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# Thermal Stability of Zirconia-coated Multiwalled Carbon Nanotubes

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## ABSTRACT

Sol-gel method has been used to coat multiwalled carbon nanotubes (MWCNTs) with zirconia at room temperature and the coated tubes were sintered at high temperature. The samples were characterised by Raman spectroscopy, x-ray diffraction, environmental scanning electron microscope, transmission electron microscopy, and energy-dispersive x-ray analyses. The performance of the coated-MWCNTs was investigated as a function of temperature. The TGA studies indicated that sintering of coated-MWCNTs has improved its oxidation resistance and this improvement is related to the proper selection of sintering temperature.

**Keywords:** Carbon nanotubes, MWCNTs, multiwalled carbon nanotubes, sol-gel, zirconia coating, thermal stability

## 1. INTRODUCTION

Carbon nanotubes (CNTs), due to their excellent physical and mechanical properties, have attracted researchers world wide as reinforcement in polymer[1,2], metal[3,4], and ceramic matrices[5-7]. However many challenges still remain before realising the full potential of CNTs as reinforcements. These challenges range from weak adhesion between the matrix and the reinforcement due to surface incompatibility of CNTs with the matrix, to processing challenges for better dispersion, which limit the original effect of CNTs as reinforcements and thus limit their applications. Therefore, there is a need for suitable surface modification of CNTs to make CNTs compatible with the matrices.

In recent years, lots of researches have been done on coating of CNTs with suitable materials to tackle the agglomeration of CNTs and the weak interface between CNTs and the matrix. Ability to deposit well-controlled coatings on CNTs would offer wide range of technological applications based on the change in their physical and chemical properties. Electroless plating[8] and dc electrophoretic[9] techniques have been used to coat CNTs with silver. Chemical method like redox reaction was employed to develop Co-B alloy coatings on CNTs[10]. Many researchers have used techniques like pulsed vapour deposition, thermal reactions to develop metal and metal oxide coatings on CNTs[11-16]. Shi[17-18], *et al.* have reported the surface modification of nano particles and CNTs by plasma coating method for better dispersion of nano materials and also for surface compatibility of the nano particles with various matrices. Theoretical possibility of uniform coating on CNTs with a monolayer of physisorbed atoms was reported by Siber[19] based on the symmetries and binding energies of the adsorbate coating as a function of CNT radius.

Developing a suitable coating layer on CNTs before using these in the ceramic matrix is now emerging as a new field of study. Efforts have been devoted to design and synthesise zirconia-coated CNTs by different techniques[20] and its composites. Here, sol-gel method is used for developing zirconia coatings on CNTs. The sol-gel method is very widely used technique for applications ranging from developing nano ceramic coatings to various ceramic composites. Incorporation of CNTs in borosilicate[21] and alumina[22] matrices through sol-gel method are reported with promising results. Sol-gel method, based on silane precursor, is also employed for surface modification of multiwalled carbon nanotubes (MWCNTs) to make these compatible with PMMA matrix[23]. Sol-gel-based zirconia-silica oxidation-resistant coatings on C-C composites were reported[24] earlier by some research groups.

In the present work, MWCNTs were coated with zirconia to tailor the surface of the CNTs for better oxidation resistance as well as to improve the compatibility of the CNTs with ceramic matrix. Coated-CNTs were sintered and the effect of sintering temperature on the performance of the coatings was investigated. These results will have implications in easy processing of CNT-reinforced zirconia-toughened alumina composites.

## 2. EXPERIMENTAL WORK

### 2.1 Materials

The MWCNTs (92 % purity) used for coating were synthesised in-house by aerosol-assisted CVD method from ferrocene toluene mixture. The synthesised CNTs were purified by heat treatment at 450 °C for 90 min to remove amorphous carbon, followed by refluxing in nitric acid to remove metal catalyst impurities. These purified

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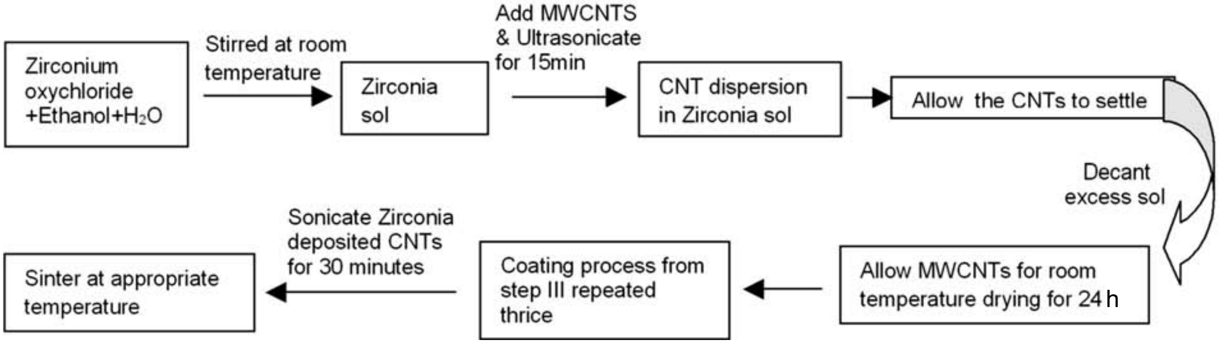


**Figure 1. Schematic representation of experimental procedure for coating on MWCNTs with zirconia.**

MWCNTs were dispersed and coated with zirconia by sol-gel method. Typical experimental procedure for coating MWCNTs with zirconia is shown as flow chart in Fig. 1. The following steps were involved:

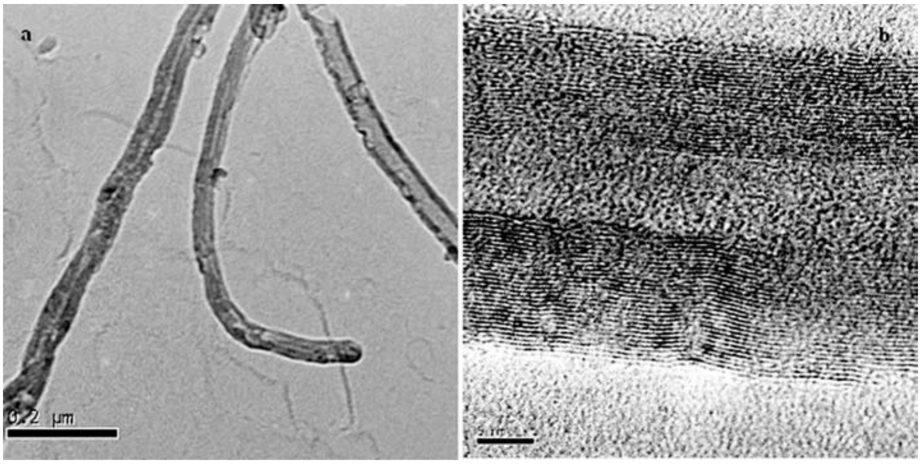
- Zirconia sol was prepared by stirring the mixture of $ZrOCl_2$ $8H_2O$/ethanol/$H_2O$ in the molar ratio of 0.05:2.38:1.11.
- Purified MWCNTs were added into the sol and the mixture was ultrasonicated in a bath type ultra sonicator for 15 min.
- Then the sol-CNT mixture was allowed to stand for 30 min allowing CNTs to settle down.
- Excess sol was decanted and the MWCNTs were allowed to undergo room temperature drying for 24 h.
- The above procedure was repeated for 3 times to obtain thick coatings of zirconia.
- Coated-MWCNTs were sintered at 700 °C and 1200 °C under nitrogen atmosphere for 1 h to improve the adhesion of ceramic layer on MWCNTs.

### 2.2 Characterisation

Coated MWCNTs were characterised using Raman spectroscopy (Horiba Zobin Yvon T64000, $Ar^+$ laser, $\lambda$=514.5 nm), x-ray diffraction (XRD) (Philips PW1830), environmental scanning electron microscopy (ESEM) (Quanta 400), and transmission electron microscopy (TEM) (FEI Tecnai 20T). The TGA studies were carried out (with temperature ramp rate of 10 °C/min under air flow of 80 ml/min) for zirconia-coated-MWCNTs before and after sintering to study the improvement in the oxidation resistance.

## 3. RESULTS AND DISCUSSION

The TEM results (Fig. 2) show that MWNTs used for coating are having outer diameter in the range of 25-50 nm, the inner diameter in the range of 5-30 nm, and lengths in tens of microns. The high resolution TEM (HRTEM) micrograph of a particular MWNT (Fig. 2(b)) shows approximately 25 well graphitised carbon lattice fringes. Raman spectroscopy result of MWNT (Fig. 3) before coating shows *G* peak at 1579 $cm^{-1}$ and *D* peak at 1345 $cm^{-1}$. Both the *G* and *D* peaks show splitting. Splitting of *G* peak is also observed for Raman shift around 1604 $cm^{-1}$which may be due to small inner diameter of the CNTs[25-26]. Low $I_G/I_D$ ratio (0.96) indicates that carbon deposits present are mostly defective. The XRD results in Fig. 4 show that initially after coating, zirconia is in amorphous phase but when sintered at 700 °C or 1200 °C, crystalline phases of zirconia were formed. All the peaks in XRD correspond



(a) (b)

**Figure 2. Particular MWNT before coating: (a) TEM and (b) HRTEM micrographs.**

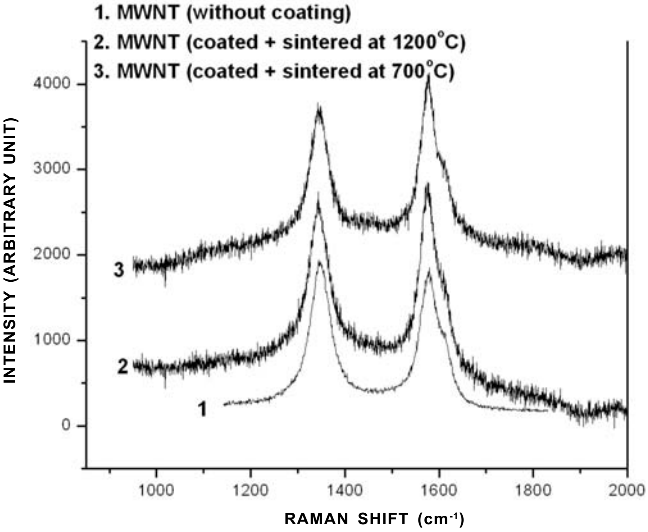


Figure 3. Raman spectroscopy analysis of MWNT without and with coating.

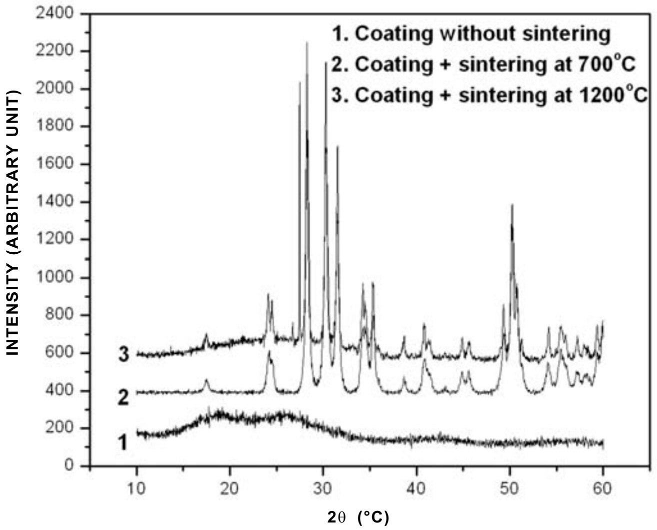


Figure 4. XRD analysis of coated MWNTs before and after sintering.

to $ZrO_2$ phase, which corresponds that no other phase was formed during coating or sintering of the coated-CNTs. Raman spectroscopic analysis of coated and sintered CNTs is shown in Fig. 3. The *D* and *G* bands for the sample sintered at 700 °C are at 1343 $cm^{-1}$ and at 1579 $cm^{-1}$, respectively.

For the sample sintered at 1200 °C, the *D* and *G* bands were observed at 1343 $cm^{-1}$ and at 1577 $cm^{-1}$, respectively. The $I_G/I_D$ ratios for the samples sintered at 700 °C or 1200 °C were 1.05 and 1.02, respectively. Generally due to high temperature treatment of CNTs, $I_G/I_D$ ratio should increase but here it has been observed that there was not so much increase in $I_G/I_D$ ratio which may be due to the fact that all the CNTs are properly coated with zirconia, therefore, these are not exposed to high temperature treatment. The ESEM images of coated-CNTs before and after sintering are shown in Fig. 5. It is observed from Fig. 5(b) that zirconia used for coating the MWNTs are mainly in agglomerate

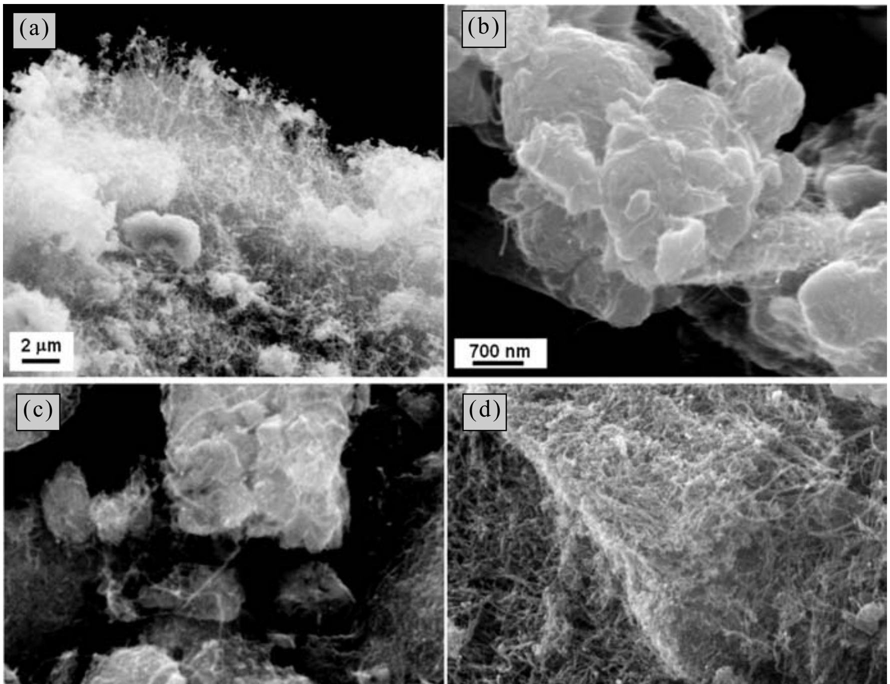


Figure 5. Environmental scanning electron microscope images of MWNTs: (a) without coating, (b) after coating, (c) coated and sintered at 700 °C, and (d) coated and sintered at 1200 °C.

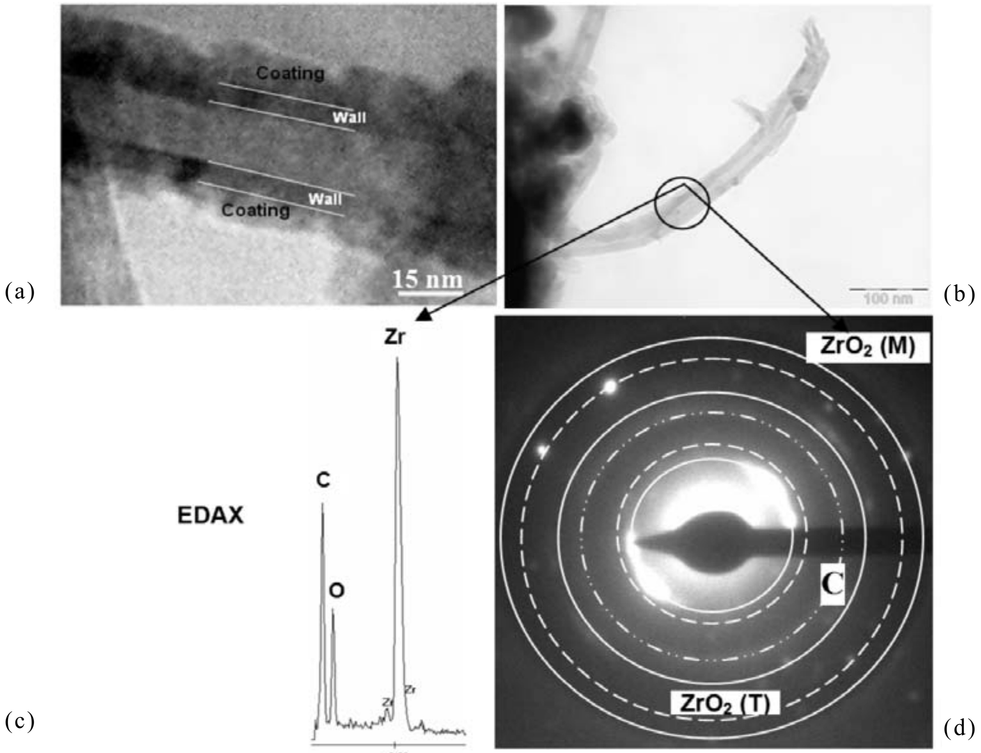


**Figure 6. (a) High magnification and (b) low magnification TEM images of coated and sintered MWNTs, (c) EDAX analysis of the coated-tube showing presence of zirconia and unmarked peaks in the centre are coming from *Cu* grid, and (d) indexed-SAD ring pattern of the tube revealing presence of zirconia in both monoclinic and tetragonal forms.**

form, but after sintering the presence of zirconia agglomerates reduces (Figs 5(c) and 5(d)). This might be due to the fact that zirconia coating on the CNTs adhers well after sintering.

The TEM images of coated-CNTs sintered at 700 $^{o}$C are shown in Figs 6(a) and 6(b). It is seen from the figure that proper coating is there on the CNT and the thickness of the coating is of the order of 10 nm. The EDAX analysis of the tube confirms the presence of zirconia as shown in Fig. 6(c). The SAD pattern from a coated-CNT is shown in Fig. 6(d). Indexing of the pattern validates the presence of zirconia both in monoclinic and tetragonal systems, which are stable at room temperature and at high temperature, respectively. The presence of tetragonal phase is very much important for using these zirconia-coated CNTs for reinforcing in zirconia-toughened alumina composites as during the processing of this material, tetragonal zirconia is converted to monoclinic phase which provides better adhesion between zirconia and alumina.

The TGA result (Fig. 7) shows that blank MWCNTs were almost completely oxidised by 530 °C. Whereas, weight loss of zirconia-coated and sintered MWCNTs starts after 600 °C while coated MWNTs without sintering does not show better oxidation resistance. This is due to the fact that when sintered, zirconia coating on the CNTs has adhered well and offered better oxidation resistance. The TGA curves also show that the MWCNTs coated with zirconia and sintered at 700 °C offer better oxidation resistance at high temperature compared to the coatings sintered at 1200 °C. The reason is attributed to the mismatch in the surface area of the zirconia layer formed with the substrate surface area for the high temperature-coated sample. This phenomenon may be very much similar to alumina coating where surface area of the sintered product depends on the temperature of the treatment. When alumina is sintered at 1200 $^{o}$C, final surface area of the sintered alumina is 10 m$^2$/g whereas for sintering[27] at 800 $^{o}$C, this is 150 m$^2$/g.

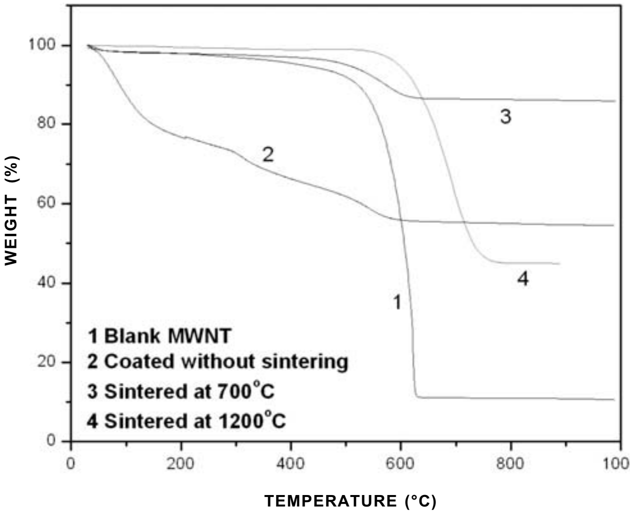


**Figure 7. TGA study showing oxidation resistance of MWNTs in different conditions.**

This has got relevance to the coating performance, as the surface area of the coating should match with the surface area of the substrate. The surface area of the MWCNTs is 150 m$^2$/g, therefore, sintering the coating at 700 °C is preferable as it matches exactly with the substrate surface area. If there is no mismatch in the surface area of the CNTs and the coating, there will be no agglomeration. But, if coated-MWCNTs are sintered at high temperature, the coating layer shrinks and gives lumps of CNTs. Due to this, for sintering at 1200 °C, all the MWCNT surface area is not protected by zirconia layer which make the bare MWCNTs to get exposed to the oxidation environment. This kind of bare CNT's surface is also not good if these ceramic-coated CNTs are to be used in the ceramic matrices as reinforcements. Therefore, proper selection of sintering temperature of coating is important to have better adhesion of the coated-CNTs with the matrix, and thereby, to improve composite properties.

## 4. CONCLUSIONS

The sol-gel method was used to coat MWCNTs with zirconia at room temperature and the coated tubes were sintered at high temperature. Sintering has improved the adhesion of the coating with CNTs and thereby improved its high temperature resistance. It is also observed that the selecting proper sintering temperature is the key to ensure a uniform coating layer on the CNTs. If this process is employed for large quantities with proper process control to remove the excess sol in each coating deposition step, it is possible to control the weight percentage of the coating deposited on the CNT surfaces, and thus, the thickness of the coating. However, these are subject to the ongoing investigation of the authors.

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