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Langmuir, **Just Accepted Manuscript** • DOI: 10.1021/acs.langmuir.5b00866 • Publication Date (Web): 21 May 2015

Downloaded from <http://pubs.acs.org> on May 24, 2015

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(revised version of Langmuir Manuscript ID la-2015-00866p, May 2015)

Unveiling the Role of CNTs on the Phase Formation of 1D Ferroelectrics

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Abstract

Carbon nanotubes (CNTs) have the potential to act as templates or bottom electrodes for three dimension (3D) capacitor arrays, which utilise one dimension (1D) ferroelectric

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3 nanostructures to increase memory size and density. However, growing a ferroelectric
4 on the surface of CNTs is non-trivial. Here, we demonstrate that multi-walled (MW)
5 CNTs decrease the time and temperature for formation of lead zirconium titanate
6 $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) by $\sim 100^\circ\text{C}$ commensurate with a decrease in activation energy
7 from 68 ± 15 kJ/mol to 27 ± 2 kJ/mol. As a consequence, monophasic PZT was obtained
8 at 575°C for MWCNT/PZT whereas for pure PZT traces of pyrochlore were still
9 present at 650°C , where PZT phase formed due to homogeneous nucleation. The
10 piezoelectric nature of MWCNT/PZT synthesised at 500°C for 1 h was proved.
11 Although further work is required to prove the concept of 3D capacitor arrays, our result
12 suggests that it is feasible to utilise MWCNT as templates/electrodes for the formation
13 of 1D PZT nano ferroelectrics.
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23 *Key words:* Carbon nanotubes, nanostructures, one dimension, ferroelectrics, lead
24 zirconate titanate, sol gel, kinetics, activation energy
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3 **1. Introduction**
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5 The major trend in recent years within the electronics industry has been the
6 ability to exponentially decrease the minimum feature size used to fabricate integrated
7 circuits in accordance with Moore’s Law.¹ However, since 2007 the International
8 Technology Roadmap for Semiconductors (ITRS) has addressed functional
9 diversification under the title “More than Moore” which highlights the need for radical
10 new technologies if further miniaturization is to be achieved. The ITRS has specifically
11 suggested that carbon based electronics may offer the potential to fabricate three
12 dimension (3D) nano-arrays using one dimension (1D) ferroelectric nanostructures to
13 increase memory capacity by 10^3 .^{1,2}
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19 The use of CNTs as templates or as bottom electrodes is a potential strategy to
20 realise 3D ferroelectric nanostructures.³⁻⁷ However, in the last years only a few reports
21 on the investigation of multiwall carbon nanotubes (MWCNT) covered with
22 ferroelectrics for 3D capacitors and related applications have been published.^{4, 5, 8-10} The
23 use of MWCNT for this application is limited by the requirement to process
24 ferroelectrics at high temperatures ($> 600\text{ }^{\circ}\text{C}$) in oxidizing atmospheres which results in
25 an exothermic reaction. From our previous studies on the thermal stability of MWCNT
26 in different atmospheres, we have demonstrated that MWCNTs are stable up to $420\text{ }^{\circ}\text{C}$
27 in air but in higher $\text{P}(\text{O}_2)$, they oxidise at $\geq 200\text{ }^{\circ}\text{C}$. However, in low $\text{P}(\text{O}_2)$ (flowing Ar
28 gas) MWCNTs can remain stable up to $1300\text{ }^{\circ}\text{C}$ with minimum sublimation¹¹. Such
29 conditions however, are not ideal for the fabrication of high breakdown strength
30 ferroelectric 1D nanostructures.
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39 In 2007 Kawasaki *et al.*⁴ reported the coverage of aligned MWCNT with lead
40 zirconium titanate (PZT) by Liquid Source Misted Chemical Deposition (LSMCD). The
41 authors found that annealing at $600\text{ }^{\circ}\text{C}$ resulted in damage of the CNT lattice and
42 reaction between the substrate and CNTs. Ashok *et al.*^{5, 12} using pulsed-laser deposition
43 (PLD) under controlled oxygen partial pressure ($70 - 80\text{ mTorr}$) successfully coated
44 MWCNT with PZT at $\sim 550\text{ }^{\circ}\text{C}$, and with $150 - 200\text{ nm}$ $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST) at $650\text{ }^{\circ}\text{C}$.
45 In addition, Yang *et al.*¹³ used PLD to form coaxial multiferroic nanowires of MWCNT
46 with CoFe_2O_3 and BaTiO_3 .
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53 As well as physical vapour deposition (PVD) techniques, chemical solution
54 deposition has also been used to coat MWCNT. In 2009, Bedekar *et al.*^{10, 14} used sol gel
55 to cover MWCNT with BaTiO_3 . Crystalline BaTiO_3 was revealed on the tubes after
56 annealing at $700\text{ }^{\circ}\text{C}$ in nitrogen. In 2012, Mohammadi *et al.*⁹ used MWCNT as a
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sacrificial template to synthesise 1D PZT tubes by sol gel. The early decomposition of MWCNT between 400 - 500 °C was observed and the authors refer to early formation of perovskite (450 °C) but no further information or explanation was provided.

The most significant progress on covering MWCNT with ferroelectrics has happened in last eight years; most of this work relates with covering MWCNT for 1D structure by physical/chemical vapor deposition methods as mentioned above and just a few studies are related to the use of chemical solution deposition methods. Moreover, except the work of Kumar *et al.*¹² no other work studied the ferroelectric properties of the CNT-FE. And the role of MWCNT on the phase formation of PZT as not been so far investigated.

From the above discussion it is clear there is need to pursue this idea and to develop techniques by which the short come of previous studies can be overcome, such as stoichiometry control, carbon lattice damage and siphoning of the using MWCNT as a substrate material. It is also necessary to conduct more systematic characterization of ferroelectric properties.

The practical use of MWCNT as bottom electrodes depends on the ability to retain their geometry and integrity during fabrication.

PZT is commercially used in a large number of microelectronic devices such as ferroelectric memories (FERAMs), electromechanical sensors and actuators, due to its high dielectric constant (~800) and polarisation (40 $\mu\text{C}/\text{cm}^2$) and large piezoelectric ($d_{33} > 300 \text{ pC/N}$) and electromechanical coupling coefficients ($k_{\text{eff}} = 0.42$).¹⁵ However, PZT from conventional solid state reaction requires high temperature, between 900 - 1000 °C¹⁶ and care must be taken to compensate for the volatilization of lead oxide.^{17, 18} PZT has been prepared by chemical methods such as hydrothermal synthesis^{19, 20}, sol gel²¹⁻²³ and co precipitation.¹⁶ These routes guarantee compositional homogeneity at the molecular level and reduce crystallization temperature.

In this work, we coat MWCNT with PZT via a chemical solution process, which offers crystallisation to the perovskite phase at low temperature. Interaction between the PZT and MWCNT as a function of the temperature is studied using thermogravimetric (DTA/TG), X Ray diffraction and microscopy characterisation. The activation energy for the perovskite phase formation is calculated and the role of MWCNT in perovskite crystallization addressed for the first time. The piezoelectric and ferroelectric responses of MWCNT coated with PZT are reported.

2. Experimental

A diol-based sol-gel was utilised to coat MWCNT. Lead acetate (99.5%, Sigma-Aldrich) was mixed with 1-2 propanol diol and acetic acid for 30 min at 60 °C. Titanium (IV) isopropoxide (97 %, Fluka) stabilized with acetyl acetone (1:2 mol ratio) was then added to the lead acetate solution followed by mixing for 30 min at 60 °C. Zirconium (IV) propoxide (70 %, Fluka) stabilized with acetyl acetone (1:2 mol ratio) was subsequently added followed by dilution with acetic acid to obtain a 0.2 M solution containing the correct proportions of Pb, Zr and Ti; more details on the PZT solution preparation are given elsewhere.²⁴

MWCNT used in this work were synthesised by chemical vapour deposition (CVD) and purified by chemical treatment.²⁵ Tubes were functionalized with 5 M nitric acid to improve their wettability. The tubes were between 15 - 60 nm diameters and ~4 µm long. ~5 wt. per cent of MWCNT were immersed in the PZT solution and ultra sonicated for >2 h (Branson, USA, 40 kHz). During the sonication process temperature stay well below 50 °C and no bubbles or precipitations occurred. The solution was then stirred on a hot plate at 70 °C for ~ 1 h and gelation occurred. The gel was dried at 120 °C for 24 h to obtain MWCNT/PZT composite powders. Similar steps were followed to obtain PZT powders.

PZT and MWCNT/PZT powders were characterized by differential thermal and thermo gravimetric analysis (DTA/ TG), carried out in a SETARAM Labsys TG-DTA12 system in air up to 700 °C with heating rate of 5 °C /min. The phase formation of PZT with MWCNT was followed by in situ XRD (Philips X'' Pert. Cu, $K\alpha$), carried out in air at 5 °C/min up to 650 °C with recording or dwell time of 13 - 14 min at each probe temperature. Ex-situ XRD (Rigaku, Geigerflex D/Max-C, Cu $K\alpha$) was used to characterize MWCNT/PZT powders heated 1 h at various temperatures. All the samples investigated in the present studies were heat treated in alumina crucibles covered with platinum foils. These MWCNT/PZT composites were further studied by Fourier Transform Infra Red (FTIR) spectroscopy (Mattson Mod 7000 FTIR spectrometer) and transmission electron microscopy (TEM) (Hitachi Microscope, Model H9000-NA and JEOL, Model 2200 FS).

The piezoelectric and ferroelectric response of MWCNT/PZT were investigated by Scanning Probe Microscopy, using an Atomic Force Microscope (AFM, Multimode Nanoscope III A), equipped with external lock-in amplifier for measuring piezo

response. Si cantilevers with platinum coating (force constant 2.4 Nm^{-1} and resonant frequency 80 kHz , MIKROMASCH) were used with an applied voltage of 5 V . Topography signals of the samples were taken simultaneously with the amplitude and phase signals and were collected in contact mode. Several hysteresis loops with bias from -40 to $+40 \text{ V}$ were obtained for each sample to ensure the reproducibility of the results, and representative loops are presented. Switchable polarization corresponds to the difference between the positive saturation polarization and negative ones ($R_m = (R_S)^+ - (R_S)^-$). As the effective piezoelectric coefficient ($(d_{33})_{\text{eff}}$) is proportional to the amplitude signal, this can be defined as $(d_{33})_{\text{eff}} \propto (\text{amplitude signal} \cdot \cos(\text{phase signal})) / V_{\text{ac}}$, where V_{ac} is the ac voltage applied.

3. Results and Discussion

Figure 1 illustrates the DTA traces conducted in air at different heating rates (5 , 10 , 20 and $30 \text{ }^\circ\text{C/min}$) for PZT (continuous line) and MWCNT/PZT samples (dashed line). For PZT heated at $5 \text{ }^\circ\text{C/min.}$, there is a small broad exothermic peak at $\sim 200 \text{ }^\circ\text{C}$ related to the release of low temperature organics. Between 200 and $350 \text{ }^\circ\text{C}$, a further broad exothermic peak occurs, attributed to the combustion of organic solvents. On increasing temperature, the next broad exotherm lies between $420 \text{ }^\circ\text{C}$ - $570 \text{ }^\circ\text{C}$ and corresponds to the formation of pyrochlore phase²⁶ followed by transformation to perovskite observed as a small shoulder at $505 \text{ }^\circ\text{C}$.

However, for MWCNT/PZT heated at $5 \text{ }^\circ\text{C/min}$, the broad exothermic peak corresponding to the formation of the pyrochlore phase begins at $\sim 350 \text{ }^\circ\text{C}$, $\sim 80 \text{ }^\circ\text{C}$ lower than PZT. Moreover, the transformation to perovskite is complete by $480 \text{ }^\circ\text{C}$ for MWCNT/PZT as opposed to $570 \text{ }^\circ\text{C}$ for PZT. According to our previous studies, the exothermic peak for the oxidation of MWCNT starts at $\sim 420 \text{ }^\circ\text{C}$ ¹¹ but in the present study this peak is not observed since it overlaps with that of pyrochlore and perovskite phase formation. From the TG analysis of PZT and MWCNT/PZT samples, four major weight loss events (I, II, III and IV) are identified (Figure 1b). The first (I), an exothermic event with $\sim 2 - 10 \text{ wt.}\%$ loss, occurs below $200 \text{ }^\circ\text{C}$ due to the evaporation of water and solvents. The second (II), also exothermic but with ~ 25 and $20 \text{ wt.}\%$ loss for PZT and MWCNT/PZT, respectively, occurs in the range 200 to $300 \text{ }^\circ\text{C}$ due to the combustion of organics. The third (III), $\sim 6\%$ for PZT between $300 \text{ }^\circ\text{C}$ and $450 \text{ }^\circ\text{C}$, may relate to the decomposition of residual organics. For PZT, a small additional weight

loss, ~3% is observed up to 560 °C (IV). For MWCNT/PZT above 400 °C, the weight loss is higher than that observed for PZT and is continuous up to 750 °C. According to our previous studies, oxidation of MWCNT occurs up to ~750 °C. In comparing the TG spectra of PZT and MWCNT/PZT the observed difference in the weight loss is ~5 %, which is approximately the wt.% MWCNT added in the MWCNT/PZT samples. Nonetheless, it is evident the formation of pyrochlore and perovskite phases takes place at lower temperature for the case of MWCNT/PZT in comparison with PZT.

To study further the phase formation, *in-situ* XRD was carried out on both PZT and MWCNT/PZT powders (Figure 2). For PZT, peaks attributed to pyrochlore appear at ~500 °C with perovskite at 550 °C (Figure 2a). However, for MWCNT/PZT small peaks ascribed to pyrochlore and perovskite appear at 450 °C. Moreover, for MWCNT/PZT perovskite peaks become sharper as temperature increases (Figure 2b) with monophasic PZT obtained at 575 °C. In contrast, for PZT, traces of pyrochlore are still identifiable at 650 °C.

(a)

(b)

Figure 1 (a) DTA and (b) TG analysis of PZT (continuous line) and MWCNT/PZT (dashed line) heat treated at different heating rates: 5, 10, 20 and 30 °C/min. DTA clearly evidences the early appearance of exothermic peaks associated with the formation of pyrochlore and perovskite around 350 °C for MWCNT/PZT samples in comparison to PZT (420 °C).

(a)

(b)

Figure 2 In-situ XRD patterns of (a) PZT and (b) MWCNT/PZT acquired from room temperature to 650 °C with an heating rate of 5 °C/min. Monophasic perovskite phase was obtained at 550 °C for MWCNT/PZT samples but was not obtained up to 650 °C for PZT.

Ex-situ XRD traces of samples calcined 1 h at different temperatures are presented in Figure 3. For MWCNT/PZT annealed at 400 °C, the volume fraction of PZT perovskite phase is enhanced when compared with in-situ XRD of MWCNT/PZT at 400 °C. For MWCNT/PZT annealed 1 h at 500 °C, only peaks associated with perovskite are present. Further increasing the annealing temperature to 550 °C sharpens the perovskite peaks, presumably due to an increase in scattering coherence length related to grain growth.

FTIR spectra of MWCNT and MWCNT/PZT samples (annealed 1 h at 400, 450, 500 and 550 °C) are shown in Figure 4. The spectrum of MWCNT has one major characteristics peaks at 1630 cm^{-1} . The transmittance bands at 3448 cm^{-1} and around 1580 cm^{-1} correspond to the stretching of O-H and C-H bonds and its occurrence in all the samples confirms the presence of organics. For MWCNT/PZT the bands at 1640 cm^{-1} and 1315 cm^{-1} correspond to acetic acid or acetate²⁷ and bands at 1436 and 1560 cm^{-1} are attributed to symmetric and asymmetric -COO^- stretching modes of the acetate groups²⁸.

Figure 3 Ex-situ XRD patterns obtained for MWCNT/PZT samples, annealed 1 h at 400, 450, 500 and 550 °C. Note the simultaneous appearance of pyrochlore and perovskite phase after 1 h at 400 °C and monophasic perovskite after 1 h at 550 °C.

MWCNT/PZT heat-treated at 400–450 °C exhibits additional peaks identified as an intermediate acetate salt whose bands occur at 1050, 1020, 940, 860, 666 and 620 cm^{-1} . The intensity of these peaks diminishes for MWCNT/PZT samples heated 1 h at 500 °C but there are additional peaks at $\sim 588 \text{ cm}^{-1}$ and 349 cm^{-1} . These two transmittance peaks are attributed to TiO_6 and ZrO_6 stretching and bending of the octahedra, respectively, confirming the formation of perovskite²⁹. MWCNT/PZT sample heated 1 h at 550 °C do not depict characteristic peaks of MWCNT and intensity of octahedral peaks further strengthen. The combination of XRD (*in-situ* and *ex-situ*), DTA/TG and FTIR studies clearly indicates that the presence of MWCNT facilitates the crystallization process of PZT and reduces the crystallization temperature by $\sim 100 \text{ }^\circ\text{C}$. However, the mechanism of PZT formation and the growth of the perovskite phase required further study using TEM.

Figure 4 FTIR spectra of MWCNT and MWCNT/PZT samples annealed 1h at 400, 450, 500 and 550 °C. The characteristic peaks of MWCNT at 1630 cm^{-1} and at 349 and 588 cm^{-1} are from octahedra of Zr and Ti and indicate the formation of a crystalline PZT.

Figure 5a is a TEM micrograph of MWCNT/PZT, dried 24 h at 100 °C, which illustrates the conformal covering of MWCNT with an amorphous PZT sol and also depicts the presence of some particulates. This sample was further analysed under high resolution TEM (HRTEM). Crystalline particles with d spacing of ~ 0.30 nm surrounded by an amorphous network are observed (Figure 5b). EDS spectra confirmed the presence of lead, zirconium and titanium (inset of Figure 5b). Similar observations have been previously reported in the literature for the growth of BaTiO_3 and ZnO . In these studies *in situ*-HRTEM indicated that Ba and Zn ions were entrapped in the amorphous network of the respective organics prepared by sol gel^{30, 31}.

In TEM micrographs of MWCNT/PZT annealed 1 h at 400 °C (Figure 5c), amorphous and crystalline phases are observed which corroborates previous XRD and FTIR analyses and confirmed the presence of perovskite and PZT. The MWCNT (diameter ~ 100 nm) have been coated with a crystalline phase of dark contrast, presumably perovskite.

The TEM images of MWCNT/PZT samples annealed 1 h at 500 °C reveal crystalline tubes of ~ 50 nm having d spacing = 0.28 nm consistent with d_{110} PZT, Figure 5d. EDS spectra (inset in Figure 5d) confirm the presence of lead, zirconium and titanium. HRTEM micrographs from one of the MWCNT covered with PZT is

illustrated in Figure 5e and reveal the MWCNT lattice (inset Figure 5e) with d spacing ≈ 0.34 nm and d_{001} PZT ≈ 0.40 nm. After annealing at 500 °C, HRTEM proves the tubes are intact, covered in a crystalline phase with d spacings characteristic of d_{001} and d_{110} PZT.

(a)

(b)

(c)

(d)

(e)

Figure 5 TEM images of MWCNT/PZT samples showing: (a) as dried sample with a conformal covering of amorphous PZT on MWCNT; (b) HRTEM micrograph of an amorphous sol accompanied by an inset EDS spectra confirming the presence of Pb, Zr, O and Ti (Cr and Cu are from sample holder); (c) a micrograph of sample annealed 1 h at 400 °C showing tubular shaped rods of ~100 nm with dark contrast; (d) a sample annealed 1 h at 500 °C illustrating long range crystalline regions of perovskite along with an inset EDS spectra confirming the presence of Pb, Zr, O and Ti and (e) a HRTEM micrograph illustrating coated MWCNT (the red circle and the inset magnified view depicts the MWCNT lattice spacing of 0.34 nm and d_{100} for PZT (0.40 nm)).

From the above TEM images, it is evident that the crystallisation of PZT is triggered by the MWCNT whose surfaces act as nucleation sites for the perovskite phase. This mechanism implies that the MWCNT lower the activation for perovskite PZT formation. The activation energy of phase formation of PZT and MWCNT/PZT may be calculated by applying the Kissinger equation³² to data from DTA (Table 1).

The maximum energy change associated with the combustion of organics, formation of pyrochlore and perovskite phase is calculated from the DTA peaks (heating rate of 5 °C/min), marked as: i) A (combustion of organics), B (pyrochlore) and C (perovskite), corresponding to 254, 453 and 505 °C, respectively for PZT (Figure 6 a) and ii) A', B' and C', corresponding to 265, 366 and 395 °C, respectively for MWCNT/PZT (Figure 6b). A Gaussian function was used to fit the DTA data for different heating rates and the associated maximum energy change (together with measurement error) are indicated in Table 1.

Kissinger's model assumes that the reaction is of first order and irreversible in nature. The calculation of the activation energy is based on the temperature at which the maximum mass loss occurs, for different heating rates and is expressed as³²:

$$\frac{d(\ln\alpha/T_p)}{d(T_p)} = \frac{E_a}{R}$$

where α stands for the heating rate (5, 10, 15 and 20 °C/min in the present study), E (kJ/mol) for the activation energy for the reaction, R (J/mol K) for the gas constant and T_p (kelvin) for peak temperature. The T_p was calculated from peak fitting and the activation energy from the slope of the variation of $\ln(\alpha/T_p)$ as a function of $1/T_p$. The activation energy for pyrochlore and perovskite phase for PZT is 248±29 kJ/mol and 68±15 kJ/mol, respectively and for MWCNT/PZT is 158±25 kJ/mol and 27±2 kJ/mol, respectively. As anticipated, the activation energy for the formation of both the pyrochlore and perovskite phase is lower for MWCNT/PZT in comparison to PZT. As shown in Figure 6 a good fitting is obtained for all the peaks. A certain uncertainty may be associated with peak A fitting, due to the combustion of the different organics present in precursor powders, still the error associated is limited.

Table 1: DTA peaks for PZT and MWCNT/PZT samples and activation energy calculated from Kissinger equation for oxidation of organics, pyrochlore and perovskite.

Heating Rate (°C/min)	Phase	Temperature of maximum energy change for PZT	Temperature of maximum energy change for MWCNT/PZT
5	organic	254	265
	pyrochlore	453	366
	perovskite	505	395
10	organic	266	276
	pyrochlore	464	386
	perovskite	587	484
15	organic	272	279
	pyrochlore	467	390
	perovskite	596	523
20	organic	278	286
	pyrochlore	476	395
	perovskite	613	582
Activation Energy (kJ/mol) for PZT sample			
pyrochlore		perovskite	
248±29		68±15	
Activation Energy (kJ/mol) for MWCNT/PZT			
pyrochlore		perovskite	
158±25		27±2

(a)

(b)

Figure 6 Gaussian fitting of differential thermal analysis peaks of (a) PZT and (b) MWCNT/PZT samples with an heating rate of 5 °C/min, marked with A (A'), B (B') and C (C') that corresponds to the maximum energy change during the combustion of organics, formation of pyrochlore and perovskite, respectively.

The origin of the lower of activation energy may be explained by a combination of factors. The presence of high surface area of the tubular MWCNT may act as heterogeneous nucleation sites for the oxide crystallization at low temperatures, reducing the activation energy for PZT in the presence of MWCNT. The perovskite formation in PZT is a sequential transition through an intermediate pyrochlore/fluorite phase. The transformation of pyrochlore into perovskite is a nucleation-controlled process where the perovskite nucleation is the rate-controlling step^{33, 34}. If the

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nucleation energy is reduced the crystallization temperature of the perovskite phase is lowered. Indeed, low processing temperature can be obtained if the underlayer provides heterogeneous nucleation sites³⁵⁻⁴¹. However, this seeding effect of MWCNT has not previously been reported. In fact, the result is somewhat unexpected, as C-based compounds have not traditionally been considered for nucleation or for substrates for these perovskite materials. In addition, the local increase in temperature in the vicinity of the MWCNT due to exothermic oxidation may also contribute to the overall lowering of the activation energy. MWCNT start to oxidize at 420 °C and around this temperature there is the simultaneous appearance of pyrochlore and perovskite phase. Nevertheless, some part of the MWCNT remain intact up to ~500 °C (Figure 5), which indicates they may be only locally oxidized, confirming the TG observations.

From the application point of view the electrical response of MWCNT/PZT is important, therefore the local piezoelectric and ferroelectric behaviour of MWCNT/PZT annealed at 500 °C for 1 h were investigated through vertical piezoresponse force microscopy (VPFM). Figure 7 represents the topography (inset in Figure 7a) and VPFM phase image (Figure 7a) of individual MWCNT/PZT tube of 80 nm in width and 180 nm in length. Phase response depicts the clear dark contrast from the tube, indicating that polar domains are aligned in the opposite direction to the applied field. MWCNT/PZT annealed at temperatures below 500 °C do not present piezoelectric response related to their incipient degree of crystallinity. The line profile analysis, corresponding to the topography and phase signals rules out topography effects on the acquired PFM signal (Figure 7b). The local hysteresis loops obtained from MWCNT/PZT depict the typical ferroelectric polarization behaviour, though with poor saturation up to applied dc bias of 40 V (Figure 7c). Various ferroelectric loops were acquired in different areas and a similar behaviour was observed. PFM measurements prove the piezoelectric and ferroelectric nature of the obtained MWCNT/PZT and that the polarization direction can be reversed with the applied field as needed for memories.

(a)

(b)

(c)

Figure 7 (a) Micrograph of VPFM phase response and topography (inset), (b) line profile from the marked area of phase and topography from MWCNT - PZT nanotube with domain 80 nm in width and 180 nm long, annealed at 500 °C 1 h. Representative remanent local hysteresis loops (c). PFM measurements prove the piezoelectric and ferroelectric nature of the obtained MWCNT - PZT.

4. Conclusions

In this study we report that ferroelectric perovskite PZT can be deposited by sol gel at low temperatures on MWCNT. A systematic study on the phase formation process by in-situ and ex-situ XRD, DTA, FTIR and HRTEM detected perovskite phase formation in the presence of the MWCNT at ~100 °C lower than without, accompanied by a decrease in activation energy from 68±15 kJ/mol for PZT and 27±2 kJ/mol. As a consequence, monophasic PZT was obtained at 575 °C for MWCNT/PZT whereas for PZT traces of pyrochlore are still identifiable at 650 °C. We proposed that MWCNT act as seeds to reduce the nucleation barrier of perovskite phase formation by providing the low energy nucleation sites and the exothermic oxidation of MWCNTs. In addition the piezoelectric nature of MWCNT/PZT synthesised at 500 °C / 1 h was proved. The results are of particular relevance in 3D ferroelectric nano capacitors in which MWCNTs are proposed as bottom electrodes.

Acknowledgements

The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT), Fundo Europeu de Desenvolvimento Regional Portugal (FEDER), QREN-COMPETE Portugal, and the Associate Laboratory CICECO (PEst-C/CTM/LA0011/2013) for funding support. Amit Mahajan acknowledges FCT for financial support (SFRH / BD / 65415 / 2009). The financial support of the OTKA NN 110676, TÁMOP-4.2.2.A-11/1/KONV-2012-0047 and TÁMOP-4.2.2.A-11/1/KONV-2012-0060 projects is also acknowledged.

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Figure caption:

Figure 1 (a) DTA and (b) TG analysis of PZT (continuous line) and MWCNTs/PZT (dashed line) heat treated at different heating rates: 5, 10, 20 and 30 °C/min. DTA clearly evidences the early appearance of exothermic peaks associated with the formation of pyrochlore and perovskite around 350 °C for MWCNT/PZT samples in comparison to PZT (420 °C).

Figure 2 *In-situ* XRD patterns of (a) PZT and (b) MWCNT/PZT acquired from room temperature to 650 °C with an heating rate of 5 °C/min. Monophasic perovskite phase was obtained at 550 °C for MWCNT/PZT samples but was not obtained up to 650 °C for PZT.

Figure 3 *Ex-situ* XRD patterns obtained for MWCNT/PZT samples, annealed 1h at 400, 450, 500 and 550 °C. Note the simultaneous appearance of pyrochlore and perovskite phase after 1 h at 400 °C and monophasic perovskite after 1h at 550 °C.

Figure 4 FTIR spectra of MWCNT and MWCNT/PZT samples annealed 1h at 400, 450, 500 and 550 °C. The characteristic peaks of MWCNT around 1630 cm⁻¹ and at 350 and 590 cm⁻¹ are from octahedra of Zr and Ti and indicate the formation of a crystalline PZT.

Figure 5 TEM images of MWCNT/PZT samples showing: (a) as dried sample with a conformal covering of amorphous PZT on MWCNT; (b) HRTEM micrograph of an amorphous sol accompanied by an inset EDS spectra confirming the presence of Pb, Zr, O and Ti (Cr and Cu are from sample holder); (c) a micrograph of sample annealed 1h at 400 °C showing tubular shaped rods of ~100 nm with dark contrast; (d) a sample annealed 1 h at 500 °C illustrating long range crystalline regions of perovskite along with an inset EDS spectra confirming the presence of Pb, Zr, O and Ti and (e) a HRTEM micrograph illustrating coated MWCNT (the red circle and the inset magnified view depicts the MWCNT lattice spacing of 0.34 nm and d₁₀₀ for PZT (0.40 nm)).

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Figure 6 Gaussian fitting of differential thermal analysis peaks of (a) PZT and (b) MWCNT/PZT samples with a heating rate of 5 °C/min, marked with A (A'), B (B') and C (C') that corresponds to the maximum energy change during the combustion of organics, formation of pyrochlore and perovskite, respectively.

Figure 7 (a) Micrograph of VPFM phase response and topography (inset), (b) line profile from the marked area of phase and topography from MWCNT - PZT nanotube with domain 80 nm in width and 180 nm long, annealed at 500 °C 1 h. Representative remanent local hysteresis loops (c). PFM measurements prove the piezoelectric and ferroelectric nature of the obtained MWCNT - PZT.

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