

# **Conjugated Microspheres FeTCPP–TDI–TiO<sub>2</sub> with Enhanced Photocatalytic Performance for Antibiotics Degradation Under Visible Light Irradiation**

Binghua Yao $^1\cdot$  Chao Peng $^{1,3}\cdot$  Yangqing  $\mathrm{He}^1\cdot$  Wen  $\mathrm{Zhang}^2\cdot$  Qinku  $\mathrm{Zhang}^1\cdot$  Ting  $\mathrm{Zhang}^1$ 

Received: 22 July 2016 / Accepted: 7 October 2016 / Published online: 28 October 2016 © Springer Science+Business Media New York 2016

**Abstract** Toluene disocyanate (TDI) was used as a bridging molecule, a bridge bonding conjugated microsphere (FeTCPP–TDI–TiO<sub>2</sub>) was successfully prepared by grafting tetra-(carboxyphenyl) porphyrin iron (FeTCPP) on the surface of TiO<sub>2</sub> microspheres. The FT-IR spectra revealed that the hydroxyl group (–OH) of TiO<sub>2</sub> microspheres surface and the carboxyl group (–COOH) of FeTCPP reacted respectively with the active isocyanato groups (–NCO) of TDI to form a surface conjugated microsphere FeTCPP– TDI–TiO<sub>2</sub>. The UV–vis DRS analysis demonstrated that the formation of FeTCPP–TDI–TiO<sub>2</sub> extended remarkably the photoresponse of as-prepared samples to visible light region. The photocatalytic activity of FeTCPP–TDI–TiO<sub>2</sub> was evaluated using the photocatalytic degradation of norfloxacin (NFC), tetracycline (TC) and sulfapyridine (SPY) antibiotics in aqueous solution under visible-light irradiation. The results showed that, TDI, as a bond unit, was used to form a steady chemical bridging bond linking between FeTCPP and the surface of  $\text{TiO}_2$  microspheres, and the prepared catalyst exhibited higher photocatalytic activity under visible-light irradiation for antibiotics degradation in comparison with P25. The degradation of antibiotics all followed the pseudo first-order reaction model under visible light irradiation, and the degradation mechanisms of NFC, TC and SPY were also proposed.

Binghua Yao bhyao@xaut.edu.cn

Wen Zhang wenzhang@uark.edu

- <sup>1</sup> Department of Applied Chemistry, Xi'an University of Technology, Xi'an 710048, China
- <sup>2</sup> Department of Civil Engineering, University of Arkansas, Fayetteville 72701, USA
- <sup>3</sup> School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, China

# **Graphical Abstract**



**Keywords** FeTCPP-TDI-TiO<sub>2</sub> complex  $\cdot$  Bridgebonding conjugated microsphere  $\cdot$  Surface modification  $\cdot$ TiO<sub>2</sub>  $\cdot$  Visible light photocatalyst  $\cdot$  Antibiotic

# 1 Introduction

Photocatalysis has attracted increasing attention as an environment friendly technology for the purification of wastewater compared to other conventional treatments [1-4]. Among various semiconductor photocatalysts, TiO<sub>2</sub> microspheres have been recognized as the most promising photocatalyst due to its unique photoactivity, nontoxicity, photostability and low cost [5–7]. However, the wide-band gap of TiO<sub>2</sub> ( $E_g = 3.2$  eV for anatase) means that TiO<sub>2</sub> can only absorb the UV light that wavelength is less than 387 nm, which seriously restricts its practical application. In addition, the high recombination rate of photoinduced electrons and holes is also a disadvantage of its application. So, much work has been devoted to extending the photoresponse of  $TiO_2$  to the visible light region and improving its photocatalytic performance via element doping, semiconductor coupling, dye sensitization and exposure of reactive face [8-14].

Among the sensitized agents, metalloporphyrins have been recognized as the most superior photo-sensitizers because of their large  $\pi$ -electron systems and strong absorption in visible light region [15–18]. Moreover, this metalloporphyrin-TiO<sub>2</sub> system can also improve the interfacial charge transfer and lower the electron-hole recombination rate. Although the above mentioned outstanding properties, metalloporphyrins adhered on the surface of TiO<sub>2</sub> by physical adsorption tend to occur partial desorption, thereby severely reducing efficiency of sensitization, lowering quantum yield and leading to the decline of photocatalytic performance [19, 20]. For overcoming this drawback, much effort has been contributed to reinforce the interaction between metalloporphyrins and TiO<sub>2</sub> surface instead of physical adsorption [21-23]. So far, numerous articles reported that anchoring groups (such as sulfonic or carboxylic acid) of metalloporphryins sensitized on the  $TiO_2$  surface is expectant to solve the desorption problem [24-26]. Unfortunately, it is rather difficult to synthesize metalloporphyrin containing anchoring groups, and time consuming [27, 28]. On the other hand, the formation of a steady chemical bond between metalloporphyrin and TiO<sub>2</sub> surface is hardly achieved due to the limited amounts of hydroxyl groups on TiO<sub>2</sub> surface [29, 30]. The introduction of bridging molecule, tolylene diisocyanate (TDI) containing bifunctional groups, was an excellent strategy for anchoring of metalloporphyrins on the TiO<sub>2</sub> surface [31– 34]. Because of its bifunctional groups, the -NCO groups of TDI molecules could react with the surface hydroxyl of TiO<sub>2</sub> and anchoring group of porphyrin respectively to form a steady bridge bond. Based on these published articles, the aim of the present work is to report a novel bridge bonding conjugated microspheres FeTCPP-TDI-TiO<sub>2</sub> and evaluate the potential utilization of this microsphere for photocatalytic degradation of antibiotics. Because antibiotics as a emerging environmental pollutant, has attracted wide attention in recent years, and the removal of antibiotics by the conventional water treatment technologies, such as biological treatment and adsorption methods, are not as efficient as anticipated [35–37]. Therefore, it is very important and urgent to develop efficient treatment methods to control the concentration level of antibiotics in aquatic environments. In this work, three representative antibiotics, norfloxacin (NFC), tetracyclines (TC) and sulfapyridine (SPY), were chosen as target degradation compounds, the visible light photocatalytic activity of FeTCPP-TDI-TiO<sub>2</sub> was investigated, and their degradation mechanisms were also proposed.

# 2 Materials and Methods

# 2.1 Reagents

All reagents were of analytical grade and used without further purification. Toluene diisocyanate (TDI, AR, Xi'an Chemical Reagent Factory), acetone (AR, Tianjin Fuyu Fine Chemical Co. Ltd.). Degussa P25-TiO<sub>2</sub> nanoparticles with an average particle size of 21 nm were purchased from Degussa Corporation, which consists of a mixture of anatase (70%) and rutile (30%) mineral phases (Germany). Tetracycline (TC, 98%) and sulfapyridine (SPY, 98%) were supplied by Wolsen and Dr. Ehrenstofer Gmbh respectively. Norfloxacin (NFC, 99%) was obtained from Shanxi Tanyuan pharmaceutical Co. Ltd. The mobile phase solvent (acetonitrile) is of HPLC grade from Sigma-Aldric Inc., USA. Tetra-(carboxyphenyl) porphyrin iron (FeTCPP) was obtained according to our previous paper [34]. Ultrapure deionized water was used throughout all experiments.

# 2.2 Preparation of FeTCPP-TDI-TiO<sub>2</sub> Microspheres

The preparation of FeTCPP-TDI-TiO<sub>2</sub> microspheres was shown in Scheme 1.  $TiO_2$  powder (Degussa P25)

was dispersed into acetone by ultrasonic technology in a three-neck flask to form a suspension. The suspension was stirred and heated slowly, while TDI (molar ratio of TiO<sub>2</sub> to TDI = 1:0.5, this optimum ratio of  $TiO_2$  to TDI has been quantify with previous work [34]) was dripped into the flask. And then the mixture solution was refluxed at 50 °C for 30 min. The mixture solution was filtered and washed with acetone 3-4 times, and dried at room temperature to obtain TDI cross-linked TiO<sub>2</sub> (TDI-TiO<sub>2</sub>). Finally, the appropriate amount of TDI-TiO2 was added into FeTCPP/ acetone (20 mg/100 mL) solution under ultrasonic dispersion for 30 min (FeTCPP/TiO<sub>2</sub> 0.1 wt%). After the mixed solution was transferred into a 250 mL three-necked flask, and then refluxed at 50 °C for 120 min in oil bath. The resulted product was washed three times with acetone, and then dried under vacuum to obtain the FeTCPP-conjugated microspheres FeTCPP-TDI-TiO<sub>2</sub>.

#### 2.3 Characterization of Samples

The FT-IR spectra were obtained using a Shimadzu FT-IR 8900 (Japan) with the reference of KBr. The morphology of samples was observed by Tescan VEGA 3 SBH with tube current of 30  $\mu$ A, and the tube voltage of 20 kV (Czech). The crystalline phase of samples was characterized by a powder X-ray diffractometer (Shimadzu XRD-7000 S, Japan) at tube current of 30 mA, tube voltage of 40 kV, and scanning speed of 10°/min. The UV–vis diffuse reflectance



Scheme 1 Schematic illustration of the preparation of FeTCPP-TDI-TiO<sub>2</sub>

spectra (UV–vis DRS) were obtained by a double-beam UV–vis diffuse reflectance spectrophotometer (TU-1901, China) with  $BaSO_4$  as reference.

# 2.4 Electrochemical Measurements

Electrochemical properties of the FeTCPP-TDI-TiO<sub>2</sub> were investigated by an electrochemical workstation (CHI 660b, Shanghai, China) in the three electrodes system, which consisted of indium-tin oxide (ITO) glass working electrode coating with the dispersed sample powders, a platinum wire as auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. The electrodes joined a cell of 5-mL volume through holes in its Teflon cover. 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte solution to carry out the electrochemical experiments at room temperature. The preparation procedure of the film ITO working electrode was as follows: 2 mg FeTCPP-TDI-TiO<sub>2</sub> was added to 2 mL ethanol under ultrasonic for 30 min to form a suspension. Consequently, the ITO glass is coated with suspension and dried in the oven at 100 °C for 2 h. Under the same conditions, FeTCPP-TiO<sub>2</sub>, TDI- $TiO_2$  and  $TiO_2$  film electrode were prepared. A 150 W Xe lamp was utilized as the light source on the measurement. The electrochemical impedance spectra Nyquist plots were recorded from 100 kHz to 0.1 Hz frequency.

# 2.5 Photocatalytic Degradation of Antibiotics

Self-made photocatalytic reaction device (as shown in Scheme 2) was used for the photocatalytic degradation of antibiotics. The device was consisted of a light source (Xe-lamp, 150 W), the sample tube (100 mL quartz tube; length 22.0 cm, diameter 2.0 cm, 10 cm away from the light source), a cold trap, an air bubbler, as well as



photocatalytic reaction device

Scheme 2 Schematic illustration of self-made photocatalytic reaction device

several additional accessories. In a typical process, 50 mg of photocatalysts and 50 mL of antibiotic solution (NFC: 25 mg/L, TC: 25 mg/L, SPY: 50 mg/L) were added to sample tube respectively. The air tube was inserted into the bottom of tube, maintaining a controlled air flow at 3 L/min to achieve the suspended catalyst in the degradation solution. The antibiotic solution was kept in dark for 30 min to reach the adsorption equilibrium in the photocatalytic system (preliminary results indicated that adsorption equilibrium could be quickly reached less than 30 min), and then samples were withdrawn at different intervals (20 min). The source of visible light was a Xe lamp, and a NaNO<sub>2</sub> solution(25 g/L) was circulated through the cooling jacket to filter out the UV emission of the lamp below 400 nm. The absorbance of the supernatant from high-speed centrifugation was measured by high performance liquid chromatography (HPLC, Shimadzu LC-20 A, Japan) system was with UV absorbance detector adjusted at 276 nm, 358 nm and 261 nm for detections of NFC, TC and SPY respectively. A reverse phase column (Shimadzu VP-ODS 5012094) with 150 nm length and 4.6 mm internal diameter was used. The mobile phase was composed of acetonitrile and ultrapure deionized water. The volume ratio CH<sub>2</sub>CN/H<sub>2</sub>O was 75/25 and the flow rates were 0.5 mL/min and 0.2 mL/ min for NFC and SPY separation, respectively. The volume ratio CH<sub>2</sub>CN/H<sub>2</sub>O was 25/75 and the flow rate was 0.3 mL/ min for TC separation. A UV-Spectrophotometer (UNICO, UV-2102 PC, American) was used to measure absorbance of antibiotics solutions. And according to the relationship between the absorbance and the concentration of antibiotic solution, the degradation rate D was calculated using the equation  $D = (A_0 - A_t)/A_0 \times 100\%$ . Where  $A_0$  is the initial absorbance of antibiotic solution,  $A_t$  is the absorbance of antibiotic solution at different degradation times, D is used to evaluate the photocatalytic activity of samples.

# **3** Results and Discussion

# 3.1 XRD Analysis

The phases and crystallinity of samples were characterized by XRD. As shown in Fig. 1, the TiO<sub>2</sub> component being the well-known commercial Degussa P25, there is no surprises regarding the crystal phase composition (70 wt% anatase/JCPDS No.21-1272, 30 wt% rutile/JCPDS No.21-1276) [38]. The characteristic diffraction peaks of TDI– TiO<sub>2</sub>, FeTCPP–TiO<sub>2</sub> and FeTCPP–TDI–TiO<sub>2</sub> in XRD patterns do not exhibit relocation or any change in the peak shape and the anatase/rutile ratio. There results indicated that the modification of TDI and sensitization of FeTCPP which chemical bonded on the surface of TiO<sub>2</sub> microsphere had no effect on the crystal structure of TiO<sub>2</sub> P25 powders.



Fig. 1 XRD patterns of TiO<sub>2</sub> and photocatalysts

#### 3.2 SEM Analysis

Figure 2 shows the SEM image of FeTCPP–TDI–TiO<sub>2</sub> sample. It was found that the FeTCPP–TDI–TiO<sub>2</sub> particles was consisted of microspheres with 30–40 nm and a uniform distribution, while no any other nanometer microsphere found, indicating that FeTCPP and bridging bond molecules were well distributed on the surface of TiO<sub>2</sub>. It is worthy to note that the surface of conjugated microspheres is much rougher than naked TiO<sub>2</sub>. In addition, as compared to the well mono-dispersed TiO<sub>2</sub>, the agglomeration of irregular particles with larger size  $(1-2 \ \mu\text{m})$  than microspheres  $(20-30 \ \text{nm})$  is observed from the image, which also clearly demonstrated the excellent adhesion and stronger interfacial bridging bond of conjugated microspheres.

#### 3.3 FT-IR Analysis

FT-IR is a reliable technique for the monitoring of the porphyrin structure variations and obtaining further information about the interaction between FeTCPP and modified  $TiO_2$  microspheres. Figure 3 shows the FT-IR spectra of TCPP and FeTCPP. From the FT-IR spectrum of TCPP, the peak at 3307 cm<sup>-1</sup> was a result of stretching vibration of the two N–H bonds at the center of porphyrin ring. Compared to TCPP, FeTCPP spectrum has peak at 1000 cm<sup>-1</sup> [39], which was attributed to the bond stretching/bending vibration between Fe<sup>3+</sup> and TCPP. Meanwhile, N-H vibration absorption peak disappeared, which caused by the formation of metal ligand. The results suggested that Fe<sup>3+</sup> has been coordinated to TCPP.

Figure 4a, b show the FT-IR spectra of TDI, TiO<sub>2</sub> and prepared samples respectively. The chemical bridging bond linking of FeTCPP to TDI-TiO<sub>2</sub> surface was confirmed by FT-IR spectra. In the FT-IR spectrum of TDI, the absorption peak at 2268  $\text{cm}^{-1}$  was due to isocyanate (-NCO) [31], which indicating that there were still residual isocyanate groups on the surface of TiO<sub>2</sub>, further confirmed the successful functionalization of TiO<sub>2</sub> surface. Simultaneously, the new peaks were observed at 1653 and 1228 cm<sup>-1</sup> due to the asymmetric stretching vibration and the symmetric stretching vibration of -NHCOOTi [32]. Additionally, the FT-IR spectrum of FeTCPP-TDI-TiO<sub>2</sub> showed that the peak at 2268  $\text{cm}^{-1}$  became weakened compared to the characteristic absorption peaks of -NCO for TDI-TiO2. It must be noted that the reactions between some amounts of -NCO on the surface of TDI-TiO2 and -COOH groups of FeTCPP led to the weakened peaks at 2268 cm<sup>-1</sup>. Meanwhile, the newly formed absorption peaks at 3323, 1630, 1535, 1420, 1381 and 1301  $\text{cm}^{-1}$  corresponding to the formation of -NHCO- are assigned as follows: two intense



**Fig. 2** SEM image of FeTCPP–TDI–TiO<sub>2</sub>



Fig. 3 FT-IR spectra of TCPP and FeTCPP



Fig. 4 FT-IR spectra of TDI, TiO<sub>2</sub> and photocatalysts (a) and their expended spectra between the range of  $1100-1900 \text{ cm}^{-1}$  (b)



Fig. 5 UV-vis DRS of TiO<sub>2</sub> and photocatalysts

peaks at 3323 and 1535 cm<sup>-1</sup> can be assigned to the antisymmetric and symmetric N–H [40], the C=O vibration at 1630 and 1381 cm<sup>-1</sup> [41, 42], the peak at 1420 cm<sup>-1</sup> could be assigned to the esterification resulted from the reaction of –NCO (isocyanate of TDI) and –COOH (carboxyl of FeTCPP) [43] and the peak at 1301 cm<sup>-1</sup> can be assigned to the N–C vibration [44]. The FT-IR spectra analyses indicated that the FeTCPP was fixed firmly on the surface of TiO<sub>2</sub> via TDI linking. However, after only sensitized by FeTCPP, there was no new peak formed in the FT-IR spectrum of FeTCPP–TiO<sub>2</sub>, which revealed that FeTCPP only could be physical absorbed on TiO<sub>2</sub> surface.

#### 3.4 UV-vis DRS Analysis

Optical property of a semiconductor is one of the important factors determining its photocatalytic performance. Figure 5 illustrates the comparison of UV–vis diffuse reflectance spectra (DRS) of samples. It can be seen that  $TiO_2$  did not absorb any light above 400 nm. After surface



Fig. 6 EIS Nyquist plots of TiO<sub>2</sub> and photocatalysts

bridging bonded, the formation of TDI–TiO<sub>2</sub> complex resulted in a red-shift of the absorption threshold towards to the visible region (up to 600 nm) and enhanced the utilization of the visible-light. An obvious red shift of the absorption edge toward to the visible region is observed for FeTCPP–TDI–TiO<sub>2</sub>, which could arise from the transitions of  $a_{1u}(\pi) - e_g^*(\pi)$  and  $a_{2u}(\pi) - e_g^*(\pi)$  attributed to FeTCPP molecule [45]. Furthermore, FeTCPP–TDI–TiO<sub>2</sub> significantly showed almost feature peaks of FeTCPP and Soret band at 420 nm, which was indicative of successful grafting FeTCPP on the TiO<sub>2</sub> surface with bridging bond molecules. In addition, it can also demonstrate from DRS data that the FeTCPP–TDI–TiO<sub>2</sub> has the visible absorption, which may use of visible light except UV light.

# 3.5 EIS Analysis

The electrical conductivity and electrons transfer of the samples were studied by analyzing the electrochemical impedance spectroscopy (EIS). Figure 6 shows the typical

Nyquist plots of FeTCPP–TDI–TiO<sub>2</sub>, FeTCPP–TiO<sub>2</sub>, TDI– TiO<sub>2</sub> and TiO<sub>2</sub>. The diameter of the semicircle in the Nyquist plots represents the electron-transfer resistance (R) of the samples [46, 47]. Noticeably, the Nyquist plot of the FeTCPP–TDI–TiO<sub>2</sub> displays the minimum semicircle diameter, indicating the lowest R and the best electrical conductivity. On the contrary, TiO<sub>2</sub> shows the largest semicircle diameter among all the samples. Furthermore, TiO<sub>2</sub> shows a value of R equal to 585  $\Omega$  which sharply reduces to 134  $\Omega$  for FeTCPP–TDI–TiO<sub>2</sub>, indicating an easy charge transfer at the sample surface of FeTCPP–TDI–TiO<sub>2</sub>. This demonstrates that the recombination of photo-induced electrons and holes in FeTCPP–TDI–TiO<sub>2</sub> is more effectively inhibited, which is consistent with the UV–vis DRS analysis and photocatalytic results.

# 3.6 Evaluation of Photocatalytic Activity for Three Antibiotics

# 3.6.1 Degradation of Norfloxacin

Norfloxacin is the major human-use fluoroquinolone antibiotic, which has been caused wide attention as an organic pollutant of wastewater [48]. Figure 7 shows the degradation rates (D%) of NFC in the presence of different catalysts. The degradation rate of NFC with FeTCPP–TDI– TiO<sub>2</sub> is much faster and higher (the degradation rate is up to 99.2%) than others. The insert of Fig. 7 (The UV–vis absorption spectrum of the photodegradation of NFC solution by FeTCPP–TDI–TiO<sub>2</sub>) shows that the characteristic absorption peak of NFC at 276 nm decreased sharply and disappeared completely after 120 min [49]. In order to better compare the effect of the different catalysts on the NFC degradation reaction, the kinetic models of antibiotic aqueous solution degradation was quantitatively studied by



Fig. 7 Degradation rates of NFC without catalyst, in the presence of different photocatalysts. The *inset* is the UV–vis absorption spectra of NFC solution in the presence of FeTCPP–TDI–TiO<sub>2</sub>

applying the Langmuir–Hinshelwood first-order model as expressed by Eq. (1):

$$\ln\left(\frac{c_t}{c_0}\right) = -kt\tag{1}$$

This model is generally used for the photocatalytic degradation process, where  $c_0$  and  $c_t$  are the concentration of initial and t time, rate constant (k) can be obtained from the slope of the curve of  $\ln(c_0/c_1)$  versus t. From the Fig. 8, the data from the experimental results fit well with firstorder kinetic model, the  $k_{\text{FeTCPP-TD-TiO}_2}$  (0.0342 min<sup>-1</sup>) is the 11.2 times higher than  $k_{\text{TiO2}}$  (0.00304 min<sup>-1</sup>). Moreover the half-life time  $t_{1/2}$  was reduced from 227 min of naked TiO<sub>2</sub> to 20.2 min of FeTCPP-TDI-TiO<sub>2</sub> (Table 1). This result suggests that FeTCPP-TDI-TiO<sub>2</sub> has the highest photocatalytic activity for the degradation of NFC. The HPLC chromatograms (inset in Fig. 8) obtained from NFC aqueous solution in presence of FeTCPP-TDI-TiO<sub>2</sub> exhibited that the intensity of the NFC peak (retention time at 3.74 min) decreased during photocatalytic process. At the same time the new peak (retention time, 13.6 min, the intermediate may be attributed to the attack of hydroxyl radicals occurs at the piperazine ring and the desethylene of NFC



Fig. 8 First-order kinetic for the degradation of NFC without catalysts, in the presence of different photocatalysts. The *inset* is the HPLC chromatograms of NFC in the degradation by FeTCPP-TDI-TiO<sub>2</sub>

 Table 1 Degradation kinetics parameters for NFC using the first-order kinetic model

Catalyst	$k/10^{-2} \min^{-1}$	<i>t</i> <sub>1/2</sub> /min	$R^2$	D/%
Blank	0.105	660	0.992	11.4
TiO <sub>2</sub>	0.304	227	0.991	28.5
TDI-TiO <sub>2</sub>	0.780	88.9	0.989	64.1
FeTCPP-TiO <sub>2</sub>	0.640	108	0.989	57.2
FeTCPP-TDI-TiO <sub>2</sub>	3.42	20.2	0.997	99.2



Fig. 9 Suggested pathway of the degradation of NFC by FeTCPP-TDI-TiO<sub>2</sub>



Fig. 10 Degradation rates of TC without catalyst, in the presence of different photocatalysts. The *inset* is the UV–vis absorption spectra of TC solution in the presence of FeTCPP–TDI–TiO<sub>2</sub>

molecule) was detected and its intensity increased with the reaction time. The suggested pathway of the degradation of NFC by FeTCPP–TDI–TiO<sub>2</sub> was depicted in Fig. 9. The degradation of NFC occurs by the attack of hydroxyl radicals on the piperazine. Then NFC undergoes piperazine side chain cleavage to form the compound **1**. Then compound **1** further loses a  $C_2H_5N$  group to produce compound **2** (intermediate) [50]. Finally above results and analyses indicated that NFC molecules were totally mineralized.

#### 3.6.2 Degradation of Tetracycline Hydrochloride

As an antibiotic, tetracycline hydrochloride (TC) is often detected in the final effluents from wastewater treatment plants [35, 51]. When the value of solution pH lies between 3.3 and 7.7, TC appears in form of non-biodegradation (TCH<sub>2</sub>) [52]. Therefore, the degradation efficient of different catalysts was evaluated by degradation of TC. As can be observed in Fig. 10, the degradation rate of TC without catalyst under direct visible light illumination was only 7.64%. However, FeTCPP–TDI–TiO<sub>2</sub> exhibited a higher degradation rate than that of other catalysts under identical conditions. Specifically, absorbance of TC at 358 nm decreased by FeTCPP–TDI–TiO<sub>2</sub> sharply with



Fig. 11 First-order kinetic for the degradation of TC without catalyst, in the presence of different photocatalysts. The *inset* is the HPLC chromatograms of TC in the degradation by FeTCPP–TDI–TiO<sub>2</sub>

the increase of irradiation time (insert of Fig. 10), and 99.7% of TC was degraded after 120 min, which was 4.4 times higher than that of naked TiO<sub>2</sub> (22.3%) [53]. As can be seen from Fig. 11, the  $\ln c_0/c_1$  values of TC degradation are very good linear with respect to the degradation times t for all catalysts. This shows that the degradation of TC follows the first order kinetics model. From Table 2, the  $k_{\text{FeTCPP-TDI-TiO}_2}$  of TC is 0.029 min<sup>-1</sup>, which is significantly higher than that of other catalysts. The greater activity of FeTCPP-TDI-TiO<sub>2</sub> is particularly notable taking into account that bridging bond and conjugated structure. The insert of Fig. 11 illustrates the HPLC chromatograms of TC degraded by FeTCPP-TDI-TiO<sub>2</sub>, the peak at retention time of 3.28 min gradually disappeared, meanwhile the two new peaks (retention time at 3.03 and 4.10 min) were detected and their intensities decreased as the reaction time increased, indicating the presence of two intermediates and final mineralization [54]. The degradation pathway of TC was shown in Fig. 12. The intermediates were observed in 3.03 and 4.10 min, resulted from the cleavage of doublebond in aromatic ring b sites and formation of the compounds 4 and 3. The peak observed in 3.03 min that the retention time is slightly shorted than that of tetracycline indicated that the more polar intermediate compound 4 was

 Table 2
 Degradation kinetics parameters for TC using the first-order kinetic model

Catalyst	$k/10^{-2} \min^{-1}$	<i>t</i> <sub>1/2</sub> /min	$R^2$	D/%	
Blank	0.075	913	0.996	7.64	
TiO <sub>2</sub>	0.234	296	0.984	22.3	
TDI-TiO <sub>2</sub>	0.611	113	0.994	53.8	
FeTCPP-TiO <sub>2</sub>	0.785	88.3	0.990	64.2	
FeTCPP-TDI-TiO <sub>2</sub>	2.97	23.2	0.997	99.7	

formed. After 120 min, most of those intermediates would be degraded and evolved to  $CO_2$ ,  $H_2O$  and inorganic ions etc.

# 3.6.3 Degradation of Sulfapyridine

Sulfapyridine (SPY), a sulfonamide antibiotic, may enter food chain and provoke acute and chronic adverse effects in the environment. In comparison to conventional water treatments, photocatalytic degradation has been proved to be a successful alternative to eliminate non-biodegradable compounds [55, 56]. Figure 13 displays the time course evolution of SPY degradation as function of time in the case of catalysts. The naked TiO<sub>2</sub> exhibited about 17.5% degradation rate of SPY after 120 min. On the contrary, the degradation rate of FeTCPP–TDI–TiO<sub>2</sub> (99.1%) displayed 5.6 times higher than that of naked TiO<sub>2</sub> (17.5%) under the same time. The UV–vis absorption spectra of SPY at the varied irradiation times using FeTCPP–TDI–TiO<sub>2</sub> were shown in the insert of Fig. 13. It is obvious that the characteristic absorption peak of SPY at 261 nm gradually



Fig. 13 Degradation rates of SPY without catalyst, in the presence of different photocatalysts. The *inset* is the UV–vis absorption spectra of SPY solution in the presence of FeTCPP–TDI–TiO<sub>2</sub>

becomes weak with the increase of reaction time, and the degradation process of SPY followed a first-order kinetic model (Table 3). As shown in Fig. 14, the  $t_{1/2}$  of SPY degradation with FeTCPP–TDI–TiO<sub>2</sub> was 21.9 min, which was about 18.7 times faster compared to that observed for naked TiO<sub>2</sub> ( $t_{1/2}$ =410 min). In addition, the  $k_{\text{FeTCPP-TDI-TiO_2}}$  (0.002 min<sup>-1</sup>) is higher than the  $k_{\text{FeTCPP-TiO_2}}$  (0.002 min<sup>-1</sup>),  $k_{\text{TDI-TiO_2}}$  (0.003 min<sup>-1</sup>),  $k_{\text{TO2}}$  (0.001 min<sup>-1</sup>) and  $k_{\text{Blank}}$  (0.0004 min<sup>-1</sup>). This comparison indicated that grafting sensitizer on the TiO<sub>2</sub> surface with bridging bond molecule played an important role in the improvement of semiconductor photocatalytic performance. These results are in good agreement with the degradation of NFC and TC, and



Fig. 12 Suggested pathway of the degradation of TC by FeTCPP-TDI-TiO<sub>2</sub>

 Table 3 Degradation kinetics parameters for SPY using the first-order kinetic model

Catalyst	$k/10^{-2} \min^{-1}$	<i>t</i> <sub>1/2</sub> /min	$R^2$	D/%
Blank	0.0456	1520	0.987	4.52
TiO <sub>2</sub>	0.169	410	0.980	17.5
TDI-TiO <sub>2</sub>	0.334	296	0.997	23.8
FeTCPP-TiO <sub>2</sub>	0.201	344	0.989	19.8
FeTCPP-TDI-TiO <sub>2</sub>	3.16	21.9	0.990	99.1



**Fig. 14** First-order kinetic for the degradation of SPY without catalyst, in the presence of different photocatalysts. The *inset* is the HPLC chromatograms of SPY in the degradation by FeTCPP–TDI–TiO<sub>2</sub>



Fig. 16 Photodegradation rates of NFC, TC and SPY in the presence of FeTCPP–TDI–TiO<sub>2</sub> for five cycles

# 3.6.4 Stability of FeTCPP-TDI-TiO<sub>2</sub> Catalyst

To evaluate the reusability of FeTCPP–TDI–TiO<sub>2</sub> catalyst, the degradation tests of three antibiotics by the recycled catalyst were carried out 5 times under identical conditions. 50 mg of FeTCPP–TDI–TiO<sub>2</sub> was dispersed into 50 mL of antibiotic solution. After 120 min of photocatalytic reaction, the FeTCPP–TDI–TiO<sub>2</sub> was separated and washed with deionized water for several times, then dried in an oven at 80 °C. As shown in Fig. 16, no obvious decrease of the degradation efficiency was observed by using the same



Fig. 15 Suggested pathway of the degradation of SPY by FeTCPP-TDI-TiO<sub>2</sub>

furthermore evidence that FeTCPP–TDI–TiO<sub>2</sub> possesses the best photocatalytic performance. The HPLC chromatograms of SPY solution degraded by FeTCPP–TDI–TiO<sub>2</sub> illustrates in the insert of Fig. 14, the chromatographic peak intensity of SPY at  $t_R = 18.9$  min was reduced with a simultaneous formation of few intermediate peaks at lower retention times. The major intermediate peak observed at  $t_R = 7.84$  min is ascribed to the sulfanilic acid, which resulted from the cleavage of the bond between the aniline ring and the sulfonic group followed by an ·OH attack to the S-N bond [55]. Moreover, their retention times were shorter than that of SPY. It indicated that the major more polar intermediate was sulfanilic acid (compound 5). The proposed intermediates and degradation pathway of SPY were depicted in Fig. 15.

batch of catalyst. This demonstrates that the stability of the synthesized FeTCPP–TDI–TiO<sub>2</sub> is very excellent under the cyclic tests, and has good potential to be used in wastewater treatment.

# 4 Conclusion

With TDI as a bridging bond molecule, the conjugated microspheres FeTCPP–TDI–TiO<sub>2</sub> were successfully obtained by grafting FeTCPP on the surface of TiO<sub>2</sub>. The characterization results showed that the FeTCPP–TDI–TiO<sub>2</sub> particles were of microsphere structure (a mixture of anatase (70%) and rutile (30%) phases) with sizes ranged

between 20 and 30 nm, and there exists obvious aggregation in the powder. As expected, the chemical interaction occurred between the FeTCPP and TiO<sub>2</sub> surface rather than physical adsorption. The FeTCPP-TDI-TiO<sub>2</sub> microspheres exhibited an excellent photocatalytic performance toward the degradation of antibiotics NFC (99.2%), TC (99.7%) and SPY (99.1%) within 120 min under visible light irradiation. According to HPLC experimental results, the possible photocatalytic mechanism of FeTCPP-TDI-TiO<sub>2</sub> for antibiotics was also discussed. Additionally, the FeTCPP-TDI-TiO<sub>2</sub> showed the long-term stability and reusability, up to 5 times without significant deactivation. Our work is not only useful in the synthesis of bridge-bond complex between sensitizer and TiO<sub>2</sub> but also provide some insight into the design of tailoring the mult-composite materials with high photocatalytic performance, which may open new field of synthesizing photocatalytic materials.

**Acknowledgments** This work was supported by the Naional Natural Science Foundation of China (No. 21276208), the International Science Technology Cooperation Program of China (2015DFR50350), the Research Fund of Shaanxi Key Laboratory of Comprehensive Utilization of Tailings Resources (No. 2014SKY-WK003), the Special Research Fund of Shaanxi Provincial Department of Education of China (No. 15JK1862), and the Research Fund for Innovation Doctoral Thesis of Xi'an University of Technology (No. 310-11202J304, 310-252071508).

# References

- Huo PW, Yan YS, Li ST, Li HM, Huang WH (2010) Appl Surf Sci 256:3380
- 2. Brigante M, Schulz PC (2011) J Hazard Mater 192:1597
- Giraldo AL, Penuela GA, Torres-Palma RA, Pino NJ, Palominos RA, Mansilla HD (2010) Water Res 44:5158
- Dimitrakopoulou D, Rethemiotaki I, Frontistis Z, Xekoukoulotakis NP, Venieri D, Mantzavinos D (2012) J Environ Manage 98:168
- 5. Nakata K, Fujishima A (2012) J Photochem Photobiol C 13:169
- 6. Su Y, Wu JS, Quan X, Chen S (2010) Desalination 252:143
- Niu JF, Yao BH, Peng C, Zhang WT, Chen YQ (2014) Integr Ferroelectr 152:163
- Zhang RH, Wang Q, Liang J, Li Q, Dai JF, Li WX (2012) Phys B 407:2709
- 9. Diker H, Varlikli C, Mizrak K, Dana A (2011) Energy 36:1243
- 10. Wang YQ, Jiang XD, Pan CX (2012) J Alloys Compd 538:16
- Kumar CV, Raptis D, Koukaras EN, Sygellou L, Lianos P (2015) Org Electron 25:66
- 12. Wei LG, Yang YL, Fan RQ, Na Y, Wang P, Dong YW (2015) Thin Solid Films 592:14
- Silva MSP, Diógenes ICN, Carvalho IMM, Zanoni KPS, Amaral RC, Iha NYM (2016) J Photochem Photobiol A 314:75
- Iqbal Z, Wu WQ, Huang ZS, Wang LY, Kuang DB, Meier H, Cao DR (2016) Dyes Pigm 124:63
- Sun WJ, Li J, Yao GP, Zhang FX, Wang JL (2011) Appl Surf Sci 258:940
- 16. Aldajaei JT, Gronert S (2012) Int J Mass Spectrom 316:68
- 17. Hasobe T, Hattori S, Kamat PV, Fukuzumi S (2006) Tetrahedron 62:1937

- Niu JF, Yao BH, Chen YQ, Peng C, Yu XJ, Zhang J, Bai GH (2013) Appl Surf Sci 271:39
- Wang C, Yang GM, Li J, Mele G, Slota R, Broda MA, Duan MY, Vasapollo G, Zhang XF, Zhang FX (2009) Dyes Pigm 80:321
- Chang MY, Hsieh YH, Cheng TC, Yao KS, Wei MC, Chang CY (2009) Thin Solid Films 517:3888
- Cai JH, Huang JW, Yu HC, Ji LN (2012) J Taiwan Inst Chem E 43:958
- 22. Gao BJ, Fang L, Men JY, Lei QJ (2012) Mater. Chem Phys 134:1049
- Murphy S, Saurel C, Morrissey A, Tobin J, Oelgemöller M, Nolan K (2012) Appl Catal B 119:156
- Daphnomili D, Sharma GD, Biswas S, Thomas KRJ, Coutsolelos AG (2013) J Photochem Photobiol A 253:88
- Kathiravan A, Renganathan R (2009) J Colloid and Interface Sci 331:401
- Xiang N, Huang XW, Feng XM, Liu YJ, Zhao B, Deng LJ, Shen P, Fei JJ, Tan ST (2011) Dyes Pigm 88:75
- 27. Seo KD, Lee MJ, Song HM, Kang HS, Kim HK (2012) Dyes Pigm 94:143
- Monteiro CJP, Pereira MM, Vicente MGH, Arnaut LG (2012) Tetrahedron 68:8783
- 29. Mallakpour S, Aalizadeh R (2013) Prog Org Coat 76:648
- Tomovska R, Daniloska V, Asua JM (2013) Appl Surf Sci 264:670
- 31. Jiang D, Xu Y, Wu D, Sun YH (2008) J Solid State Chem 181:593
- 32. Jiang D, Xu Y, Hou B, Wu D, Sun YH (2007) J Solid State Chem 180:1787
- Yao BH, Peng C, Zhang W, Zhao J, Niu JF (2015) Appl Catal B 174:77
- Peng C, Yao BH, Zhang W, Niu JF, Zhao J (2014) Chin. J Chem Phys 27:200
- 35. Sarmah AK, Meyer MT, Boxall ABA (2006) Chemosphere 65:725
- Yang SF, Lin CF, Wu CJ, Ng KK, Lin AYC, Hong PKA (2012) Water Res 46:1301
- 37. Ahmed MJ, Theydan SK (2014) J Taiwan Inst Chem E 45:219
- Zhang ZW, Zhou YM, Zhang YW, Sheng XL, Zhou SJ, Xiang SM (2013) Appl Surf Sci 286:344
- Marijuan AF, Barandika G, Bazán B, Urtiaga MK, Arriortua MI (2011) Polyhedron 30:2711
- Jeong EY, Ansari MB, Mo YH, Park SE (2011) J Hazard Mater 185:1311
- 41. Managa M, Antunes E, Nyokong T (2014) Polyhedron 76:94
- Uribe CED, Daza MC, Martínez F, Mozo EAP, Guedes CLB, Mauro ED (2010) J Photochem Photobiol A 215:172
- 43. Mallakpour S, Barati A (2011) Prog Org Coat 71:391
- 44. Wang Y, Jiang PP, Zhang WJ, Zheng JW (2013) Appl Surf Sci 270:531
- 45. Huang HY, Gu XT, Zhou JH, Ji K, Liu HL, Feng YY (2009) Catal Commun 11:58
- 46. Hao NH, Gyawali G, Sekino T, Lee SW (2016) Prog Nat Sci Mater 26:4.
- Dai GT, Zhao L, Wang SM, Hu JH, Dong BH, Lu HB, Li J (2012) J Alloy Compd 539:25
- 48. Haque MM, Muneer M (2007) J Hazard Mater 145:51
- Ahmad I, Bano R, Musharraf SG, Sheraz MA, Ahmed S, Tahir H, Arfeen Q, Bhatti MS, Shad Z, Hussain SF (2015) J Photochem Photobiol A 302:1
- 50. Liu C, Nanaboina V, Korshin GV, Jiang WJ (2012) Water Res 46:5235
- 51. Daghrir R, Drogui P (2013) Environ Chem Lett 11:209
- Hou LW, Wang LG, Royer SB, Zhang H (2016) J Hazard Mater 302:458

- 53. Liu S, Zhao XR, Sun HY, Li RP, Fang YF, Huang YP (2013) Chem Eng J 231:441
- 54. He D, Sun YB, Xin L, Feng JW (2014) Chem Eng J 258:18
- Challis JK, Carlson JC, Friesen KJ, Hanson ML, Wong CS (2013) J Photochem Photobiol A 262:14
- 56. Galán MJG, Cruz MSD, Barceló D (2012) Water Res 46:711