thermal stability, electrical, mechanical and optical properties etc. Recently, we started to work on property studies of individual BNNTs inside TEM. For the first time, we used an AFM-TEM sample holder to perform a direct force measurements under bending of well-structured multi-walled BNNTs of various diameters [5]. The BNNTs were slowly bent inside TEM between a movable Al wire and a Si cantilever. A thick tube and thin tube with diameters of ~100 nm and ~40 nm were investigated. The real force-displacement curves during the deformation were recorded. It was estimated that the bending stresses were ～100 and ～260 MPa, respectively, and the calculated values of the elastic modulus (based on the Euler formula) were 0.5-0.6 TPa. Such values were consistent with the theoretical predictions and the experiments using a resonance technique.

Thermal/electrical stabilities of individual nanotubes were also investigated [6]. A BNNT was bridged between two electrodes inside TEM. Two Schottky barriers were formed between the nanotube surface and the electrodes. The electrical conductivity of BNNT was very low. As the high bias was kept for a while, the current slowly increased and finally the nanotubes were broken. The closed caps were formed at the

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burnt end and within the inner channel. Amorphous balls appeared on the walls and within the tube, as shown in Figure 2. These balls were made of elemental B as revealed by energy-filtered elemental maps. The breakdown temperature was found to depend on a local electrical field. Keeping in mind the partially ionic nature of a B-N bond, we suggest that the failure of a BNNT is electrically assisted thermal decomposition. The high electrical fields and defects within the nanotubes play the key roles in lowering the decomposition temperature. Based on the thermionic field-emission model, the decomposition temperature was estimated to be around 1275 K. Such relatively low temperature implies the key role of electrical field in breakdown of BNNTs.

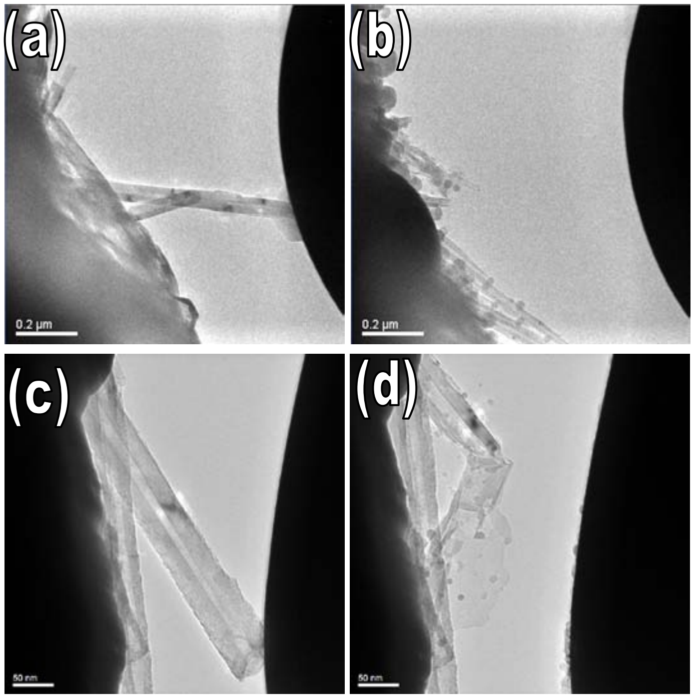

Fig. 2. (a) and (b) TEM images of a BNNT before and after electrical breakdown; (c) and (d) analogous images for another BNNT sample.

IV. COMPOSITE APPLICATIONS

The usage of BNNTs as nanofillers for composites is governed by their superb mechanical properties and high thermal conductivities. BNNTs are electrically insulating fillers, which guarantees insulating composites suitable for applications in electrical circuits packaging. We fabricated polystyrene-BNNTs composites and studied a mechanical reinforcement effect of BNNTs. To improve BNNTs' dispersibility and interfacial interactions between BNNTs and polystyrene, PmPV was used as a surfactant. With a 1 wt. % BNNTs fraction, the elastic modulus of polystyrene was raised by 21% [7]. With the use of covalently functionalized BNNTs (hydroxylated BNNTs) as fillers, the improvement of matrix's strength was even more effective, e.g. the elastic modulus was improved by 31% and the yield strength was increased by 9%.

In addition, we also used BNNTs as nanofillers to fabricate highly thermo-conductive electrically insulating polymeric composites [8]. We developed an absorbing-filtering method to embed high fraction of BNNTs in a polymeric matrix. Then the performance of obtained composites was thoroughly evaluated. For example, with 24 wt.% BNNTs embedding in ploymethyl methacrylate (PMMA), its thermal conductivity was improved 21-fold. The coefficient of thermal expansion of PMMA was reduced from 164×10^{-6} to 21×10^{-6} K^{-1}. Moreover, the composites kept decent hardness and high breakdown voltage.

V. SUMMARY

We develop an effective CVD method for the large scale synthesis of highly pure multi-walled boron nitride nanotubes. Based on high-quality-BNNTs, their optical, electrical, mechanical and thermal properties were systematically investigated. Moreover, the pioneering explorations of BNNTs' applications in polymeric composites were performed. Various composites were fabricated, and they indeed revealed superb mechanical and thermal properties. Our studies confirmed that BNNTs are very promising nanofillers in composites towards their mechanical reinforcement, improvement of thermal conductivity, and lowering a coefficient of thermal expansion.

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