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Fabrication of Carbon Nanotube/Titanium Dioxide Nanocomposite Photocatalyst Using Sol-Gel Method

In this work, functionalized multi-walls carbon nanotubes (FMWCNTs) were prepared and mixed with titanium dioxide nanoparticles by sol-gel chemical method using titanium tetrachloride ($TiCl_4$) as a source. A cretin amount of MWCNTs were soaked in a mixture of 0.2ml $TiCl_4$ and 0.1ml HCl forming MWNTs/TiO_2 nanocomposite as efficient photocatalytic material. Characterization and measurements on the prepared samples before and after adding TiO_2 include x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). The results reveal deposition TiO_2NPs on FMWCNTs surface after leaving soaking in mixture of $TiCl_4$ for 24h and that caused to fill the MWCNTs with TiO_2 NPs and decorating surface of MWCNTs resulting in formation MWNTs/TiO_2 nanocomposites.

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1. Introduction

Titanium dioxide is described as a low-cost photocatalyst substance to degrade environmental pollutants from industrial wastewater because of its ability to oxidize a broad range of Pollutants and long term stability of thermodynamic using specific experiment conditions [1,2]. Also, this feature has been helpful in deactivation of bacteria and harmful components from wastewater and air, as well as in self-cleaning or self-sterilizing surfaces for places such as health centers [3-5].

Among these techniques, carbon nanostructures as adsorbent assist photocatalyst have concerned great interest due to higher potential. Later, additional types of Carbon nanostructures (mainly carbon nanotubes CNTs) are proposed as substitute carriers of mostly TiO_2 because of the combine effects of electronic and adsorption characteristics. Carbon Nanotubes in general are categorized into Multi Walled carbon nanotubes and Single Walled carbon nanotubes (MWCNTs and SWCNTs). The exceptional electronic characteristics of MWCNTs can slow down the time of electron hole recombination, which leads to enhance the photocatalytic achievement of TiO_2 [6-8]. In special, manufacture of Functionalized MWCNTs base procedure that supported with other metal oxides becomes more appropriate than other modified procedures. currently, a variety of metal oxides like TiO_2, SnO_2, ZnO and Fe_2O_3, are be notified to alter MWCNTs. Nowadays finding a simple and low cost approach to modify MWCNTs with the metal oxides is still an active study [9-13]. In resent a large amount of publishing papers have concentrated on coated and filled of MWCNTs by metals and metal oxides [14]. MWCNTs/TiO_2 nanocomposite substances have concerned interest of authors in due to the treated of contamination water and air using heterogeneous photocatalysits, Hydrogen development, CO_2 photo-reduction, and Dye sensitize Solar Cells. All of composite substances have been created by extent of various techniques, involving mixed of Titanium dioxide and MWCNTs mechanically [15], using Sol-Gel production of TiO_2 and MWCNTs [16], electro-spin technique [17] and chemical vapor deposition (CVD) [18]. Decoration of MWCNTs with metal oxide forming Composite materials makes their physical characteristic depend on the route of modifying. On the other hand these routes are difficult and require particular preparation. The modifying MWCNTs with Sol-Gel technique produce heterogeneous and non-uniform decorated and aggregated of TiO_2 NPs or TiO_2 clusters on the surface of MWCNTs [19]. In this study, modified MWCNTs with TiO_2NPs were prepared using sol-gel method from Tetra Chloride Titanium $TiCl_4$ as catalyst materials forming MWNTs/TiO_2 nanocomposites as efficient photocatalytic material because of MWCNTs surface-to-volume ratio and are ideal supports in composites.

2. Experimental Part

The MWNTs and TiO_2 nanocomposites are manufactured using a Sol-Gel technique. Multi-walled carbon nanotubes (MWCNTs) of 0.1g, purity >95 wt.%, outside diameter: 5-15nm using HRTEM was added to mixture of 100ml of HCl and $TiCl_4$ solution. The method is represented by: First, MWNTs are functionalized by concentrated acid mixture of 95% H_2SO_4 and 65% HNO_3 at temperature 25°C for one hour in ultrasonicated water bath. After that, the mixture was dilute in 400 mL of Deionized Water (D.I) and Vacuum-filter using a 0.22 µm polycarbonate membrane and dry at 90°C for an overnight. Second, a particular quantity of $TiCl_4$ (0.2ml) is added dropwise to deionized water (100ml), followed by addition a small quantity of HCl (0.1ml) to deionized water before dissolving $TiCl_4$ in the water. Then, 0.1mg of functionalized MWNTs dissolved in the above solution and sonicated for 15min with pH=2.5. Moreover, the mixture sonicated for 5min and stirred for 30min with increasing pH up to 2 using NH_4OH (1%) dropwise. After that the mixture suspension (sol) of MWCNTs forming TiO_2 resulting from chemical mixing method is kept for 24h at room temperature. Then the precipitate of socking MWCNTs and TiO_2 is filtering and washing several times with deionized water and dried at 100°C for 24 h.

The morphology of MWCNTs/TiO_2 nanocomposite was performed by transmission electron microscope (TEM) analysis using Philips EM208 instrument to investigate the modification and measurement of diameter of MWCNTs and particle size of decorated titanium dioxide as a photocatalyst materiel. The x-ray diffraction (XRD) analysis was performed using Shimadzu 6000 instrument with wavelength λ=0.15418nm to characterize the crystallite size and analyze the phase composition of MWCNTs/TiO_2 nanocomposite and. The Fourier-transforms infrared (FTIR) analysis was carried out using Shimadzu 8400S spectrophotometer to determine strong absorption peak of MWCNTs before adding TiO_2 and of MWCNT/TiO_2 nanocomposites.

3. Results and Discussion

Figure (1) reveals the FTIR spectra of MWCNTs before adding TiO_2 and MWCNT/TiO_2 nanocomposites. As shown in Fig. (1a), two strong absorption peaks at 2870 and 2997cm^{-1} are associated to symmetric and asymmetric stretching vibration modes of methylene group (CH_2 and CH_3), which point that the methylene structure of carbon nanotubes is not damaged. Besides, two absorption peaks at 1716 and 1521cm^{-1} are related to the formation of carboxyl groups and carbonyl groups in the functionaliztion method. The peak at 1680cm^{-1} is related to the stretch MWCNTs backbone. Additionally, the peaks from 3685-3427cm^{-1} are related to hydroxyl functional groups (OH) and stretch from carboxyl functional groups (O=C–OH, C–OH). In Fig. (1b), the FTIR spectrum of the TiO_2/MWCNT nanocomposite shows peak at 586cm^{-1}, which is related to stretching vibration of Ti-O-Ti bonds and formation of covalent bonds Ti-O-C is related to the peak at 1053cm^{-1}. This result indicates the reduction of energy band gap for photo-generated electrons and holes.

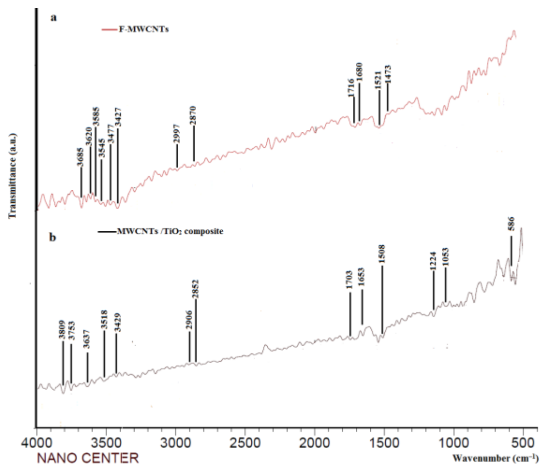


Fig. (1) FTIR spectrum related to (a) functionalized FMWCNTs and (b) MWCNTs/TiO_2 nanocomposite

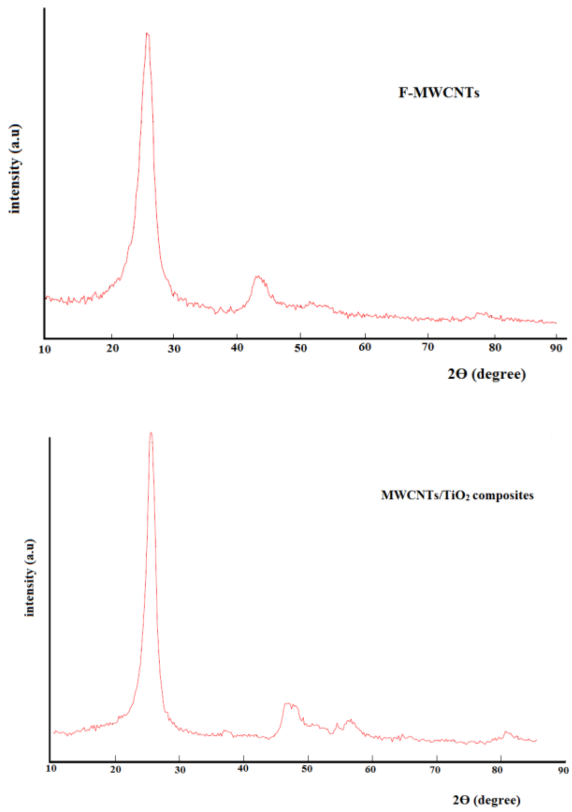


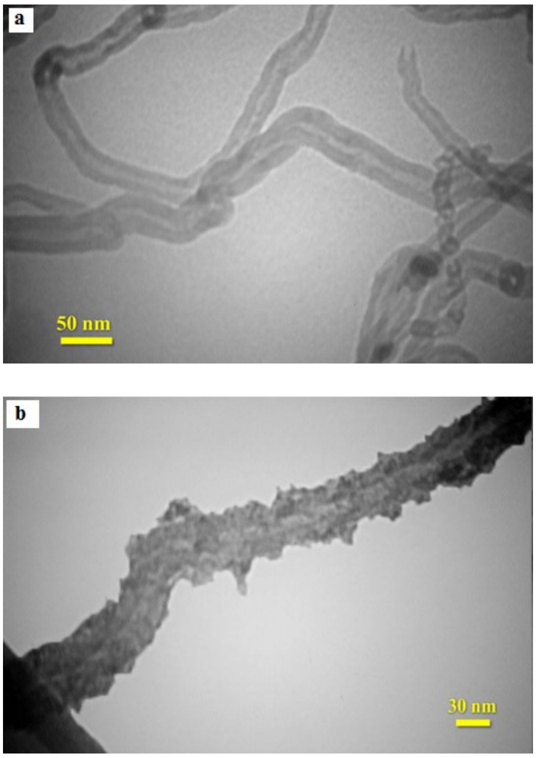
Fig. (2) XRD analysis (a) functionalized FMWCNTs and (b) MWCNTs/TiO_2 nanocomposite

The XRD patterns of the products in Fig. (2a,b) shows the highly crystalline structures of treated MWCNTs and TiO_2/MWCNTs composites, respectively. In Fig. (2a), XRD patterns of the functionalized FMWCNTs shows tow peaks at 2θ=25.8 and 43.6 corresponding to the (002) and (100) planes for treated MWCNTs with concentrated acids. The peaks at 25.3, 37.9, 48.2

and 54.3° are attributed to diffractions of 101, 004, 200 and 211 planes of anatase TiO_2, respectively, which indicating the developed TiO_2/MWCNTs nanocomposites existed in anatase state as shown in Fig. (2b). This result demonstrates the deposited TiO_2 on MWCNTs in sample prepared by sol gel mixing under the experimental conditions.

The morphology and microstructure of MWCNTs without TiO_2NPs and with TiO_2 decorating MWCNTs forming MWCNTs/TiO_2 nanocomposite that prepared by sol-gel method have been elucidated by TEM analysis (TEM, EM208, Philips, Day Petronic Co., Iran) as shown in Fig. (3a,b,c), respectively. Figure (3a) shows TEM image of functionalized F-MWCNTs by concentrated acids with less agglomeration and with a diameter of about 25-30nm. From the TEM image in Fig. (3b), it can be seen that there is a distribution of nearly spherical photocatalyst TiO_2NPs coating the surface of MWCNTs and filling the tube during the socking for 24h. So, it was considered that the interval space of these F-MWCNT networks was filled with TiO_2 nanoclusters of less than 10nm as reveals by size distribution in Fig. (3d).

Moreover, the TEM analysis shown in Fig. (3c) demonstrates the attachment and partially covered of well spread TiO_2NPs, with narrow size on the surface of MWCNTs with an average size less than 10nm as shown in size distribution in Fig. (3e) forming MWCNTs/TiO_2 nanocomposite materials.



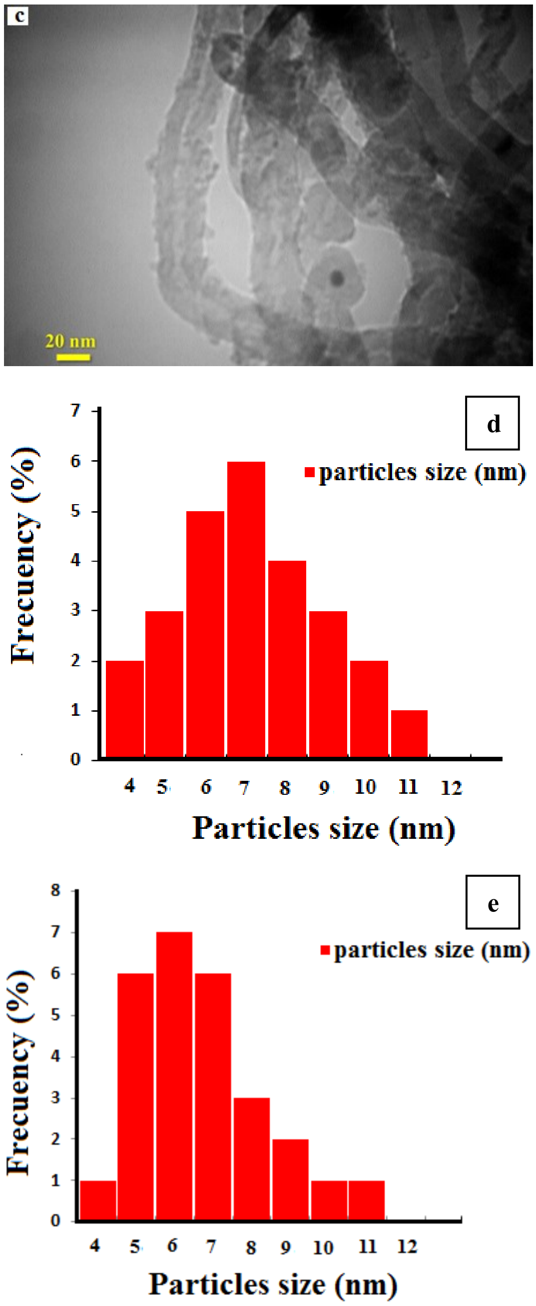


Fig. (3) TEM images of (a) functionalized F-MWCNTs, (b) TiO_2NPs coating the surface of MWCNTs forming MWCNTs/TiO_2 nanocomposite by mixing process, (c) partially covered of TiO_2NPs, on the surface of MWCNTs by mixing process, and (d) and (e) the corresponding size distribution of TiO_2NPs attachment and interaction of TiO_2NPs with MWCNTs

These results confirm that functionalized F-MWCNTs results introduce a number of active sites on MWCNTs created by the acid treatment and make them as carrier of TiO_2NPs and increase the photocatalyst activity of MWCNTs/TiO_2 nanocomposite by simple mixing process.

4. Conclusion

The results reported that using certain quantity of $TiCl_4$ as titanium source produces large amount of Ti ions that adsorbed to F-MWCNTs surfaces because of the electrostatic attraction, which leads to decorate the surface of F-MWCNTs with TiO_2 NPs. It also results in filling MWCNTs with TiO_2 NPs during the long-time soaking for 24h as improved by TEM results. The results revealed that the amount of $TiCl_4$ as precursor and soaking time have an important role on quantity of decoration TiO_2 on MWCNTs as shown by XRD and FTIR results forming MWCNTs/TiO_2 nanocomposite .

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