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Studies on Preparation and Photocatalytic Performance of Polythiophene/TiO_2 Composite Nanoparticles

YANG BAI[1,*], PING-YA LUO[1], PING-QUAN WANG[1], JIAN-YI LIU[1], ZHOU FAN[1], GUANG-DONG ZHANG[1] and ZHI-WEI QIAN[2]

[1]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, P.R. China
[2]Petro China Great Wall Drilling Engineering Company, Panjin 124000, Liaoning Province, P.R. China

*Corresponding author: Tel/Fax: + 86 28 83036809; E-mail: baiyanghyq@foxmail.com

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Titanium(IV) dioxide can photocatalyze degradation of organic pollutants and has been widely used in our daily life. In order to improve its photocatalytic activity, the polythiophene/TiO_2 (PTh/TiO_2) composite nanoparticles were prepared by *in situ* chemical oxidative polymerization of thiophene onto the TiO_2 particles. Structures of the PTh/TiO_2 composite particles were characterized by Fourier transform infrared spectroscopy and X-ray diffraction. Phenol solution was used as the target pollutant to investigate the photocatalytic activity of the composite particles. The PTh/TiO_2 composite nanoparticles can degrade phenol solution effectively under UV irradiation. Their photocatalytic activities were better than that of TiO_2, 1 % PTh/TiO_2 composites achieved the maximum. The PTh/TiO_2 composites presented in this paper are expected to be applied in the photocatalytic areas such as degrading pollutants and water purification.

Key Words: Polythiophene/TiO_2, Composite nanoparticles, Photocatalytic, Phenol.

INTRODUCTION

In recent years, the global environment pollution is more serious. Waste gas, waste water and waste residue have made water and air be affected by different degrees of hazards. How to handling pollutants effectively, has become one of the most active research areas.

Since Honda and Fujishima[1] discovered the photocatalytic splitting of water on TiO_2 electrodes in 1972, photocatalysis by TiO_2 semiconductors has received much attention and has been widely studied, with the final aim of converting solar light energy into useful chemical energy efficiently[2-4]. People wish to use clean, safe and inexhaustible solar light energy to catalyze oxidation of organic pollutants in water and air, achieving degradation of pollutants. TiO_2 semiconductor nanoparticles are ideal photocatalysts due to their chemical stability, nontoxicity and high photocatalytic reactivity in the elimination of pollutants in air and water. At present, TiO_2 nanoparticles have been gradually applied in pollutants degradation, treatment of waste water, water purification, air purification and other areas[5-8]. Although semiconductor TiO_2 could photocatalyze degradation of organic pollutants and has been widely used in our daily life. TiO_2 only absorbs UV energy to generate electron-cavity pairs and electron-cavity pairs recombine easily, which lead to lower photocatalytic activity[9]. Moreover, TiO_2 particles aggregate heavily in the organic medium and they may degrade organic medium[10], so the use of TiO_2 in photocatalytic materials is finally restricted.

To overcome these shortages, plenty of researches have been carried out *e.g.*, transition metal ions doping[11], semiconductor compound[12], precious metals deposition[13], dye sensitization[14] and polymer/TiO_2 doping[15], *etc*. They can prolong composite time of photo-induced electrons and cavities, improve life of photo-induced electrons and cavities, thereby improving the photo quantum efficiency. Among them, polymer/TiO_2 doping is the most promising way. In the polymer/TiO_2 doping field, conductive polymers such as polythiophene, polypyrrole, polyacetylene, polypyridine, polyfluorene, polyaniline and their derivatives can play the role of photocatalysis[16]. Among these conjugated polymers, polythiophene has the characteristics of high conductivity to and high stability. By means of doping with TiO_2, it can reduce surface polarity of TiO_2, improve efficiency of photocatalysis and light absorption[17]. Therefore, polythiophene is the best choice.

In this paper, polythiophene/TiO_2 (PTh/TiO_2) composite particles were prepared by the *in situ* chemical oxidative polymerization. Then the structures of the PTh/TiO_2 composite particles were characterized by FT-IR and XRD. Phenol solution was used as the target pollutant to investigate the photocatalytic activity of the composite particles.

EXPERIMENTAL

TiO_2 (anatase, specific surface area = 122 m^2/g, mean particle size = 25 nm) was supplied by Panzhihua Iron and Steel Group Co. (Panzhihua, China). The thiophene monomer was obtained from Xilong Chemical Co. (Shantou, China), anhydrous ferric chloride ($FeCl_3$), chloroform ($CHCl_3$), methanol and phenol were all purchased from Chengdu Kelong Chemical Reagents Co. (Chengdu, China). They were all analytical grade and used as received.

Preparation of the PTh/TiO_2 composites: The PTh/TiO_2 composites were prepared by the *in situ* chemical oxidative polymerization of thiophene onto the TiO_2 particles. Certain amount of TiO_2 nanoparticles were first dried at 100 ºC for 2 h before use. Subsequently, they were added to a round-bottom flask with 50 mL chloroform solution and dispersed by ultrasound at 200 W for 15 min. After that, thiophene was added and the mixture was stirred for 0.5 h. Then $FeCl_3$ dissolved in chloroform was added to the mixture, the resulting mixture was stirred in an ice bath for 4 h. After finishing the reaction, the colour of the solution changed from gray to dark. The products were precipitated in methanol, filtered and dried. Then the composites were extracted with methanol at 75 ºC for 48 h to remove residual $FeCl_3$. During this procedure, the colour of the composites changed from black (PTh in oxidized state) to red (PTh in reduced state), indicating successful reduction of the polymer. The composites were dried at 60-80 ºC for 3 h to obtain PTh/TiO_2 composite particles and they were kept in dark place. According to this preparation method, a series of PTh/TiO_2 composite particles with different contents of PTh were synthesized *via* controlling the ratio of thiophene/TiO_2, including: pure TiO_2, 1 % PTh/TiO_2, 2 % PTh/TiO_2, 5 % PTh/TiO_2 and pure PTh, referring to PTh content in the composites.

Fourier transform infrared spectra were obtained with the Nicolet-5700 spectrophotometer with a resolution setting of 4 cm^{-1}. The scanning range was altered from 4000 to 400 cm^{-1}. X-ray diffraction patterns of PTh, TiO_2 and PTh/TiO_2 composites were measured with an X'Pert PRO MPD (Philips Co.) X-ray diffractometer using CuK_α radiation, 40 kV, 40 mA.

Photocatalytic degradation of phenol: Phenol as the target pollutant was used to investigate the photocatalytic activities of the prepared PTh/TiO_2 composites. Photocatalysis experiments were performed under UV irradiation. The source of UV was two 10 W germicidal lamps with a maximum wavelength of 253.7 nm. The experimental procedure of photocatalytic degradation of phenol is as follows. First, 10 mg of TiO_2, 1 % PTh/TiO_2, 2 % PTh/TiO_2 and 5 % PTh/TiO_2 composites were added into four quartz glass tubes, respectively. Then 10 mL of phenol solution (C = 80 mg/L) was added to each of the tube. Photocatalysis was initiated by turning on the UV lamps. All the samples were magnetically stirred under UV irradiation for 30, 60, 90 and 120 min, respectively. The obtained solutions were centrifuged at 5000 rpm for 15 min. The changes of the concentrations of phenol were monitored by measuring the absorbance at λ_{max} = 510 nm with a UV-VIS spectrophotometer (U-4100, Hitachi Co., Japan). In this paper, the degradation ratios of phenol were calculated by eqn. (1):

$$\eta = [(C_0-C_t)/C_0] \times 100\ \% \qquad (1)$$

where, C_0 is the concentration of the phenol solution at the beginning of the photocatalytic reaction and C_t is the phenol concentration at various degradation time t.

RESULTS AND DISCUSSION

Characterization of the PTh/TiO_2 composites: A series of PTh/TiO_2 composite particles with different contents of polythiophene were successfully prepared by the *in situ* chemical oxidative polymerization. In order to characterize their structures accurately, FT-IR transmission spectra of polythiophene, TiO_2 and the PTh/TiO_2 composites were determined. Fig. 1 shows the FT-IR spectra of (a) polythiophene, (b) TiO_2 and (c) 1 % PTh/TiO_2 composites. Several low-intensity peaks are present in the FT-IR spectrum of PTh between 3100-2800 cm^{-1} and they can be attributed to aromatic C-H stretching vibrations. The 1500-600 cm^{-1} region is the fingerprint region of PTh. The peaks at 695 and 784 cm^{-1} are usually ascribed to the C-H out-of-plane deformation mode. The peak at 1487 cm^{-1} is a combination of C=C asymmetric and symmetric stretching vibrations of the 2,5-thiophenylene units (Fig. 1a). The FT-IR spectrum of the TiO_2 particles (Fig. 1b) has a characteristic Ti-O-Ti absorption band peaked at 476 cm^{-1}. Fig. 1c shows the spectrum of the PTh/TiO_2 composites, characteristic absorption bands from both TiO_2 and polythiophene are present in this spectrum, including the band originating from TiO_2 located at 476 cm^{-1} and the peaks originating from polythiophene located at 2800-3100, 1490 and 788 cm^{-1}. The results show that the composites are composed of polythiophene and TiO_2.

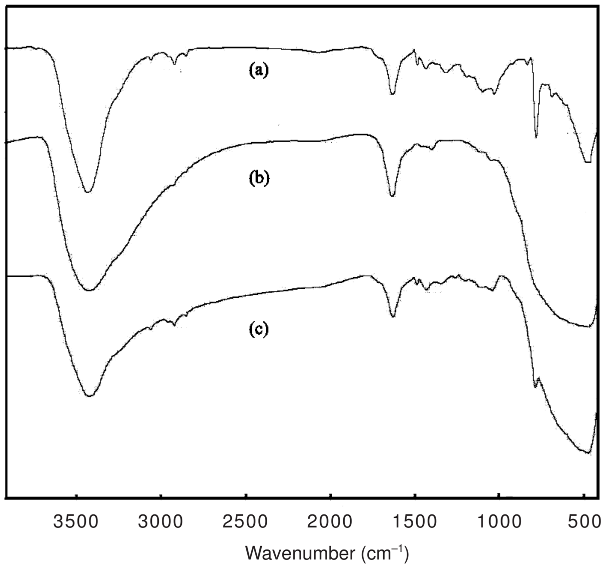

Fig. 1. FT-IR spectra of (a) polythiophene, (b) TiO_2 and (c) 1 % PTh/TiO_2 composites

The structures of the PTh/TiO_2 composites were further confirmed by X-ray diffraction. The XRD patterns of the (a) polythiophene, (b) TiO_2 and (c) 1 % PTh/TiO_2 composites are displayed in Fig. 2. Fig. 2a is the XRD pattern of polythiophene sample, as can be seen from the figure, polythiophene has an amorphous structure, the broad peak in the range of 20-40º centered at 25.3º is corresponded to the intermolecular π-π transition absorption peak. Fig. 2b shows the XRD patterns of TiO_2 particles, the peaks at $2\theta = 25.18°, 37.75°, 47.89°, 53.90°$ and 62.51° are assigned to the (101), (004), (200), (106) and (215) lattice planes of TiO_2, which are the characteristic peaks of the anatase TiO_2. As shown in Fig. 2c for the PTh/TiO_2 composites, both characteristic peaks of TiO_2 and the broad peak of PTh are existed. And because of the existence of PTh, compared with the pure TiO_2, TiO_2 characteristic peaks of PTh/TiO_2 composite are obvious weakened. In addition, because TiO_2 has the strongest peak at 25.18°, the broad PTh peak of PTh/TiO_2 composites at 25.3° is overlapped. Through FT-IR and XRD results, it can be verified that the PTh/TiO_2 composite particles have been successfully prepared.

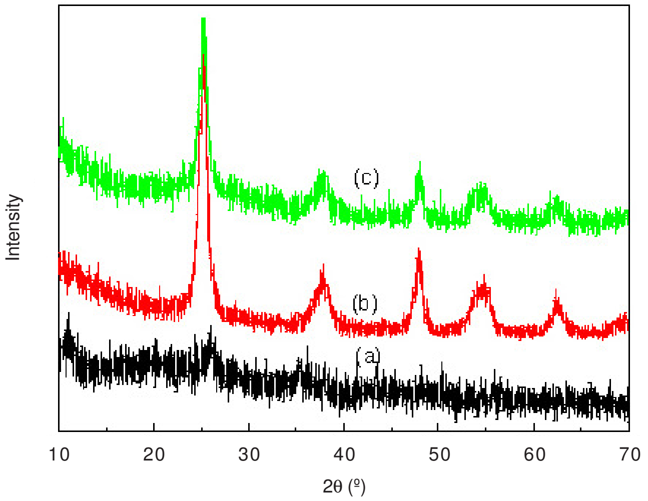

Fig. 2. XRD patterns of (a) polythiophene, (b) TiO_2 and (c) 1 % PTh/TiO_2 composites

Photocatalytic degradation of phenol: UV-visible spectrophotometer was performed to determine the phenol solution after photocatalytic degradation using PTh/TiO_2 composites as photocatalyst. Absorbance can reflect changes in the phenol concentration. The concentration of phenol solution can be calculated from measured absorbency by the following standard curve equation: $A = 0.135\ C - 0.032$. Then photocatalytic degradation rate of phenol solution can be obtained.

Fig. 3 shows the degradation ratios of phenol solution at different UV irradiation time with a series photocatalys. They are (a) TiO_2, (b) 1 % PTh/TiO_2, (c) 2 % PTh/TiO_2 and (d) 5 % PTh/TiO_2 composites. As can be seen from the curves in the figure, all the samples show rapid degradation rates of phenol with increasing UV irradiation time. For TiO_2 sample (Fig. 3a), the degradation rate is 12 % after 0.5 h of UV irradiation, at 2 h time point, it increases to 43 %. Fig. 3b shows the degradation rate of 1 % PTh/TiO_2, the degradation rate increases from 13 % to 45 % at 2 h, which is always higher than that of TiO_2. Degradation ratio of 2 % PTh/TiO_2 is displayed in Fig. 3c, 12 % at 0.5 h and 44 % at 2 h, its degradation rate is also higher than that of TiO_2 but lower than 1 % PTh/TiO_2. Seen from Fig. 3d, it is notable that 5 % PTh/TiO_2 exhibits a lower degradation rate, the initial degradation rate is only 8 % at 0.5 h, which is significantly lower than all the samples above. The degradation rate increases from 8 to 38 % after 2 h degradation, it is still lower than TiO_2, 1 % PTh/TiO_2 and 2 % PTh/TiO_2. To sum up, the degradation rate of phenol has the following order: 1 % PTh/TiO_2 > 2 % PTh/TiO_2 > TiO_2 > 5 % PTh/TiO_2. 1 % PTh/TiO_2 shows the highest degradation rate, while 5 % PTh/TiO_2 exhibits the lowest degradation rate. In the experiment to degrade phenol, 1 % PTh/TiO_2 and 2 % PTh/TiO_2 have stronger photocatalytic degradation ability than that of TiO_2, while the degradation ability is weaken for 5 % PTh/TiO_2. The results indicate that the PTh/TiO_2 composites are effective photocatalysts for the degradation of phenol under UV irradia-tion. Small amount of polythiophene can improve the efficiency of photocatalytic degradation of phenol, but with the polythiophene content increasing, photocatalytic efficiency can be decreased for the PTh/TiO_2 composites, even lower than that of pure TiO_2, such as 5 % PTh/TiO_2. The reason is that the ability of photocatalytic degrading phenol for PTh/TiO_2 composite nanoparticles is closely related to the polythiophene and TiO_2 content. If polythiophene content is too low, it can not play the role of transmission surface charges of TiO_2 very well, so separation efficiency of charges and cavities by TiO_2 can not be improved most effectively, photocatalytic activity of TiO_2 can not get the maximum degree of improvement. Conversely, if excessive polythiophene is introduced, they will be adsorbed on the surface of TiO_2, they will affect the use UV light by TiO_2, photocatalytic activity of TiO_2 is reduced on the contrary.

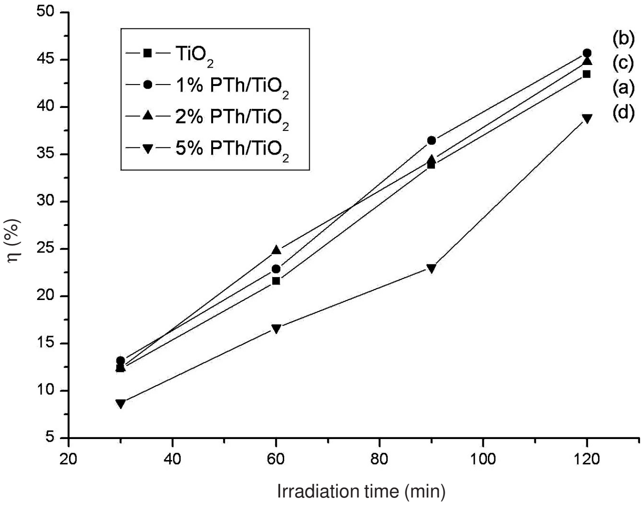

Fig. 3. Degrading ratio of phenol as a function of UV irradiation time in the presence of (a) TiO_2, (b) 1 % PTh/TiO_2, (c) 2 % PTh/TiO_2 and (d) 5 % PTh/TiO_2 composites

According to the data in Fig. 3, we can use the first-order kinetic equation to describe the degradation reaction.

$$\ln(C_0/C_t) = k_t$$

where, C_0 and C_t are the concentration of phenol solution at initial and certain time of UV irradiation, respectively. t is the illumination time and k is the constant of first-order kinetic equation.

Fig. 4 shows that the linear fitting curves between $\ln(C_0/C_t)$ and UV irradiation time are consistent with apparent first-order kinetics. With different photocatalysts of TiO_2, 1 % PTh/TiO_2, 2 % PTh/TiO_2 and 5 % PTh/TiO_2 composites, their first-order kinetic equation, reaction rate constant (k) and relativity coefficient (R) are listed on Table-1. The reaction rate constant k is 0.00407, 0.00437, 0.0042 and 0.00331 min^{-1} for TiO_2, 1 % PTh/TiO_2, 2 % PTh/TiO_2 and 5 % PTh/TiO_2 composites, respectively. In the presence of different PTh/TiO_2 potocatalysts, 1 % PTh/TiO_2 and 2 % PTh/TiO_2 always show more excellent photocatalytic activity than that of TiO_2. But with further increasing of polythiophene content, the reaction rate constant is reduced on the contrary for 5 % PTh/TiO_2 composites. The main reason is that when the polythiophene content is high, TiO_2 will be wrapped by excessive polythiophene. It can prevent $\cdot OH$ and $\cdot O_2^-$ from contacting with contaminants, so the reaction rate of degrading phenol slows. From the obtained results, it is concluded that a moderate content of polythiophene is beneficial for the photocatalytic activity of PTh/TiO_2 composites, while the excessive content of polythiophene can decrease the photocatalytic activity of the composites. The relativity coefficients (R) for the fitted lines were calculated to be between 0.974 and 0.999 (Table-1), which indicates that the photocatalytic degradation of phenol can be described by the first-order kinetic model.

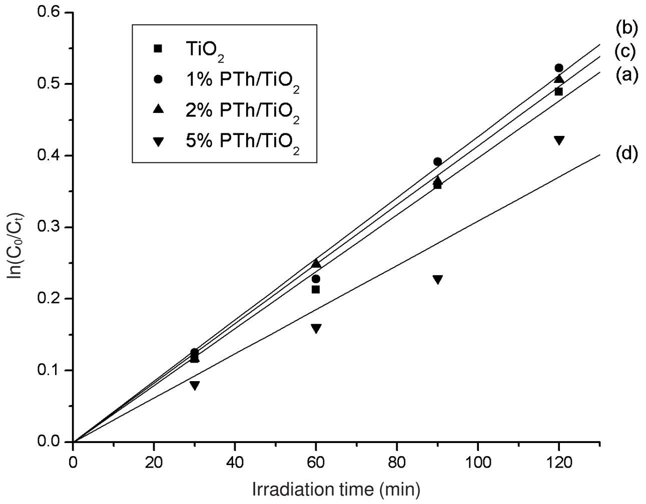

Fig. 4. Apparent first-order linear transform $\ln(C_0/C_t) = k$ of the phenol degradation kinetic plots for (a) TiO_2, (b) 1 % PTh/TiO_2, (c) 2 % PTh/TiO_2 and (d) 5 % PTh/TiO_2 composites under UV irradiation

TABLE-1
FIRST-ORDER KINETIC EQUATIONS AND THE PARAMETERS WITH DIFFERENT PHOTOCATALYSTS: TiO_2, 1% PTh/TiO_2, 2 % PTh/TiO_2 AND 5 % PTh/TiO_2 COMPOSITES

Photo-catalysts	First-order kinetic equation	k×10^2 (min^{-1})	Relativity coefficient (R)
TiO_2	$\ln(C_0/C_t) = 0.00407\ t-0.00886$	0.407	0.997
1 % PTh	$\ln(C_0/C_t) = 0.00437\ t-0.0091$	0.437	0.998
2 % PTh	$\ln(C_0/C_t) = 0.0042\ t-0.00498$	0.420	0.999
5 % PTh	$\ln(C_0/C_t) = 0.00331\ t-0.02039$	0.331	0.974

Conclusion

PTh/TiO_2 composites nanoparticles were successfully prepared by *in situ* chemical oxidative polymerization of thiophene onto the TiO_2 particles. Structures of the PTh/TiO_2 composites were characterized by FT-IR and XRD. In order to investigate photocatalytic activity of the composites, phenol solution was used as the target pollutant. The PTh/TiO_2 composites nanoparticles can degrade phenol solution effectively under UV irradiation. Their photocatalytic activities were better than that of TiO_2. We hope these PTh/TiO_2 composites will find potential applications in the photocatalytic areas such as degrading pollutants and water purification.

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