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Synthesis and crystallization of lead-zirconium-titanate (PZT) nanotubes at the low temperature using carbon nanotubes (CNTs) as sacrificial templates

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ABSTRACT

Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT) nanotubes with diameters of 80–100 nm and a wall thickness of 15–20 nm were prepared by sol–gel template technique and using multi-walled carbon nanotubes (MWCNT) as sacrificial templates. The coating process of MWCNT with PZT precursor sol and removal of the carbon nanotubes by an interrupt heat treatment were discussed and studied by Raman spectroscopy. Simultaneous thermal analysis (STA) revealed that PZT nanotube crystallized at the low temperature of 410 °C by the significantly low activation energy of crystallization of 103.7 kJ/mol. Moreover, based on the X-ray diffraction (XRD) pattern and selected area electron diffraction pattern the crystal structure of the PZT nanotube was determined as perovskite. High resolution transmission electron microscope (HRTEM) and field-emission scanning electron microscope (FE-SEM) images proved that the final PZT had a tubular structure.

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1. Introduction

Lead zirconium titanate (PZT), a solid solution of the perovskites lead zirconate and lead titanate, is a prominent ferroelectric material that has stimulated tremendous fundamental and applied research due to its high spontaneous polarization abilities, piezoelectric coefficient, dielectric permittivity and pyroelectricity [1,2]. The highest values for both, the piezoelectric coupling coefficient (k_p) and the permittivity (ε_r) have been observed for chemical composition of Pb(Zr_{0.52}Ti_{0.48})O₃, the so-called morphotropic phase boundary (MPB), at which the rhombohedral and tetragonal phases coexist [3,4]. The reason for this behaviour is currently believed to be the relatively large ionic displacements associated with stress, although various other mechanisms have also been proposed.

One-dimensional (1D) nanostructures of ferroelectric materials exhibit significant properties which recently motivated many indepth researches on potential applications [5–7]. Synthesis of 1D PZT nanostructures has attracted significant attention due to the ferroelectric properties of the material. The presence of ferroelectric properties and domains in the nano dimension is the key of having such modern applications since usually decreasing the size of most ferroelectrics leads in vanishing of the ferroelectric properties [8]. Determining the ferroelectric properties of 1D

E-mail addresses: mrm41@cam.ac.uk, mohammadi@sharif.edu (M.R. Mohammadi). nanostructures needs developing modeling theories and piezoresponse force microscopy measurements. Applications of PZT nanotubes include tunable photonic crystals, ferroelectric random access memories, terahertz emission, fluidic delivery, nanosensors and NEMS [9–12]. Arrays of PZT nanotubes could be exploited in ferroelectric random access memory (FRAM) devices [13] due to a unique polar axis of each tube in the array that can be inversed in direction by application of external electric field. In addition, the significant need of miniaturization of electronic devices leads to more extensive usage of PZT FRAMs based on nanotubes.

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Amongst many suitable methods for the preparation of nanostructured PZT materials, including magnetron sputtering, pulsed laser deposition, chemical vapor deposition (CVD), photochemical deposition [14–17], sol–gel process is one of the promising routes, as it leads to materials with high chemical homogeneity and purity at comparably low temperatures [18–21]. PZT nanotubes have only been produced so far by using anodic aluminum oxide (AAO) templates, which was coated by a sol–gel process and subsequently removed with concentrated NaOH, [9,21,22]. This technique provides vertically aligned pores, rather than individual tubes, requires high temperature processing and in addition allows little control over pore width and wall thickness. Therefore, in the present work we demonstrate how CNTs can be used as templates to produce PZT nanotubes at the low temperature with good control of morphology and dimensions.

MWCNTs have been frequently used as sacrificial templates for the preparation of metal oxide nanowires and nanotubes, such as

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Al₂O₃, SiO₂, Fe₂O₃, ZrO₂, TiO₂, ZnO, CeO₂ and etc. [23–28]. This method is a two step process comprising of (a) coating of MWCNTs with the target material and (b) subsequent combustion of

MWCNTs. This synthesis route has a significant potential for synthesis of almost all oxides in various nanostructures such as, nanotubes, nanowires, nanobeads and also nanocomposites. The



Fig. 1. Simultaneous thermal analysis of CNT-PZT hybrid at the rate of (a) 5 °C/min, (b) 10 °C/min, (c) 15 °C/min, (d) 20 °C/min and (e) 25 °C/min. Exothermic peaks are shown upward.

Table	1

Description of peak position and weight loss of CNT-PZT hybrid determined by STA analysis.

Heating rate (°C/min)	Stage	Peak position (°C)	Weight loss (%)
5	Water evaporation	RT-200	5
	Decomposition of organic compounds	268	21
	CNT combustion	407	20
10	Water evaporation	RT-200	5
	Decomposition of organic compounds	288	25
	CNT combustion	427	21
15	Water evaporation	RT-200	6
	Decomposition of organic compounds	300	23
	CNT combustion	430	21
20	Water evaporation	RT-200	5
	Decomposition of organic compounds	304	22
	CNT combustion	452	20
25	Water evaporation	RT-200	4
	Decomposition of organic compounds	308	22
	CNT combustion	463	20

technique promises a faster and easier route to obtain the desired structure with more accurate geometry in the nano scale in comparison to other techniques for preparation of similar nanostructures or nanocomposites [29-33]. Virtually all morphological features of the oxide nanotubes can be controlled with this route, such as the length and inner diameter by the dimensions of the CNTs, the wall thickness by the CNT to metal precursor ratio and the particle size by various sol-gel process parameters. In comparison to the above mentioned simple oxides, the synthesis of highly complex PZT in nanotubular form by this method involves additional challenges; to obtain uniform coating of PZT on CNTs and the desired phase composition. In the present work we report, for the first time, the synthesis of PZT nanotubes using MWCNT as a template. The aim of this study is preparation of uniform and soundness PZT nanotube by controlling the processing parameters of the present method.

2. Experimental

2.1. Template

MWCNTs were produced by a modified CVD process in a tube furnace at a reaction temperature of 760 °C. A mixture of 4.0 wt.% ferrocene as catalyst precursor and toluene as the carbon feedstock was continuously injected at a rate of 5.6 ml/hour into the quartz tube using argon as a carrier gas. The collected CNTs are vertically aligned ("carpets") with an average outer diameter of 70–90 nm and lengths around 30–50 μ m.

2.2. Sol preparation and coating process

A conventional sol-gel process was used to synthesize PZT in the desired chemical composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$. Lead (II) acetate trihydrate, titanium (IV) isopropoxide, and zirconium (IV) propoxide (70 wt.% in propanol) were used as metal precursors, while acetic acid, 1,2-propanediol, acetyl acetone and benzyl alcohol were used as solvents. Briefly, lead (II) acetate, acetic acid and 1,2-propanediol were refluxed at 100 °C for 1 h to obtain Pb sol. A solution of zirconium (IV) propoxide in 1,2-propanediol was added into the Pb sol and the resulting mixture was refluxed at 80 °C for 1 h to obtain Pb-Zr sol. Finally, titanium (IV) isopropoxide was dissolved in acetyl acetone, added to the combined Pb–Zr sol and refluxed at 70 °C for 1 h.

The hydrophobicity of the CNTs is known to hamper the deposition of any hydrophilic metal oxide coatings. A common route to alter their chemical nature is the partial oxidation of the surface with HNO₃ and H₂SO₄ [34]. This acid-treatment introduces a variety of hydrophilic functional groups, such as hydroxyl and carboxyl groups, but does, however, not allow sufficient control over their number, type and location (i.e. side-walls vs. tip) [35]. As a consequence, the oxide coatings are often irregular and incomplete. Therefore, we used an alternative route, which was recently introduced for the coating of pristine CNTs with TiO₂ [36], that does not require covalent functionalisation. In this process, benzyl alcohol is used as a linking agent that adsorbs on the hydrophobic CNT surface via π - π interactions with its benzene ring, while at the same time rendering it hydrophilic by providing a high density of hydroxyl groups. The weight ratio of the materials for functionalizing was MWCNT:BA = 1:25. The functionalized MWCNTs were coated with PZT sol with weight ratio of MWCNT:PZT = 1:5.

2.3. Template removal and characterization

Simultaneous thermal analysis (STA) was carried out for ascoated MWCNT, using TA Instruments Q600. The activation energy of crystallization of PZT-MWCNT hybrid material was calculated by STA analysis at various heating rates. It was found that PZT nanotube are formed by an interrupt annealing process at the rate of 5 °C/min up to 430 °C rather than a continuous annealing treatment. Therefore, the sample was heated at a rate of 5 °C/min up to 100, 200, 300, 400 and 430 °C and held at these temperatures for 1 h. In some experiments, the sample was kept at 430 °C for an additional hour to ensure complete crystallization and simultaneous removal of MWCNTs. The structure and chemical composition of the samples were characterized by X-ray diffraction (XRD) (Philips X'pert PW3020, Cu- K_{α} radiation) and EDS mapping using transmission electron microscopy (TEM) (JEOL HRTEM 3010). Additionally, Raman spectroscopy was carried out by a WITec GmbH CRM200 confocal Raman microscope under Nd-doped YAG laser of excitation wavelength of 633 nm. The morphology of the samples was characterized using a field emission microscope (FE-SEM) FEI Ouanta 200 F and a high resolution transmission electron microscope (HRTEM) JEOL 3010.

3. Results and discussion

Fig. 1 illustrates STA results of as-coated MWCNT at various heating rates, namely 5, 10, 15, 20 and 25 °C/min. It can be ob-



Fig. 2. Starink's plot for calculation of crystallization activation energy. The inset shows approximation of E_{a} . The estimate error was about 2%.



Fig. 3. XRD patterns of (a) CNT-PZT hybrid, (b) PZT nanotube and (c) PZT powder annealed at 500 $^\circ C.$

served that, all samples showed weight loss less than or about 5 wt.% below 200 °C with no distinct peak. This weight loss is probably due to the gradual evaporation of physisorbed water and other solvents. It is believed that a gradual evaporation of water with a constant rate occurs up to 200 °C due to the constant slope of the weight loss curve between room temperature and 200 °C. Since the amount of weight loss is relatively small, it can be deduced that less material was evaporated relative to the whole sample and evaporation occurred continuously and constantly in a wide range. Therefore, no sharp endothermic peak is observed. Above 200 °C there is a broad exothermic peak at 269, 288, 300, 304 and 308 °C for the heating rates of 5, 10, 15, 20 and 25 °C/ min, respectively. These peaks which are accompanied by 20-25 wt.% weight loss can be related to combustion of chemisorbed organic compounds. The sharp exothermic peak at 410 °C for the heating rate of 5 °C/min (and at 427 °C for 10 °C/min, 433 °C for 15 °C/min. 453 °C for 20 °C/min. and 465 °C for 25 °C/min) is related to amorphous to crystalline phase transformation of PZT (as confirmed by XRD analysis) and burning out of MWCNTs. The weight loss around 20 wt.% for all samples corresponds well with the initial CNT:PZT ratio in the sol. The peak position and weight loss are listed in Table 1. In comparison to the reported crystallization temperatures of sol-gel derived PZT powders and films (i.e., around 500 °C) [37,38], we succeeded to produce PZT nanotubes at the low temperature of 410 °C. Besides controlling the phase structure, composition homogeneity and microstructure, the cost of the product is also an important concern. Therefore, reducing the crystallization temperature of PZT nanotube may reduce the total cost of the production and, therefore, has a good potential for industrial application.

The oxidation temperature of CNTs in the presence of PZT is remarkably decreased compared with the uncoated CNTs (~670 °C). This phenomenon is attributed to a self-catalysed process, upon which the metal oxide coating aids the oxidation of CNTs via lattice oxygen following a Mars-van Krevelen type mechanism. Depending on the type of metal oxide, the oxidation temperature of MWCNTs can be increased (i.e. Al_2O_3) or decreased to values as low as 330 °C (i.e. Bi_2O_3). It the present case, the CNT oxidation proceeds at roughly the same temperature as the crystallization. It is thus likely, that the heat released upon PZT crystallization aided further the oxidation of carbon nanotubes.

The activation energy of crystallization can be calculated by semi-empirical formulae proposed by Kissinger [39], Ozawa [40] and the modified type by Starink [41]. The activation energy of crystallization of PZT nanotubes was calculated by the Starink's modified formula, as plotted in Fig. 2:

$$\ln\left(\frac{\beta}{T_f^{1.8}}\right) = -A\frac{E_a}{RT_f} + \cos\tan t \tag{1}$$

where β is heating rate in *K*/min, T_f is peak temperature of transformation in *K*, *R* is gas constant, E_a is activation energy in J/mol and $A = 1.007 - 1.2 \times 10^{-5} \dot{E}_a$ \dot{E}_a is determined by the plot slope of $\ln(T_f^{1.8}/\beta)$ versus $1/RT_f$. The activation energy of crystallization is then calculated to be 103.7 kJ/mol which is significantly lower than the values reported for sol–gel derived PZT powders and films (i.e.,



Fig. 4. Raman Spectra of pristine CNT, CNT-PZT hybrid and PZT nanotube.



Fig. 5. FE-SEM micrographs PZT nanotube.

141–494 kJ/mol) [42,43]. The estimated error of STA measurements was around 2% and was determined by the standard deviation of several measurements. Although the activation energy of crystallization of sol-gel derived materials depends on nature of the precursors, preparation method and the final geometry of the product, this significantly low value can be explained firstly, due to the nanosized grains which provide high surface area to volume ratios and increasing the total surface energy and secondly, due to the synergistic effect of simultaneous oxidation of MWCNTs and crystallization of PZT. Moreover, CNT is an excellent thermal conductive material and eliminates heat transport limitations as a part of the activation barrier. Consequently, the apparent activation energy of crystallization of PZT nanotube was decreased down to 103.7 kJ/mol. From the economical point of view, the activation energy of crystallization is an important factor. The lower the activation energy of crystallization, the lower cost of the final product.

Kinetics of crystallization of sol-gel derived PZT materials is believed to follow Avrami-type equations.

XRD pattern of as-coated MWCNTs (Fig. 3a) shows a peak at $2\theta = 26.4^{\circ}$ that corresponds to the diffraction from (0 0 2) planes of MWCNTs [44]. The absence of other diffractions indicates that the PZT coating is amorphous at this stage. XRD pattern of PZT nanotube annealed at 430 °C (Fig. 3b) is completely different form that of CNT-PZT hybrid, corresponding to Pb(Zr_{0.52}Ti_{0.48})O₃ composition (matched with JCPDS card number 73–2022) with perovskite structure. Furthermore, the absence of the (0 0 2) peak from CNTs clearly confirms the removal of the template via combustion, in line with the STA results. It is important to note that despite the complexity of PZT it was indeed possible to obtain a coating with the desired chemical composition by the presented method.

The average crystallite size of PZT material was calculated by the Scherrer equation [45]:



Fig. 6. (a) TEM image of pristine CNT and (b) HRTEM lattice image of pristine CNT.



Fig. 7. (a) TEM image of CNT-PZT hybrid and (b) TEM-EDS spectrum of CNT-PZT hybrid. The Cu peak is due to the TEM grid.

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(2)

$$d = k\lambda/B\cos\theta$$

where *d* is the crystallite size, *k* a constant of 0.9, λ the X-ray wavelength of Cu which is 1.5406 A°, θ the Bragg angle in degrees, and *B* the full width at half maximum (FWHM) of the peak. Keeping in mind XRD pattern of PZT powder (Fig. 3c), it is evident that the average crystallite size of PZT on CNTs is slightly smaller than that of in absence of CNTs (i.e., PZT powder), being 3.1 nm for PZT nanotube and 5.1 nm for PZT powder. This phenomenon has been previously reported for TiO₂. Presumably, CNTs due to their high thermal conductivity can act as heat sinks during the crystallization of PZT, conducting away any excess heat otherwise consumed by grain growth.

Fig. 4 shows the Raman spectra of pristine CNT, CNT-PZT hybrid and PZT nanotube. The pristine MWCNTs, characterized by the absence of the radial breathing mode (RBM), in the range 75–300 cm⁻¹ [46] and the presence of D, G and G' bands at 1350, 1581 and 2688 cm⁻¹, respectively. The relatively high intensity ratio of D band to G band suggested the high concentration of defects in the pristine MWCNTs. This was also confirmed by TEM images. For as-coated MWCNTs (CNT-PZT hybrid), the fluorescent base line and the peaks at 1400 and 415 cm⁻¹ can be related to the presence of the organometallic agents in the sol. Interestingly, the PZT coating was considerably altered the intensities of both, the D and G' bands, with respect to the uncoated CNTs. Thus, the intensity of the D band was decreased, whereas the intensity of the G' band was increased in case of CNT-PZT hybrid. A similar behavior was reported for the adsorption of benzene on the surface of CNTs, indicating the presence of $\pi - \pi$ interactions. This result is

important as it confirms the role of benzyl alcohol as a linking agent in the present work. In Raman spectrum of the final PZT nanotubes the signatures of MWCNTs was completely disappeared, leaving small peaks at 270, 593 and 724 cm⁻¹ corresponding to the $E(silent) + B_1$, $A_1(3TO)$ and $A_1(3LO)$ modes, respectively belonging to tetragonal PZT with P4mm space group.

Fig. 5 shows low-magnification SEM images of PZT nanotubes and reveals that the sample consisted homogeneously of bundles of nanotubes. Interestingly, no additional particles were observed, suggesting that all of the PZT sol had been consumed in the CNT coating. The PZT nanotubes were up to 20 μ m long and so of similar length as the CNTs. It is thus expected that the use of longer CNTs – lengths of up to mm have yet been achieved – would result in longer PZT tubes.

Fig. 6 shows HRTEM images of pristine MWCNTs. The dark spots within the hollow core (inner diameter of 7.2 nm) highlight the presence of iron residues from the CNT synthesis [47], while those within the walls are remnants of structural defects, whose presence was indicated by the high D:G ratio in Raman spectroscopy.

Fig. 7a illustrates TEM image of as-coated MWCNT. The surface of the CNT clearly is decorated with an array of poorly interconnected disc-like particles with diameters of about 15 nm. It appears that the coating consisted only of a single rather than of multiple layers. The exclusive mono-layer deposition provides a convenient means to control the thickness of the final oxide. The thickness of the particles is remarkably uniform and of the order of 10 nm. Advantage of such mono-layer deposition is that the thickness of the final oxide nanotubes depends on the thickness of the particles and hence can be controlled by various process



Fig. 8. (a) and (b) TEM images of PZT nanotubes, (c) SAED pattern of PZT nanotube and (d) lattice image of PZT nanotube. The distance between arrows is 0.285 nm, corresponding to PZT (1 1 0) planes.





Fig. 9. TEM-EDS elemental map of PZT nanotubes. Presence of carbon is due to the graphitic layer on TEM grid.

parameters (e.g., reaction temperature and etc.). In the present case, the thickness of the individual particles is remarkably uniform and of the order of 10 nm. TEM-EDS spectrum of this sample (Fig. 7b) confirmed the presence of constituting materials of the sol (i.e., Pb, Zr, Ti and O).

There is a fundamental relationship between the synthesis conditions (i.e., processing parameters) and the final morphology of PZT NTs. It was found that three synthesis conditions, namely concentration of the PZT sol, the PZT:CNT weight ratio and heat treatment, influence on morphology of PZT nanotubes, PZT sol with high concentration resulted in a thick and non-uniform PZT coat on CNTs. Such a non-uniform coat with high thickness helps crack nucleation in the coating due to high surface roughness and consequently leads to a collapsed structure of the NTs and producing PZT nanoparticle rather than the PZT nanotube. The same conclusion can be explained for the effect of PZT:CNT weight ratio on morphology of PZT-CNT hybrid. Both high and low PZT:CNT weight ratios resulted in very thick and very thin PZT coat, respectively and therefore a collapsed structure was obtained. However, in case of very low PZT:CNT weight ratio no PZT nanotube can be produced. Consequently, two processing parameters of concentration of the PZT sol and PZT:CNT weight ratio were optimized to obtain uniform and soundness PZT nanotube.

It is worth mentioning that, the interrupted annealing procedure was applied to avoid collapsing of newly formed PZT nanotubes due to possible thermal shocks of heating process. Without applying of such a treatment the final structure was determined, by electron microscopy, to be remnants of collapsed and broken tubes. TEM image of the final PZT nanotube (heat-treated sample) is shown in Fig. 8a, b, which illustrates a tubular structure with a remarkably uniform inner core of approximately 30 nm. The average outer diameter of these tubes is in the range 50–60 nm with the wall thickness of 10 nm. Considering that the PZT particles on CNTs were poorly interconnected prior to the CNT oxidation, it is remarkable that the template removal did not result in just sintered particles or at least nanostructures with collapsed pores. In contrary, the particles appear to have sintered upon heat treatment, and, supported by the CNTs, formed an interconnected coating, which preserved its tubular morphology after the removal of the template. The selected area electron diffraction pattern of the final PZT nanotube is shown in Fig. 8c which confirms the presence of the desired perovskite structure. In addition, Fig. 8d highlights a d-spacing of 0.285 nm, corresponding to $(1\ 1\ 0)$ planes in Pb(Zr_{0.52}Ti_{0.48})O₃.

TEM-EDS elemental mapping (Fig. 9) reveals that all elements, Pb, Zr, Ti and O, were uniformly distributed along the PZT nanotubes. Furthermore, carbon was present over the whole area, as expected from the carbon-coated TEM grid. The absence of additional carbon in the PZT nanotube confirms the removal of CNTs.

4. Conclusions

PZT nanotubes have been successfully prepared using a conventional sol-gel method aided by MWCNT as a template. STA results confirmed that crystallization of PZT nanotube with perovskite structure occurred at the low temperature of 410 °C. Raman spectroscopy and X-ray diffraction studies showed that the MWCNT template left the final product by a subsequent interrupt annealing. FE-SEM and HRTEM images verified the tubular nanostructure of the PZT product. Furthermore, SAED and XRD patterns confirmed the perovskite structure of PZT nanotubes.

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