

Effects of Nanoparticle Size on Catalytic and Photocatalytic Activity of Carbon Nanotubes-Titanium Dioxide Composites

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Continuous changes in production techniques of composites have attracted the attention of researchers in the various branches of science, starting from academic research and ending in engineered materials. These techniques aim to preserve their beneficial properties and try to increase their efficiency with the introduction of new standards to this component which may not be already owned or efficient in a few capacities and are intended to be introduced to the composites [1]. One of the most important properties is produces nanomaterials along with the improvement of its physiochemical properties, due to the unique importance in the technology of its applications [2]. TiO_2 is a common semiconductor material that is used in this way due to many causes such as it being inexpensive, and nontoxic [3], and its relatively high reactivity and chemical stability under ultraviolet light [4]. Photocatalytic reactions at the surface of titanium dioxide have been used in many applications such as environmental cleaning for self-cleaning material on the surface coating of, glasses, and windows [5]. This new carbon-material, consists of Carbon nanotube CNTs, which appeared to have become a reality for science thanks to Iijima [6], and which was a challenge and temptation at the same time due to it being unknown to some extent, it's amazing physiochemical properties [7], and the variety of types of single-walled carbon nanotubes (SWNTs), few-walled carbon nanotubes (FWCNTs), and multi-walled carbon nanotubes (MWNTs). Many attempts brought together a, high surface area, fascinating electronic, chemical and mechanical properties for CNTs [8] with a low surface area for TiO_2 , in addition to the properties mentioned above. The addition of CNTs to TiO_2 created new properties and structural stability, which improved their activities compared to the pristine TiO_2 particle size, thus representing the key to understanding or at least finding a suitable proposal for this behavior. Raman spectroscopy [9] and XRD represent powerful methods for the investigation of the particle size effect in the activities of these nano- materials. The relations between the surface structure and particle size were translated into creating new bounds between them. Two types of binary composite were synthesized by using MWNTs, and SWNTs, which were purchased from (Aldrich). According to the product specifications, the two compounds were fabricated by the chemical vapor deposition method. SWNT constancies of more than 90% carbon included 77% SWNTs, with a diameter of 0.7-1.1 nm. The MWNT 95% carbon nanotubes with a mode diameter of 5.5, and the TiO_2 sample were purchased from Degussa, Germany (TiO_2 -P25). 0.5% CNT/ TiO_2 was prepared by an impregnation method. First, SWNTs, or MWNTs were treated with a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ acid (1/3) in an ultrasonic water bath for 7h to make activation for the surfaces [10]. After that 1g of the TiO_2 photocatalyst was suspended in an ultrasonic water bath in 100 ml of distilled water for 30 min. which contained the desired percentage weight of CNTs (0.5%). The mixed suspension was filtered by using a vacuum evaporator (Rota vapor re121 BUSHI 461 water Bath) at 45°C to accelerate the evaporation of the water. After the water had evaporated, the composite was dried overnight in an oven at 104°C. The samples were characterized using, Brunauer, Emmett and Teller BET to measure the specific surface area of the materials, the XRD pattern, and Raman spectroscopy. The effect of the existence of 0.5% CNTs a summarized in (Table 1) by using the full-width at half-maximum (FWHM) of the given bands, which were found by using the origin program8.

As shown in (Figure 1), the Raman spectra of the pristine TiO_2 , 0.5% SWNT/ TiO_2 , and 0.5% MWNT/ TiO_2 , represented by the five Raman-active modes of the anatase phase with symmetries of $2E_g$, A_{1g} , B_{1g} , and E_g , at 145.1, 198.0, 398.0, 515.5 and 638.5 cm^{-1} respectively, and E_g with a very small intensity at 445 cm^{-1} . TiO_2 -P25, as a mixture of anatase and rutile, has five Raman peaks (at 145.1, 198, 398, 516.5 and 6398.5 cm^{-1}) corresponding to the anatase, but just one peak, at 445 cm^{-1} , corresponding to the rutile [11]. Comparing TiO_2 with the synthesized materials shows: i- FWHM of the TiO_2 , increased with the existence of SWNTs and MWNTs, which increased within the SWNTs more than the MWNTs, ii- the shift in wavenumber for high values within the SWNTs and MWNTs, which showed more deviation with the SWNTs. As shown in (Figure 2), the low ratios of CNTs in the composites did not cause large or clear changes in the crystallography of the TiO_2 which may be related to covering the composites by the much more intense peak for the large ratio of the TiO_2 , however the effect of CNTs was limited to the small change in the width of the peaks with a shift towards a higher 2θ , which is summarized in (Table 2), in addition to a decrease with particle size which can be found from the Debye-Scherrer equation($d=K \lambda/\beta \cos\theta$) [12]. The CNTs showed two characteristic peaks at $2\theta=25.9^\circ$ and 43.2° , which can be attributed to the diffraction from the C(100) and C(002) planes of the carbon nanotube; the second peak was more intense in the MWNTs than the SWNTs [13], which may explain the value of the surface area for 0.5% MWNT/ TiO_2 (64 m^2/g), which was more than 0.5% SWNT/ TiO_2 (54 m^2/g) and TiO_2 (51 m^2/g). The test of the activities was done by using Cobalamin ($\text{C}_{63}\text{H}_{88}\text{CoN}_{14}\text{P}$), which is vitamin B12, as a complex compound of an organometallic species with a cobalt atom that is distinguished in a Corrine ring [14] which at the same time may give the explanation for the adsorption properties in the following sequences: 0.5% MWNT/ $\text{TiO}_2 > 0.5\%$ SWNT/ $\text{TiO}_2 > \text{TiO}_2$.

Sample	E_g	E_g	B_{1g}	A_{1g}	E_g
TiO_2	145.1(11.38)	198.0(5.69)	398.0(7.85)	515.5(7.85)	638.5(9.48)
0.5% SWNT / TiO_2	147.0(14.46)	201.3(6.32)	399.5(9.03)	517.0(9.03)	639.0(10.48)
0.5% MWNT / TiO_2	145.8(13.84)	198.2(5.85)	398.0(7.89)	515.5(7.89)	639.0(11.07)

Table 1: The effect of the existence of 0.5% CNTs

Samples	BET (m^2/g)	Particle size (nm)	C_{ppm}	$k(\text{s}^{-1})$
TiO_2	51	23.09	≈40	0.0648
0.5% SWNT / TiO_2	56	15.41	36.80	0.0769
0.5% MWNT / TiO_2	64	20.84	31.20	0.0743

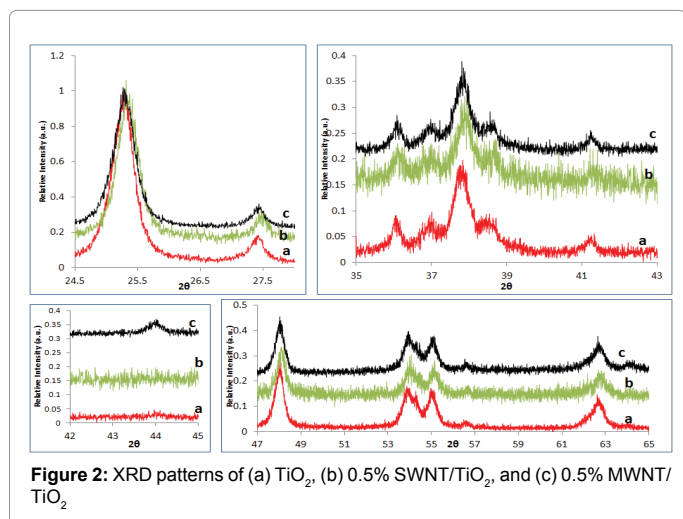
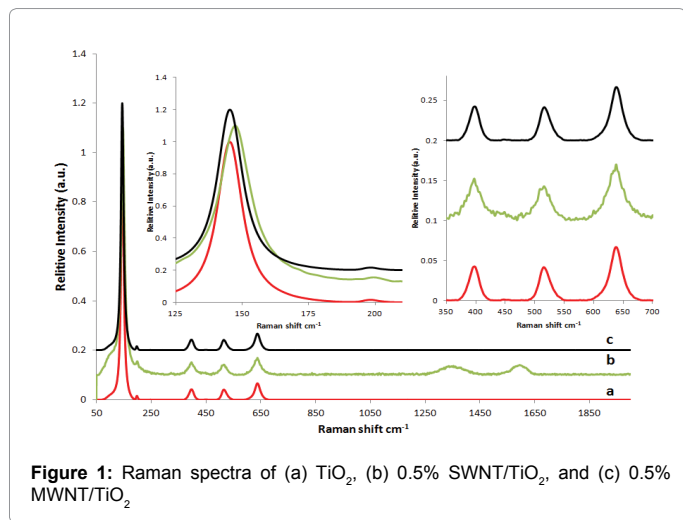
Table 2: The effect of CNTs with a shift towards a higher 2θ

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Received February 24, 2015; Accepted February 25, 2015; Published February 28, 2015

Citation: Abdulrazzak FH, Hussein FH (2015) Effects of Nanoparticle Size on Catalytic and Photocatalytic Activity of Carbon Nanotubes-Titanium Dioxide Composites. J Environ Anal Chem 2: e110. doi:10.41722380-2391.1000e110

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This refers to the homogenous distribution of SWNTs in the composite which is more than MWNTs, thus the sequences of photocatalytic degradation are: 0.5% SWNT/ TiO_2 > 0.5% MWNT/ TiO_2 > TiO_2 .

There is a shift in the Raman bands towards a higher wavenumber with a decrease in the intensities of the peak with a reduction the value of the particle size on the nanoparticle scale [9,15]. The change in intensity and brooding and the effects of the SWNTs more than the MWNTs are as a result of the lower densities of the SWNTs [16], which makes the distribution of SWNTs with particles of titanium dioxide more regular and homogenous than MWNTs, due to the abilities of SWNTs and MWNTs to distribute and reduce the agglomerates of the TiO_2 particles.

In conclusion, titanium dioxide as a semiconductor can improve the activities by adding different types of CNTs, which could increase the adsorption and photoactivity for TiO_2 . The Raman spectrum and XRD with the measurement of the surface area represent the ideal ways for explaining the change in the activities of TiO_2 .

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