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# Preparation of titania covered multi-walled carbon nanotube thin films

Zoltán Németh [a,b], Endre Horváth [c], Arnaud Magrez [c], Balázs Réti [a], Péter Berki [a], László Forró [c], Klára Hernádi [a,*]

[a] Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Béla tér 1, Szeged H-6720, Hungary
[b] Laboratory of High Performance Ceramics, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, Dübendorf CH-8600, Switzerland
[c] Laboratory of Physics of Complex Matter, École Polytechnique Fédérale de Lausanne, Ecublens CH-1026, Switzerland

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ABSTRACT

The aim of this work was to investigate the effects of relative humidity on the formation of titania layers on the surface of multi-walled carbon nanotubes under regulated conditions in a sealed system. Reactive precursor compounds such as titanium (IV) oxychloride hydrochloric acid and titanium (IV) bromide were used as precursor to cover the surface of multi-walled carbon nanotubes (MWCNTs) under solvent conditions. The mixtures of MWCNTs and titania compounds were not stirred or sonicated. The effect of relative humidity was influenced using the mixture of sulphuric acid and water in desiccators. As-prepared titan-dioxide ($TiO_2$) layers were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TG), X-ray diffraction (XRD) and Raman spectroscopy. Our results revealed that $TiO_2$ layers with different thicknesses can be obtained using this simple sealed system. These $TiO_2$ covered multi-walled carbon nanotube films can be ideal candidates for different kinds of applications (e.g. sensors, virus filtration or catalysts).



## 1. Introduction

Carbon nanotubes (CNTs) have exceptional properties of strength, high surface area, thermal stability, optical activity, thermal and electrical conductivity [1], thereby resulting in many potential applications [2,3]. Due to their high specific surface area and adsorption capability CNTs have been increasingly used in environmental applications [4]. Recently, multi-walled and single-walled CNT filters were developed and found to be effective for multilog microbial removal from contaminated water by physical straining, puncture and depth filtration [5–8]. Furthermore, Gao et al. [9] reported a mechanically stable, electrically conductive and flexible CNT-PVDF membrane and demonstrated that the filter can be effective and efficient for single pass nitrobenzene mineralization by sequential reduction-oxidation.

Combining their remarkable electrical, thermal and mechanical properties with other special properties of conjugated components is also a promising direction to constitute composite materials [10] for nanotechnological and environmental applications such as solar cells, nanoelectric devices, fuel cells, hydrogen storage, adsorptive and degradative water treatment, etc. [11]. In the last couple of years many chemical researches were concerned with the combination of carbon nanotubes with polymers or metal-oxide nanoparticles [12,13]. The applications of these composite materials are very extensive, which usually determines the performance of the composites. The well-known $TiO_2$ is one of the most important n-type semiconductor materials, which is applied as white pigment, catalyst and/or support owing to its excellent physical and chemical properties [14]. Since CNTs can show good electrical conductivity and with their properties mentioned before, they are excellent candidates to be supports for $TiO_2$-based nanocomposites to be used as filters for virus removal from water [15] or photocatalysts [16].

$TiO_2$-MWCNT nanocomposites have been prepared by a number of different techniques including sol–gel synthesis of $TiO_2$ in the presence of CNTs [17,18], electro-spinning method [19], electrophoretic deposition [20], hydrothermal treatment [21,22], hydrolysis [23], chemical vapor deposition (CVD) [24], dip-coating [25] and layer-by-layer (LBL) technique [26].

The uniformity of the $TiO_2$ coating and the physical properties of the composite materials may vary depending on the applied preparation method. Though homogeneous coating of $TiO_2$ on CNTs may be achieved by CVD and electro-spinning methods, these techniques are not simple. They require specialized equipment and it may be difficult to quantify the ratio between composite compounds. Sol–gel method is still the most preferred one, although they usually lead to a heterogeneous, non-uniform coating of CNTs by $TiO_2$, showing bare CNT surfaces and random aggregation of $TiO_2$ onto the CNT surfaces [16]. Yu et al. studied the synthesis of $TiO_2$-MWCNT heterojunction arrays on Ti substrate with a controllable thickness of $TiO_2$ layer for photodegradation of phenol [27]. Wang et al. used a modified sol–gel method to prepare $TiO_2$-MWCNT nanocomposites that exhibited photocatalytic activity under both UV and visible light [28]. Eder and Windle reported the preparation of CNT–$TiO_2$ hybrid material and the key achievement of this work was the control of morphology and structure of the $TiO_2$ coating on the surface of CNTs [29]. An et al. [30] deposited anatase $TiO_2$

* Corresponding author.
*E-mail address:* hernadi@chem.u-szeged.hu (K. Hernádi).

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onto MWCNTs via hydrolysis of titanium isopropoxide in supercritical ethanol and investigated the photocatalytic activity of the composites. Sol–gel technique was utilized to deposit anatase $TiO_2$ thin films on the grown MWCNTs. $TiCl_4$ was added dropwise to absolute ethanol with a volume ratio of 1/20 while it was stirred. Since $TiCl_4$ shows a strong reaction with water and even humid air, usually $TiO_2$ is produced by hydrolysis of chemically pure $TiCl_4$ in absolute ethanol [31]. Recently we have reported the preparation of MWCNT based $TiO_2$ composites using organometallic [32] and inorganic [33] titanium compounds as precursors by a simple impregnation technique. It was demonstrated that the speed of the hydrolysis of precursors highly affects the quality and homogeneity of the titanium layers on the surface of MWCNTs. In accordance with the purpose the coating may consist of separated titania nanoparticles [30] or can be fully homogeneous [31] depending on the applied precursor compound and the speed of the hydrolysis process. In addition, the aforementioned methods of fabricating CNT/$TiO_2$ nanocomposites have been mostly used for the generation of bulk nanocomposites and do not provide a straightforward method for creating conformal thin films and coatings with precisely regulated composition and properties. Based on our previous results [30,31] a sealed system is proposed in order to investigate the effect of hydrolysis more accurately by changing the relative humidity and to avoid standalone inorganic particles as a side product. The generation of $TiO_2$/MWCNT thin films would enhance the utility of these nanocomposites in various applications.

In this study, $TiO_2$/MWCNT nanocomposite membranes were prepared by a modified hydrolysis method. The aim of our work was to elaborate a controlled and regulated process which provides different thickness and homogeneity of $TiO_2$ layers on the surface of multi-walled carbon nanotubes thereby improving the physical and chemical properties of composite materials. Using this process completely covered MWCNTs could be produced in large quantities, which were strongly influenced by the applied relative humidity values. The resulting thin films can be used in further applications. One of our main goals in the near future is to develop innovative nanocomposite based depth filters to investigate surface properties and adsorption capability in order to improve drinking water quality by removing viruses from contaminated water.

## 2. Experimental

### 2.1. Materials

MWCNTs were prepared with the chemical vapor deposition (CVD) technique: acetylene was decomposed in a rotary oven at 720 °C using Fe,Co/$CaCO_3$ as catalyst [34]. Using this synthesis method only MWCNTs were formed without amorphous carbon or other carbonaceous particles [35]. Fig. 1a and b shows SEM image and the Raman spectrum of pristine MWCNTs. The spectrum shows strong peaks at 1342.7 $cm^{-1}$, 1572.2 $cm^{-1}$ and 2680.1 $cm^{-1}$ which correspond with the D, G and G′ peaks of MWCNTs [36]. There are also weak second-order peaks at 2443.9 $cm^{-1}$, 2917.3 $cm^{-1}$ and 3220.0 $cm^{-1}$. The intensity ratios between the three main peaks ($I_D/I_G = 0.51$, $I_{G'}/I_G = 0.69$ and $I_D/I_{G'} = 0.74$) indicate good $sp^2$ structure and confirm the high-quality of multi-wall carbon nanotubes. The following precursor compounds were used: $TiBr_4$ (Aldrich) and $TiOCl_2 \times 2HCl$ (Aldrich), and ethanol (EtOH) was applied as solvent (HPLC grade from Reanal). PVDF filter membranes (pore size: 0.1 μm, diameter: 47 mm) (Aldrich) were used to prepare MWCNT films. The relative humidity was regulated by changing the concentration of sulphuric acid ($H_2SO_4$ — Aldrich) – (distilled) $H_2O$ mixtures in different desiccators.

### 2.2. Preparation of MWCNT based films

First, 50 mg of purified MWCNTs was added into 500 $cm^3$ EtOH and then it was suspended via sonication for 10 min. In the next step 100 $cm^3$ portions of this suspension was filtered through a PVDF membrane in order to prepare a MWCNT film. In the meantime calculated amount of precursor compound (15 mg of $TiBr_4$ or 26 mg of $TiOCl_2 \times 2HCl$) was dissolved in 20 $cm^3$ EtOH. In the following step the MWCNT film and the previously prepared solution of the precursor were put into a beaker. Desiccators were applied in order to investigate the effect of relative humidity (RH) and the ratio of the sulphuric acid and distilled water were changed inside the desiccators to obtain different RH values [37]. The applied RH values were ranged from 10% to 60%. As the final step we putted the beaker inside the desiccator and closed it for 24 h. The as prepared MWCNT film was dried at 50 °C for 12 h.

### 2.3. Sample characterization

For qualitative characterization the obtained films were investigated by scanning electron microscopy. SEM investigation was performed by a Hitachi S-4700 Type II FE-SEM operating in the range of 5–15 kV. Prior to the measurement the samples were mounted on a conductive carbon tape and these were coated with a thin Au/Pd layer in Ar atmosphere. The energy-dispersive X-ray spectroscopy (EDS) measurement was completed by the scanning electron microscope and a Röntec XFlash Detector 3001 SDD device. Thicknesses of as-prepared $TiO_2$ layers were investigated using iTEM software from Olympus Soft Imaging Solutions. Thermogravimetric analysis (TG) measurements were performed by a NETZSCH STA 409 PC device in airflow (temperature range: 25–1000 °C, heating rate: 10 °C/min, flow rate: 40 $cm^3$/min). Based on the results of TGA the heat treatment was performed in Type F21100 Tube Furnace applying quartz boat, quartz tube, and $N_2$ atmosphere. Nanocomposite samples were annealed at 700 °C for 3 h. The crystalline structure of the inorganic layer was also studied by powder X-ray diffraction method – XRD – by a Rigaku Miniflex II Diffractometer

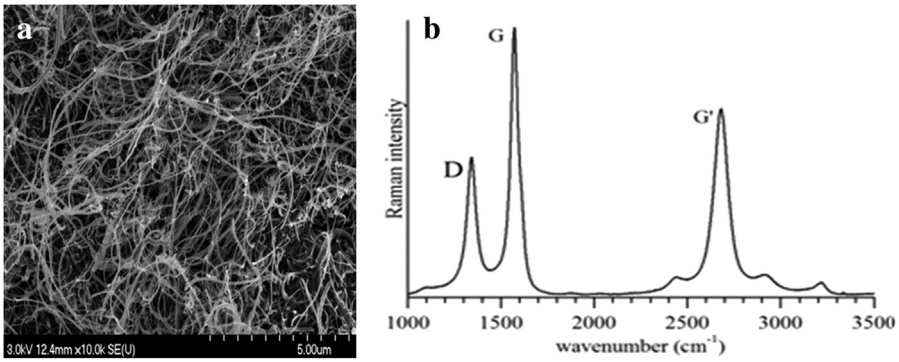


**Fig. 1.** SEM micrograph (a) and Raman spectrum (b) of pristine MWCNTs.