Synthesis and Characterization Hybrid Materials (TiO$_2$/MWCNTS) by Chemical Method and Evaluating Antibacterial Activity against Common Microbial Pathogens

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TiO$_2$/MWCNTs hybrid material was prepared by sol–gel method using mixture of TiCl$_4$ and HCl as source of TiO$_2$. In this method a certain amount of MWCNTs was added to mixture of TiCl$_4$, HCl andsocking overnight followed by calcining at 650 °C for 2 h forming MWCNTs/TiO$_2$ hybrid. The modified MWCNTs with TiO$_2$ nanoparticles have been characterized by X-ray diffraction and transmission electron microscopy which reveals the formation of TiO$_2$ nanoparticles and decorated MWCNTs surface through soaking in mixture of TiCl$_4$ overnight. Besides, the antimicrobial activity of MWCNTs and TiO$_2$/MWCNTs hybrid material was evaluated against Gram-positive and Gram-negative pathogenic bacteria to improve the possibility of samples as a new antibacterial strategy to reduce the rate of infections.

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1. Introduction

Carbon nanotubes (CNTs) are considered as remarkable materials due to their unique structural and mechanical properties such as high electrochemical stability, low resistivity, and high surface-to-volume ratio. In general, carbon nanotubes are divided into two categories: single wall carbon nanotubes (SWCNTs) and multi wall carbon nanotubes (MWCNTs) [1]. Modification of CNTs has generated a great deal of interest as model system for fundamental scientific research with the potential technological applications. In particular, fabrication of CNTs modified with metal oxides is more applicable than non-modified devices. Currently, finding a simple and low cost approach to modify MWCNTs with the metal oxides is still an active study. In recent years, a large amount of publishing papers have concentrated on coating and filling of MWCNTs by metals and metal oxides [2–4]. Up to now, various metal oxides such as TiO$_2$, SnO$_2$, ZnO, Fe$_2$O$_3$, AgNO$_3$, MnO$_2$, and RuO$_2$ have been reported to modify CNTs [5].

In the last decades, titanium dioxide, TiO$_2$, is the most promising semiconductor catalyst because of easy production, non-toxicity and its biological and chemical inertness [6]. The morphological properties of titanium dioxide NPs greatly influence their applications [7]. TiO$_2$ nanostructures are attractive in a wide range of applications such as photocatalysis, dye sensitized solar cells, gas sensors, photo degradation of organic compounds, and inactivation of bacteria and harmful components from water and air [8–10]. TiO$_2$ acquires antibacterial properties due to its strong oxidation activity in the presence of light and the generation of reactive oxygen species such as hydroxyl radicals OH, hydrogen peroxide H$_2$O$_2$, and superoxide ions O$_2^−$ from photocatalytic reaction [11]. Recently, several methods of synthesis of semiconductors at the nanoscale have been used, such as electrosprin technique, chemical vapor deposition (CVD), and sol–gel [12]. The modifying MWCNTs with sol–gel technique produce heterogeneous and aggregated of TiO$_2$ NPs or TiO$_2$ clusters on the surface of MWCNTs [13, 14]. In the present paper, we studied the sol–gel method in producing TiO$_2$/MWCNT hybrid from tetra chloride titanium TiCl$_4$ as catalyst materials and the effect of soaking on the structure and evaluating the antibacterial activity of hybrid structure (TiO$_2$/MWCNTs) against a Gram negative and Gram positive bacteria as compared with MWCNTs in same experimental conditions.

2. Experimental part

2.1. Synthesis TiO$_2$/MWCNTs hybrid material

TiO$_2$/MWCNTs hybrid were synthesized using a sol–gel method using a mixture of TiCl$_4$ (0.4 ml), which is added drop wise to deionized water (100 ml), followed by addition of a small quantity of HCl (0.2 ml) to deionized water before dissolving TiCl$_4$ in the water. Then, 0.1 mg of functionalized MWCNTs were dissolved in the solution and sonication for 15 min with pH = 2.5. Moreover, the mixture was sonicated for 3 min and stirred for 30 min with increasing pH up to 2 using NH$_4$OH (1%) drop wise as shown in Fig. 1.

After that the mixture suspension (sol) of MWCNTs forming TiO$_2$ resulting from chemical mixing method

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was kept for 24 h at room temperature. Then the precipitation of socking MWCNTs and TiO\(_2\) (gel) is filtering and washing several times with deionized water and dried at 150°C for 24 h then heat treated (calcinated) at 650°C for 2 h. The prepared TiO\(_2\)/MWCNTs hybrid was characterized by transmission electron microscope analysis (TEM, EM208, Philips) and X-ray diffraction (XRD, 6000-Shimadzu) with wavelength \(\lambda = 0.15418\) nm. Besides, the antibacterial activity of prepared samples was evaluated by disk diffusion method against Gram-negative and Gram positive pathogenic bacteria to improve the possibility of them as a new antibacterial strategy and environmental health.

### 2.2. Antibacterial activity of MWCNTs and TiO\(_2\)/MWCNTs hybrid material

Antibacterial activity of MWCNTs before and after decoration by TiO\(_2\)NPs against a Gram negative bacterium *Escherichia coli* (*E. coli*) and Gram positive bacterium *Staphylococcus aureus* (*S. aureus*) were investigated using disk diffusion method. In the first step, both bacteria samples were cultured in an LB medium at 37°C for 24 h. The bacteria cultures were diluted to reach approximately the concentration of bacteria corresponding to the MacFarland scale (10\(^7\) CFU/ml). Following this step, there were placed sterile paper discs (10 mm) that were soaking in samples MWCNTs and TiO\(_2\)/MWCNTs hybrid solvents, respectively on the inoculation (MHA) agar and incubating at 37°C for 24 h. After incubation, the zones of clearing around the desk are measured.

### 3. Results and discussion

The crystalline phases of the MWCNTs and TiO\(_2\)/MWCNTs hybrid samples have been analyzed by X-ray diffraction (XRD), and the results reveal different crystal structures as shown in Fig. 2a and b, respectively. In Fig. 2a, it can be observed that functionalized MWCNTs exhibit two peaks at 2\(\theta\) = 26.04° and 43.8° corresponding to the (002) and (100) planes for treated MWCNTs with concentrated acids [2–4]. Besides, the observed diffraction patterns revealed the peaks related to MWCNTs and TiO\(_2\) in TiO\(_2\)/MWCNTs hybrid as shown in Fig. 2b. The peak at 2\(\theta\) = 27.3° typical for the (002) diffraction of MWCNTs and this shift reveals the effect of calcination for 2 h at \(T = 650°C\) on the hybrid and confirms the presence of CNTs in the sample while the peaks at 2\(\theta\) = 27.5°, 36.25°, 41°, 54.4°, 63.2°, and 69° which is related to diffraction peaks (110), (101), (111), (105), (211), (002), and (112), respectively of TiO\(_2\) rutile structure as compared with the American Society of Testing Materials (ASTM) since there is no traces of anatase in TiO\(_2\)/MWCNTs hybrid sample. This results demonstrates the deposited TiO\(_2\) on MWCNTs prepared by converting TiCl\(_4\) to rutile through post heating at \(T = 650°C\) under the experimental conditions.

![Fig. 1. Digital photograph of synthesis of TiO\(_2\) decorating MWCNTs using TiCl\(_4\) by a sol–gel method.](image1)

![Fig. 2. XRD patterns of (a) MWCNTs and (b) TiO\(_2\)/MWCNTs hybrid material.](image2)
The samples are investigated by TEM analysis in order to observe the interaction and composition among the constituents in the MWCNTs and TiO$_2$/MWCNTs hybrid as shown in Fig. 3 at different magnifications. The TEM images in Fig. 3 determined the deposition of TiO$_2$ nanoparticles of average particle size less than 10 nm on MWCNTs (diameter of about 25–30 nm) without noticeable agglomerations at different magnifications. This is probably because of the surface functional groups on the treated MWCNTs with acids, such as the carboxylic (–COOH) and carbonyl (–C=O) groups, which may help the dispersion of TiO$_2$ NPs, providing a further higher level of interaction between the MWCNTs and TiO$_2$. Besides, TEM analysis reveals the attachment
Inhibition zones diameters in mm of MWCNTs and TiO$_2$/MWCNTs hybrid against *S. aureus* and *E. coli* bacteria.

| Bacteria                | E. coli | S. aureus |
|-------------------------|---------|-----------|
| MWCNTs                  | 18 mm   | 15 mm     |
| TiO$_2$/MWCNTs hybrid   | 20 mm   | 18 mm     |

Fig. 6. SEM images of adhesion (a) *E. coli* and (b) *S. aureus* on TiO$_2$/MWCNTs hybrid.

The effect of decorating MWCNTs with TiO$_2$ on growth of *E. coli* and *S. aureus* was performed as compared with treated MWCNTs, as shown in Fig. 5a and b. The zone of clearance around the desk was measured by the diameter of the inhibition circle, as shown in Table I.

The results reveal free oxygen formed on the surface of TiO$_2$/MWCNTs hybrid because of injection of electrons from MWCNTs to TiO$_2$ due to the reduction of band gap energy for photogeneration of electrons and holes and formation of active radicals ions could penetrate and damage the thin cell well and external membrane during the interaction with cell. This is shown in Fig. 6a and b as SEM images of adhesion of *E. coli* and *S. aureus* on TiO$_2$/MWCNTs, while the hybrid and functionalized MWCNTs have small effect on *S. aureus* because of thick cell membrane.

### 4. Conclusion

The results of this work improved the role of TiCl$_4$ in formation TiO$_2$ NPs rutile structure adsorbed on treated MWCNTs through post heating at $T = 650°C$ for 2 h under the experimental conditions. Since large amount of Ti ions, through sol–gel method, gets adsorbed on treated MWCNTs surfaces due to electrostatic attraction, this leads to decoration the surface of treated MWCNTs with TiO$_2$ NPs. This also results in the filling MWCNTs with TiO$_2$ NPs during the long time of soaking for 24 h as improved by XRD and TEM results with average particle size less than 10 nm on MWCNTs. The antibacterial activity of MWCNTs and TiO$_2$/MWCNTs hybrid released the effect of decoration MWCNTs with TiO$_2$ on growth of *E. coli* and *S. aureus* was higher than treated MWCNTs. Besides, the effective of soaking time on the modification of functionalized MWCNTs with TiO$_2$NPs leads to oxidative stress of cell membrane of *E. coli* as shown in SEM analysis.

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