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Preparation of Photoactive Tungsten-doped Anatase Nanotubes Using Hydrothermal Technique

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TITANIA (TiO_2) and tungsten doped titania (W-TiO_2) nanoshpheres were prepared by the sol-gel method, while tungsten doped titania nanotubes was formed by the hydrothermal process. The structure and the morphology of the prepared photocatalysts have been characterized using X-ray diffraction (XRD) and high resolution transmission electron microscope (HRTEM) techniques, respectively. XRD results of the W-TiO_2 powder, prepared by the sol - gel method and the hydrothermal method showed that anatase structure was formed. HRTEM images illustrate that the average diameter of the as-synthesized W-TiO_2 nanosphers was about 70 nm and the nanotubes ,W-TiO_2 NT, have an outer diameter ranging from 8 to 10 nm and inner diameter of 2 to 3 nm and a length of few hundreds of nanometers. The photocatalytic performance of the prepared photocatalysts was studied through the degradation of acid orange dye (AO7). Higher efficiency for degradation of AO7 was obtained using W-TiO_2 NT compared with TiO_2 and W-TiO_2 nano-powders. The results show that the dye removal was 99.88, 95.00 and 81.00 % within 60minutes in the case of using W-TiO_2 NT and W-TiO_2 nanospheres and TiO_2 nanospheres, respectively and the absorption edge shifts toward visible light region for both W- TiO_2 nano-powders and NT.

Keywords : Hydrothermal, Sol-gel, Nanotubes, Titanium dioxide, Tungsten doped titania.

Photocatalytic degradation of some organics has been studied using some metal oxide or sulfide photocatalysts. The most commonly studied photocatalysts include: TiO_2, ZnO, WO_3, Fe_2O_3, and ZnS[(1)].

The oxidation ability is an important factor for degradation of organics using photocatalytic oxidation technique. The photo generation of valence band holes (h_{vb}) and creation of hydroxyl radicals (HO• ads) are the key factors for using the photocatalyst in the degradation of organic compounds. This is also true if the excited conduction band electrons (e^-_{cb}) have reducing power that is sufficient for the reduction of oxygen molecules to superoxide [(2)].

The electron-hole pairs formation is considered to be an important key factor in the photocatalytic oxidation processes of organics for H_2O and CO_2. The energy of the semiconductor's band gap may define the irradiation energy that may be required

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for excitation an electron from the valence band to the conduction band, resulting in leaving a positively charged hole in the valence band, h^{+}_{vb}. If the needed excitation energy of a given semiconductor to form charge carriers is outside the wavelength range of the incident irradiation energy, the photocatalyst is useless for the degradative oxidation of organic compounds without electronic modification [3-5].

Titanium dioxide (TiO_2) photocatalyst has good oxidation ability as well as band gap energy that could absorb UV radiation. The ultraviolet radiation is considered to make up only about 5% of the solar energy. The doping of titanium dioxide with metals, non-metals and other metal oxides is of great interest for the improvement of visible light absorption and/or the decrement of recombination rate of excited electrons and holes. The reductive deposition of some noble metals (*e.g.* Pt or Au) onto the titanium dioxide surface is considered to be one of the most promising doping techniques. The splitting of water into H_2 and O_2 could not be carried out by photocatalysis techniques using undoped TiO_2. When nanoparticles of platinum are deposited on the surface of titanium dioxide, an increment in the H_2 production rate from adsorbed water molecules may be observed [6]. This may be attributed to the transfer of electrons from the TiO_2 surface to the metal resulting in the reduction of water molecules to hydrogen. The high prices of noble metals make them difficult to be used for industrial scale. Some transition metals, *i.e.* Fe and Cr, have been used as dopants ; in conclusion, these metals are considered to act as electron and hole traps as well as decrease the recombination rate of electron hole pairs [7-10].

Doping with tungstate has shown a shift of the band gap of TiO_2 to be closer to the visible spectrum (2.86 eV vs. 3.21 eV for pure anatase). This result is highly promising since increment the solar energy absorption is considered to be one of the important goals of titanium dioxide scientific research. The enhancement of photocatalytic degradation rate is also mentioned for many of these photocatalysts compared to pure anatase and Degussa. This improvement in the phtotcatalytic reaction may be attributed to an increment of surface acidity of the photocatalyst surface as well as the trapping of charge carriers [11, 12]. Azodyes are chemical dyes that are hazardous to environment [13]. The discharge of large amounts of these dyes into the environment via the dye effluents from textile mills causes problems for municipal wastewater treatment facilities.

The present work concerns with the preparation of TiO_2 nanosphere, W-TiO_2 nanosphere and W-TiO_2 nanotube photocatalysts. The oxidative efficiency of the prepared photocatalysts has been evaluated by the degradation of *azo*dye such as Acid Orange 7 (AO7).

Experimental Procedures

Preparation of anatase & tungsten -doped anatase nanoparticles

A TiO_2 transparent sol was prepared by mixing of 17.5 g titanium(IV) butoxide $Ti(O\text{-}nBu)_4$ reagent grade (Sigma-Aldrich), 120 ml ethanol, 15 ml acetic acid, and 5 ml deionized water. The mixture was aged for 24 hr and was stirred at ambient

temperature. In case of preparation of tungsten doped titania, 60 ml of aqueous solution containing 4.56 g ammonium paratungestate (Sigma-Aldrich, ≥ 99%) ($(NH_4)_{10}W_{12}O_{41}$, F.W.= 3042.55) was added under vigorous stirring to titania sol dropwise over 2 hr until the W-TiO_2 gel is formed. The TiO_2 gel was aged two days. The W-TiO_2 gel was then dried with a rotary evaporator at 150 ^oC. After drying, the samples were collected and ground using a mill. The TiO_2 powder was calcinated at 450 ^oC for three hours [14] .

Preparation of W-TiO_2 nanotubes

W-TiO_2 nanotubes were synthesized by the hydrothermal method. A conversion from nanoparticles to nanotubes was achieved by treating the W-TiO_2 nanoparticle with 10 M NaOH (ADWIC, 96%) at 150 °C for 24 hr in a Teflon-lined autoclave. The precipitates were neutralized thoroughly with HCl, then washed with deionized water, filtered and dried at 100°C. The detailed procedure is reported elsewhere [15, 16] .

Characterization

X-ray diffraction (XRD) analysis of the prepared powders was performed using BRUKUR D8 ADVANCE with secondary monochromatic beam CuKα radiation at 40 Kv and 40 mA, whereas the microstructure of the prepared powders was examined using high resolution transmission electron microscope (HRTEM), JEOL, JEM-2100 working voltage at 200kV. The morphology of TiO_2 doped with tungsten was examined using Field emission scanning electron microscopy (FESEM) using JOEL Model JED-2300 instrument. The tungsten was observed by Energy-dispersive X-ray spectroscopy (EDX). The EDX spectra of the TiO_2 doped with tungsten was recorded on a JOEL Model JED-2300 instrument.

Photocatalytic experiments

The experiments were carried out using a photoreactor with fifteen fluorescent bulbs generating approximately 120 W m^{-2} from 365-600 nm. Prior to irradiation, all of the samples were sonicated for 10 min to break up the photocatalyst agglomerates powder. During the photoreaction, the samples were stirred and the temperature held constant at 25-30 ˚C. For all runs, the amount of photocatalyst suspended in the dye solution was kept constant at 100 mg/l. the initial dye concentration was 250mg/l. The photocatalyst dose among the various runs was kept constant. A magnetic stirrer guaranteed satisfactory powder suspension and the uniformity of the reacting mixture. Oxygen was bubbled during this stage in order to ensure the availability of the oxidant gas in the solution. The irradiation time was taken at the moment when the lamp was switched on. Samples for analyses were withdrawn at fixed intervals of time. The dye concentration was analyzed using UV-visible spectrophotometer (Agilent-Carry 100). The maximum absorption wavelength for the acid orange 7 dye (λ_{max}) is 480 nm. The removal dye efficiency was estimated by applying the following Equation (1):

$$\text{Removal Dye Efficiency (\%)} = (C_0\text{-}C/C_0) \times 100 \quad (1)$$

where C_o is the original dye content and C is the residual dye in solution.

The chemical oxygen demand (COD) was determined by an open-reflux dichromate titrimetric procedure, as described in standard methods [17].

Results and Discussions

Phase composition of the as-synthesized samples and hydrothermally treated samples

Figure 1 shows XRD patterns of the as-synthesized W-TiO_2 powder, prepared by the sol - gel method and hydrothermal method. As indicated in these patterns, both two samples exhibit anatase structure according to JCPDS 21-1272; *i.e.* 25.33(101), 37.88(004), 47.98(200), 54.74(105), 62.80(204), 70.00(116), 75.16 (301).

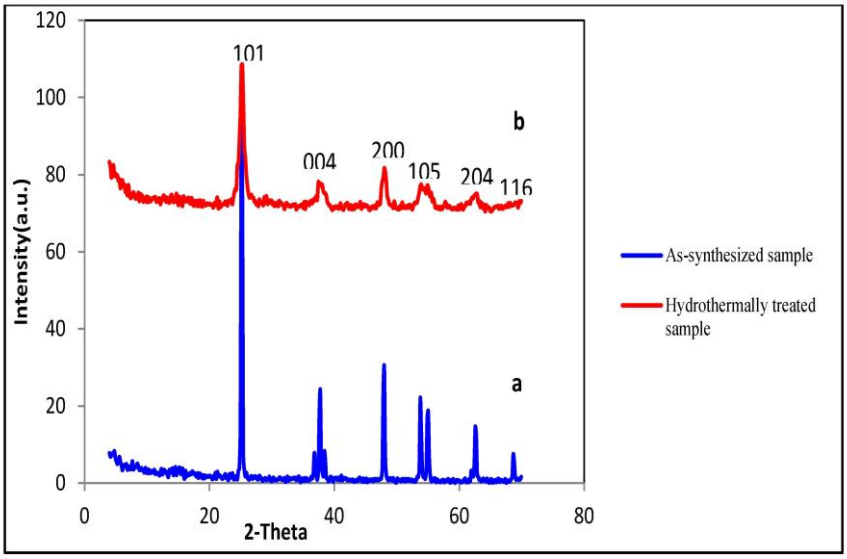
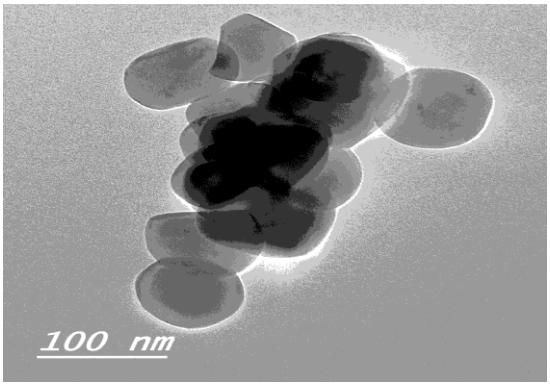


Fig. 1. XRD patterns of the as-synthesized W-doped TiO_2 powders: a) sol-gel sample b) Hydrothermally treated for 24 hr at 150 °C.

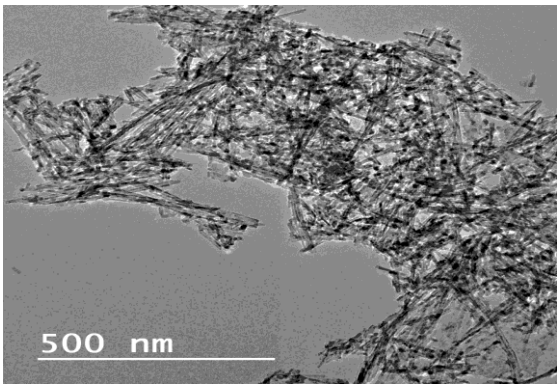
Morphology of as-synthesized W-TiO_2 and W- TiO_2 NT

Figure 2 (a, b and c) shows HRTEM images of as-synthesized W-TiO_2 nanoparticles and the obtained W-TiO_2 NT after the hydrothermal treatment with low and high-magnification, respectively. As-synthesized W-TiO_2 is nano-particle of pure anatase with an average diameter of about 70 nm as shown in Fig. 2(a).

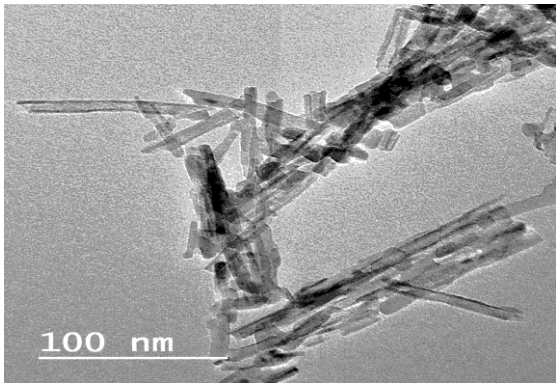
The as-grown W- TiO_2 NTs are generally homogeneous, (Fig.2b), fine hollow open-ended tubes with a uniform diameter along their lengths. The nanotubes have an outer diameter ranging from 8 to 10 nm and inner diameter of 2 to 3 nm and a length of few hundreds of nanometers, showing narrow size distribution, as shown in Fig.2(c). It is clear from these figures a well identified multi walled nanotubular structure can be formatted as it is clear from these figures.



(a)



(b)



(c)

Fig.2. Typical HR-TEM images of as-prepared a) W-doped TiO_2 and b) W-doped TNTs c) high-magnification W-doped TNTs.

One of the proposed mechanisms of the nanotube formation via the hydrothermal reaction is the formation of titanate containing alkali metal, first, during the hydrothermal treatment process using sodium hydroxide. Second, the ion exchange process of the alkali metal element has been occurred. The protonated titanate is then formed as a nano-sheet. Finally, the nano-sheet converts to be a tubular structure by scrolling process for lowering the surface energy [18].

SEM/ EDAX analysis of the W-TiO_2 NTs

The SEM image revealed that the W-TiO_2 NT has smooth surfaces and uniformities in diameter size (Fig. 3a). Furthermore, the electron dispersive spectrum of the W–TiO_2 NT is made. From this EDX spectrum, (Fig. 3b), a very weak signal for W and a very strong signal for Ti can be observed. The quantitative analysis of the W–TiO_2 NT based on this spectrum showed that about 2.5 % of W was present. This is consistent with the nominal amount of doped tungsten.

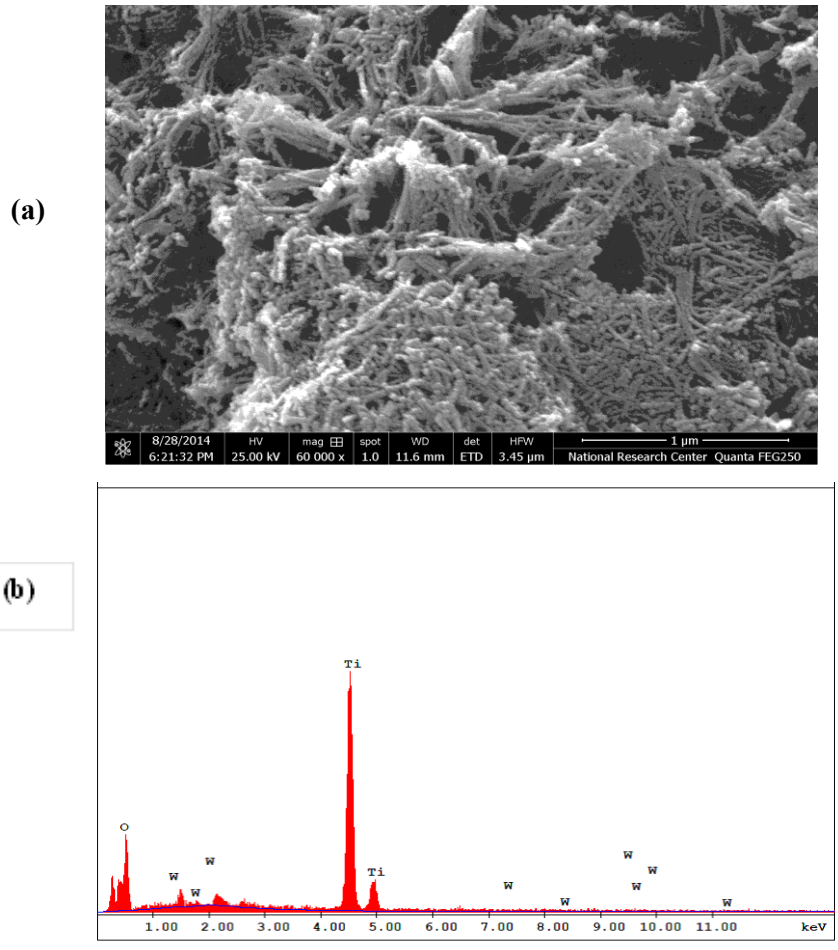


Fig. 3. (a) SEM image for W-doped W–TiO2 NT, (b) EDS spectra for W-doped W–TiO2 NT.

Photocatalytic performance

The photocatalytic degradation of AO7 was studied using the prepared photocatalysts. The structure of AO7 is shown in Fig. 4. The photolysis of AO7 dye was carried out in the absence of photocatalyst. The results showed that no significant dye or COD removal within 60 min of irradiation, (Fig. 5).

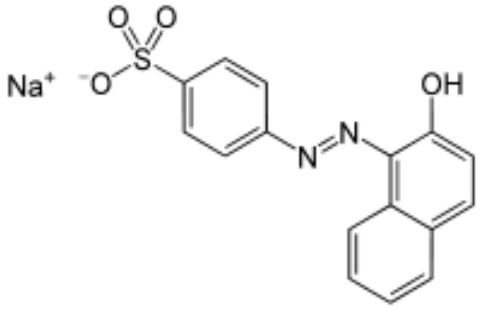


Fig. 4. Structure of Acid Orange (AO7) dye .

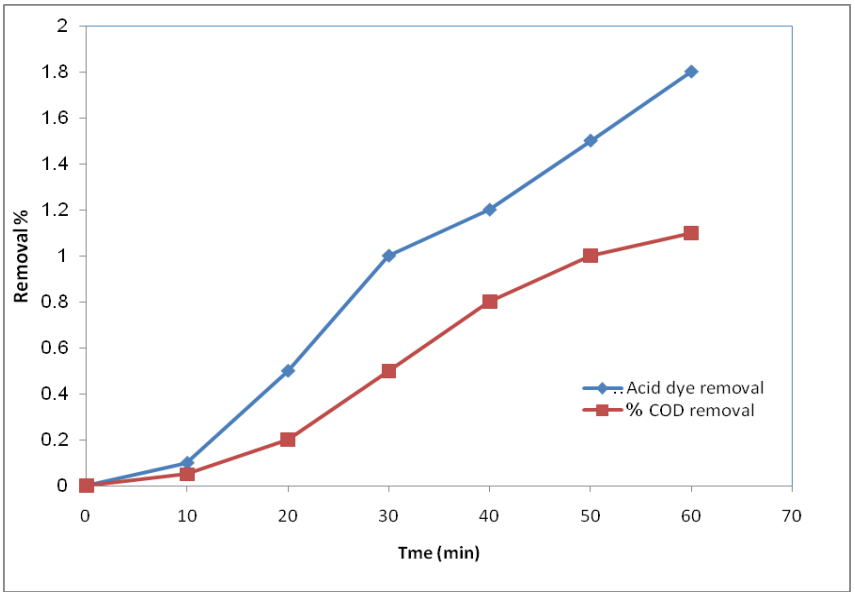


Fig. 5. Relationship between time of photolysis and the percentage of total dye and COD removal of acid orange dye in absence of Photocatalyst: pH= 5, and Temp= 25 °C.

The photocatalytic oxidation of AO7 experiment shows that the dye removal results were 99.88, 95.00 and 81.00 % in the case of using W-TiO_2 NT, W-TiO_2 nanospheres and TiO_2 nanospheres, respectively (Fig. 6). While the results of COD removal were

96.00, 90.00 and 62.00 % in the case of using W-TiO_2 NT, W-TiO_2 nanospheres and TiO_2 nanospheres, respectively, as shown in Fig. 7.

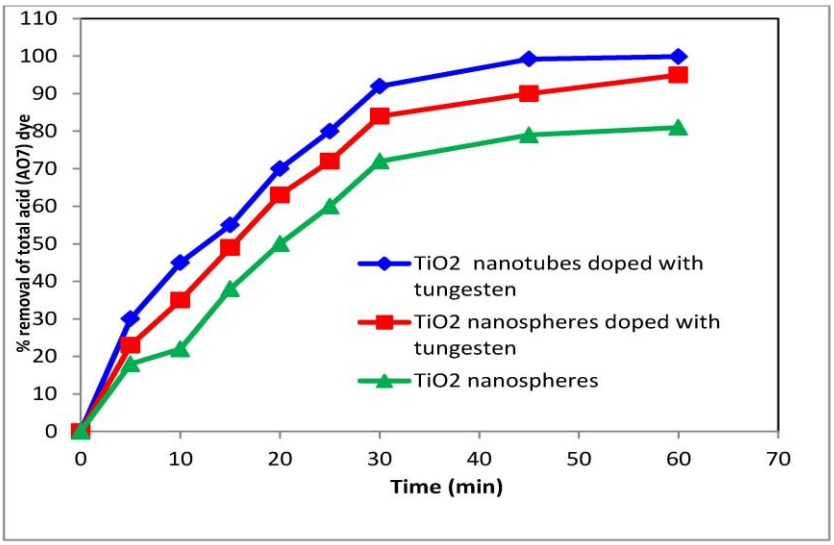


Fig. 6. Relationship between time of irradiation and the percentage of total Acid Orange dye removal using different photocatalysts. Photocatalyst: 100 mgl^{-1}, pH= 5 and Temp= 25 ^{o}C.

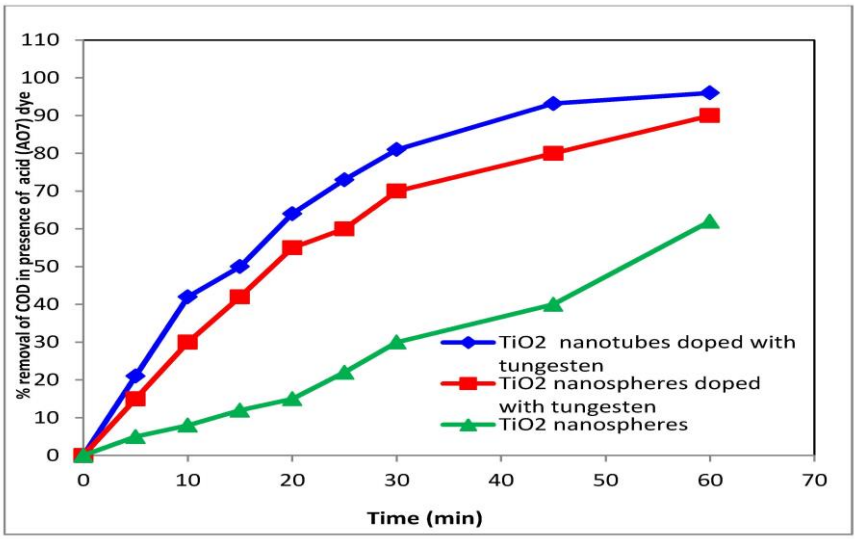


Fig. 7. Relationship between time of irradiation and the percentage of total COD removal in presence of acid orange dye using different photocatalysts. Photocatalyst: 100 mgl^{-1}, pH= 5, and Temp= 25 ^{o}C.

TiO_2 only exhibit the fundamental absorption band in the UV light region, while the absorption edge shifts towards the visible light region obviously for the W-TiO_2 and W-TiO_2 NT. The same behavior was observed with doping with earth ion [19]. The results indicate that the photocatalytic efficiency is relatively high in case of using nanotube morphology of TiO_2 due to increment in the photocatalyst surface area [20]. This increment of photocatalytic efficiency was attributed to that when W ions in contact with the TiO_2 surface; it could trap excited electrons in the W-TiO_2 photocatalyst. During irradiation of W-TiO_2 photocatalyst, the excited electron may transfer from O^{2-} to $W^{6+}$and the W^{6+} reduces to W^{5+} as the electron trapping process is occurring. The oxidation of W^{5+} to W^{6+}may be performed by the oxygen present in the reaction mixture that could again trap the electrons resulting in increment of the photocatalytic activity [21] . Doping of TiO_2 with tungsten may form junction that contributes in the separation of the photogenerated electron–hole pairs. This may enhance the photocatalytic activity of the doped photocatalyst[22,23] . The crystallinity of nanotubes may decrease the electron-hole recombination probability in bulk as well as increase the diffusion efficiency of electrons and holes to adsorbed reactants on the TiO_2 surface to participate in the photocatalytic degradation reaction [24] .

Conclusions

Titania (TiO_2) and tungsten doped titania (W-TiO_2) nanoparticles were prepared using sol-gel technique. Then transformation of tungsten doped titania nanoparticles into nanotubes (W-TiO_2 NT) was achieved using hydrothermal technique. Comparison of the photocatalytic activity of the three photocatalyst was made. The results of the photocatalytic oxidation of AO7 showed that the dye removal was 99.88, 95.00 and 81.00 % in the case of using W-TiO_2 NT, W-TiO_2 nanospheres and TiO_2 nanospheres, respectively and the absorption edge shifts towards visible light region obviously for the W- TiO_2 and W- TiO_2 NT. COD removal was 96.00, 90.00 and 62.00 % in the case of using W-TiO_2 NT, W-TiO_2 nanospheres and TiO_2 nanospheres, respectively.

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تحضـر ثـاني أكسـيد التيتـانيوم (الأنـاتيز) المطعـم بالتنجسـتن فـي صورة أنابيب نانومترية باستخدام المعالجة الحرارية المائية

حسام الدين عبد الفتاح الناظر و أميرة محمد الرافعى*
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تم في هذا البحث تحضير حوافز ضوئية كروية و أنبوبية في حجم النانو مصنوعة من ثاني أكسيد التيتانيوم (الأناتيز) و أيضا ثاني أكسيد التيتانيوم المطعم بعنصر التنجستين. واستخدمت تقنية المحلول الغروى في تحضير الحوافز الكروية و تقنية المعالجة الحرارية المائية في تحضير الحوافز الأنبوبية النانومترية، لتتم مقارنة النتائج المتحصل عليها باستخدام كلتا التقنيتين. و قد تم توصيف الحوافز المحضرة باستخدام تقنيات حيود الأشعة السينية و المجهر الالكتروني النافذوقد اوضحت نتائج الاشعة السينية تكون طور الاناتيز. وأوضحت صور المجهر الالكتروني النافذ أن متوسط قطر الكريات النانومترية لأكسيد التيتانيوم المطعم بالتنجستين كان حوالي ٧٠ نانومتر أما الأنابيب النانوية مترية فقد كان القطر الخارجي لها تتراوح من ٨ إلى ١٠ نانومتر، وقطرها الداخلي ٢-٣ نانومتر، ويبلغ طولها بضع مئات من النانومتر. وتم قياس كفاءة المحفزات الضوئية المحضره في عملية الأكسدة الحفزية الضوئية للصبغة العضوية (البرتقالية الحامضية) في وجود الأشعة الفوق بنفسجية و الضوء المرئي. وأوضحت النتائج العملية أن كفاءة الحافز الضوئي المحضر من ثاني أكسيد التيتانيوم المطعم بعنصر التنجستين في صورة الأنابيب النانومترية أعلى من المحضر في الصورة الكرويه النانومترية حيث أن نسبة كفاءة تكسير الصبغة البرتقالية وصلت الى ٩٩,٨٨%. و أظهرت النتائج ايضا أن تطعيم الحافز الضوئي بعنصر التنجستين قد رفع من كفاءة امتصاص الحافز للضوء المرئي.