Mechanical and Electrical Properties of CNT/Inorganic Nanocomposites Fabricated by Molecular Level Mixing Process

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ABSTRACT

CNT/Inorganic nanocomposites with homogeneously distributed CNTs in inorganic matrix with strong interfacial strength are fabricated by a novel fabrication process, i.e. molecular level mixing process. Molecular level mixing process enables CNTs to be mixed and react with ions of inorganic matrix in molecular level overcoming agglomeration problem of CNTs. The fabricated CNT/Inorganic nanocomposites show outstanding multifunctional behavior for various applications. For the structural applications of CNT nanocomposites, CNT/Cu nanocomposite could be fabricated with excellent strength, increased by 3 times, and high elastic modulus, increases by 1.6 times, compared to those of Cu. For functional applications of CNT nanocomposites, the CNT/Co nanocomposite can be applied to high-efficiency field emitter for applications as back light unit, field emission display. CNT/Inorganic nanocomposites can be applied to various applications EMI shielding materials and electrode materials for energy storage and conversion.

Keywords: carbon nanotube, nanocomposites, fabrication process, molecular level mixing process

1 INTRODUCTION

Several researchers have attempted to fabricate CNT reinforced metal or ceramic matrix nanocomposite materials by means of traditional powder metallurgy process,[1-3] which consists of mixing CNTs with matrix powders followed by sintering or hot pressing. However, these attempts were not successful to fabricate CNT/Inorganic nanocomposites with homogeneously dispersed CNTs in the matrix. This is mainly due to strong agglomeration of CNTs in powder forms: the van der Waals forces between CNTs cause them to mutually attract each other rather than homogeneously disperse. Furthermore, if CNT/Inorganic nanocomposites are manufactured by the conventional process, most of the CNTs are preferentially located on the surfaces of the metal or ceramic powders after mixing.[1-3] The conventional process inhibits the diffusion of matrix materials across or along the powder surfaces; hence, sintering cannot proceed without damaging the CNTs or removing them from the powder surfaces. Even if sintering is successful, CNTs are mostly located at grain boundaries of the matrix and are insignificant in improving material performance. At the same time, the most important processing issue is how to obtain good interfacial bonding between carbon nanotubes and matrix. In the case of CNT/polymer nanocomposites, the interfacial strength between the CNTs and the polymer matrix is strong because they interact at molecular level.[4] In the case of CNT/metal or CNT/ceramic nanocomposites, however, the interfacial strength cannot be expected to be strong because the CNTs and the matrix are merely blended.

2 EXPERIMENTAL PROCEDURES

The strategy for developing a novel fabrication process for CNT/Inorganic nanocomposite basically involves molecular level mixing of the reinforcement(CNT) and the matrix material in a solution instead of the conventional powder mixing. This new process produces CNT/Inorganic

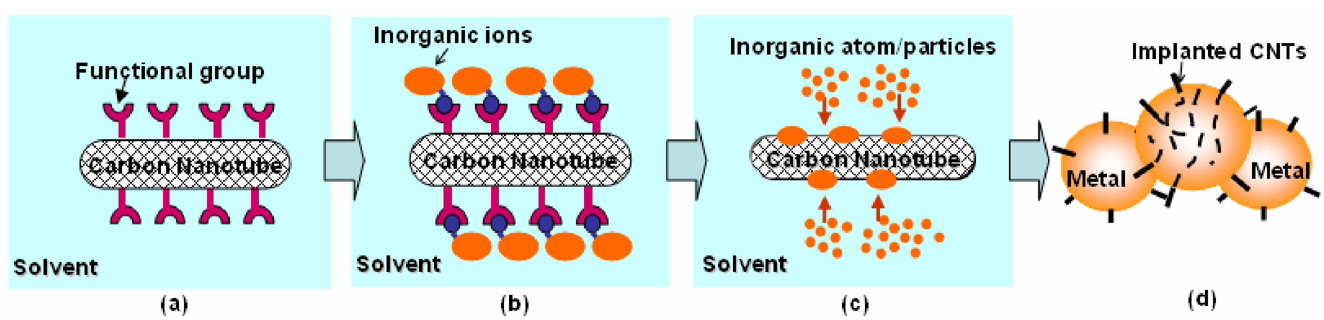

Fig. 1. Schematics depicting strategies and procedures for the molecular level mixing process, (a) functionalization of carbon nanotube, (b) reaction between the ions and the functional group on the carbon nanotube surface, (c) nucleation and growth of inorganic particles by reduction or solvent evaporation, (d) carbon nanotube/metal nanocomposite powders in which carbon nanotubes are homogeneously implanted.

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composite powders where the CNTs are mainly located within the inorganic powders rather than on surfaces of them; the chemical bonding between the CNTs and the inorganic matrix ions provide homogeneous distribution of CNTs as well as high interfacial strength between CNT and inorganic matrix.

The molecular level mixing process for fabricating CNT/Inorganic composite powders consists of 4 steps. First, CNTs are dispersed in a solution, to make a stable suspension by attaching functional groups on the CNT surfaces. (Fig. 1a) There are several chemical methods for attaching functional groups on the CNT surfaces.[5] Once the functional groups are attached on the CNTs, the electrostatic repulsive force between the CNTs could overcome the Van der Waals force to form a stable suspension within the solvent. Second, a soluble salt containing matrix ions is dissolved in the CNT suspension. Sonication treatment is introduced to disperse the inorganic matrix ions among the suspended CNTs and to promote chemical reaction between the ions and the functional groups on CNT surfaces. The third step is to dry the solution consisted of CNTs and ions. During this process, the solvent and ligands are removed and the inorganic matrix ions on CNTs are oxidized to form powders. The fourth step is calcination and reduction processes to obtain chemically stable crystalline nanocomposite powders. The nanocomposite powders obtained in the third step are generally existed as oxides. These powders are changed into CNT/Metal nanocomposite powders by a reduction process. The reduced CNT/Inorganic nanocomposite powders show that the CNTs are homogeneously implanted in inorganic matrix as shown in Fig. 1d.

3 RESULTS AND DISCUSSION

3.1 Microstructure of CNT/Inorganic Nano-composites

The CNT/Cu nanocomposite powders fabricated by molecular level mixing process consisted of homogeneously dispersed CNTs within Cu powders as shown in Fig. 2. The most important feature of this process is that CNTs and matrix ions are mixed each other at molecular level. That is, the CNTs are located within the powders rather than on the powder surfaces. The morphologies of the CNT/Cu and CNT/Co powders show an ideal composite microstructure, which displays that CNTs are homogeneously implanted in the powders (Fig. 2).

The CNT/Metal nanocomposite powders fabricated by the molecular level mixing process was consolidated into bulk CNT/Metal nanocomposite by spark plasma sintering process, which can produce a high heating rate of 100°C/min and rapid consolidation through high joule heating and generation of spark plasma between powder-to-powder contacts. The consolidated CNT/Metal nanocomposite shows homogeneous distribution of carbon nanotubes within the matrix (Fig. 3).

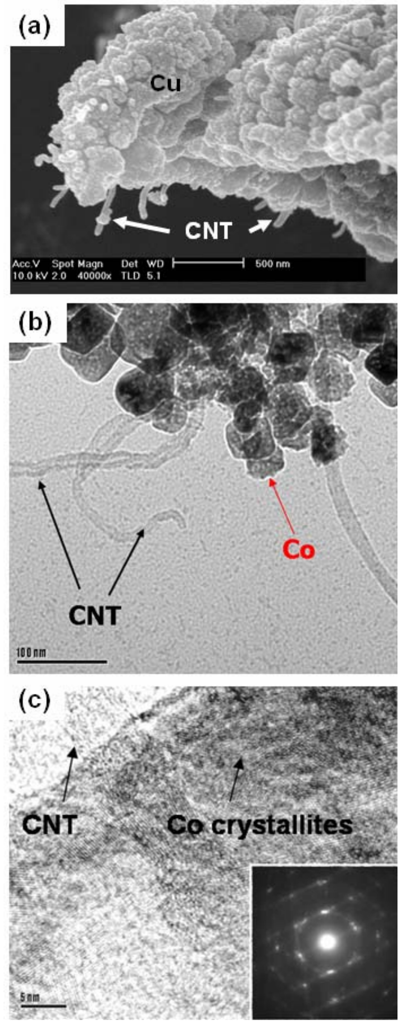

Fig. 2. Microstructures of carbon nanotube/metal nanocomposite powders, (a) SEM image of implanted type carbon nanotube/Cu nanocomposite powders [6], (b) TEM image of necklace type carbon nanotube/Co nanocomposite powders, (c) HRTEM Image of necklace type carbon nanotube/Co nanocomposite powders.[8]

3.2 Mechanical Properties of CNT/Cu Nano-composites

The mechanical properties of CNT/Cu nanocomposite were characterized by compressive test. As shown in Fig. 4a, the compressive yield strengths of CNT/Cu nanocomposites were much higher than that of Cu matrix, which is fabricated by the same process without adding CNTs. 5 volume percent CNT reinforced Cu matrix nanocomposite shows yield strength of 360MPa, which is 2.3 times higher than that of Cu. In the case of 10 volume percent CNT reinforced Cu, the yield strength is 485MPa, which is more than 3 times higher than that of Cu. Moreover, Young's modulus of CNT/Cu nanocomposite increases as the volume fraction of carbon nanotubes is increased, as shown in Fig. 4b[6].

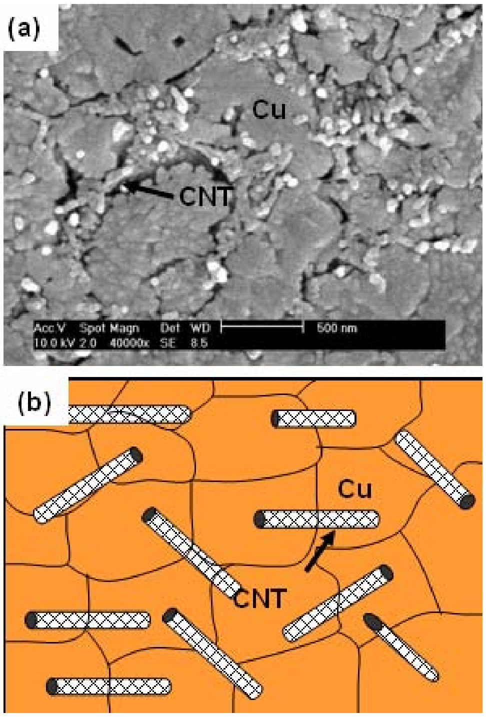

Fig. 3. Microstructure of sintered CNT/Cu nanocomosite (a) SEM microstructure of CNT/Cu nanocomposite showing homogeneous distribution of CNTs within Cu matrix, (b) schematics microstructure of CNT/Cu nanocomposites.

The remarkable strengthening effect of CNTs in CNT/Cu nanocomposite was due to a high load-transfer efficiency caused by strong interfacial strength between CNTs and Cu, which originated from strong chemical bonds formed during the molecular level mixing process. The strengthening efficiency (R) of reinforcement can be expressed as

$$R = (\sigma_c - \sigma_m) / V f \sigma_m$$

R : Strengthening efficiency of reinforcement
σ_c: yield strength of composite
σ_m: yield strength of matrix
V_f: volume percent of reinforcement

The strengthening efficiency, defined as the strengthening effect of a given volume percentage of reinforcement on the matrix, for carbon nanotubes is much higher than those of SiC particles or SiC whiskers, which are the most widely used reinforcements for metal matrices.[6] This indicates that carbon nanotubes are the most effective reinforcements. Such a high strengthening effect of CNTs has been confirmed in other CNT/Inorganic nanocomposites such as CNT/Co nanocomposite[7] and CNT/Alumina nanocomposite[9] fabricated by molecular level mixing process.

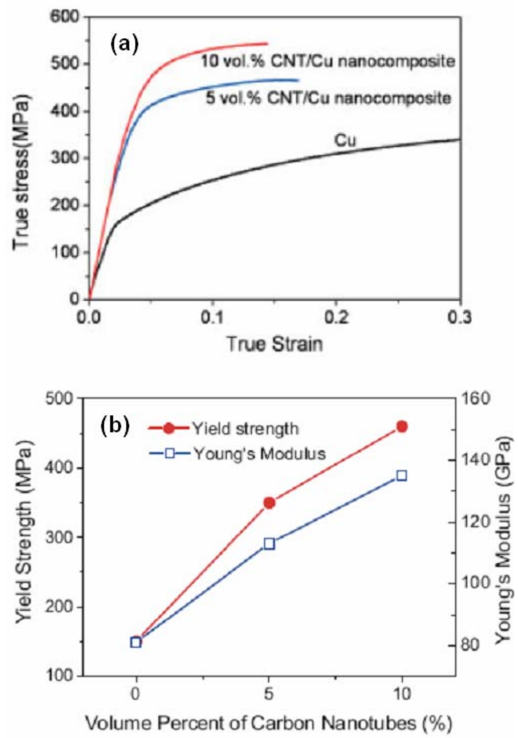

Fig. 4. Mechanical properties of CNT/Cu nanocomposites. (a) the stress-strain curves of CNT/Cu nanocomposites obtained by compressive test, (b) yield strength and Young's modulus of CNT/Cu nanocomposites according to the volume percentage of CNTs[6].

3.3 Electrical Properties of CNT/Co Nano-composites

CNT/Metal nanocomposites can be applied to not only structural material but also functional materials such as field emitter. The CNT-implanted Co nanocomposite field emitter is fabricated from necklace type CNT/Co nanocomposite powders by a screen-printing process followed by a sintering process as shown in Fig 5a. Before sintering, the necklace type CNT/Co nanocomposite powders are buried in organic binders (Fig. 5b), which are thermally decomposed during the sintering process (Fig. 5c). During the sintering process, the Co nanoparticles are sintered together and form a dense metallic layer in which the CNTs are implanted. CNTs are straightened and aligned perpendicular to the substrate so that they stand upright on the surface of metallic layer as shown in Fig. 5d. The CNTs tend to be aligned perpendicular to the substrate because the base of the CNT is implanted in the Co metal layer during the sintering process.[8]

CNT/Co nanocomposite field emitter, fabricated by sintering of CNT/Co nanocomposite powders, shows good field emission properties with low turn-on field of 1.28V/µ m, high current density of 4.5mA/cm^2 at 3V/µ m and homogeneous field emission as shown in Fig. 6b. Good field emission properties were due to low electrical resistivity by strong interfacial bonding between CNTs and Co and homogeneous dispersion of CNTs in Co matrix.

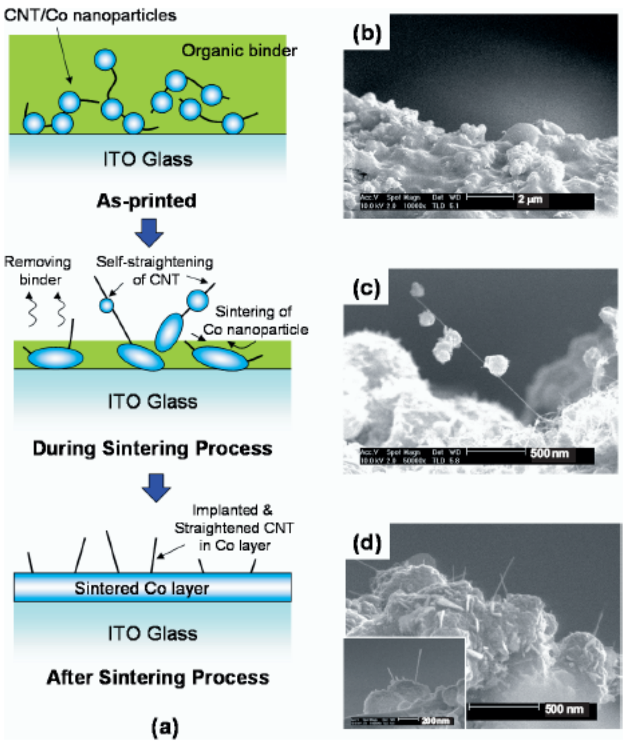

Fig. 5. Fabrication process of CNT/Co nanocomposite field emitters. (a) Schematic depiction of the fabrication process and formation mechanism for CNT-implanted Co nanocomposite emitters. (b) Cross-sectional SEM image of screen-printed necklace type CNT/Co powders with an organic binder, (c) SEM image showing Co nanoparticles threaded by a straight CNT after sintering, and (d) SEM images of the CNT-implanted Co nanocomposite emitter after sintering.[8]

4 CONCLUSIONS

The critical issues on fabrication of CNT/Inorganic nanocomposites are homogeneous dispersion of CNTs and strong interfacial bonding between CNTs and matrix. Molecular level mixing process is a novel process to solve critical issues. CNT/Inorganic nanocomposites with homogeneously dispersed CNTs within the matrix were fabricated and showed highly enhanced mechanical properties by effective load transfer and excellent field emission properties by low electrical resistivity due to strong interfacial bonding between CNTs and the matrix. It is expected that molecular level mixing process can contribute not only for development of high strength/modulus structural components but also for development of various functional materials such as field emitters, EMI shielding materials and electrode materials for energy storage and conversion applications.

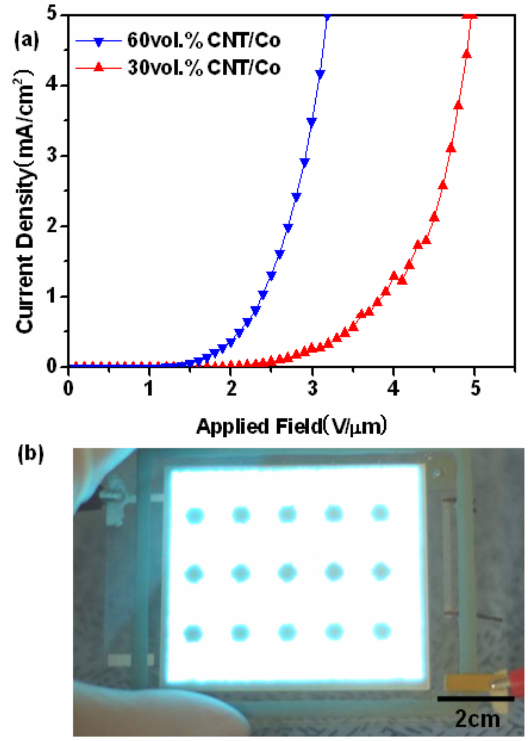

Fig. 6. Fied emission properties of CNT/Co nanocomposites. (a) Field emission curves of 60vol.% CNT/Co and 30vol.% CNT/Co nanocomposite field emitters, (b) field emission image of CNT/Co nanocomposite field emitters.

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