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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 and socking overnight followed by calcinating 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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PACS/topics: antimicrobial agents, TiO_2 nanoparticles, carbon-based nanoparticles, photocatalytic materials, TiO_2/MWCNTs, hybrid material

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_2O_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_2O_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 electrospin 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 socking 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 MWNTs were dissolved in the solution and sonication for 15 min with pH = 2.5. Moreover, the mixture was sonicated for 5 min and stirred for 30 min with increasing pH up to 2 using NH_4OH (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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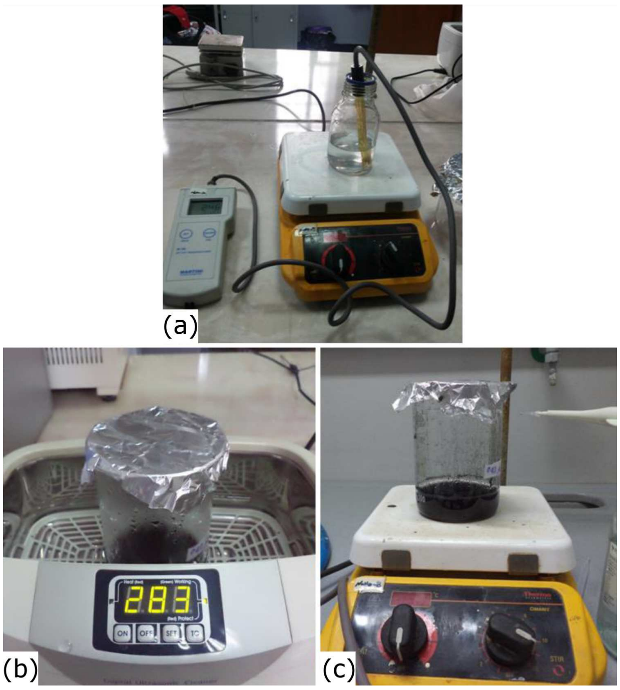

Fig. 1. Digital photograph of synthesis of TiO_2 decorating MWCNTs using $TiCl_4$ by a sol–gel method.

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_2NPs 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 anatace 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.

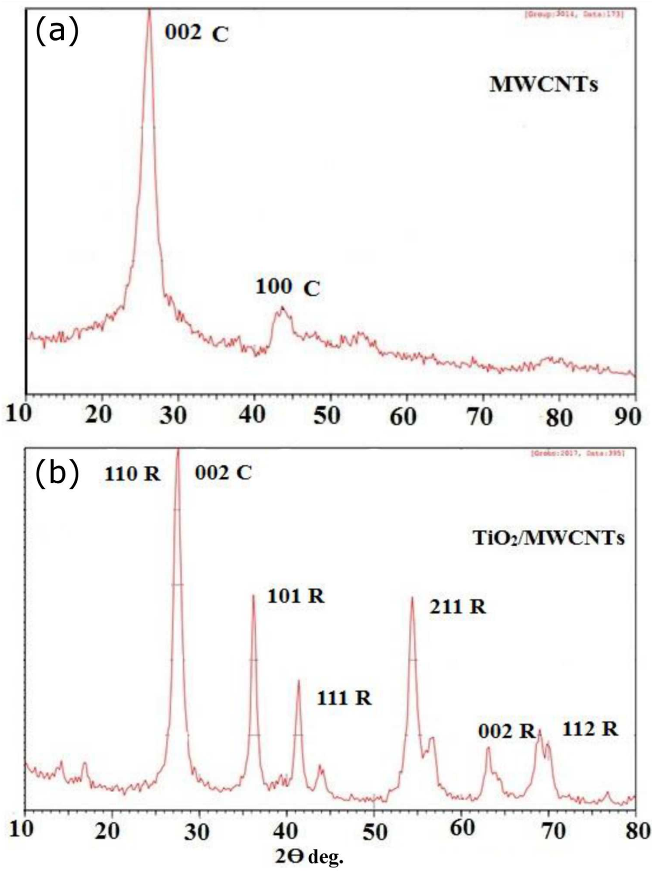

Fig. 2. XRD patterns of (a) MWCNTs and (b) TiO_2/MWCNTs hybrid material.

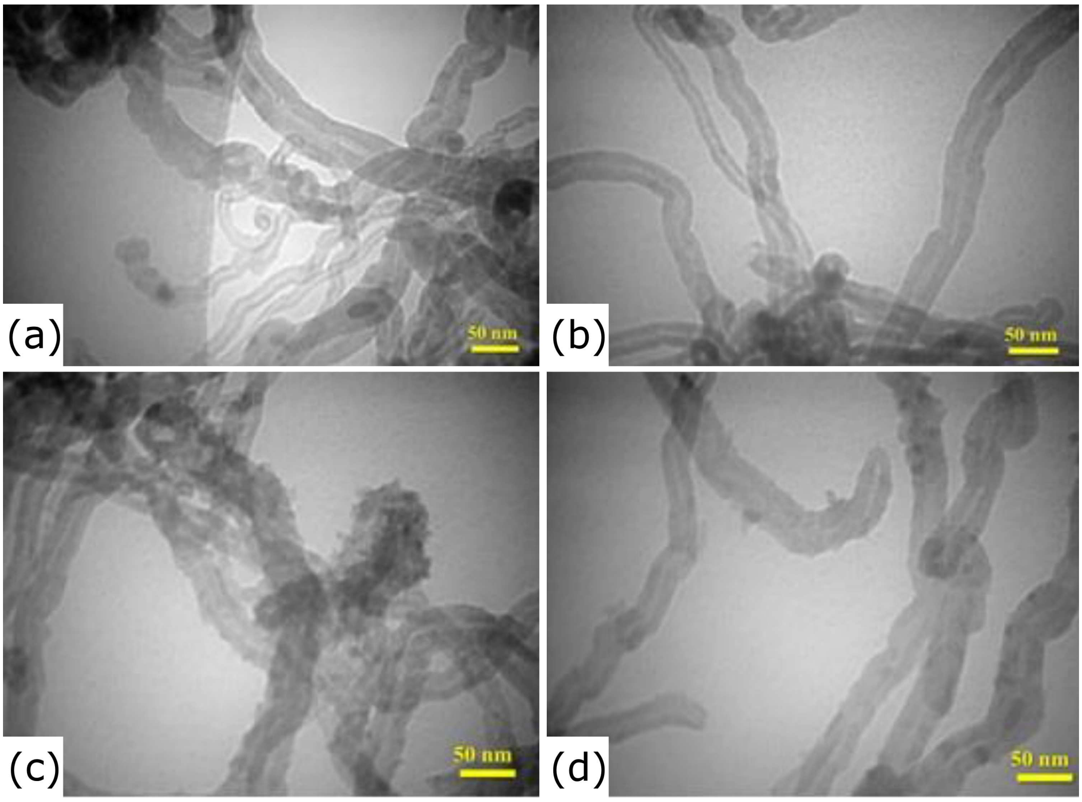

Fig. 3. TEM image of (a) raw MWCNTs and (b)–(d) TiO_2 decorated MWCNTs in TiO_2/MWCNTs.

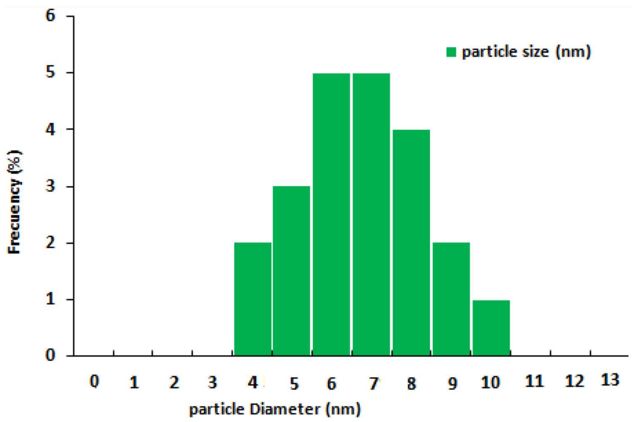

Fig. 4. The corresponding size distribution of TiO_2NPs attachment of TiO_2NPs with MWCNTs.

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

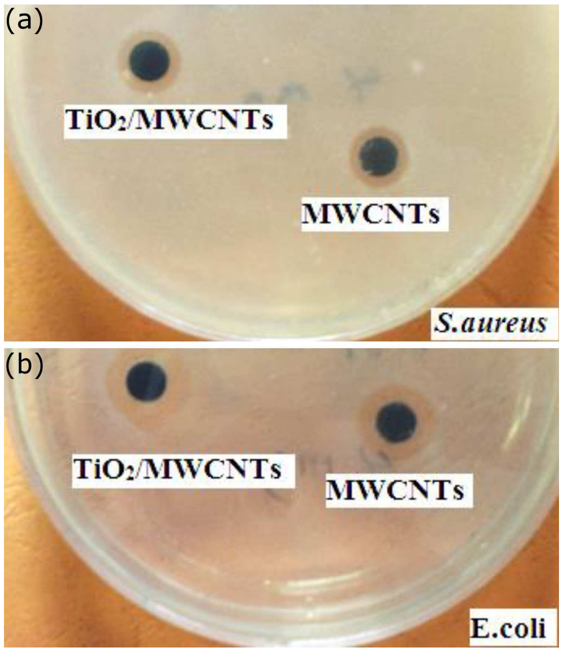

Fig. 5. Inhibition zones diameters in mm of MWCNTs and TiO_2/MWCNTs hybrid against (a) *E. coli* and (b) *S. aureus* bacteria.

TABLE I

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

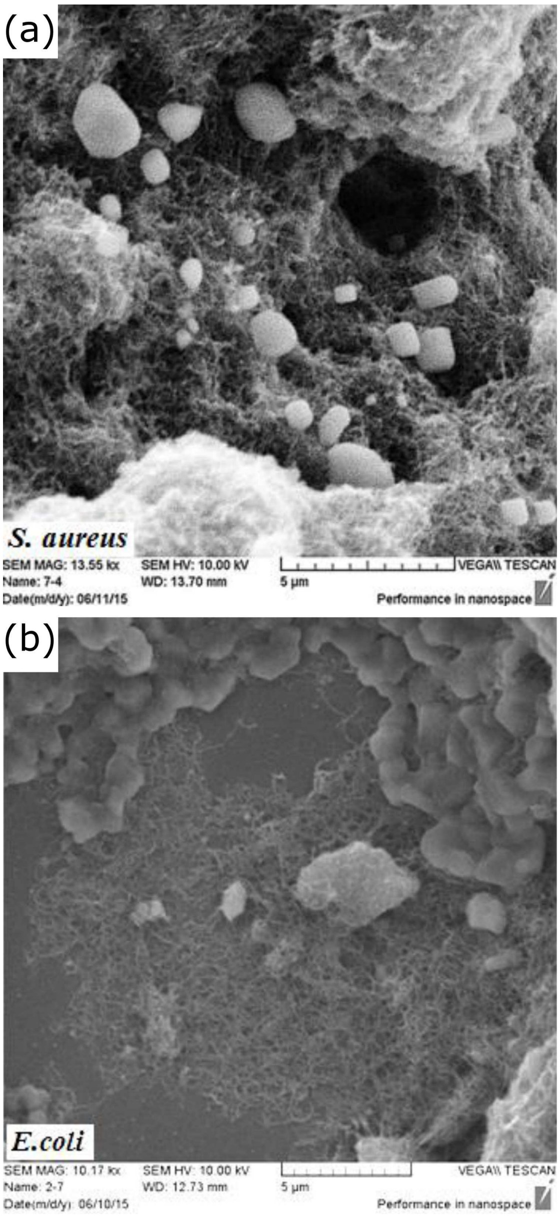

Fig. 6. SEM imeges of adhesion (a) *E. coli* and (b) *S. aureus* on TiO_2/MWCNTs hybrid.

and partial coverage of spread of TiO_2NPs, with small size on the surface of MWCNTs with an average size less than 10 nm as shown in size distribution in Fig. 4 forming MWCNTs/TiO_2 hybrid materials.

The antibacterial activity of MWCNTs and TiO_2/MWCNTs hybrid, respectively are tested against standards of the *E. coli* and *S. aureus* by using disc diffusion method to determine the clear inhibition zone, 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 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, respectively. Besides, Table I reveals a clear inhibition zone against *E. coli* treated with TiO_2/MWCNTs hybrid while smaller inhibition zone is treated with MWCNTs, whereas the TiO_2/MWCNTs hybrid and MWCNTs samples show smaller zone of inhibition against *S. aureus*. These results demonstrate the effective of socking time on the modification of functionalized MWCNTs with TiO_2NPs and in disruption and oxidative stress of cell membrane of *E. coli* as compared to MWCNTs.

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 $T = 650\,^{\circ}\mathrm{C}$ 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 socking 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 socking time on the modification of functionalized MWCNTs with TiO_2NPs leads to oxidative stress of cell membrane of *E. coli* as shown in SEM analysis.

Acknowledgments

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