Applied Surface Science 257 (2011) 2275–2280

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Preparation and performance of photocatalytic TiO_2 immobilized on palladium-doped carbon fibers

Yaofeng Zhu[a,b], Yaqin Fu[a,*], Qing-Qing Ni[a,b]

[a] Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, China
[b] Graduate School of Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386-8576, Japan

ARTICLE INFO

Article history:
Received 29 June 2010
Received in revised form
23 September 2010
Accepted 24 September 2010
Available online 8 October 2010

Keywords:
Titanium dioxide
Pd particles
Carbon fiber
Photocatalytic
Acid orange

ABSTRACT

Pd-modified carbon fibers (CFs) are obtained by a facile oxidation–reduction method and then dip-coated in a sol–gel of titanium dioxide (TiO_2) to form supported TiO_2/Pd-CF photocatalysts. The morphology of the Pd-modified CFs and the amount Pd deposited are characterized by field emission scanning electron microscopy and atomic absorption spectrometry, respectively. X-ray diffraction is used to investigate the crystal structures of the TiO_2 photocatalyst. Acid orange II is used as a model contaminant to evaluate the photocatalytic properties of the photocatalyst under UV irradiation. TiO_2/Pd-CF exhibits higher catalytic activity than TiO_2/CF towards the degradation of acid orange II. Optimum photocatalytic performance and support properties are achieved when the Pd particle loading is about 10.8 mg/g.

1. Introduction

Since Fujishima and Honda discovered the photoelectrocatalyzed decomposition of water at *n*-type semiconductor titanium dioxide (TiO_2) electrodes [1], TiO_2 has been studied extensively by researchers in different fields. The excellent physical and chemical properties of TiO_2 make it a potential photocatalyst and it has been widely used as an antibacterial agent as well as for deodorization, purification of polluted air and wastewater treatment [2–4]. However, the energy gap of TiO_2 is larger than 3.2 eV, which only ultraviolet light (wavelength < 380 nm) can overcome. This results in TiO_2 having a very low quantum efficiency for photocatalysis [5]. Recently, the problem of separating TiO_2 powder catalysts from the working system has been resolved empirically by preparing photocatalytic thin films of immobilized TiO_2 [6,7]. However, the immobilized TiO_2 films exhibit relatively low photocatalytic activity because of their low surface area.

In the present study, the catalytic activity of immobilized photocatalytic materials were improved by taking two measures: (1) determining the best process for fabricating a thin film of TiO_2 and modifying its surface, and (2) selecting the appropriate carrier material. The catalytic activity of a material can be improved by a synergistic effect in the composite formed between a carbon-like material and a TiO_2 thin film. Several methods have been used to enhance the photocatalytic activity of TiO_2 such as preparing as nano-titanium dioxide [8,9], metal doping and coating with metals [10,11], and semiconductor-coupled modification [12]. It has been found that the modification of TiO_2 surfaces with a noble metal is one of the most effective ways to improve the photocatalytic efficiency [5,13]. The disparity of the Fermi levels in a noble metal and TiO_2 changes the electronic distribution of the system, continuously promoting the transfer of electrons to the metal particles. As a consequence, the rate of photoelectron transfer and oxygen adsorption can be improved. Moreover, the Schottky barrier formed at the interface between a noble metal and TiO_2 could further prevent hole–electron recombination. However, in heterogeneous photocatalysis, the activity of the catalyst is significantly influenced by the amount of loaded noble metal. This means determining a suitable amount of loaded noble metal is a crucial problem in the preparation of photocatalytic materials with high catalytic activity.

It has been reported that the catalytic activity of palladium (Pd)-modified TiO_2 is better than that of unmodified TiO_2. The TiO_2 thin film usually used to prepare Pd-modified TiO_2 by redox processes is a composite with a common structure. However, this composite has some disadvantages. On one hand, it decreases the number of catalytic active sites in TiO_2 and increases the UV-shielding ability of the composite films formed, resulting in a reduced proportion of photons used. On the other hand, the noble metals deposited on the surface of the TiO_2 thin film increase the selectivity of the com-

---

* Corresponding author. Tel.: +86 571 86843607; fax: +86 571 86843607.
E-mail address: fuyaqin@yahoo.com.cn (Y. Fu).

0169-4332/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2010.09.087

posite photocatalyst for the photocatalytic degradation of organic compounds.

In the present investigation, polyacrylonitrile carbon fiber (PAN-CF) was used as a catalyst support for photocatalytic TiO_2. Pd-modified CF was fabricated through a facile oxidation–reduction method and photocatalytic TiO_2 films supported on Pd-modified CF (TiO_2/Pd-CF) were prepared by sol–gel dip-coating. The photocatalytic performance of the composite photocatalyst materials is evaluated.

2. Experimental

2.1. Materials

PAN-CF (T300C), with a diameter of about 5–6.5 μm, was provided by Toray Inc. Tetrabutyl orthotitanate (CP grade) was provided by Wuxi Zhanwang Chemical Reagent Co. Ltd., China. Palladium chloride (AR grade) was purchased from Shanghai Jiuling Smelting Co. Ltd., China. All commercial chemicals were used as received without further purification.

2.2. Preparation of TiO_2 supported on Pd-modified CF

PAN-CF (0.1 g per fiber was oxidized in concentrated nitric acid (160 mL) by heating under reflux for 4 h in an oil bath at 115 °C. After cooling and washing with demineralized water until the pH was >6, the fibers were dried in an oven at 80 °C. Initial concentrations of $PdCl_2$ solutions were 0.1, 0.3, 0.5, 0.7 and 0.9 g/L, which were prepared by dissolving $PdCl_2$ in concentrated hydrochloric acid (37%). The oxidized CFs were dipped into $PdCl_2$ solutions (100 mL) for 10 min and then dried in an ambient atmosphere at room temperature. The samples were then immersed in a solution of $SnCl_2$ (10 g/L, 100 mL) to reduce the palladium ions. Residual ions on the surface of the substrate were removed by washing with deionized water. The CFs modified with 0.1, 0.3, 0.5, 0.7 and 0.9 g/L $PdCl_2$ solutions are denoted as M1-Pd-CF, M3-Pd-CF, M5-Pd-CF, M7-Pd-CF and M9-Pd-CF, respectively.

A TiO_2 sol was prepared using tetrabutyl orthotitanate as the titanium precursor and alcohol as the solvent. $Ti(OBu)_4$ (17.08 mL) was dissolved in a mixture of ethanol (69 mL), acetic acid (2.9 mL) and acetylacetonate (0.5 mL). After stirring for 1 h, the solution was hydrolyzed by adding a mixture of water (1 mL) and EtOH (10 mL) dropwise with stirring over 1 h. The solution was maintained at room temperature for 3 days to complete the hydrolysis, forming the TiO_2 sol.

The Pd-modified CF substrates were dip-coated in the TiO_2 sol for 10 min and pulled out slowly with a uniform pulling rate. The substrate was allowed to dry in an ambient atmosphere at room temperature. Finally, the coated CF substrates were calcined in a nitrogen environment at 600 °C for 2 h to give the composite photocatalysts of TiO_2 thin films supported on Pd-modified CFs (TiO_2/Pd-CF). The composite photocatalysts are denoted as M1TiO_2/Pd-CF, M3TiO_2/Pd-CF, M5TiO_2/Pd-CF, M7TiO_2/Pd-CF and M9TiO_2/Pd-CF, depending on the concentration of the $PdCl_2$ solution used (0.1, 0.3, 0.5, 0.7 and 0.9 g/L, respectively).

2.3. Characterization

The surface morphology of the Pd-modified CFs and TiO_2 immobilized on CFs were investigated by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The crystal structure of the TiO_2 was determined using a Bruker AXS (Bruker AXS, D8-Discover) X-ray diffractometer with Cu Kα radiation. The accelerating voltage and the applied current were 40 kV and 35 mA, respectively.

2.3.1. Determination of Pd content

The mass of Pd particles was determined using standard atomic absorption spectrometry (AAS) after aqua regia digestion as described in NY/T1613-2008 [14]. The mass of Pd particles deposited on the CF was determined through quantitative analysis. The mass of Pd particles deposited on the surface of the CF was expressed as the mass fraction W (mg/g) described by:

$$W = \frac{(\rho - \rho_0) \times V}{m} \quad (1)$$

where ρ (mg/L) is the mass concentration of Pd deposited on the surface of samples and ρ_0 (mg/L) is the mass concentration of the blank sample solution. V (L) is the volume of the solution, which is constant, and m (g) is the mass of sample used.

2.3.2. Evaluation of photocatalytic activity and interface performance

The photocatalytic activity of the prepared samples was evaluated from the photocatalytic degradation of acid orange II in aqueous solution. The sample was placed in a Pyrex tube containing an aqueous solution of acid orange II (100 mg/L, 25 mL) at pH 3. The sample was then irradiated with a 500 W mercury lamp as a UV source. To measure the acid orange II concentration, the absorption at 484 nm, which corresponds to the maximum adsorption of acid orange II, was monitored using a UV–Vis spectrophotometer. The interface performance of the composites was evaluated by using the samples repeatedly.

3. Results and discussion

3.1. Surface morphology of samples

The morphology of the oxidized and Pd-modified CFs is shown in Fig. 1. It can be seen that a number of particles are deposited on the surface of the Pd-modified CFs compared with the CFs oxidized with nitric acid. Furthermore, the particles deposited on the CFs uniformly with no aggregation of the Pd particles. This indicates that the facile oxidation–reduction process was used successfully. The uniform distribution of the Pd particles may contribute to stable performance of the composite photocatalysts. FE-SEM images in Fig. 2 show morphologies of the composite photocatalysts after calcination process (nitrogen atmosphere, 600 °C, 2 h). As shown in Figs. 2(a)–(f), continuous TiO_2 film was immobilized both on CFs and Pd-modified CFs. Moreover, it did not show obvious difference between the TiO_2/Pd-CF and TiO_2/CF by the morphological comparison.

3.2. Crystal structure of TiO_2

A model TiO_2 powder was prepared using the same heat treatment process as the TiO_2 films and then used to analyze the crystal structure of the sample. The X-ray diffraction (XRD) pattern of the TiO_2 powder calcined at 600 °C for 2 h is presented in Fig. 3. The XRD pattern shows that only the anatase phase is present, as confirmed from JCPDS NO. 21-1272. The average crystal size was determined from parameters in the XRD pattern according to the Scherrer equation (2).

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (2)$$

where D represents the average crystal size, β is the full width at half-maximum (FWHM), and θ is the diffraction angle. The average crystal size of TiO_2 was determined to be 15 nm calculated using the characteristic anatase peak at $2\theta = 25.3°$.

Fig. 4(a) shows the XRD spectra of unmodified CFs, TiO_2/CF and M7TiO_2/Pd-CF. The peaks of carbon fiber at 26° is related to the

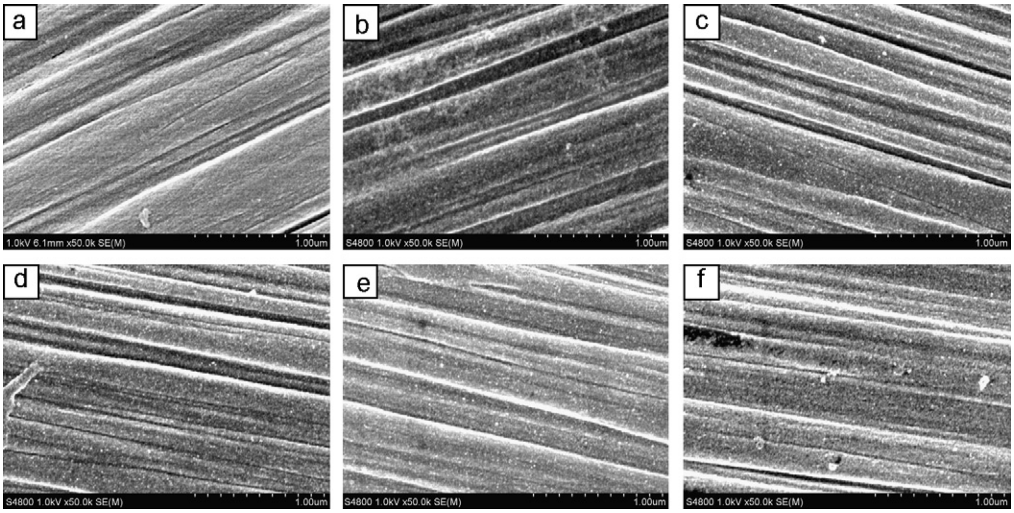

Fig. 1. Surface morphology of CF with deposited Pd particles (a) CF, (b) M1-Pd-CF, (c) M3-Pd-CF, (d) M5-Pd-CF, (e) M7-Pd-CF, and (f) M9-Pd-CF.

diffraction of the (0 0 2) planes of graphite and the broad peak at 43.6° represents both the (1 0 0) and (1 0 1) planes of graphite. This typical peak still appears in the XRD spectra of TiO_2/CF and M7TiO_2/Pd-CF. Simultaneously, the typical diffraction peaks of anatase TiO_2 were detected in the TiO_2/CF and M7TiO_2/Pd-CF [15]. However, the part of diffraction peaks of anatase-form TiO_2 is not clearly detected yet, which may be attributed to the lower content of TiO_2 on carbon fibers. Compared with the diffraction peaks of samples, we found that the peaks of graphite (0 0 2) and anatase TiO_2 (1 0 1) overlap each other due to their closely location of diffraction peaks. It can be seen from Fig. 4(b) and (c), which shows the original and Gaussian fitted curves of the TiO_2/CF and M7TiO_2/Pd-CF at $2\theta = 20–35°$, respectively. The original XRD curve can be well fitted by two peaks of graphite (0 0 2) and anatase TiO_2 (1 0 1), respectively.

3.3. Pd content on the CF surfaces

The mass of Pd particles deposited on the surface of the CFs was determined using AAS after digestion with aqua regia, and the results are shown in Fig. 5. The concentration of the $PdCl_2$ solution used to coat the CFs has a significant effect on the amount of Pd particles deposited on the surface of the CFs. The amount of Pd particles deposited increased as the $PdCl_2$ concentration increased, with W of 2.3, 5.3, 7.5, 10.8 and 12.6 mg/g for samples fabricated using $PdCl_2$ solutions with concentrations of 0.1, 0.3, 0.5, 0.7 and 0.9 g/L, respectively.

3.4. Photocatalytic activity of the samples

The photocatalytic activity of the samples was evaluated by their degradation of acid orange II, a typical azo dye. The TiO_2/CF photocatalytic degradation of solutions of acid orange II is shown in Fig. 6. The catalytic activity of the composite photocatalysts is influenced significantly by number of Pd particles deposited on the surface of the CFs. After irradiation for 15 min with a 500 W UV light, 22% of acid orange II was degraded by TiO_2/CF, whereas >64% was degraded by the Pd-modified TiO_2/CF samples. M7TiO_2/Pd-CF showed the optimum catalytic performance of the Pd-modified samples; 70% of acid orange II was degraded by M7TiO_2/Pd-CF after irradiation for 15 min. However, as the reaction proceeded, the degradation rate slows because the concentration of the reaction solution decreases continuously, which may be the factor dominating the catalytic reaction rate. As the surface morphology of TiO_2/Pd-CF is almost the same as that of TiO_2/CF, differences in the structure and properties (such as the physical adsorption prop-

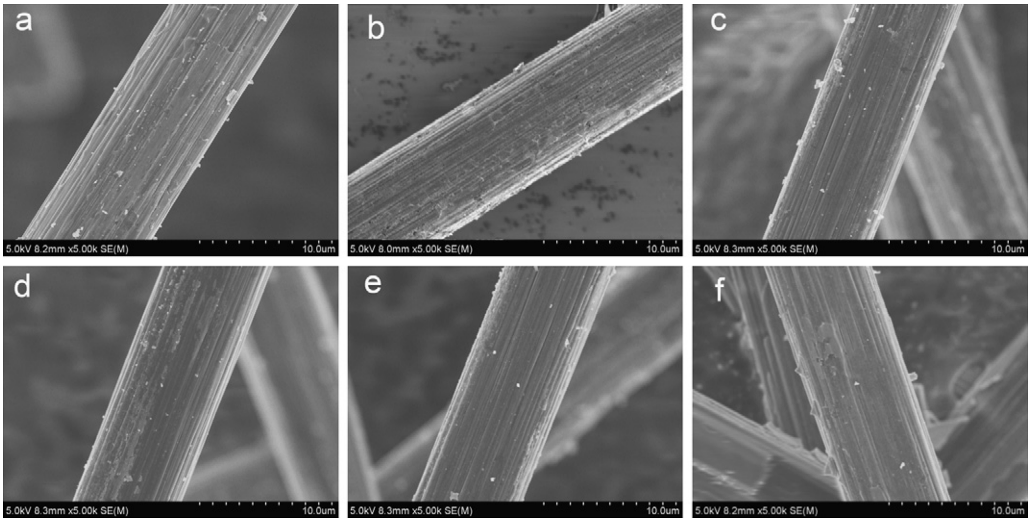

Fig. 2. Surface morphology of TiO_2/CF and TiO_2/Pd-CF (a) TiO_2/CF, (b) M1TiO_2/Pd-CF, (c) M3TiO_2/Pd-CF, (d) M5TiO_2/Pd-CF, (e) M7TiO_2/Pd-CF, and (f) M9TiO_2/Pd-CF.

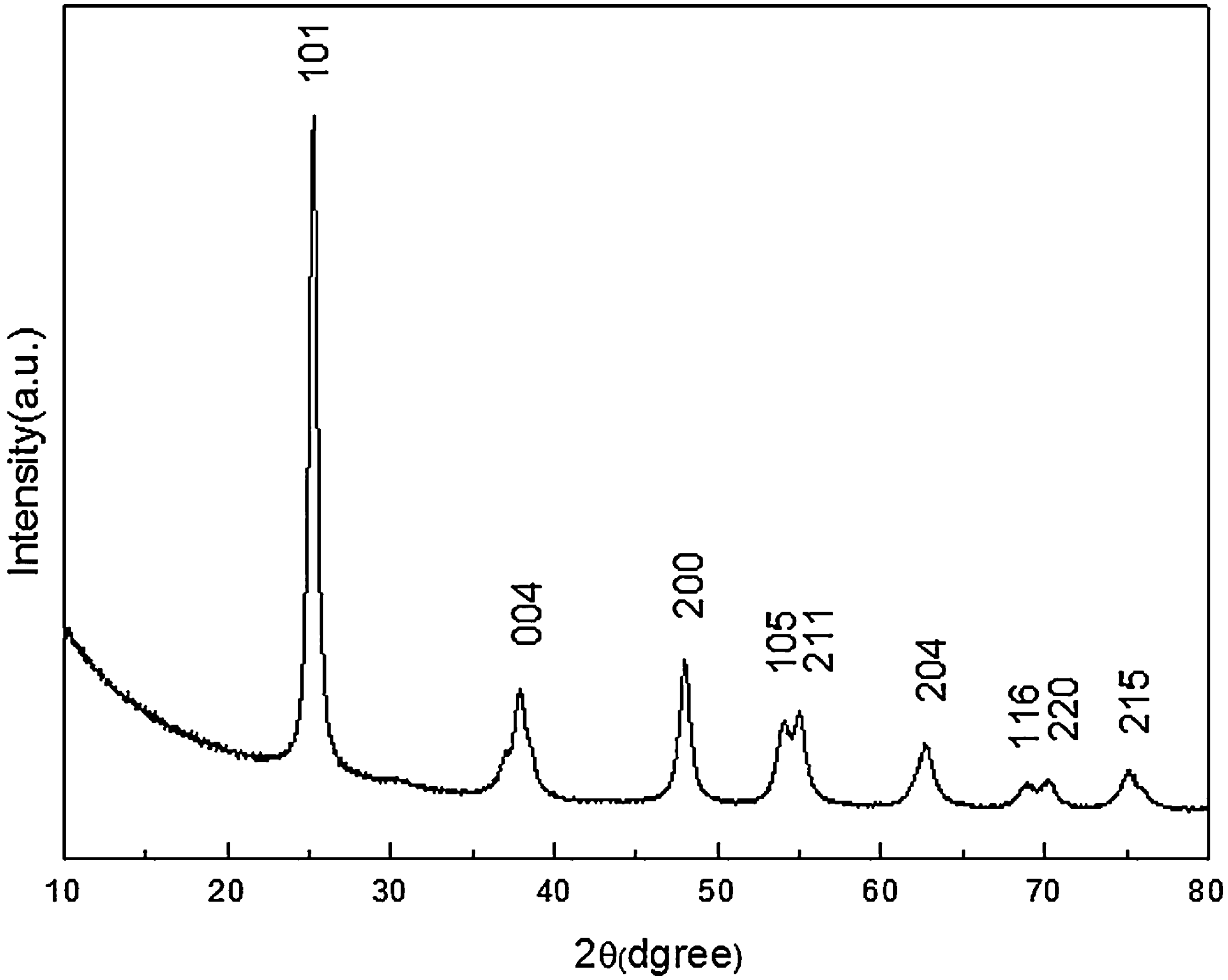

Fig. 3. XRD pattern of TiO_2 powder.

erties, catalytic active site and the absorption of UV light) of the samples before and after modification should be minor, as shown in Fig. 2. It is believed that the deposited Pd particles act as trapping sites to capture photogenerated electrons from the TiO_2 conduction band, separating the photogenerated electron–hole pairs. This should improve the photocatalytic activity of the samples, accelerating the degradation of acid orange II. After irradiation for 2 h, M7TiO_2/Pd-CF still showed the highest photocatalytic activity of

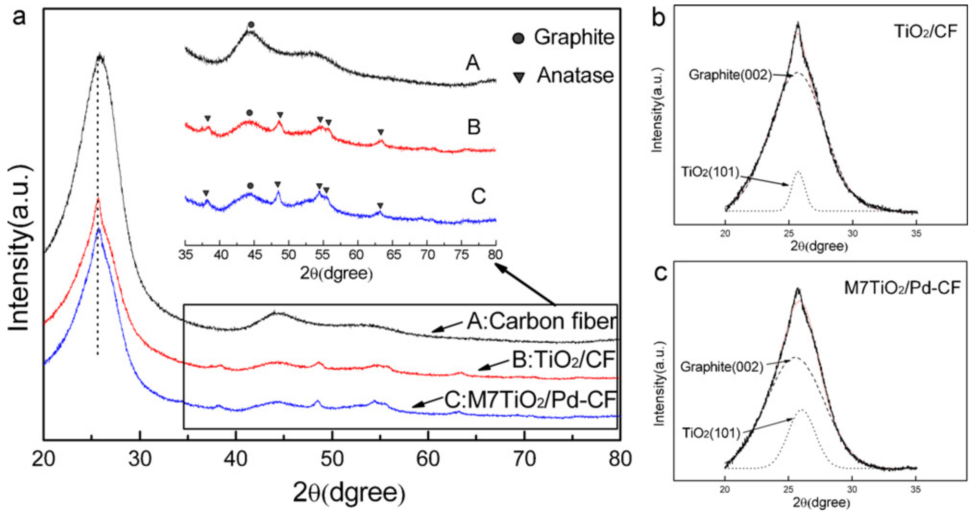

Fig. 4. (a) XRD patterns of unmodified CFs, TiO_2/CF and M7TiO_2/Pd-CF, insets represent the magnified image of the samples at $2\theta = 35–80^{\circ}$, (b) and (c) are the Original and Gaussian fitted curves of the TiO_2/CF and M7TiO_2/Pd-CF at $2\theta = 20–35^{\circ}$, respectively.

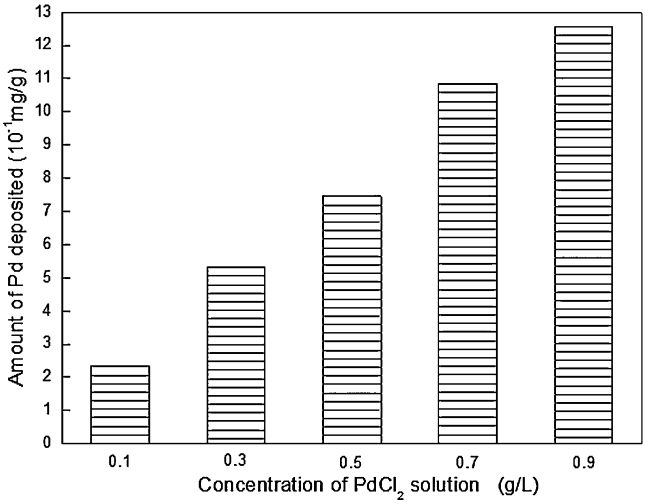

Fig. 5. Relation between the concentration of the $PdCl_2$ solution and amount of Pd particles deposited.

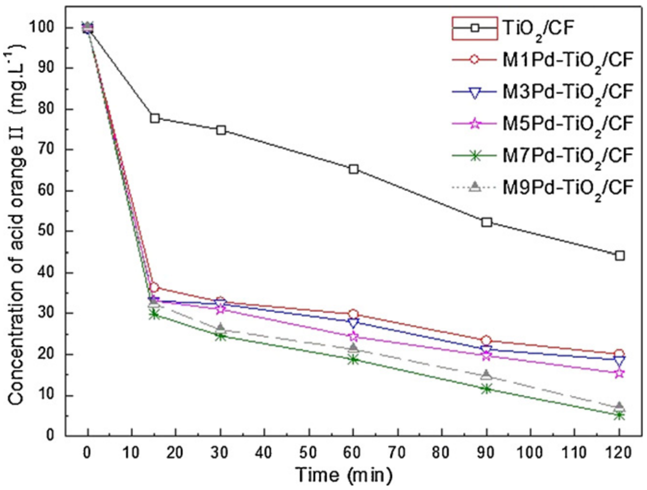

Fig. 6. TiO_2/CF photocatalytic degradation of acid orange II.

the samples, with a degradation ratio of acid orange II that was 70% greater than that of unmodified TiO_2/CF.

Fig. 7 shows the effect of the amount of Pd particles deposited on the CFs on the degradation behavior of acid orange II photocatalyzed by TiO_2/CF and TiO_2/Pd-CF under UV irradiation for 2 h.

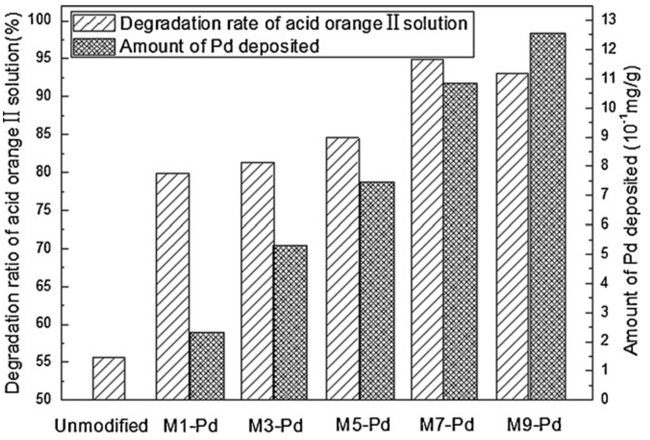

Fig. 7. Effect of Pd particle content on the degradation ratio of acid orange II.

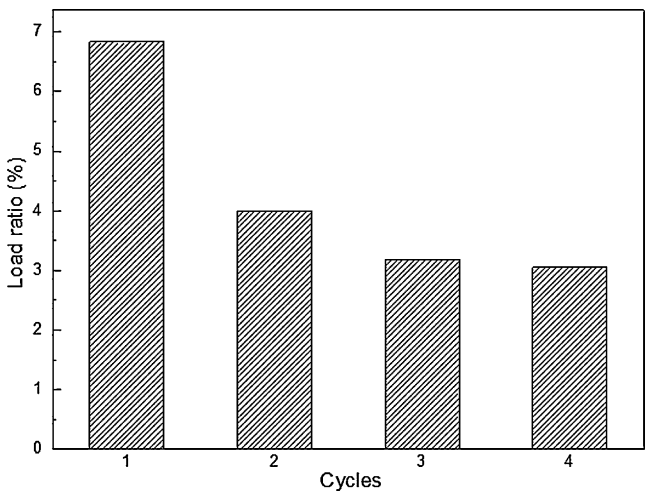

Fig. 8. Effect of repeated use on the load ratio of M7Pd-TiO_2/CF.

The photocatalytic activity of TiO_2/Pd-CF is strongly dependent on the amount of Pd particles present. As the content of Pd particles increased, the degradation ratio of acid orange II first increases, with a maximum degradation ratio (95%) appearing when the amount of Pd on the TiO_2/Pd-CF is 10.8 mg/g, and then decreases as the amount of Pd particles increases further. This indicates that the activity of the catalyst depends on the amount of Pd particles deposited on the CF surface, because it has an effect on the probability of electron–hole pairs recombining. When the Pd loading is below the optimum amount, the number of Pd nanoparticles formed at the composite interface is insufficient to allow effective hole–electron recombination. However, when Pd loading exceeds the optimum amount, the Pd particles begin to act as hole–electron recombination centers, decreasing the photocatalytic activity of the TiO_2/Pd-CF catalysts. Thus, the appropriate amount of deposited Pd particles is an important factor in the preparation of effective photocatalysts [11,16].

3.5. Effects of repeated use on the Pd load ratio and photocatalytic properties of the catalysts

Fig. 8 shows the effect of cycling on the load ratio of M7TiO_2/Pd-CF. The load ratio K can be expressed as follows:

$$K = \frac{W_x - W_0}{W_0} \times 100\% \qquad (3)$$

where W_0 is the dry weight of Pd-modified CF and W_x is the dry weight of M7TiO_2/Pd-CF before use or the dry weight of M7TiO_2/Pd-CF after recovery. The load ratio reduces rapidly after the initial cycle, decreasing from 6.8% to 4.0%, which is attributed to the presence of carbon on the surface of the composites after thermal treatment in a nitrogen environment. However, load ratio of M7TiO_2/Pd-CF catalyst is almost unchanged between the third and fourth cycles, with load ratios of 3.2% and 3.1%, respectively. These results suggest that the samples exhibit high load ratios and that CF behaves as a suitable support for the TiO_2 catalyst.

The effect of repeated use on photocatalytic activity of M7TiO_2/Pd-CF is shown in Fig. 9 (photocatalyzed the degradation of acid orange II 2 h for each cycle). The figure shows that the degradation ratio of acid orange II in the first cycle reached 94%, and this ratio was remained above 80% after four cycles. The decrease in the degradation ratio is caused by the decreased loading ratio of the M7TiO_2/Pd-CF sample resulting from strong magnetic stirring. On the other hand, it may be attributed to the adsorption of

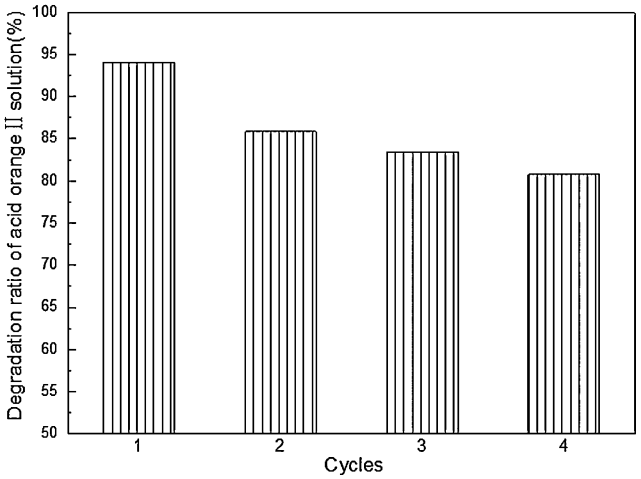

Fig. 9. Effect of repeated use on photocatalytic activity of M7TiO_2/Pd-CF.

M7TiO_2/Pd-CF, which is the adsorption capability of M7TiO_2/Pd-CF almost reached saturation after four cycles.

The above analysis indicates that the catalysts possess good stability and photocatalytic activity, exhibiting the potential for TiO_2 supported on Pd-modified CF to be used as a composite photocatalyst for industrial organic wastewater treatment.

4. Conclusions

Pd-modified CFs were obtained through a facile oxidation–reduction method and then coated with TiO_2 by sol–gel dip-coating. The structure and properties of the resulting TiO_2/Pd-CF photocatalysts were studied. The amount of Pd particles present in the catalyst was increased by increasing the concentration of $PdCl_2$ in the fabrication process, and the Pd particles dispersed uniformly on the CFs. The photocatalytic activity of the Pd-modified TiO_2/CF photocatalysts for the degradation of acid orange II was significantly improved compared with unmodified TiO_2/CF. The TiO_2/Pd-CF catalyst containing 10.8 mg/g of Pd exhibited the optimum catalytic efficiency for acid orange II, which was about 70% higher than that of TiO_2/CF. The TiO_2/Pd-CF catalyst containing 10.8 mg/g of Pd exhibited favorable stability and photocatalytic activity after recycling, revealing the potential of such a composite photocatalysts for industrial organic wastewater treatment.

Acknowledgments

This work was supported by the Natural Science Foundation of Zhejiang Province, China (Grant number: Y406310) and the Grant-in-Aid Global Center of Excellence (COE) program from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37–38.

[2] D. Gebeyehu, C.J. Brabec, N.S. Sariciftci, Solid-state organic/inorganic hybrid solar cells based on conjugated polymers and dye-sensitized TiO_2 electrodes, Thin Solid Films 403–404 (2002) 271–274.

[3] B.R. Sankapal, M.C. Lux-steiner, A. Ennaoui, Synthesis and characterization of anatase-TiO_2 thin films, Appl. Surf. Sci. 239 (2005) 165–170.

[4] L. Ge, M.X. Xu, H.B. Fang, Synthesis and characterization of the Pd/$InVO_4$–TiO_2 co-doped thin films with visible light photocatalytic activities, Appl. Surf. Sci. 253 (2006) 2257–2263.

[5] Z.B. Wu, Z.Y. Sheng, Y. Liu, H.Q. Wang, N. Tang, J. Wang, Characterization and activity of Pd-modified TiO_2 catalysts for photocatalytic oxidation of NO in gas phase, J. Hazard. Mater. 164 (2009) 542–548.

[6] A. Fernández, G. Lassaletta, V.M. Jiménez, A. Justo, A.R. González-Elipe, J.M. Herrmann, H. Tahiri, Y. Ait-Ichou, Preparation and characterization of TiO_2 photocatalysts supported on various rigid supports (glass, quartz and stainless steel) comparative studies of photocatalytic activity in water purification, Appl. Catal. B 7 (1995) 49–63.

[7] D.P. Xua, Z.H. Huang, F.Y. Kang, M. Inagakic, T.H. Kod, Effect of heat treatment on adsorption performance and photocatalytic activity of TiO_2-mounted activated carbon cloths, Catal. Today 139 (2008) 64–68.

[8] Z.B. Wu, H.Q. Wang, Y. Liu, Z.L. Gu, Photocatalytic oxidation of nitric oxide with immobilized titanium dioxide films synthesized by hydrothermal method, J. Hazard. Mater. 151 (2008) 17–25.

[9] A.J. Maira, K.L. Yeung, J. Soria, J.M. Coronado, C. Belver, C.Y. Lee, V. Augugliaro, Gas-phase photo-oxidation of toluene using nanometer-size TiO_2 catalysts, Appl. Catal. B 29 (2001) 327–336.

[10] V. Brezová, A. Blažkov, Ľ. Karpinskŷ, J. Grošková, B. Havlínová, V. Jorík, M. Čeppan, Phenol decomposition using Mn+/TiO_2 photocatalysts supported by the sol–gel technique on glass fibers, J. Photochem. Photobiol. A 109 (1997) 177–183.

[11] B.P. Xie, Y. Xiong, R.M. Chen, J. Chen, P.X. Cai, Catalytic activities of Pd–TiO_2 film towards the oxidation of formic acid, Catal. Commun. 6 (2005) 699–704.

[12] L.R. Hou, C.Z. Yuan, Y. Peng, Synthesis and photocatalytic property of SnO_2/TiO_2 nanotubes composites, J. Hazard. Mater. 139 (2007) 310–315.

[13] Z.Y. Sheng, Z.B. Wu, Y. Liu, H.Q. Wang, Gas-phase photocatalytic oxidation of NO over palladium modified TiO_2 catalysts, Catal. Commun. 9 (2008) 1941–1944.

[14] NY/T1613-2008, Soil quality-analysis of soil heavy metals-atomic absorption spectrometry with aqua regia digestion, Agricultural Industry Criteria of China, Chinese, 2008.

[15] P.F. Fu, Y. Luan, X.G. Dai, Preparation of activated carbon fibers supported TiO_2 photocatalyst and evaluation of its photocatalytic reactivity, J. Mol. Catal. A: Chem. 221 (2004) 81–88.

[16] J.B. Zhong, Y. Lu, W.D. Jiang, Q.M. Meng, X.Y. He, J.Z. Li, Y.Q. Chen, Characterization and photocatalytic property of Pd/TiO_2 with the oxidation of gaseous benzene, J. Hazard. Mater. 168 (2009) 1632–1635.