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Magnetic field effect on the photocatalytic activity of self-organized TiO_2 nanotubes

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ABSTRACT

In the present paper, the magnetic field effect on the photocatalytic activity of self-organized TiO_2 nanotube arrays has been studied. Highly ordered TiO_2 nanotube arrays with an average pore diameter of about 100nm and an average length of about 2μm were grown on a titanium foil by anodic oxidation. Photocatalytic experiments were conducted in a photoreactor, in which the anodized sample was surrounded by an electromagnetic device with the magnetic field direction vertical to the axes of the reactor. Experimental results showed that the photodegradation efficiency increases slightly by the increase of the magnetic field, indicating that the electron–hole pairs could be separated by applying magnetic field, and consequently enhancing photocatalytic activity.

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KEYWORDS

Anodic oxidation;
Magnetic field;
Nanotubes;
Photocatalytic activity;
Titanium dioxide.

INTRODUCTION

Over the past few decades, photocatalytic degradation of organic pollutants in waste water using semiconductor nanomaterials, such as Fe_2O_3, NiO, WO_3, ZnO, SnO_2, ZrO_2, CdS, etc. has attracted much attention[1]. Among these various photocatalysts, titanium dioxide (TiO_2) has proven to be the most suitable material in photocatalysis due to its relatively high efficiency, low cost, excellent charge transport property, nontoxicity and photostability[2-4].

The photocatalytic characteristics of TiO_2 are greatly enhanced due to the advent of nanotechnology. At nanoscale, not only the surface area of titanium dioxide particle increases dramatically but also it exhibits other effects on optical properties and size quantization. An increased rate in photocatalytic reaction is observed as the redox potential increases and the size decreases. In some cases energy from any ambient light source can be used effectively as an energy source of photocatalysis instead of UV light[5]. While the photoexcited state of most semiconductors is generally unstable and can easily break down, titanium dioxide, on the other hand, remains stable even when it is photoexcited. This is one of the reasons that TiO_2 makes an excellent photocatalyst[6]. However, conventional powder photocatalysts are not always suitable for large-scale applications, because they exhibit high recombination efficiency of photogenerated electron–hole pairs, and they are difficult to separate after reaction, therefore, several meth-

ods for fabricating fixed TiO_2 photocatalyst on solid support substrates have been studied[7-10].

As an effective fabrication technology, the electrochemical anodization technique shows its advantage on preparing highly ordered TiO_2 nanotube arrays, which possesses good mechanical adhesion strength and electronic conductivity since it is directly grown from titanium metal substrate[11,12]. In addition, the properties and morphology of such a TiO_2 film are easily controlled by tailoring the anodization conditions such as the anodization time, applied voltage, electrolyte composition and thermal treatment conditions[13-15].

Recently, research on using TiO_2 nanotube arrays as photo-catalysts has been performed[16]. However, very few reports concerning the magnetic field effect on photocatalytic reactions, although considerable efforts have been focused on the study of magnetic field effects on the kinetics of chemical reactions after the discovery of nuclear and electronic spin polarization phenomena during chemical reactions[17,18]. Since the common characteristic of all photocatalytic degradation reactions is the generation of extraordinarily reactive free radicals and radical ions, it is believed that the behavior of the photoinduced electrons and holes, together with the radicals and radical ions produced, may be affected by magnetic field[19].

In this paper, the effect of the magnetic field on the photocatalytic degradation of methyl orange over the self-organized TiO_2 nanotube arrays has been studied. The results indicate that the photodegradation efficiency can be slightly enhanced by the applied magnetic field.

EXPERIMENTAL

Self-organized TiO_2 nanotube arrays were grown on a titanium foil (99.6% purity, Tite Inc., Shanghai) with thickness of about 3μm by anodic oxidation. Before the electrochemical processing, the titanium foil was chemically etched in 30% HCl solution for 30 minutes at 80°C, afterwards rinsed with deionized water and dried in air. The anodization process was performed in a two-electrode electrochemical cell, with a platinum counter electrode at constant voltage of 30V for 40 minutes in an electrolyte of ethylene glycol containing ammonium fluoride (NH_4F) with the concentration of 0.5 wt%. The anodized sample was then annealed at 450°C for 1 hour with heating and cooling rates of 20°C/min. After cooling, the sample was cut into four equal pieces (about $2cm^2$).

Each piece was then tested for the degradation of methyl orange (MO) under different magnetic field intensities (0, 0.3, 0.5, 0.7T) using a DXSB-100 double-yoke double-tuning adjustable air gap electromagnet. The photocatalytic experiments were carried out by immersing the TiO_2 nanotube arrays film in 20 ml glass beaker containing methyl orange (MO) solution with the concentration of 20mg/L. Prior to irradiation, TiO_2 nanotube arrays film was soaked in MO solution for 30 min in a dark environment to achieve the equilibrium of adsorption and desorption. A UV-lamp (λ = 360 nm) was fixed about 15cm above the surface of the solution. The absorbance changes of MO were measured using a UV spectrophotometer at different time intervals (0, 10, 20, 40 and 60 min) during the whole photodegradation process. Figure 1 shows the photocatalytic reactor diagram.

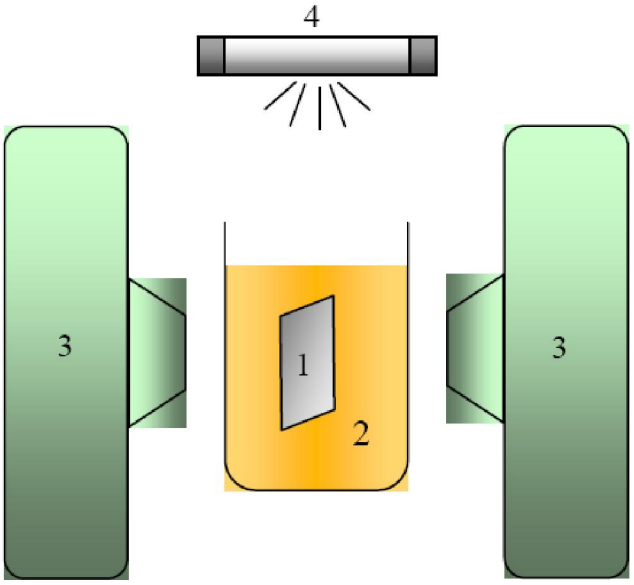

Figure 1 : Schematic diagram of the photocatalytic reactor; (1) anodized sample, (2) MO, (3) electromagnet, (4) UV lamp.

The surface morphology and dimension characterization (top-view and cross-section view) of the anodized samples were observed by scanning electron microscopy (SEM, JEOL JSM-6700F). The cross-section images were taken from mechanically cut samples. The elemental composition of the anodized sample was analyzed using the energy dispersive X-ray diffraction technique (EDX).

RESULTS AND DISCUSSION

Figure 2 shows the SEM images of the anodized sample after annealing. The sample exposes nanotube arrays with pore diameter of about 100 nm and an average nanotube length of about 2μm (see figure 2(a)).

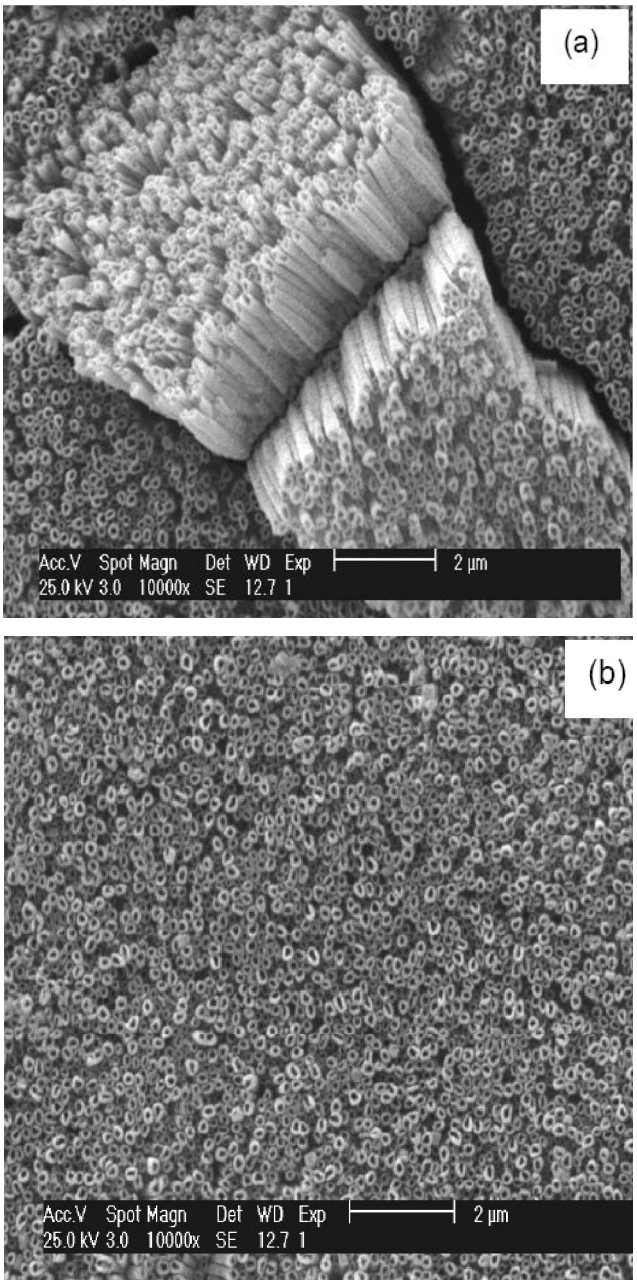

Figure 2 : SEM images of the self-organized TiO_2 nanotubes grown on titanium foil; (a) side view and (b) top view

Elemental analysis using the energy dispersive X-ray diffraction (EDX) technique reveals that Ti and O are the major elements without the existence of any impurity peaks as can be seen from figure 3. The quantitative analysis shows that the atomic ratio of Ti:O is about 1:2, which confirms the composition of TiO_2.

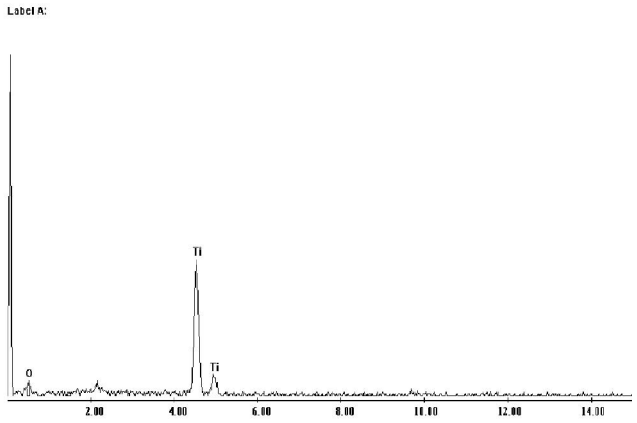

Figure 3 : EDX spectrum of the anodized sample

Figure 3 shows the relative concentration of MO as a function of time at different applied magnetic fields (0 - 0.7T). From this figure it is apparent that the magnetic field has a slight effect on the photocatalytic activity, where changing the magnetic field from 0.3-0.7 T resulted in a slight change in the concentration of the MO.

The degradation efficiency of MO after 20 min at different applied magnetic fields is summarized in TABLE 1. It was observed the photodegradation efficiency of the nanotube arrays increases gradually by the increase of the magnetic field, where at magnetic field strength of 0.7T the highest degradation efficiency was achieved (68%) after UV exposure for 20min, while in the absence of the magnetic field (0 T) only 63.5% of MO was decomposed, indicating that there is an enhancement in the degradation efficiency by a factor of 5%.

TABLE 1 : Summary of the degradation efficiency of MO in 20 minutes at different applied magnetic fields

Magnetic field strength (Tesla)	0	0.3	0.5	0.7
Degradation efficiency after 20 min (%)	63.5	66	67.9	68

Since the common characteristic of all photocatalytic degradation reactions is the generation of extraordinarily reactive free radicals and radical ions and according to the theory of photocatalysis, the efficiency of photocatalysis decreases mostly due to the recombination of photo-generated electron–hole pairs, so it is predicted that the magnetic field across the photocatalyst can promote the separation of photo-gener-

ated electrons and holes and prevent them from recombination, thus enhances the photocatalytic efficiency of the catalyst. Although we couldn't investigate the photocatalytic activity at high magnetic fields due to the high fluctuation in the intensity of the UV light at magnetic field intensities higher than 0.7T, we believe that noticeable effect can be achieved at higher magnetic fied intensities.

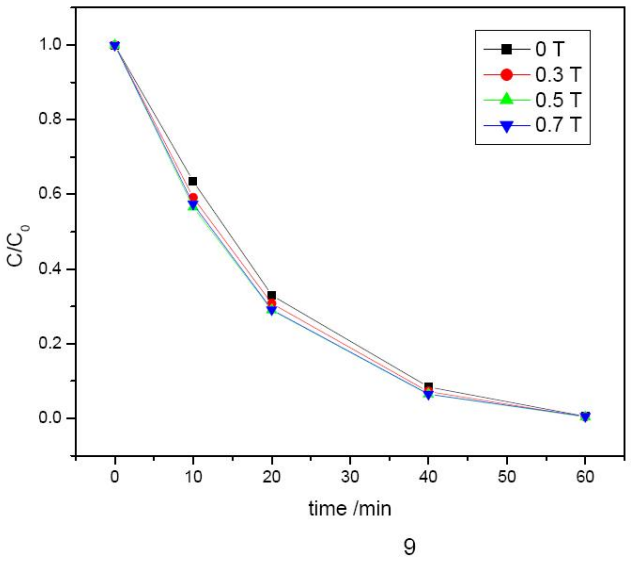

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Figure 4 : Relative reduction of MO concentration as a function of time at different applied magnetic fields

CONCLUSION

Highly ordered TiO_2 nanotube arrays with average length and pore diameter of 2mm and 100nm, respectively, were grown by anodic oxidation on titanium foil. The effect of the magnetic field on the degradation of methyl orange was studied at different magnetic field strengths (0, 0.3, 0.5 and 0.7T). The results showed that the degradation efficiency increases by the increase of the magnetic filed. The mechanism of this enhancement effect was attributed to the promotion of the separation of photo-generated electron– hole pairs inside the semiconductor by the magnetic field.

REFERENCES

[1] M.A.Gondal, M.N.Sayeed, A.Alarfaj; Chem.Phys.Lett., **445**, 325 **(2007)**.

[2] Y.Li, W.Xie, X.Hu, G.Shen, X.Zhou, Y.Xiang, X.Zhao, P.Fang; Langmuir, **26**, 591 **(2010)**.

[3] K.Vinodgopal, I.Bedja, P.V.Kamat; Chem.Mater., **8**, 2180 **(1996)**.

[4] F.Zhang, S.S.Wong; Chem.Mater., **21**, 4541 **(2009)**.

[5] Y.Wang, M.Zhong, F.Chen, J.Yang; Applied Catalysis B: Environmental, **90**, 249 **(2009)**.

[6] G.L.Puma, A.Bono, D.Krishnaiah, J.G.Collin; J.Haz.Mat., **157**, 209 **(2008)**.

[7] T.A.Egerton, M.Janus, A.W.Morawski; Chemosphere, **63**, 1203 **(2006)**.

[8] J.Q.Li, L.P.Li, L.Zheng; Electrochimica Acta, **51**, 4942 **(2006)**.

[9] B.B.Lakshmi, C.J.Patrissi, C.R.Martin; Chemistry of Materials, **9**, 2544 **(1997)**.

[10] C.He, X.Z.Li, N.Graham; Applied Catalysis A: General, **305**, 54 **(2006)**.

[11] V.Zwilling, E.Darque-Ceretti, A.Boutry-Forveille; Surface and Interface Analysis, **27**, 629 **(1999)**.

[12] G.K.Mor, O.K.Varghese, M.Paulose; J.Materials Research, **18**, 2588 **(2003)**.

[13] A.Elsanousi, J.Zhang, H.M.H.Fadlalla, F.Zhang, H.Wang, X.X.Ding, Z.H.Huang, C.Tang; J.Mater.Sci., **43**, 7219 **(2008)**.

[14] R.Beranek, H.Hildebrand, P.Schmuki; Electrochem.Solid State Lett., **6**, B12 **(2003)**.

[15] J.S.Choi, R.B.Wehrspohn, J.Lee, U.Gosele; Electrochim.Acta, **49**, 2645 **(2004)**.

[16] X.Zeng, Y.X.Gan, E.Clark, L.Su; Journal of Alloys and Compounds, **509**, L221 **(2011)**.

[17] U.E.Steiner, T.Ulrich; Chem.Rev., **89**, 51 **(1989)**.

[18] S.Maiti, D.Bag; Indian J.Chem., **34A**, 673 **(1995)**.

[19] B.Brocklehurst; Chem.Soc.Rev., **31**, 301 **(2002)**.