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 physicochemical properties, due to the unique importance in the technology of its applications [2]. TiO₂ 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 (MWCNTs). Many attempts brought together a high surface area, fascinating electronic, chemical and mechanical properties for CNTs [8] with a low surface area for TiO₂, in addition to the properties mentioned above. The addition of CNTs to TiO₂ created new properties and structural stability, which improved their activities compared to the pristine TiO₂ 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 MWCNTs, 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 MWNMT95% carbon nanotubes with a mode diameter of 5.5, and the TiO₂ sample was purchased from Degussa, Germany (TiO₂-P25). 0.5% CNT/TiO₂ was prepared by an impregnation method. First, SWNTs, or MWCNTs were treated with a mixture of HNO₃/H₂SO₄ acid (1/3) in an water bath in 100 ml of distilled water for 30 min. After that 1g of the TiO₂ 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 TiO₂, 0.5% SWNT/TiO₂, and 0.5% MWNMTiO₂, represented by the five Raman-active modes of the anatase phase with symmetries of 2Eg, A₁g, B₁g, and E, at 145.1, 198.0, 398.0, 515.5 and 638.5 cm⁻¹ respectively, and E with a very small intensity at 445 cm⁻¹. TiO₂-P25, as a mixture of anatase and rutile, has five Raman peaks (at 145.1, 198, 398, 515.5 and 638.5 cm⁻¹) corresponding to the anatase, but just one peak, at 445 cm⁻¹, corresponding to the rutile [11]. Comparing TiO₂ with the synthesized materials shows: i- FWHM of the TiO₂ increased with the existence of SWNTs and MWNMTs, which increased within the SWNTs more than the MWNMTs, ii- the shift in wavenumber for high values within the SWNTs and MWNMTs, 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 TiO₂, which may be related to covering the composites by the much more intense peak for the large ratio of the TiO₂, 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/λβcosθ) [12]. The CNTs showed two characteristic peaks at 2θ=25.9° and 43.2°, which can be attributed to the diffraction from the (110) and (002) planes of the carbon nanotube; the second peak was more intense in the MWNMTs than the SWNTs [13], which may explain the value of the surface area for 0.5% SWNT/ TiO₂ (64 m²/g), which was more than 0.5% SWNT/TiO₂ (54 m²/g) and TiO₂ (51 m²/g). The test of the activities was done by using Cobalamin (C₁₂H₁₉CoN₄P), which is vitamin B12, as a complex compound of an organometallic species with a cobalt atom that is distinguished in a Coocene ring [14] which at the same time may give the explanation for the adsorption properties in the following sequences: 0.5% MWNMTiO₂>0.5% SWNT/TiO₂> TiO₂.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO₂</th>
<th>0.5% SWNT/TiO₂</th>
<th>0.5% MWNMTiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁</td>
<td>145.1(11.38)</td>
<td>147.0(14.46)</td>
<td>148.5(13.84)</td>
</tr>
<tr>
<td>E₂</td>
<td>198.0(6.69)</td>
<td>201.3(3.62)</td>
<td>198.2(5.85)</td>
</tr>
<tr>
<td>E₃</td>
<td>396.0(7.85)</td>
<td>399.5(9.03)</td>
<td>398.0(7.89)</td>
</tr>
<tr>
<td>A₀</td>
<td>515.5(7.65)</td>
<td>517.0(9.00)</td>
<td>515.5(7.69)</td>
</tr>
<tr>
<td>E₄</td>
<td>638.5(9.48)</td>
<td>639.0(10.04)</td>
<td>639.0(11.07)</td>
</tr>
</tbody>
</table>

### Table 2: The effect of CNTs with a shift towards a higher 28

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET (m²/g)</th>
<th>Particle size (nm)</th>
<th>Copen</th>
<th>K(s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>51</td>
<td>23.09</td>
<td>240</td>
<td>0.0648</td>
</tr>
<tr>
<td>0.5% SWNT/TiO₂</td>
<td>56</td>
<td>15.41</td>
<td>36.80</td>
<td>0.0769</td>
</tr>
<tr>
<td>0.5% MWNMTiO₂</td>
<td>64</td>
<td>20.84</td>
<td>31.20</td>
<td>0.0743</td>
</tr>
</tbody>
</table>

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In conclusion, titanium dioxide as a semiconductor can improve the activities by adding different types of CNTs, which could increase the adsorption and photocactivity 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$_2$.

References


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 nanoparticule 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.

Figure 1: Raman spectra of (a) TiO$_2$, (b) 0.5% SWNT/TiO$_2$, and (c) 0.5% MWNT/TiO$_2$.

Figure 2: XRD patterns of (a) TiO$_2$, (b) 0.5% SWNT/TiO$_2$, and (c) 0.5% MWNT/ TiO$_2$.