تحضير وتحديد خصائص منظومة الأقطاب النانونية لتيتانات الفاناديوم فى تطبيقات معالجة المياه

محمد عبدالفتاح؛ أحمد الغامدى؛ فريد الطنطاوى؛ طه حنفى؛ حسام رجب

تم بنجاح تحضير المركبات النانونية لتيتانات الفاناديوم كمحفز لأغراض معالجة المياه، وذلك بواسطة الحرارة الهيدروجينية. كما تم التعرف على المحفز الصلب بواسطة الأشعة السينية، والميكروسكوب الإلكترونى الماسح، والميكروسكوب الإلكترونى العاكس.

وقد تم تقييم نشاط المركبات النانونية للمحفز من خلال التحلل بالتحفيز الضوئى بمادة ريمازول ب تحت الإشعاع الضوئى المرئى. واتضح أن التيتانيا التى تم تنشيطها فى مركبات الفاناديوم النانونية قد أظهرت تحسن كبير فى النشاط الضوئى للمحفز مقارنة بالأنابيب النانونية للتيتانات، والجزيئات النانونية لأكسيد التيتانات، ويرجع حدوث هذا التحسن إلى نتيجة التأثير المتناغم للتصميم البنائى للجزيئات النانونية للفاناديوم والتيتانيوم.

Figure 3
TEM image of titanium oxide nanotubes.

Figure 4
SEM (a, b) images of VO_x/TiO_2.

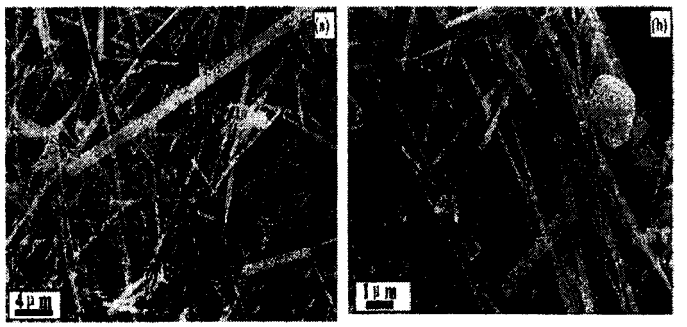


Figure 5
The normalized absorbance changes of all the samples with irradiation time under visible light irradiation

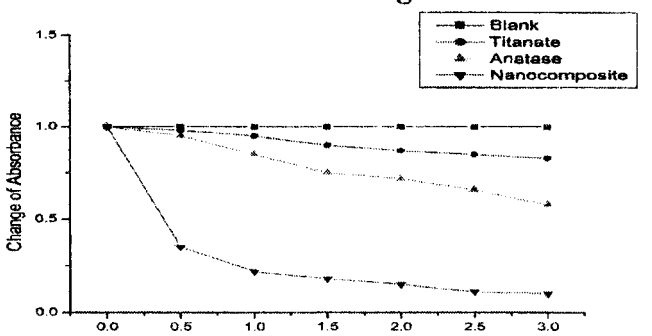


Figure 1
XRD of titanium oxide nanotubes (a) and VO_x/TiO_2 (b).

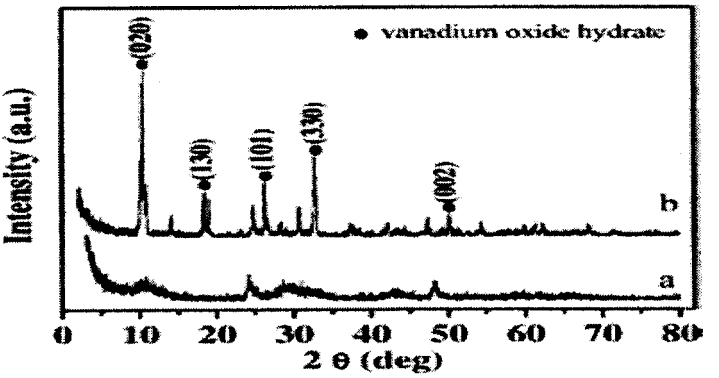
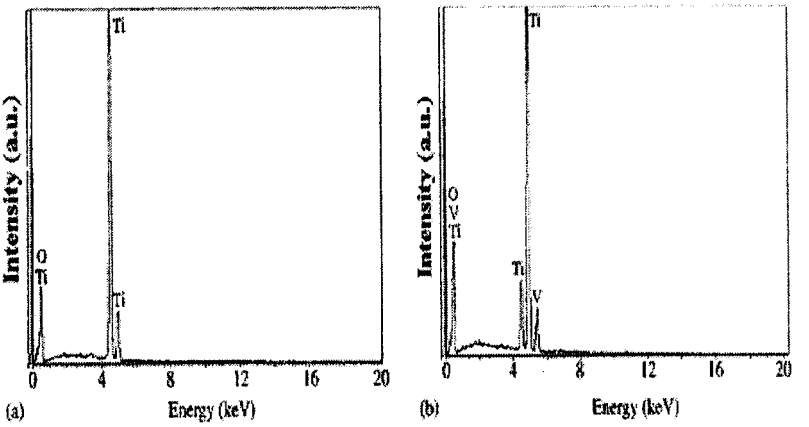


Figure 2
EDAX spectra of titanium oxide nanotubes (a) and VO_x/TiO_2 (b).



21 - Lee, Woo-Jin Alhosan, M.; Sara Yohe, L.; Nathan, Macy L. and William, H., Smyrl. J. Electrochem. Soc., 155, 2008, p. 915.
22 – Lai, Y. K.; Sun, L.; Chen, Y. C.; Zhuang, H. F.; Lin, C. J. and Chin, J. W., Electrochem. J. Soc, 153, 2006, p. 123.
23 – Zhu, H. Y.; Gao, X. P.; Lan, Y.; Song, D. Y.; Xi Y.X. and Zhao, J. C., Am, J. Chem. Soc., 126, 2004, p. 8380.
24 – Yu, J. G.; Yu, H. G.; Cheng, B and Trapalis, C., Mol. J. Catal., A 249, 2006, p.135.
25 - Contescu C., Popa; V.T., Miller, J. B., Ko; I. E., Schwarz; J. A., J. Solar Energy Eng., 199, 1997, p. 120.
26 - Zhang, F. X., Guan, N. J., Li, Y. Z., Zhang, X. J., Chen J. X. and Zeng, H. S., Langmuir., 19, 2003, p. 8230.
27 - Navío, J. A., Testa, J. J.; Djedjeian, P., Padrón, J. R., Rodríguez D. and Litter, M. I., Appl. Catal. A. Gen., 178, 1999, p. 191.
28 - Li, Y. Z., Hwang, D. S.; Lee N. H. and Kim, S. J., Chem. Phys. Lett., 404, 2005, p. 25.
29 - Asahi, R.; Morikawa, T., Ohwaki, T., Aoki K. and Taga, Y., Science, 293, 2001, p. 269.
30 - Chen, D., Yang, D., Wang, Q. and Jiang, Z. Y., Ind. Eng. Chem. Res., 45, 2006, p. 4110.
31 - Fu, X.; Clark, L. A.; Yang Q. and Anderson, M. A., Environ. Sci, Technol., 30, 1996, p. 647.
32 – Jung, K. Y. and Park, S.B., J. Photochem. Photobiol. A: Chem., 127, 1999, p. 117.
33 - Jung J. Y., and Park, S. B., Appl. Catal. B: Environ., 25, 2000, p. 249.
34 - Zhang, Q. H.; Gao, L.; Sun, J.; Zhang, S., Chem. Lett., 2002, p. 226.
35 - Chandrappa, G. T.; Steunou, N.; Cassaignon, S.; Bauvais, C.; Livage, J.; Catal. Today, 78, 2003, p. 85.
36 - Alonso, B.; Livage, J.; Solid J., State Chem, 148, 1999, p. 16.
37 - Chen, Q., Du, G.H; Zhang, S., Peng, L.M., Acta Crystallogr, 58, 2002, p. 587.
38 - Sun; X. M., Li; Y.D., Chem. Eur. J., 9, 2003, p. 2229.
39 - Fukahori, S.; Ichiura, H.; Kitaoka, T.; Anaka, H.T., Environ. Sci. Technol., 37, 2003, pp. 1048–1051.

References

1 – Wilson, S. C.; Burnett, V.; Waterhouse, K. S. and Jones, K.C., Environ. Sci. Technol; 28, 1994, p. 259.

2 – Ollis, D. F.; Pelizzetti, E. and Serpone, N., Environ. Sci. Technol., 25, 1991, p. 1522.

3 – Macak, J. M.; Zlamal, M.; rysa, J. K. and Schmuki, P., Small., 3, 2007, p. 300.

4 – Khan, M. A; Jung, H. T. and Yang, O.B., J. Phys. Chem., B 110, 2006, p. 6626.

5 – Chen, Y. S.; Crittenden, J. C.; Hackney, S.; Sutter, L. and Hand, D. W., Environ. Sci. Technol, 39, 2005, p. 1201.

6 – Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T. and Niihara, K., Adv. Mater. 11, 1999, p. 1307.

7 - Du, G. H.; Chen, Q.; Che, R.C.; Yuan, Z.Y. and Peng, L. M., Appl. Phys. Lett., 79, 2001, p. 702.

8 – Lakshmi, B. B.; Patrissi, C. J.; and Martin, C. R., Chem. Mater, 9, 1997, p. 2544.

9 – Zwilling, V.; Darque-Ceretti, E.; Forveille, A. B.; David, D.; Perrinl, M.Y. and Aucouturier, M., Surf.Interface Anal, 27, 1999, p. 629.

10 – Choi, A.; Termin, W.; and Hoffmann, M. R., J. Phys. Chem., 98, 1994, p. 13669.

11 – Wang, K. X.; Yao, B. D.; Morris, M. A. and Holmes, J. D., Chem. Commun, 17, 2005, p. 4825.

12 – Hu, Y, and Yuan, C. W., Cryst, J. Growth, 274, 2005, p. 563.

13 – Candal, R. J.; Zeltner, W. A.; and Anderson, M. A., Environ. Sci. Technol0; 34, 2000, p. 3443.

14 – Ong, K. G; Varghese, O. K.; Mor, G. K.; Grimes, C. A., Nanosci, J. Nanotechnol., 5, 2005, p. 1801.

15 – Cao, F.; Oskam, G.; Meyer, G. J.; Searson, P. C., Phys. J. Chem., 100, 1996, p.17021.

16 – Macak, J. M.; Sirotna, K. and Schmuki, P., Electrochim, Acta., 50, 2005, p. 3679.

17 - Cai, Q. Y; Paulose, M; Varghese, O. K.; Shankar, K, and Grimes, C. A., Mater J. Res., 20, 2005, p. 230.

18 – Macak, J. M.; Tsuchiya, H.; Taveira, L.; Aldabergerova, S., and Schmuki, P. Angew, Chem. Int. Ed, 44, 2005, p. 7463.

19 – Paulose, M.; Shankar, K.; Yoriya, S.; Prakasam, H. E.; Varghese, O. K.; Mor, G. K.; Latempa, T. A.; Fitzgerald, A., and Grimes, C. A., Phys, J. Chem. B, 110, 2006, p.16179.

20 - Lee, Woo- Jin Alhoshan, M.; and Smyrl, W. H., Electrochem. Soc., 153 (11), 2006, p. 499.

effect of vanadium and titanium nanopartcicles as reported in BPA/TiO2/zeolite system by Fukahori et al[39].

4 - Conclusion

Titanium dioxide has long been used to remediate organic substances present in wastewater. Consequently significant effort has been directed during the last several years towards modification of this semiconductor material to suite other applications. In the present work, we have summarized the various ways of TiO_2 photocatalytic modifications successfully utilized for the degradation of organic dyes, especially aiming at high efficiency, activity in visible range of the solar spectrum and effective reuse of the catalyst. Modifications have been achieved using vanadium oxide. Means of photosensitization of TiO_2 with organic dyes and co-modification for TiO_2 have been critically analyzed. While such modifications have demonstrated significant improvement in the ability of Ti-oxide system to remediate wastewater in laboratory scale, it is apparent that the need to develop pilot scale treatment systems and to apply the technique in cost effective dyehouse effluent purification processes stipulates continued in depth research. Thus extensive possibilities exist in this promising area of research, which need to be bring full attention and the outcome of such investigation should benefit commercial sector both in terms of ecology and economy. Since there are no detailed reports on the metal-doped TiO_2 nanotube arrays electrode and its photocatalytic characteristics, this study gives evidence of the best conditions required for the photoactivity of vanadium oxide/titanate composites nanotubes.

3 - Results and discussion

Figure 1a illustrates the XRD pattern of synthesized titanate nanotubes, which is indexed to H_2 Ti_3 O_7 according to Chen and Sun[37-38], that might be described as $K_xH_{2-x}Ti_3O_7$ *(x ≈ 0.27)* according to our EDAX results, figure 2a. The patterns of VO*x*/titanate-CNRs, fig. 1b, indicate the presence of two phases, titanate and a vanadium oxide. According to JCPDS X-ray powder data files (28-1433), the powder XRD pattern of the vanadium phase indicates that the vanadium oxides acquires the structure of vanadium oxide hydrate ($V_3O_7 \cdot H_2O$), with orthorhombic symmetry and lattice parameters of *a* = 9.34 Å, *b* = 17.0Å, *c* = 3.626 Å. EDAX analysis of VO*x*/titanate-CNRs is shown in fig. 2b exhibiting the existence of O, Ti and Vat a ratio (weight) of Ti/V of 1:6.

Figure 3a, exhibit the TEM image of titanate nanotubes whereas, the morphology of VO*x*/titanate-CNRs is shown in fig. 4a and b, showing the final VO*x*/titanate-CNRs as consisting mainly of nanorods. It can be seen clearly, that VO*x*/titanate-CNRs are orderly grown together in the form of bundles and handsome rigidity. The typical VO*x*/titanate-CNRs length is measured at about 10 μm, but its length ranges from 10 to 20 μm with a diameter ranging from 100 to 300 nm. Length and diameter of the VO*x*/titanate-CNRs were found to depend on the preparation conditions, such as the dimension of template material and reaction time. The VO*x*/titanate-CNRs acquire a black-green color, indicating some vanadium in a IV oxidation state.

Figure 5 exhibits the normalized absorbance changes of all the solutions with irradiation time under visible light. Degradation of RzB dye was observed to resist degradation by visible light, while in presence of the titanate, anatase and nanocomposite, the normalized absorption of the solutions has decreased with the prolonged irradiation time indicating progressive dye degradation. From fig. 5, it is clear that RzB/composite system showed the minimum normalized absorbance after irradiation for 3 hrs which means that the vanadium titanate nanocomposites functions its best photocatalytic activity in comparison with those of other nanotubes such as pure anatase and titanate nanoparticles. This observation is likely due to the synergistic

g of titanate nanotubes were then added to the $V_2O_5 \cdot nH_2O$ sol (weight ratio titanate nanotubes: V_2O_5 = 1: 10) producing a brown mixture that was stirred for 24 hrs. The brown mixture was then placed in Teflon-lined autoclave with a stainless-steel shell, maintained at 200°C for 48 hrs. The solid black-green powder was then washed with distilled water and ethanol several times until clear filtrate. Finally, the solid is dried at 60°C for 5 hrs. and the VO*x*/titanates were then characterized before activity tests are considered.

B - Structural characterization

Structural and chemical characterization of all solid vanadium oxide doped titania samples were examined using powder X-ray diffraction (Oxford, England) operating with Cu Kα radiation, scanning electron microscope SEM (Schimadzu, Japan), transmission electron microscope TEM (Hitachi-600) and energy-dispersive spectrometer EDAX (Link-200).

C - Photocatalytic activity

In order to investigate the photocatalytic activity of the samples, photodecolorization of Remazole B (RzB) under visible light irradiation was carried out in the presence of nanocomposites at room temperature. A 300W halogen lamp as the visible light source was placed in a cylindrical glass vessel with a recycling water glass jacket; meanwhile a cut-off filter was placed outside the water jacket to completely remove any radiation at wavelengths below 420 nm, thereby ensuring illumination by visible light only. Reaction suspension was prepared by adding 80 mg of the solid catalyst sample into a 100 mL beaker containing 80 mL × 10^{-5} M of the RzB dye. Prior to illumination, the suspension was magnetically stirred for 30 min. in dark to establish an absorption/desorption equilibrium of RzB dye. Subsequently, the dispersion containing RzB and photocatalyst was irradiated under visible light. At given intervals, 3mL of the suspensions were sampled and subsequently centrifuged at a rate of 9000 rpm for 15 min. UV–VIS absorption spectra of the supernatant were then measured using a Perkin Elmer UV WinLab Lambda 35 spectrophotometer. For comparison, similar measurements were also carried out on as-prepared nanotube, and pure anatase and titanate nanopartilce.

applied potential, anodization duration and electrolyte composition[16-21]. The effect of crystallinity and length of TiO_2 nanotubes on the photodegradation of methylene blue in aqueous solution has been investigated by Lai et al[22]. However, the effect of tube wall thickness on the photocatalytic ability, which might play a key role on the charge transfer and the separation of electron–hole pairs, was not attended to. The effect of the calcination temperature on the overall photocatalytic activity of TiO_2 catalysts was also studied and reported[23-24]. In addition, doping of TiO_2 with metals such as Pt, Ag and Fe[25-27] or with selected non-metal elements such as N, C and B[28-30] proved to improve photocatalytic activity of TiO_2 under UV and even visible light. Induced structural and physicochemical properties, such as high thermal stability, quantum-sized crystalline and good surface wettability were convincingly reported[31-33].

In the present work, photochemical activity of Vanadium oxide doped TiO_2 prepared via a hydrothermal method targeting photocatalytically active small-sized anatase crystallite of metal doped titania with of unique nanotubular structure. The morphological structure of the metal doped titania and their photocatalytic degradation of Remazole B, under visible light irradiation, are reported herein.

2 - Experimental techniques

A - Synthesis of vanadium oxide/titanate composites nanotubes

Titanate nanotubes were prepared[33-34]. Anatase titanium dioxide (0.5g) and 32 ml of a 10M KOH aqueous solution were mixed homogeneously in a Teflon-lined autoclave with a stainless steel shell. The mixture was placed in the baking oven at 200°C for 20 hr. After cooling to room temperature to ambient, gradually, the final white product was vacuum-filtered, neutralized with 1M HCl, washed with distilled water till pH= 7 then finally dried at 60°C for 5 hrs.

$V_2O_5 \cdot nH_2O$ solutions were synthesized by dissolving one gram of V_2O_5 in 50 ml. of hydrogen peroxide solution (30%) forming V(V) peroxo complexes[35-36]. The product of the exothermic reaction is a bright orange solution that is formed after about 20 min at a final pH ≈ 1.5. The solution gradually turns into a red-brown gel after 24 hrs. 0.1

also to decompose natural organic matter that has environmental and industrial negative impacts. This technology also might be useful for water pre-treatment of desalination process especially with reverse osmosis technique.

Organic dyes and aromatic hydrocarbons are typical pollutants emitted from industrial and domestic activities[1]. Among the technologies developed for the treatment of harmful pollutants is the photocatalytic oxidation process using heterogeneous photocatalysis which is regarded as a promising technology to decompose harmful pollutants to final non-toxic products. Titanium dioxide has been proved to be a very efficient photocatalyst for the degradation of harmful pollutants in water and air due to its high stability, nontoxicity and inexpensiveness[2].

As nano-structured TiO_2 proved higher photochemical reactivity than that of bulk TiO_2 particles[3-5], further advances in the nano-scale technology is now adopted for synthesizing titania with a unique nano-architecture that is consisting of vertically oriented, immobilized, highly ordered and high-aspect ratio nanotubes such as hydrothermal technique[6-7], template synthesis[8], and anodic oxidation[9]. However, the photocatalytic oxidation technology involving TiO_2 photocatalysts always suffers from the difficulties of separating suspended TiO_2 nanoparticles from aqueous solution as well as of the low quantum yield achieved caused by the rapid combination of photogenerated electrons and holes[10]. In comparison, the immobilization of TiO_2 film on a solid carrier by spin[11] or dip-coating[12] methods are more desirable for photocatalytic application, rather of functional defects such as poor adhesion of TiO_2 film to supporting carriers[13] and low surface area of supported TiO_2 photocatalyst exposed to solution. Accordingly, TiO_2 nanotube-array film using anodization process would provide greater surface area for photochemical action that is easily accessible to the redox couples in the electrolyte and offers the ability to influence the absorption and propagation of light by precisely designing and controlling the geometrical parameters of the architecture[14-15] even to atailored morphology of such a nanotubular TiO_2 film through controlled

SYNTHESIS AND CHARACTERIZATION OF VANADIUM TITANATE NANORODS ARRAYS FOR WATER TREATMENT APPLICATION

Mohamed Abdelfattah[1][2], Ahmed Al-Ghamdi[3], Farid El- Tantawy[4], Taha Hanafy[5][6], Hossam Ragab

Titanate/vanadium nano-composites nanotubes as catalysts for water treatment purposes were successfully prepared via a hydrothermal method. The solid catalysts were characterized by means of X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). The activity of the nanocomposites catalysts was assessed through the photocatalytic degradation of Remazole B under visible light irradiation. It is concluded that titania doped vanadia nanocomposites exhibit a much improved photocatalytic activity in comparison with titanate nanotube, and anatase TiO_2 nanoparticle. This observation is explained as likely due to the synergistic effect of vanadium and titanium nanopartcicles architecture.

1 - Introduction

In recent years, interest has been focused on the use of semiconductor materials as photocatalysts for the decomposition of pollutants in wastewater effluents of industrial waste and normal household's disposals. Moreover, photocatalysts can be utilized for the decomposition of inorganic compounds, and for removal of trace metals as well as destruction of viruses and bacteria. It can be used

1 - Department of Chemisty, Faculty of Sciene, University of Tabuk 71491, Saudi Arabia.
2 - Department of Chemistry, Faculty of Education, El-Arish, Egypt.
3 - Department of Physics, Faculty of Science, King Abdel Aziz University, Jeddah 21589, Saudi Arabia.
4 - Department of Physics, Faculty of Science, Suez Canal Univrsity, Ismailia, Egypt.
5 - Department of Physics, Faculty of Science, Univrsity, of Tabuk 71491, Saudi Arabia.
6 - Department of Physics, Faculty of Science, Fayoum University, 63514 EL Fayoum, Egypt.