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A microscopy study of Multiwall Carbon Nanotubes (MWCNTs)/$BaTiO_3$

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Due to its high dielectric permittivity (ε_r), piezoelectric response and semiconductor behavior when doped, $BaTiO_3$ (BT) is an interesting dielectric material with vast microelectronic applications such as capacitors, resistors, actuators, among others. In the last decade, considerable efforts have been made towards the miniaturization of microelectronic devices, and considerable challenges are being faced as in the case of Ferroelectric Random Access Memories (FeRAMs). In order to reduce chip size and enhance storage capacity a three dimensional (3D) geometry for the design of the memory cell is being considered. Within this context the use of carbon nanotubes (CNTs) as templates or bottom electrodes for one dimensional (1D) pillars of the 3D structure is a possible strategy worth to be explored [1]. MWCNTs have been used as fillers in composites with BT to improve electrical and thermal properties [2]. However, covering CNTs with FE is not a trivial task and many aspects are still unexplored and unclear. Therefore, in this work a systematic microscopy study of the coverage of multiwall CNTs (MWCNTs) with BT by a sol gel hydrothermal method is presented.

Pristine CNTs (10 - 35 nm in diameter and ~10 μm in length) are hydrophobic and, as a consequence difficult to wet the surface. Therefore, the CNTs used in this work were functionalized with 5M HNO_3 in order to improve the wetablility of the tubes as shown in Fig. 1 (a) (inset illustrates no wetting for as received MWCNTs). BT sol gel solution was prepared by mixing barium acetate and titanium isopropoxide precursor. MWCNTs were dispersed in this BT solution using ultra high -sonication. MWCNTs-BT solution was precipitated with the addition of potassium hydroxide solution. The precipitated solution was transferred to the autoclave and the hydrothermal reaction was carried at 160 ºC for different times. XRD confirms the formation of monophasic BT at 160 ºC for the processing time of 10 h and above (Fig. 1 (b)). FTIR transmittance spectra of functionalized MWCNTs depicts peaks at ~3442 and 1385cm^{-1} indicating the presence of hydroxyl groups (OH) and a peak at 1055cm^{-1} confirming the formation of carboxylic groups. FTIR peak at 1625 cm^{-1} is due to stretching of C=C bond from CNTs skeleton and the peaks at 580 and 403 cm^{-1} are from crystalline BT, both confirming the presence of MWCNT after the synthesis of BT (Fig 1(c)).

Fig. 2 (a) shows TEM (Hitachi H9000) micrographs of MWCNTs uniformly covered with BT with coating thickness of 50 nm. In the dark field image (Fig. 2 (b)) the bright contrast from BT confirms the covering of MWCNTs. EDS of the MWCNTs covered with BT further verifies the presence of barium and titanium elements (Fig. 2(c)).

Fig. 3 (a-b) depicts the HRTEM (Jeol model 2200FS) micrograph of the MWCNTs semi covered with BT particles with size of 20-30 nm. The MWCNTs surrounded by the BT are intact with d spacing of 0.34 nm and BT particle having lattice spacing of 0.28 nm which correspond to (101) planes. The studies prove the coverage of MWCNTs with a ferroelectric oxide by low cost technique.

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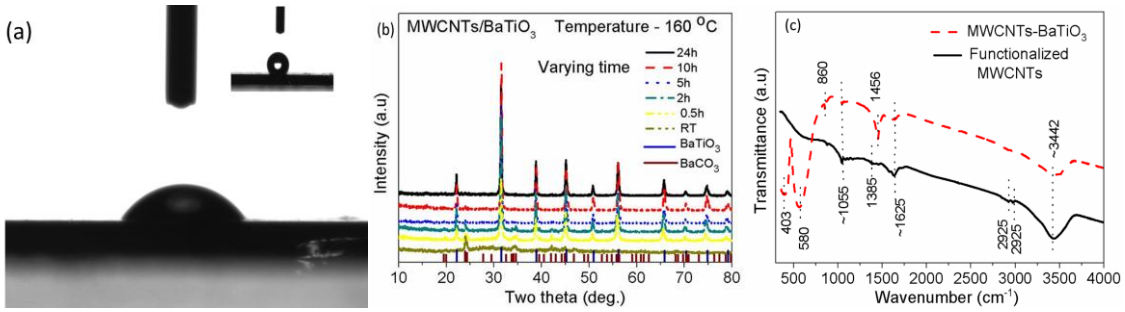

Figure 1. (a) Optical micrograph shows wetting of functionalized MWCNTs with water (insert show no wetting of pristine MWCNTs); (b) XRD of MWCNTs-BT at 160 ^{o}C with varying synthesis time. (c) FTIR of functionalized MWCNTs and MWCNTs-BT synthesised at 160 ^{o}C for 10 h.

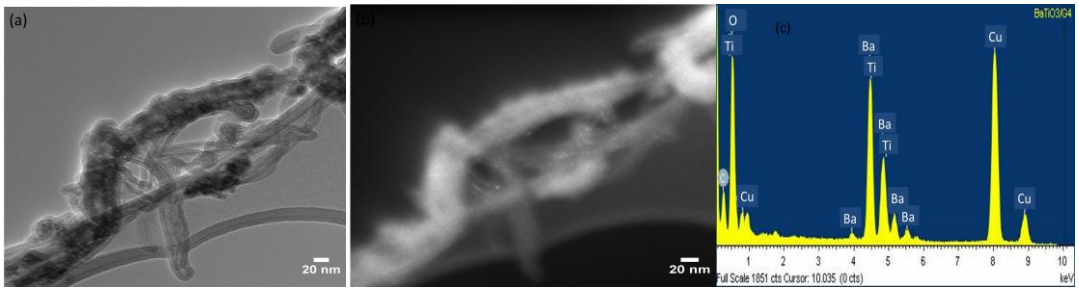

Figure 2. TEM micrograph of MWCNTs-BT synthesised at 160 ^{o}C for 10 h: (a) bright field and (b) dark field images and (c) EDS spectra, confirming the presence of Ba and Ti elements.

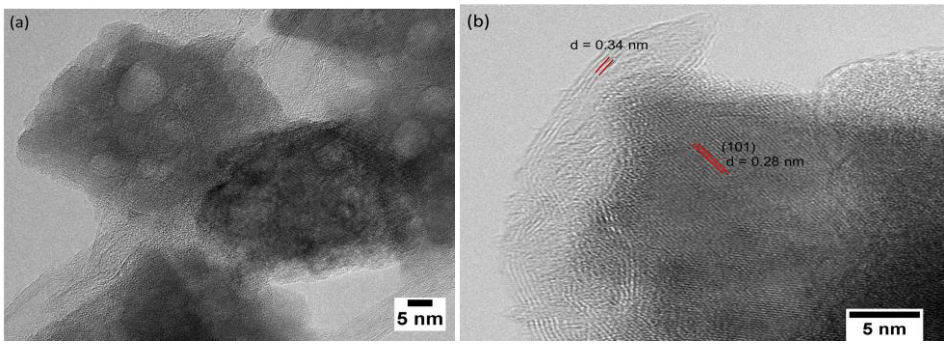

Figure 3. HRTEM of MWCNTs-BT synthesised at 160 ^{o}C for 10 h: (a) BT particles at the surface of the tubes and (b) details of the interfaces between the tubes and BT.

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