Synthesis and Characterization the Photocatalytic Activity of CNT/TiO_2 Nano-Composite

Shakiba Sadeghian[1*], Mohammad Reza Khanlari[2]

[1, 2]Department of Physics, Imam Khomeini International University, Iran.

* Corresponding author. Tel.: +989122681134; email: shakiba.sadeghian.333@gmail.com
Manuscript submitted June 8, 2014; accept September 10, 2014.
doi: 10.7763/IJAPM.2014.V4.309

Abstract: In this paper, synthesis of titania (TiO_2) thin film and a nanocomposite of multi-walled carbon nanotubes (MWCNTs) and titania, as MWCNT-TiO_2 by sol-gel method, are reported. The samples produced have been studied by XRD diffraction pattern, dispersive micro-raman backscattering spectroscopy and UV-Vis spectroscopy. Results showed that MWCNT/TiO_2 nanocomposite has two phases of carbon nanotubes and TiO_2 anatase, as expected. The homogeneous sol was prepared by using magnetic stirrer in high rate status and also adding basic material drop by drop. It as observed that the photocatalytic properties of nanocomposite have progressed.

Key words: Carbon nanotubes, nano-composite, sol-gel, titania.

1. Introduction

Optical and electrical properties of semiconductors at nano-scale are different from that at bulk scale. The concept of nanocomposites has attracted very interest in recent decades. Sol-gel method is known as a primary method of producing the nanocomposites. One advantage of this method is producing carbon nanotubes coated with nanoparticles as dopants. Carbon nanotubes are a specific class of materials that have attracted the attention of many researchers due to its mechanical and electronic properties. Composition of nanotubes with nanocrystals, has many applications in photocatalysts, sensors, nanoelectronics, oxygen and information storing, and in reinforcement of the polymers, ceramics and composite materials [1]. Today, TiO_2 nanoparticles are used in the fields of environment catalysis [2]. These materials have optical properties in Near-UV region of light. Photocatalytic activity of TiO_2 can be improved with the addition of nano-scale semiconductor. This issue has been identified that a proper combination of TiO_2, can improve the photocatalytic activity and this effect is more observable with in combination with anatase TiO_2 nanoparticles [3]. Recently, several methods to synthesis of semiconductors at the nano-scale have been used, such as chemical vapor deposition (CVD), sol-gel, etc. [4]. The present paper, studied the sol-gel method used in producing a nanocomposite of titanium dioxide (TiO_2) nanoparticles and multi-walled carbon nanotubes (MWCNT) in order to improve the photocatalytic activity. In this research, the physical properties of samples produced have been studied by XRD patterns, laser Raman scattering and UV-Vis spectroscopies. PUBLISHING reserves the right to do the final formatting of your paper.

2. Experimental

2.1. Synthesis of Titanium Dioxide Thin Films

Titanium dioxide thin films were stacked on the substrates from the appropriate sol using sol-gel method and by spin-coating technique. To prepare the appropriate sol, at first 50 ml of ethanol (CH3CH2OH) with a purity of 99.9% and 5 ml of acetic acid (CH3COOH) with a purity of 99.5%, stirred with the magnetic stirrer for 5 min. Then, titanium isopropoxideTi[OCH(CH3)2]4 with a purity of 98% was added drop-wise to the solution. Resulting solution was stirred for two minutes using a magnetic stirrer. Immediately after it was prepared, the solution was coated on the glass or quartz substrates, which we prepared it before, using spin-coating method. All substrates were cleaned first with neutral detergent and water in an ultrasonic bath and then with DI water. Next, ethanol was used to clean them better and finally, acetone was used to remove stains and eliminate the possible fat. For deposition on the substrates, spin coater device (Model S.C.S 86, Speed: 3000 rpm) was used at room temperature for 30 seconds. After each coating step on the substrates, they were heated in a dryer in 150°C for 15 minutes in order to dry thin film. Then another layer is coated on previously coated layer on same substrate with the order mentioned above to make a thicker film. To anneal the substrates, furnace was raised from the room temperature to 550 °C with a rate of 1 degree per minute. Then the sample was held at this temperature for half an hour. After that, the sample was returned to the room temperature.

2.2. Synthesis of CNT/TiO_2 Nanocomposites

In this section, the sol-gel method was used. To produce CNT/TiO_2 nanocomposite, first 0.1 mole of titanium is opropoxide Ti[OCH(CH3)2]4 with a purity of 98% and 200 ml of ethanol (CH3CH2OH) with a purity of 99.9%, were stirred with a magnetic stirrer for 30 minutes. Then 1.6 ml of nitric acid (65 wt%) was added to the above solution. In this study, samples with different percentages of CNT were synthesized in order to study the possible differences in crystal structures of the produced nanocomposites. To this end, once 0.2 g of multi-walled carbon nanotubes with a purity of 0.95% and once 0.6 g of that, was added to the solution and was stirred with a magnetic stirrer for about 45 min while the beaker was covered with an end-cap. After the solution was prepared, in order to aging, it was in the presence of air for a few, until its water evaporated completely. Thus, the resulting nanocomposite is prepared in powder form. To anneal, nano-powder was placed in a furnace in nitrogen gas atmosphere at 400 °C for 2 h.

3. Disscussion

3.1. Investigation of Raman Spectra

Raman spectra of these samples, were investigated by Almega Thermo Nicolet Dispersive Raman Spectrometer with wavelength of 523 nm and Nd:YLF laser with power of 30mW. In Fig. 1, Raman spectrum of carbon nanotube is shown. Peaks 1362 cm-1 , 1610 cm-1 , 2652 cm-1 related to D, G and G', respectively. Others observed peaks are due to catalyst and impurities created from it [5].

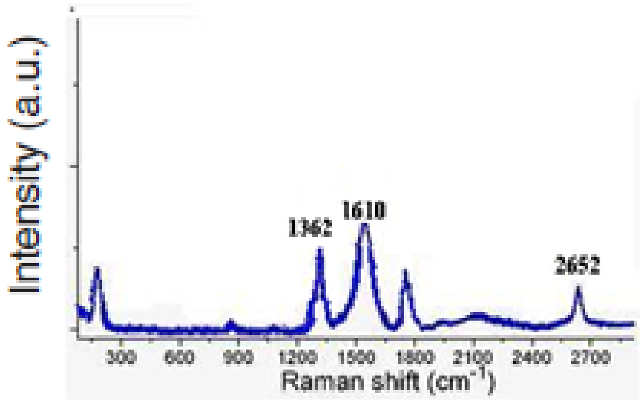


Fig. 1. Raman spectrum of carbon nanotube.

In Fig. 2, Raman spectra of titanium dioxide thin film synthesized at 550 °C, are shown. Peaks present in the figure, indicate the anatase phase of titanium dioxide [6].

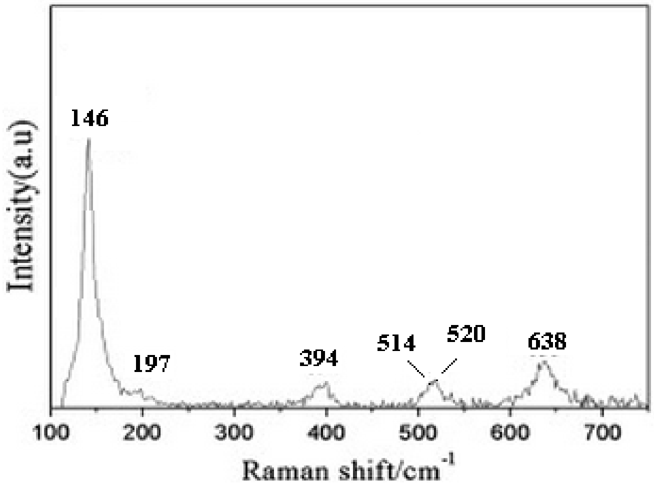


Fig. 2. Raman spectrum of titanium dioxide thin film.

Group theory, predicts the existence of six symmetrical optical modes, A1g +2B1g +3Eg, in anatase titanium dioxide [7] .

$$A1g + 2B1g + 3Eg = \Gamma optical$$

As we can see in Fig. 2, the strong peak at 146 cm^{-1} indicates Eg mode. The peak at 197cm^{-1} also indicates Eg mode. The peak at 394 cm^{-1} indicates B1g. Peak at 514 cm^{-1} indicates A 1g. The peaks at 520cm^{-1} and 638 cm^{-1}, indicate B1g and Eg mode, respectively [8]. Fig. 3 shows the Raman spectrum of CNT/TiO_2 nanocomposite synthesized at 400 °C.

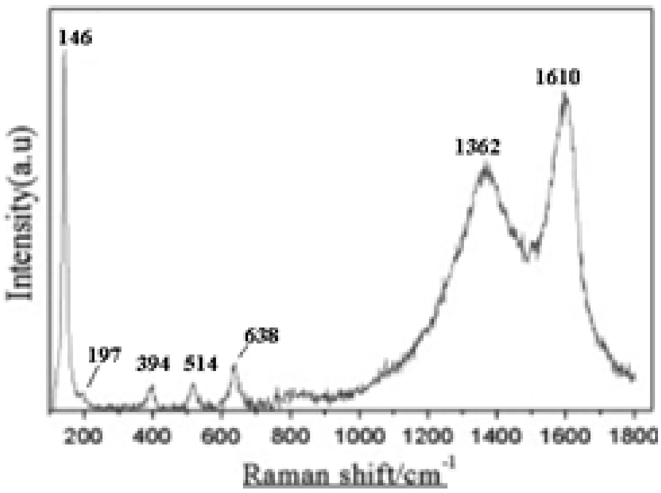


Fig. 3. Raman spectrum of CNT/TiO2 nanocomposite.

As shown in Fig. 3, there are peaks in the synthesized nanocomposite that related to both titanium dioxide and carbon nanotubes. According to Fig. 3, the peak at 146 cm^{-1} that shows Eg mode of anatase titanium dioxide, has been sharper.

On the other hand, the peak at 1610 cm^{-1}, is graphite peak (G) of carbon nanotube. It is seen that the peak intensity in nanocomposite is increased than the initial nanotube. In Fig. 3, the peak at 1362cm^{-1} is related to the D Band. By Comparing Fig. 2 and Fig. 3, we can see a reduction in the intensity of peak D than peak G.

It should be noted that the process of adding TiO_2 to CNT to produce CNT/TiO_2 nanocomposites, could be useful until a certain value. After that, this increasing, in turn would be a factor to creation of more defects and thus increasing the intensity of peak D. Raman spectrum taken from a sample with higher percentage of titanium dioxide than CNT in the final composite, is seen in Fig. 4. According to the figure, we find that the intensity of peak G of carbon nanotube in nanocomposite, has been decreased. FWHM of the main peak of anatase 146cm^{-1} related to Eg mode is increased from 10/65 cm^{-1} for titanium dioxide to 11/34 cm^{-1} for CNT/TiO_2 nanocomposite.

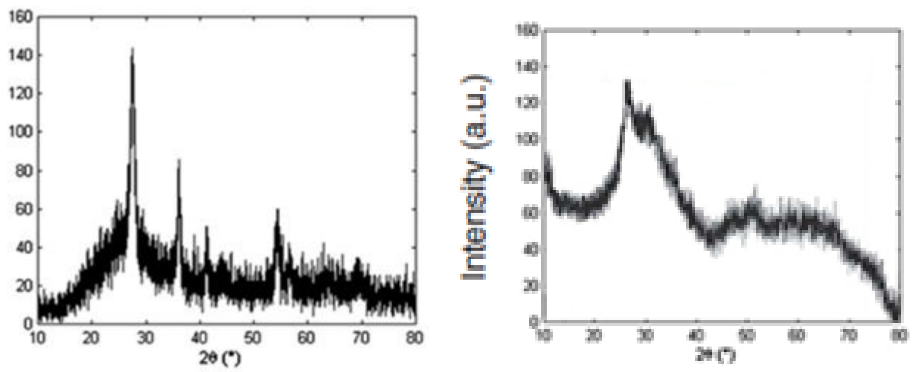
3.2. Investigation of X-ray Diffraction Patterns of the Samples

X-ray diffraction patterns, were studied using X'Pert XRD; PHILIPS with wavelength of 1.54 Å.

Sample (1) was deposited for four times with the rate of 3000 rpm, thickness of 149 nm and annealing temperature of 550 °C.

Sample (2) was deposited for three times with the rate of 3000 rpm, thickness of 119 nm and annealing temperature of 550 °C.

It can be seen that both samples, have tetragonal structure and have the peaks of (101), (004), (200) and (105). In both samples, preferred peak of (101) is exist (Fig. 5).



a) b)

Fig. 5. Comparison of the spectra of X-ray diffraction pattern: a): a film with thickness of 119 nm. b): a film with thickness of 149 nm.

In Fig. 6, we investigate X-ray diffraction pattern of CNT/TiO_2 nanocomposite. We can see peaks at 2θ angles of 26° and 44° related to the Bragg reflection planes of (002) and (100).

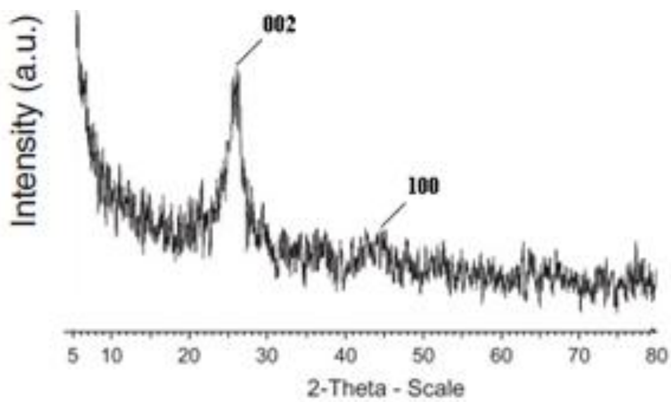


Fig. 6. X-ray diffraction pattern of the initial carbon nanotube.

Diffraction pattern of titanium dioxide thin film is related to four main diffraction peaks at 2θ angles of 26°, 38°, 48° and 54° related to the crystal planes of (101), (004), (200) and (105), respectively (Fig. 7).

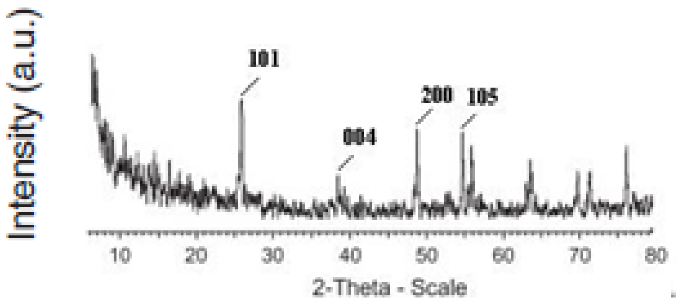


Fig. 7. XRD patterns of titanium dioxide thin film.

We can see from XRD pattern of the final composite that it has peaks composed of peaks of the initial carbon nanotube and titanium dioxide thin film.

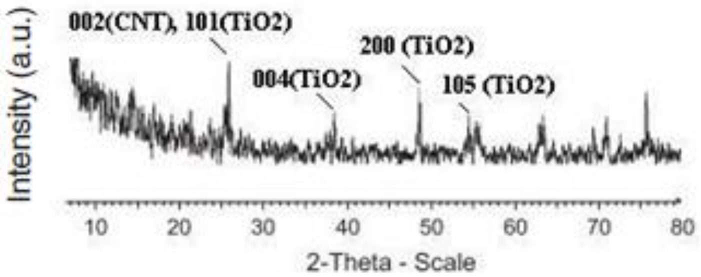


Fig. 8. X-ray diffraction pattern of CNT/TiO_2 nanocomposite.

As can be seen in Fig. 8, diffraction peaks indicate the presence of anatase titanium dioxide in nanocomposites that it is in good agreement with the files of JCPDS 78-2486. Bragg reflection plane (101) related to anatase phase, is overlapped with carbon nanotubes' plane (002).

Different percentages of the carbon nanotube reduce to somewhat the intensity of peaks and increase to somewhat the width of peaks. We can conclude that the grain size is decreased by increasing the concentration of CNTs in the solution. This is due to the fact that carbon atoms are linked together that prevents the crystal growth of TiO_2 within the nanocomposite. Calculations performed based on Debye - Scherrer relation, estimated the grain size of titanium dioxide thin films about 20 nm, and same calculations, estimated the grain size of CNT/TiO_2 nanocomposite about 17 nm.

3.3. Investigation of UV-Vis Spectrum of the Samples

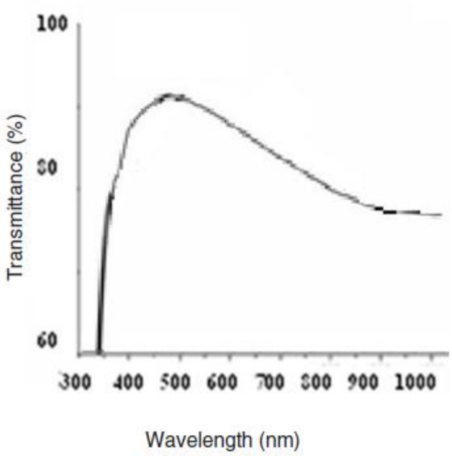


Fig. 9. Transmission spectrum of titanium dioxide thin film with thickness of 119 nm.

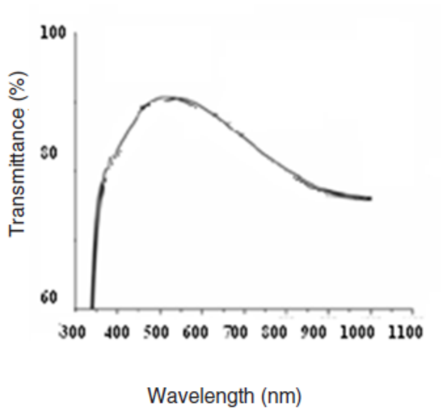


Fig. 10. Transmission spectrum of titanium dioxide thin film with thickness of 149 nm.

Absorption and transmission spectroscopies were performed by RAY LEIGH device (Model 2601 UV). UV-visible spectrum of titanium dioxide thin films coated on glass with thicknesses of 119 and 149 nm was investigated in order to examine their optical properties. Transmission spectrum of the annealed sample was investigated. As we can see in Fig. 9, maximum transmission occurs in the range of 515-560 nm. In addition, we can observe that by increasing the thickness of samples, transmission peak shifts towards the higher wavelengths. This may be due to the change in the optical energy bandgap in thicker layers. Relatively high transmission through the film indicates low roughness and high uniformity of the film's surface [9].

In Fig. 11, we can see UV absorption spectrum of the synthesized titanium dioxide thin film. According to the figure, an absorption band near the wavelength of 387 nm is seen related to titanium dioxide particles, which lies in ultraviolet region of light.

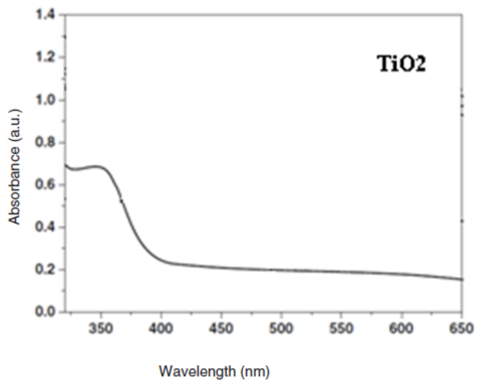


Fig. 11. UV absorption spectrum of titanium dioxide thin film.

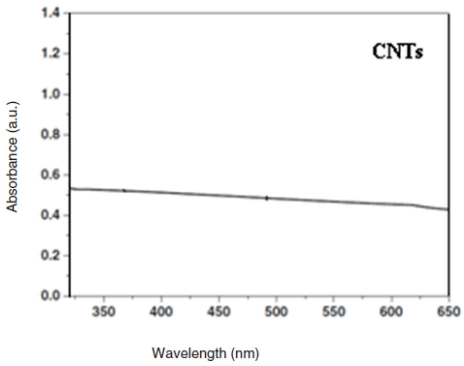


Fig. 12. Absorption spectrum for pure CNTs.

Pure carbon nanotube shows absorption over the entire range of visible light.

Sample (1) consists of 0.2 g and sample (2) consists of 0.6 g of CNT. Formation of TiO_2 nanoparticles within carbon nanotubes implies that in production process, the growth TiO_2 at nano-scale is effectively restricted. This result already has been confirmed by Raman spectroscopy and X-ray diffraction pattern. Results show that in both samples a wide optical absorption is present in the visible region of light, in addition to the absorption band near the wavelength of 387 nm. The peak observed in absorption spectra of both samples (see Fig. 13), shifts towards the blue compared to the absorption spectrum of titanium oxide (see Fig. 14). This blue shift can be due to the effect of particle size. In addition, we can see that the visible light absorption spectrum of titanium oxide coated on carbon nanotube, increases by increasing CNTs in the composite (visible light absorption spectrum of the sample (2) is more than of the sample (1). In ddition, the possibility of increasing the surface charge of titanium dioxide in the composite due to the addition of carbon nanotube is present. This may alter the process of arrangement of the electron – hole pairs and the photocatalytic activity under visible light irradiation [10].

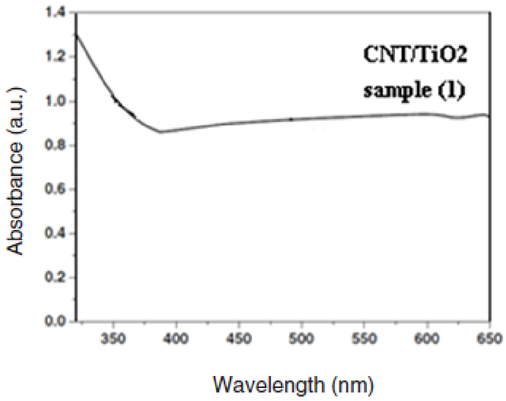


Fig. 13. Absorption spectrum for nanocomposite consisting of 0.2 g of CNTs.

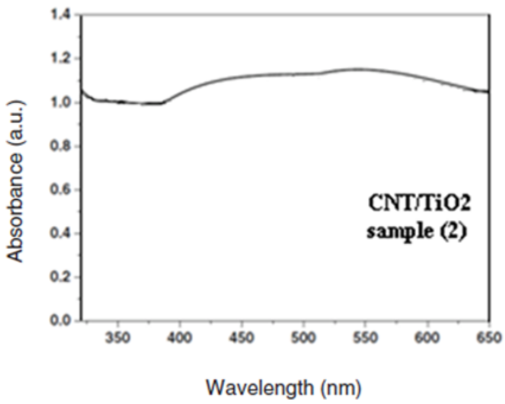


Fig. 14. Absorption spectrum for nanocomposite consisting of 0.6 g of CNTs.

4. Conclusion

In this research, titanium dioxide thin films and CNT-TiO_2 nanocomposite are synthesized using sol-gel method. Characterizations of the samples have been studied by XRD diffraction pattern, dispersive micro-raman backscattering spectroscopy and UV-Vis absorption and transmission spectroscopies. Results show the presence of only titanium dioxide anatase phase. The preferred peak of crystal growth of TiO_2 anatase is (101). X-ray diffraction pattern of CNT-TiO_2 nanocomposite indicates the overlapping of (101) planes of titanium dioxide and (002) planes of carbon nanotube. By comparing the grain sizes of thin film and nanocomposite, we can see the decreasing of the particles, due to the presence of CNTs. By increasing the thickness of thin films, the grain sizes are also increased. By increasing the thickness of titanium dioxide thin films, the transmission peak shifts to the higher wavelengths. This may be due to the change in the optical energy bandgap in thicker layers. Relatively high transmission through the film indicates low roughness and high uniformity of the film's surface. Producing the nanocomposite, improves the crystal structure of TiO_2 and we observe that the Eg peak related to anatase dioxide titanium, is sharper. The presence of TiO_2 in nanocomposite resulted to reducing the disordering peak (D) and increasing the graphite peak (G). By comparing UV-Vis absorption spectra of TiO_2 and CNT/TiO_2 nanocomposite, we can see a blue shift in absorption band of the nanocomposite. This may have occurred due to the addition of CNTs to TiO_2 and decreasing in particle sizes. By addition of CNTs, we observe an increasing in absorption in visible region of light and increasing of surface charge and enhancement of photocatalytic activity of CNT/TiO_2.

References

[1] Pender, M. J., Sowards, L. A., Hartgerink, J. D., Stone,M. O., & Naik, R. R. (2006). *Nano Lett.*, *6*, 40-45.

[2] Vautier, M., Guillard, C., & Herrmann, J. (2001). Photocalytic degradation of dyes in water. 46-50.

[3] Fuerte, A., Hermandez, A., Lonso, M. D., Garcia, M., & Conesa, J. C. (2002). Effect of doping level in the photocatalytic degradation of toluene using sunlight-type excitationNano Ti-W size mixed oxides. *212*, 1-9.

[4] Sales, L. S., Robles, P., Nune, D., Mohallem, N., Gusevskaya, E., & Sousa, E. (2003). Characterization and catalytic activity studies of sol-gel CNT-SiO2 nanocomposites. *Mater Charact*, *50*, 95-99.

[5] Dresselhaus, M. S., *et al*. (2005). Raman spectroscopy of carbon nanotubes. *Physics Reports*, *409*, 47-99.

[6] Reinaldo, J., & Gonzalez, R. (1996). *Infrared, X-Ray, and EELS Studies of Nanophasetitania*. Dissertation, Faculty of the Virginia Polytechnic Institute and StateUniversity, Blacksburg, Virginia.

[7] Bersani, D., & Lottici, P. P. (1998). *Appl. Phys. Lett.*, 72-73.

[8] Jiang, D., Xu, Y., Hou, B., Wu, D., & Sun, Y. (2008). *Eur. J. Inorg. Chem.*, 1236-1240.

[9] Hemissi, M., Amardjia-Adnani, & Digest, H. (2007). *Journal of Nanomaterials and Biostructures*, *2(4)*, 299.

[10] Wang, W., Serp, P., Kalck, P., & Faria, J. L. (2005). Visible light photodegradation of phenol on MWNT-TiO_2 composite catalysts prepared by a modified sol-gel method. *Journal of Molecular Catalysis A*, *235(1-2)*, 194–199.

Shakiba Sadeghian was born on February 14, 1987. She received her B.S. degree from ShahidRajaee Teacher Training University in 2010, and M.S. degree in condensed matter physics from Imam Khomeini International Universityin 2012. She once was a teacher in Pre University and High School Physics. Her reseach interests are in nano-composite, thin films, carbon nanotubes.

She published the paper entitled Synthesis and Characterizing the Photocatalytic Activity of CNT/TiO_2 Nano-Composite, in Indian Journal of Scientific Research. She attended the 2th National Conference on Nanotechnology Applications in Pure and Applied Sciences, Kermanshah, Iran.