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Enhancement of photoelectric catalytic activity of TiO_2 film via Polyaniline hybridization

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ABSTRACT

A Polyaniline (PANI)/TiO_2 film coated on titanium foil was successfully prepared using the sol–gel method followed by a facile chemisorption. Compared with pristine TiO_2, the photocatalytic (PC) and photoelectrocatalytic (PEC) degradation rates of 2,4-dichlorophenol (2,4-DCP) with the PANI/TiO_2 film were enhanced by 22.2% and 57.5%, respectively. 2,4-DCP can be mineralized more effectively in the presence of PANI/TiO_2 film. The best PEC degradation efficiency of 2,4-DCP with the PANI/TiO_2 film was acquired at an external potential of 1.5 V with a layer of 1 nm thick PANI. The PANI/TiO_2 film was characterized by Raman spectra, Fourier transform infrared spectra (FT-IR), Auger electron spectroscopy (AES), and electrochemical analysis. These results indicated that there was a chemical interaction on the interface of PANI and TiO_2. This interaction may be of significance to promote the migration efficiency of carriers and induce a synergetic effect to enhance the PC and PEC activities.

1. Introduction

Photocatalysis has been extensively studied as an emerging successful technology for water treatment [1]. In current researches, TiO_2-based photocatalysts are still the most promising photocatalysts due to their high oxidative efficiency, photochemical stability and low-cost [2–4]. However, the high photoinduced charge recombination rate and low charge separation efficiency has hindered the application of this technology. Several methods have been performed to increase the efficiency of the photocatalytic (PC) process of TiO_2. Photoelectrocatalytic (PEC) oxidation has been proven to be more efficient than PC oxidation by driving the photogenerated electrons to a counter electrode via an external bias potential, thus the quantum efficiency can be improved consequently [5–7]. Moreover, TiO_2 in an immobilized film form is more practical than that in a powdery form for application.

Nowadays, delocalized conjugated structures have been proven to arouse a rapid photoinduced charge separation and decrease the charge recombination rate in electron-transfer processes [8,9]. Recently, our group has developed some semiconductors hybridized by delocalized conjugative π structure material as efficient photocatalysts, such as C_{60} [9], graphene-like carbon [10]. Polyaniline (PANI) is one of the conducting polymers with the delocalized conjugated structure, and its benzenoid and quinonoid units has several redox states with extensive interesting properties. Moreover, PANI is a promising candidate for a large scale application due to its high conductivity, good environmental stability, and ease of preparation [11,12]. Recently, some studies have focused on the combination of PANI and TiO_2 to improve their electronic conductivity and solar energy transfer [13–20]. Li and co-workers synthesized PANI-TiO_2 nanoparticles by chemical oxidative polymerization, and found that PANI-TiO_2 composites exhibited higher PC activity than that of pristine TiO_2 under visible light irradiation [17]. Mo and co-workers prepared PANI-TiO_2 by in situ polymerization of aniline, and found that the nanocomposite exhibited higher dielectric constants and dielectric losses [16]. Dey and co-workers synthesized PANI-TiO_2 from a colloidal sol of TiO_2 nanoparticles, and found the nanocomposite yielded a large dielectric constant [18]. We have already carried out the research on TiO_2 nanoparticles modified by PANI and found the PC activity of the PANI-modified TiO_2 nanoparticles was improved remarkably [15]. To the best of our knowledge, there has been no report regarding the application of the PANI-modified TiO_2 in the PEC degradation of organic contaminants. In the present study, a series of PANI/TiO_2 films with different PANI contents were prepared by a facile chemisorption approach. 2,4-Dichlorophenol (2,4-DCP) was chosen as a model pollutant for PC and PEC degradation. 2,4-DCP is common used as a chemical intermediate for manufacture of pesticides and herbicides and as a precursor in the production of certain methyl compounds used in mouth antiseptics and seed disinfectants [21]. It has been reported that 2,4-DCP may induce some pathological changes to endocrine systems of human [22]. The degradation

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results indicated that the introduction of PANI to TiO_2 can effectively enhance its PC and PEC activity. The optimal external potential and PANI content were also investigated. Furthermore, the PANI/TiO_2 films were chemically stable even after UV illumination for 418 h.

2. Experimental section

2.1. Preparation of the photocatalyst

Preparation of TiO_2 film: titanium foils (approximately 250 μm thick, purity 99.4%, Beijing Cuibolin Non-Ferrous Technology Developing Co., Ltd.) after chemical polishing were dipped into the sol (the volume ratio of Tetrabutyl titanate to ethanol solution (containing 1% deionized water) is 1:7.5) for 3 min and lifted at a speed of 3 cm/min to form a film. After drying at 80 °C, the film was calcined at 450 °C for 1 h in an air flow muffle. The thickness of the TiO_2 film could be adjusted by repeating the cycle from dipping to heat treatment.

Preparation of PANI/TiO_2 film: PANI (molecular weight, $\sim 10^5$, Jilin Zhengji Corp.) was dissolved in tetrahydrofuran (THF) to obtain a concentration series of 30, 50, 60, 70, 80, and 90 mg/L. The typical preparation of the PANI/TiO_2 film was as follows: TiO_2 film was dipped into the PANI solution for 30 min, and then dried at 80 °C for 24 h in an air flow oven.

2.2. Characterization

The phase composition of the samples was determined by Microscopic Confocal Raman Spectrometer (Renishaw, RM2000) using 632.8 nm as the light source. Fourier transform infrared (FT-IR) spectra were measured by a Perkin Elmer System 2000 infrared spectrometer with KBr as the reference sample. The thickness of the PANI layer was determined by a PHI700 Auger electron spectroscopy (AES). The beam voltage was 3.0 KeV and the beam current was 0.5 μA. During the depth profile analysis, the energy and beam current of the Ar ion beam were 3.0 keV and 6 μA, respectively. According to the sputtering rate and N and Ti curves' crosspoint, the thickness of the PANI layer can be calculated. The concentration of 2,4-DCP was examined by a High-Performance Liquid Chromatography (HPLC) (LUMTECH) system with a Venusil XBP-C18 (Agela Technologies Inc.) column and using a UV absorbance detector (K 2501) operated at 278 nm. The mobile phase was 1.0 mL/min of methanol and deionized water (containing 1% acetic acid) (70:30 v/v). The mineralization of the 2,4-DCP was followed by measuring the total organic carbon (TOC) concentration, utilizing a Analytik Jena MultiN/C 2100 TOC/TN Analyzer.

2.3. Measurement of photoelectric performances

The PC and PEC degradation experiments were performed in a rectangular (50 mm × 50 mm × 140 mm) quartz reactor. The reactor was placed 4 cm in front of an 18 W germicidal lamp (λ=254 nm, Institute of Electric Light Source, Beijing, China). The intensity of light at the PANI/TiO_2 film was 1.60 mW/cm^2. All electrochemical and photoelectric studies were performed on a CHI660B electrochemical system (Shanghai, China) using a standard three-electrode cell with a working electrode (20 mm × 36 mm), a platinum wire as counter electrode, and a standard calomel electrode (SCE) as reference electrode. 0.1 M Na_2SO_4 was used as electrolyte solution. The photocurrents of UV light on and off were measured at 0.0 V. Electrochemical impedance spectra (EIS) was recorded in the open circuit potential mode. A sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range of 0.05×10^5 Hz. The PC and PEC activities of the samples were all evaluated by the removal of 2,4-DCP (with an initial concentration of 50 mg/L) in 0.1 M Na_2SO_4 solution.

3. Results and discussion

3.1. Interaction between PANI and TiO_2

Fig. 1 showed the Raman spectra of TiO_2 and PANI/TiO_2 films. It can be clearly seen that the main characteristic peaks of PANI and anatase TiO_2 all appear in the PANI/TiO_2 film. The peaks at 142, 398, 516, and 635 cm^{-1} were characteristic of anatase TiO_2 [7]. In the Raman spectra of PANI/TiO_2 film (inset of Fig. 1), the peak at 1596 cm^{-1} could be attributed to the C–C stretching vibration of the benzenoid, the peak at 1510 cm^{-1} corresponding to the N–H stretching mode, the peak at 1394 cm^{-1} could be assigned to the C–C stretching vibration of the quinonoid rings, the peak at 1333 cm^{-1} was related to the C–N$^+$ stretching mode, and the peak at 1167 cm^{-1} was attributed to the C–H bending vibration of the benzenoid [20,23]. Compared with the spectrum of pristine PANI, the peaks of PANI/TiO_2 all shifted to lower wavenumbers for about 2–9 cm^{-1}. The red shift of the bands indicated that the conjugated system of PANI was weakened, and an intensive interaction between PANI and TiO_2 occurred [15]. In addition, PANI exists in three principal forms: leucoemeraldine (totally reduced), emeraldine (semioxidized), and pernigraniline (totally oxidized), only the emeraldine favors conductivity. The existence of peaks in the vicinity of 1300–1350 cm^{-1} is inherently associated with the protonation process via polysemiquinone radical formation mechanism and is a direct proof that the PANI used in this research is in its conducting state [24].

The FT-IR spectra of PANI, TiO_2, and PANI/TiO_2 were shown in Fig. 2. The peaks of pristine PANI at 1558 cm^{-1} (attributed to the C=C and C=N stretching modes for the quinonoid units) and 1466 cm^{-1} (associated with the C=C and C=N stretching modes for the benzenoid rings) all shifted to lower wavenumbers for about 14–16 cm^{-1} [11,18]. These red shift was due to the decrease in the vibrational frequency of C=N and C=C bond, indicating that the bond strengths of C=N and C=C were weakened. This result might origin from stretched conjugated system of PANI and a more widely conjugated system containing PANI and TiO_2. It was consistent with the Raman spectra.

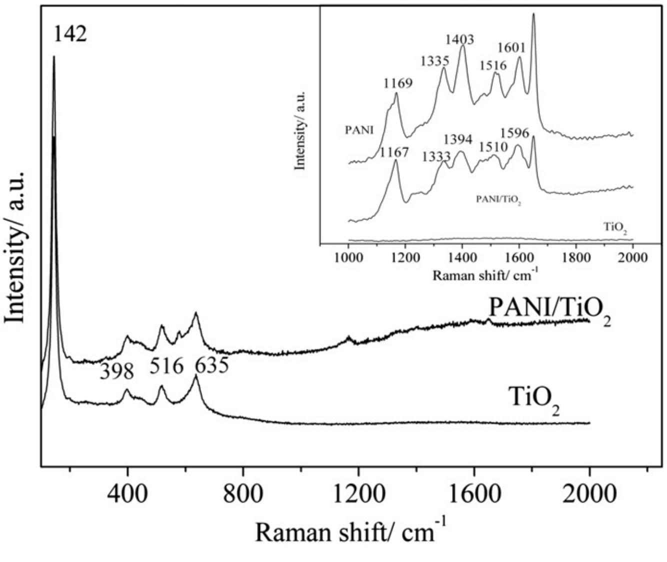

Fig. 1. Raman spectra of TiO_2 and PANI/TiO_2. Inset of Fig. 1 showed the detailed Raman information of PANI, TiO_2, and PANI/TiO_2.

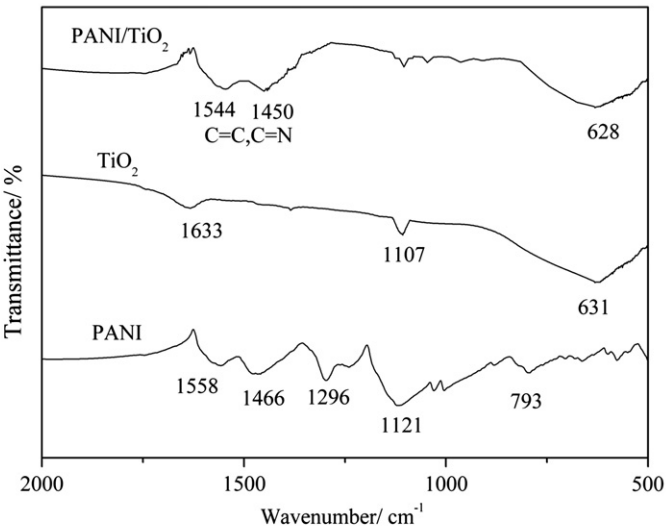

Fig. 2. FT-IR spectra of PANI, TiO_2, and PANI/TiO_2.

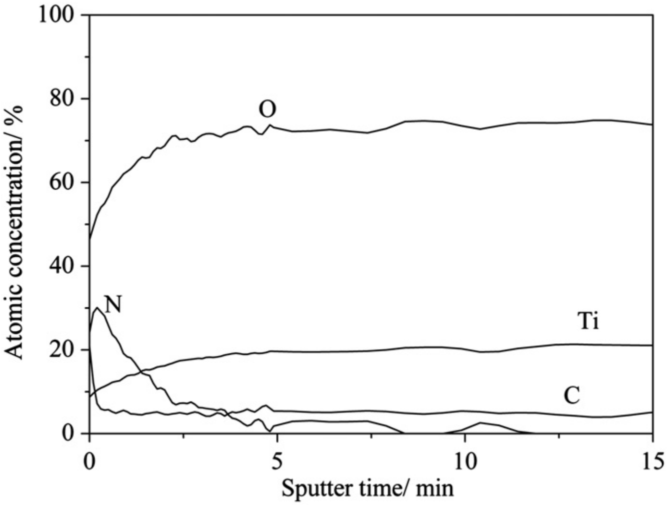

Fig. 3. AES depth profile of PANI/TiO_2 film.

According to the results of Raman and FT-IR, the conjugated system of PANI was weakened, and there was a strong interaction between PANI and TiO_2 [11,15]. This chemical interaction may be of significance to transfer carriers and induce synergetic effect to enhance PC and PEC activities [15].

The thickness of PANI layer was measured using AES (Fig. 3), and the sputtering rate was 0.5 nm/min for a thermally oxidized SiO_2 thin film. After adjusting the N and C elements, the thickness of PANI layer on PANI/TiO_2 film (PANI: 70 mg/L) was calculated as about 1 nm.

3.2. Enhancement of PC and PEC activity

PC, electro-oxidation and PEC degradation of 2,4-DCP at the external potential of 1.5 V were performed. It is well recognized that the PC, electro-oxidation, and PEC degradation of organic pollutants follows pesudo-first-order kinetics [25]. The rate constants of 2,4-DCP degradation were shown in Fig. 4. Compared with pristine TiO_2, the PC and PEC degradation efficiency of PANI/TiO_2 film were clearly enhanced. The rate constant of PC degradation of PANI/TiO_2 was $0.73 \times 10^{-2}\ \text{min}^{-1}$, which was 30.4% higher than that of pristine TiO_2 ($0.56 \times 10^{-2}\ \text{min}^{-1}$). The rate constant of PEC degradation of PANI/TiO_2 was $1.26 \times 10^{-2}\ \text{min}^{-1}$, which was 57.5% higher than that of pristine TiO_2. Within 120 min, 77.4% of 2,4-DCP was degraded in the presence of the PANI/TiO_2 film. These results indicated that PANI coated on TiO_2 film can remarkably enhance the PC and PEC activity of TiO_2 film. In addition, as shown in Fig. 4, the pseudo-first-order kinetic constant of 2,4-DCP for PEC degradation is larger than the sum of the electro-oxidation and PC degradation individually. It was reasonable to conclude that a synergetic effect occurred in the PANI/TiO_2 film during the PEC degradation of 2,4-DCP [25].

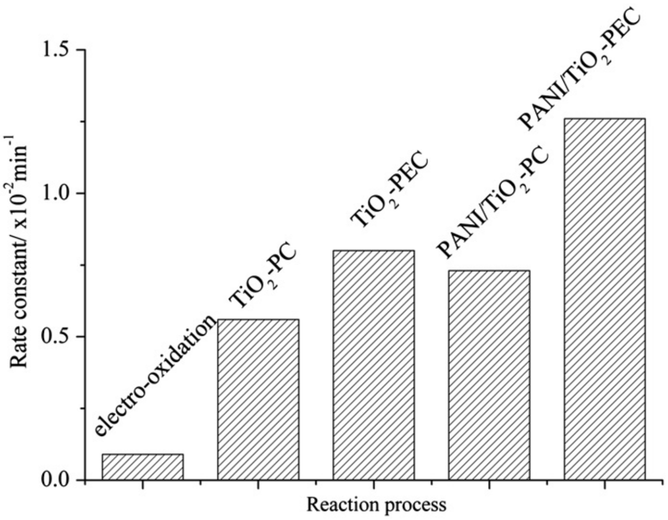

Fig. 4. Pseudo-first-order rate constants of 2,4-DCP degradation under various conditions (2,4-DCP initial concentration = 50 mg/L, external potential = 1.5 V, reaction time = 2 h).

To further understand the mineralization property of the as-prepared photocatalyst, the decrease of TOC in the PEC degradation of 2,4-DCP was determined. When 77.4% of 2,4-DCP was degraded in PANI/TiO_2 film PEC degradation in 2 h, about 51.2% of mineralized degree was reached. While 31.6% of mineralized degree of 2,4-DCP was achieved after 2 h TiO_2 film PEC degradation. After PANI modification, the mineralization property of TiO_2 film was effectively enhanced.

3.3. Synergetic effect of photocatalysis and electro-oxidation

To analyze the synergetic effect of PANI and TiO_2, the effect of PANI content on photoelectric properties of PANI/TiO_2 films was determined (Fig. 5). The used PANI concentrations were 30, 50, 60, 70, 80, and 90 mg/L. As shown in Fig. 5(A), the photoelectric property was enhanced gradually with the concentration of PANI increasing. When the concentration got to 70 mg/L, the as-prepared PANI/TiO_2 film exhibited an optimal photocurrent of 0.15 mA/cm^2, almost twice as high as that of pristine TiO_2. Further increasing the concentration of PANI, the photocurrent decreased gradually though it remained larger than that of pristine TiO_2. Fig. 5(B) showed the EIS spectra of TiO_2 and PANI/TiO_2 films under UV irradiation. The arc radius on EIS spectra first decreased and then increased with the concentration of PANI increasing. The smallest arc radius occurred when the concentration of PANI was 70 mg/L. Since the radius of the arc on the EIS spectra reflects the reaction rate occurring at the surface of electrode [26,27], it suggested that a more effective separation rate of photogenerated electron–hole pairs and a faster interfacial charge transfer occurred on PANI/TiO_2 film under this condition [25]. Moreover, since all the arc radius on the EIS Nynquist plot were smaller than that of pristine TiO_2, it clearly indicated that the combination of TiO_2 and PANI can effectively enhance the separation efficiency of

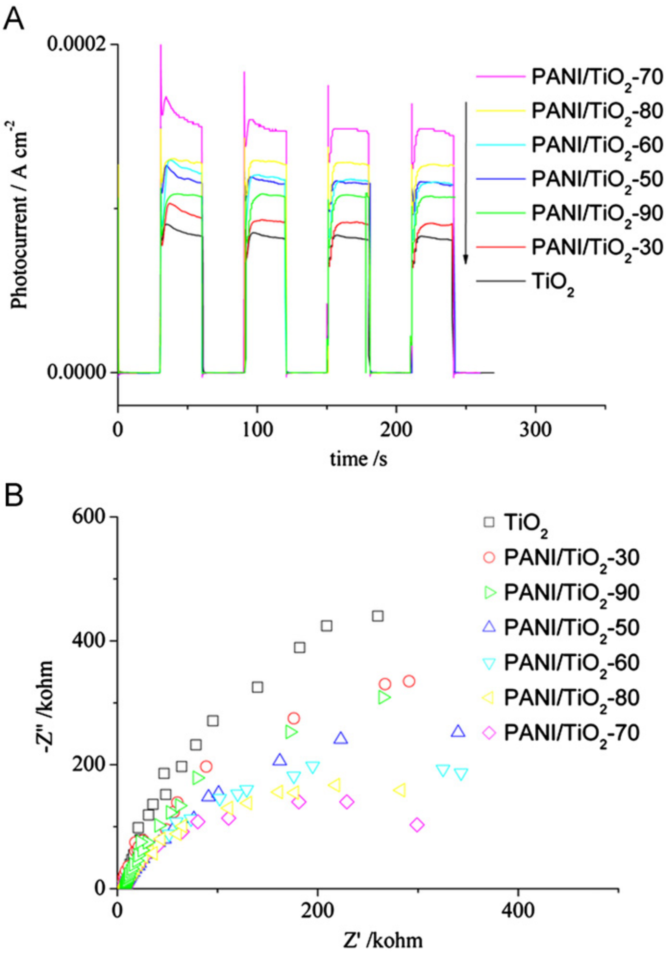

Fig. 5. (A) The photocurrent spectra on the TiO_2 and various PANI/TiO_2 films and (B) EIS spectra of the TiO_2 and various PANI/TiO_2 films.

photogenerated electron–hole pairs, thus improving the PC and PEC activity. According to the results of photocurrent and EIS spectra, the PANI/TiO_2 film prepared with the PANI solution of 70 mg/L had an optimal photoelectric performance.

The effect of PANI content on the PEC degradation of 2,4-DCP was also determined (Fig. 6). The PEC activity was enhanced gradually with increased concentration of PANI. When the concentration of PANI reached 70 mg/L, the as-prepared PANI/TiO_2 film exhibited the highest activity of degrading 2,4-DCP by 77.4% in 120 min. Further increasing the concentration of PANI, the degradation rate constant *k* declined gradually though it remained consistently higher than that of pristine TiO_2. According to the results of photoelectric performance and the PEC degradation, PANI concentration of 70 mg/L is the optimal condition. At the time, the thickness of PANI layer is about 1 nm (determined by AES). Moreover, these results demonstrated that the synergetic effect of TiO_2 and PANI can effectively enhance the PEC activity.

According to the cyclic voltammetry (Fig. 7), the redox potential of 2,4-DCP was 0.8 V. The effect of the external potential on the PEC degradation of 2,4-DCP was shown in Fig. 8. PEC degradation of 2,4-DCP was performed at potentials of 0, 0.3, 0.5, 0.8, 1.0, 1.3, 1.5, and 2.0 V, respectively. As the external potential increased, the PEC activity did not enhance monotonously. The PEC degradation rate constants of 2,4-DCP increased at first but then decreased above 1.5 V. When the external potential was lower than 0.8 V (the redox potential), the potential only promoted the separation of photogenerated holes and electrons, as a consequence, the degradation rate of 2,4-DCP

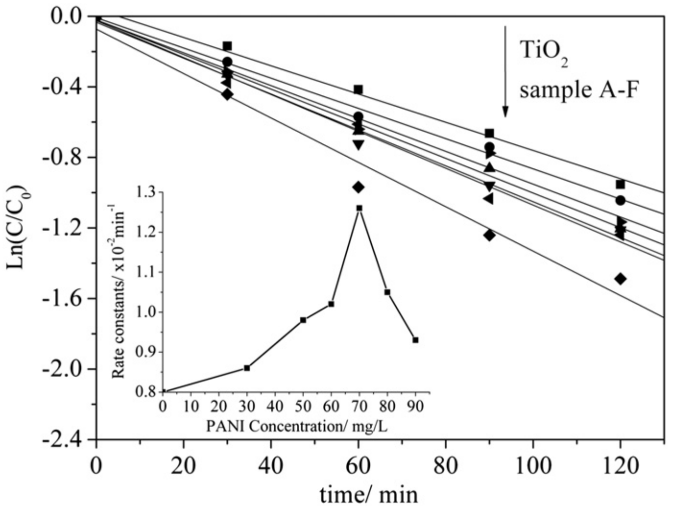

Fig. 6. The effect of PANI content on 2,4-DCP degradation with initial concentration of 50 mg/L, external potential = 1.5 V. Samples A–F represented PANI/TiO_2 photocatalysts with PANI concentration = 30, 90, 50, 60, 80, and 70 mg/L, respectively. Inset of Fig. 6 showed the degradation rate constants of various PANI/TiO_2 films.

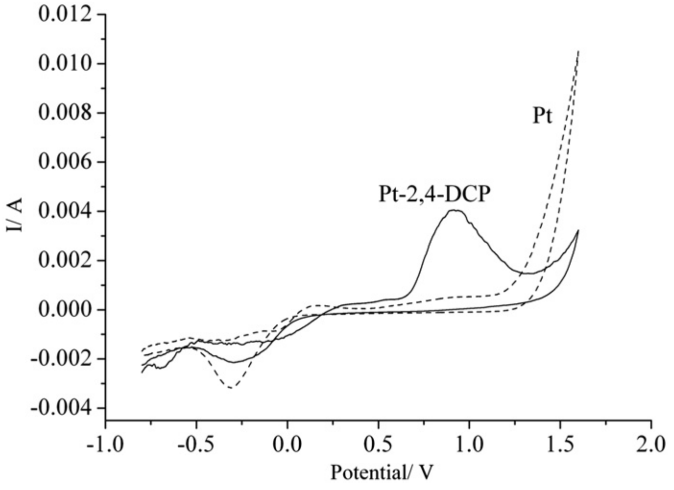

Fig. 7. Cyclic voltammetry scan curves of 2,4-DCP in 0.1 M Na_2SO_4 solution.

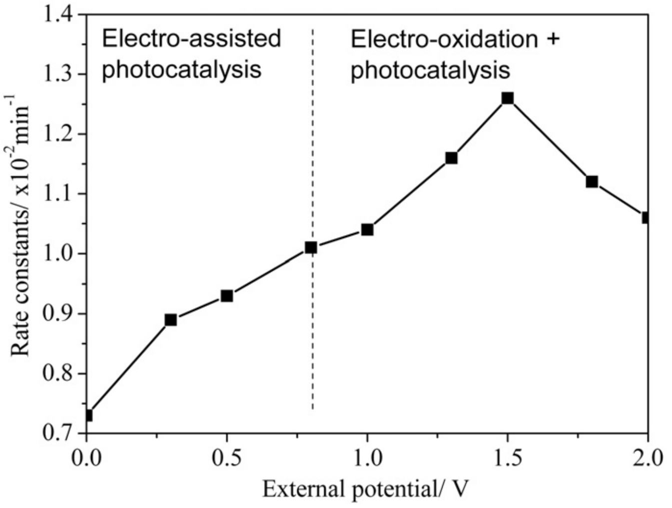

Fig. 8. The effect of the external potential on 2,4-DCP degradation with initial concentration of 50 mg/L, PANI concentration = 70 mg/L.

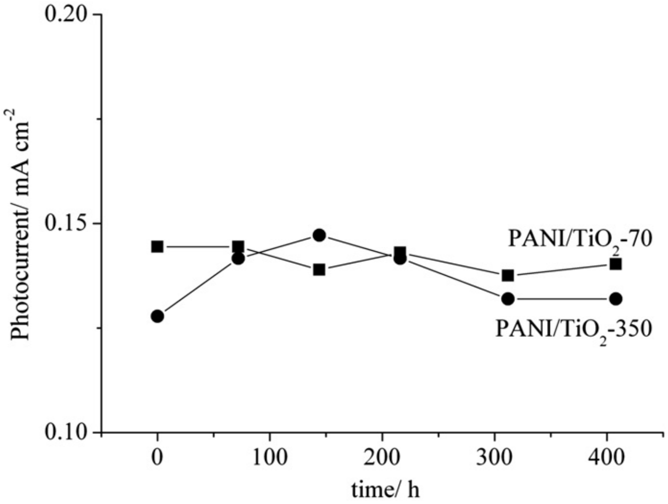

Fig. 9. The influence of various UV light illumination time on photocurrent of the PANI/TiO_2 films.

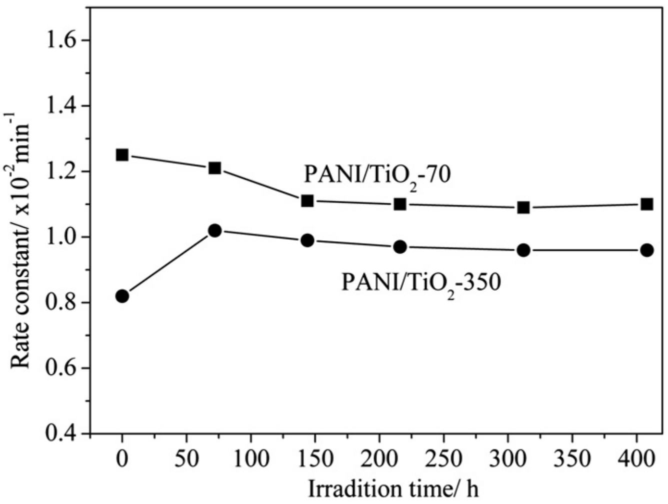

Fig. 10. The influence of various UV light illumination time on PEC degradation of the PANI/TiO_2 films.

increased. When the external potential got to 0.8 V (the redox potential), the electro-oxidation and PC degradation of 2,4-DCP both taken place on the surface of the PANI/TiO_2 photocatalyst simultaneously [28]. The external potential not only can separate the holes and electrons but also can directly electro-oxidize 2,4-DCP. The degradation rate reached a maximum at 1.5 V when the electro-oxidation and PC degradation achieved an optimal synergetic effect. It indicated an effective separation of the photogenerated electron–hole pair and a fast interfacial charge transfer [25]. Moreover, when the external potential greater than 1.5 V, the faster electropolymerization of 2,4-DCP occurred on the surface of PANI/TiO_2 which blocked the current transfer and destroyed the synergetic effect of the system, so that the PEC activity decreased gradually [29].

3.4. Mechanism on enhancement of PEC activity

As discussed above, the introduction of PANI to the TiO_2 obviously enhanced the PC and PEC activity. The Raman and IR results indicated that a strong interaction existed at the interface of PANI and TiO_2. When the PANI/TiO_2 film is irradiated with UV light, electrons in the valence bands (VB) of TiO_2 can be excited to their conduction bands (CB) [26]. Since the VB of TiO_2 matches well with the highest occupied molecular orbital (HOMO) level of PANI [15], the generated holes in VB of TiO_2 can directly transfer to the HOMO level of PANI. The electrons can transfer to the other side of the system via the external circuit so that the holes on the surface could oxidize the adsorbed contaminations directly. Accordingly, a rapid photogenerated charge separation and relatively slow charge recombination was achieved, which significantly enhanced the PEC activity of the as-prepared PANI/TiO_2 films.

3.5. Photostability of PANI/TiO_2 films

To examine the stability of the PANI/TiO_2 films, two photocatalysts were synthesized with different concentrations of PANI (70 and 350 mg/L). The PANI/TiO_2 films were able to maintain photocurrent stability after 418 h UV light illumination (light intensity was 2 mW/cm^2) (see Fig. 9). The photocurrent of the PANI/TiO_2 film (PANI: 70 mg/L) decreased a little and then remained steady in 0.14 mA/cm^2; meanwhile the photocurrent of the PANI/TiO_2 film (PANI: 350 mg/L) also finally steadied in 0.13 mA/cm^2.

Fig. 10 showed the PEC degradation rate constant of PANI/TiO_2 films after the long time UV light illumination. The PEC activity of the PANI/TiO_2 film (PANI:70 mg/L) decreased a little and the gradation rate constant k reduced from 0.0125 to 0.0111 min^{-1}, then remained steady in 0.0111 min^{-1}, while the PEC activity of the film (PANI: 350 mg/L) increased slightly and then steady in 0.0096 min^{-1}. These results indicated that these two PANI/TiO_2 films was chemical stabile even after UV illumination for 418 h.

4. Conclusions

PANI/TiO_2 films were prepared via a simple chemical adsorption method. The synergetic effect between PANI and TiO_2 caused a rapid charge separation and a slow charge recombination. The PC and PEC activities of the PANI/TiO_2 film were both efficiently enhanced by 22.2% and 57.5% than that of pristine TiO_2. The present hybrid photocatalyst is a promising photocatalytic material of good potential applications for environmental purification.

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