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Humic acid-mediated visible-light degradation of phenol on phosphate-modified and Nafion-modified TiO₂ surfaces

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ABSTRACT

Although humic acid (HA) can inhibit TiO₂ photocatalysis, it can sensitize TiO₂ and induce significant visible-light (VL) activity in phenol degradation. This favorable effect of HA was negligible on phosphate-modified TiO₂ (P-TiO₂), but significantly stronger on Nafion-modified TiO₂ (Nf-TiO₂). The reaction rate constants for phenol degradation on Nf-TiO₂ increased from (0.003±0.001) to (0.025±0.003) min⁻¹ when the reaction was performed in the presence of 20 mg/L HA. The different effects of HA on P-TiO₂ and Nf-TiO₂ photocatalysis cannot be attributed to adsorption changes, because the adsorption capacities of P-TiO₂ and Nf-TiO₂ were only slightly lower than that of TiO₂ at an initial HA concentration of 20 mg/mL. Scavenger tests, electron paramagnetic resonance spectroscopy, and H₂O₂ detection were taken to understand the low VL activity of the P-TiO₂/HA suspension. The main active species for phenol degradation in the TiO₂ and Nf-TiO₂ suspensions were superoxide radicals. There were negligible amounts of superoxide radicals in the P-TiO₂/HA suspension, possibly because a direct four-electron oxygen reduction reaction occurred. The better VL activity of Nf-TiO₂ was rationalized on the basis of Mott–Schottky and electrochemical impedance plots. Nafion modification resulted in cathodic shifts of the energy band positions, increased electron density, and less resistance to electron transfer across the interface between TiO₂ and electrolytes. All these factors facilitated electron transfer and improved the production of active species. Phosphate modification therefore did not improve the VL response of HA sensitized TiO₂, and low concentrations of HA can facilitate VL photocatalytic degradation of organic pollutants on Nafion surface-modified TiO₂.

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1. Introduction

Photocatalytic water treatment has shown great potential as a cost-efficient technique for the removal of recalcitrant organic pollutants in water [1–6]. Although hundreds of new photocatalysts have been developed by using approaches such as engineered nanoarchitectures or band energy structures

[7–13], TiO₂ is still the most promising material for water purification because of its advantages such as robustness, low cost, and safety [14,15]. Photocatalytic processes and their reaction kinetics depend greatly on the surface properties of TiO₂, therefore, surface modification has been intensively investigated in TiO₂-mediated photocatalysis [16–21]. Among species that can be used to alter the surface properties of TiO₂, Nafion

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and phosphate are two readily available candidates. Nafion, which is an anionic perfluorinated polymer consisting of a hydrophobic polytetrafluoroethylene backbone and side chains with hydrophilic sulfonate groups, is chemically and photochemically inert under both oxidative and reductive conditions [22–24]. Nafion-modified TiO_2 (Nf- TiO_2) has shown significantly enhanced photocatalytic activity in the degradation of cationic substrates (e.g., herbicides, dyes, and tetramethylammonium) [25–30]. This could be because of improved adsorption of cationic species at ion-exchange sites in Nafion [25–30]. The photocatalytic degradation of organic compounds in water can be influenced by coexisting inorganic anions (e.g., phosphate) that can strongly bind to the TiO_2 surface and alter the surface charge properties [31]. It has been reported that phosphate-modified TiO_2 (P- TiO_2) positively influences degradation of compounds that adsorb poorly on TiO_2 by increasing the production of hydroxyl radicals; however, it decreases the degradation of strongly adsorbing compounds [31–33]. The enhanced performance of phosphate-modified TiO_2 has also been attributed to facilitated electron transfer and improved oxygen adsorption [21,34,35]. Although photocatalytic reactions involving band gap excitation of phosphate- or Nafion-modified TiO_2 have been reported, there have been few studies of the photoreactions of these modified TiO_2 materials under ambient conditions with coexisting dissolved natural organic matter (NOM) and under daylight irradiation.

NOM, which is pervasive in water, always decreases the degradation efficiency of target prior pollutants by photocatalysis or other advanced oxidation processes [32,36–39]. This inhibitory effect is mainly attributed to competitive reactions with reactive oxygen species (ROS) and competitive adsorption between NOM and target pollutants [32,39]. Surface modification to alter the adsorption of NOM and modulate photocatalytic processes has shown great potential in counteracting inhibitory effects [32]. However, ROS can be photochemically produced in aerobic water containing NOM, and this facilitates the photosensitized degradation of waterborne organic pollutants [40–45]. Photoionization of NOM by light of wavelength 300–500 nm can produce triplet states ($^3\text{NOM}^*$) and hydrated electrons (e^-) [43,46]. Vinodgopal et al. [47] reported charge injection from excited NOM into semiconductor colloids; this indicates that electrons photoproduced from NOM can be trapped by semiconductor nanoparticles, to produce superoxide radicals ($\text{O}_2^{\bullet-}$) through a single-electron oxygen reduction reaction (ORR). NOM therefore favorably affects TiO_2 photocatalysis by serving as sensitizers that extend the photocatalytic function to the visible-light (VL) range. It is a challenge to strengthen this favorable effect but avoid the inhibitory effect of NOM, and achieving this is important in pilot studies of TiO_2 photocatalytic water treatment.

Humic acid (HA), a representative NOM containing abundant phenolic, hydroxyl, and carboxylic groups, adsorbs strongly on TiO_2 with a high Langmuir binding constant (0.12–0.90 L mg^{-1}) [48]. In this study, we compared the sensitizing effects of HA on Nafion- and phosphate-modified TiO_2 materials under VL irradiation. Phenol was used as a model pollutant to probe the photocatalytic activity because of its

non-ionic properties and negligible adsorption on TiO_2 . The mechanism of the effect of HA on the two modified TiO_2 materials was explored based on analyses of the degradation kinetics, adsorption, main active species, and semiconductor properties. Clarification of the effects of surface species on the VL activity of TiO_2 in water containing NOM is important in understanding the photochemical activity and toxicity of nanoparticles, and will help in the development of effective photocatalytic materials for pilot studies of water purification.

2. Experimental

2.1. Materials

Humic acid sodium (HA), furfuryl alcohol (FFA), phenol, NaH_2PO_4 , isopropyl alcohol (IPA), *p*-benzoquinone (BQ), and *N,N*-diethyl-*p*-phenylenediamine (DPD) were all obtained from Sigma Aldrich, USA. Nafion (5 wt% solution in a mixture of ethanol, 1-propanol, and water) was purchased from the Dupont Co., Ltd., USA. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was obtained from the Adamas Co., Ltd., China. Peroxidase (POD, horseradish, RZ > 1.5) was obtained from the Sangon Biotech Co., Ltd., China. All other reagents were purchased from the Shanghai Chemical Reagent Co., Ltd., China.

Commercial Degussa P25 TiO_2 (a mixture of 71% anatase and 29% rutile) was used for all tests. To avoid desorption, P- TiO_2 was obtained by photocatalytic degradation in a suspension of TiO_2 and 2 mmol/L NaH_2PO_4 . Nf- TiO_2 was prepared using a previously reported method [28]. Briefly, Nafion solution and TiO_2 powder, at a ratio of 50 mg (Nafion)/g (TiO_2), were added to deionized water (10 mL). The suspension was stirred for 6 h to ensure homogeneous coating of the TiO_2 nanoparticles with Nafion. The product was dried in a vacuum oven at 30 °C for 24 h to give Nf- TiO_2 .

2.2. Photocatalytic degradation experiments

The light source was a 500-W xenon lamp with a 420 nm cutoff filter and a filter to remove infrared light. In the phenol degradation tests, a suspension of the photocatalyst (0.5 g/L) was mixed with phenol (10 mg/L) in a 50 mL quartz vessel; various amounts of HA were then added. In all the tests, the initial pH values of the suspensions were carefully adjusted to 3.0 with HClO_4 to minimize desorption of phosphate or Nafion from TiO_2 . The suspension was kept in the dark at room temperature for 30 min to achieve adsorption–desorption equilibrium, and was then illuminated to start the photocatalytic degradation. At predetermined times, samples were collected and filtered through a 0.45 μm polyethersulfone (PES) filter. The residual phenol concentrations were determined using a high-performance liquid chromatography system (LC-2010AHT, Shimadzu) equipped with a C-18 column. A binary mixture of phosphoric acid solution (0.1 wt%) and methanol at a volumetric ratio of 70:30 was used as the mobile phase, and the detection wavelength was 270 nm. Apparent first-order degradation rate constants (k) were obtained for all photocatalytic processes. The ratio (R) between the reaction

rate constants in the absence (k_0) and presence of HA (k) was used as a measure of the inhibitory or favorable effect of HA. The concentration of HA in all tests, unless specified, was 20 mg/L.

The concentration of H_2O_2 in the illuminated suspension was determined using a modified DPD–POD method [49,50]. Briefly, the solution obtained after filtration (1 mL) was transferred to a 10 mL volumetric flask and mixed with phosphate buffer (3 mL, 0.5 mol/L, pH = 6). Then DPD solution (50 μL , 10 mg/mL) and POD solution (50 μL , 1 mg/mL) were pipetted into the mixture and deionized water (10 mL) was added. The H_2O_2 concentration was obtained by measuring the absorbance at 551 nm (UV-vis spectrophotometer, T6-New Century, Purkinje General).

The electron paramagnetic resonance (EPR) signals for $\text{DMPO-O}_2^{\cdot-}$ adducts were recorded using an EPR spectrometer (MS 5000, Magent Tech), with DMPO as the spin trap. A catalyst suspension (0.5 g/L) in methanol was irradiated for 5 min under VL in the presence of DMPO (20 mmol/L). A sample of the suspension (about 0.5 mL) was removed, filtered through a 0.22 μm PES filter, immediately transferred to a flat quartz EPR cell, and the EPR spectrum was recorded. The EPR settings were center field, 336 mT; sweep width, 10 mT; sweep time, 60 s; modulation, 0.2 mT; resonance frequency, 9.464 GHz; and microwave power, 20 mW. X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical-A, Shimadzu) with a monochromatic Al K_α source (1486.6 eV). P-TiO₂ samples for XPS were prepared by dispersing TiO₂ in a NaH_2PO_4 solution (2 mmol/L). The solid was separated by filtration and freeze-dried.

2.3. (Photo)electrochemical tests

Electrochemical measurements were performed using a CHI 760E electrochemical system with a three-electrode cell. The light source was a 500-W xenon lamp with a cutoff filter ($\lambda > 420$ nm). A Pt plate and Hg/HgCl_2 electrode were used as the counter electrode and reference electrode, respectively. The working electrode was prepared by coating a slurry of the sample on a cleaned indium tin oxide glass substrate by the doctor blade method. The slurry was prepared by dispersing the powder sample (0.2 g) in absolute ethanol (1 mL). The coated electrodes were heated at 200 °C in air for 2 h to improve adhesion. In all the tests, the available surface area of the working electrode was 1 cm^2 .

Impedance–potential tests were performed in a three-electrode cell, using previously reported procedures [51]. The ac amplitude and frequency were set at 5 mV and 1.5 kHz, respectively. Electrochemical impedance spectroscopy (EIS) was performed by applying an open circuit voltage bias (0.2 V) and were recorded over the frequency range 0.1–10⁵ Hz at an ac amplitude of 5 mV. The electrolyte for current–time and EIS tests was a 0.1 mol/L sodium perchlorate solution of pH = 3.5, and for the impedance–potential tests it was a 0.5 mol/L Na_2SO_4 aqueous solution of pH = 5.5. The electrolyte was purged with nitrogen for 20 min prior to each test and continuously purged during the measurements.

2.4. Adsorption experiments

TiO₂ (25 mg) or Nf-TiO₂ (25 mg) was added to HA aqueous solutions (50 mL, 20, 40 or 60 mg/L), and the suspension pH was adjusted to 3.0. To determine the effect of phosphate modification, HA solutions were prepared in the presence of 2 mmol/L phosphate solutions. The suspensions were stirred at 30 °C for 1 h to reach adsorption equilibrium. In time-dependence tests, samples were withdrawn at predetermined times. The concentration of HA was determined by measuring the absorbance at 254 nm and calibrating using standard samples.

3. Results and discussion

Fig. 1(a–c) show the effects of HA on VL degradation of phenol over TiO₂ and surface-modified TiO₂. About 26% ($\pm 0.9\%$) phenol was removed on pristine TiO₂ by VL irradiation for 120 min. This is attributed to the formation of phenolic complexes on the TiO₂ surface, which enabled ligand-to-metal charge transfer in the VL range [52]. Unlike the inhibitory effect of HA in phenol degradation over TiO₂ under UV irradiation [32], VL degradation of phenol was greatly enhanced in the presence of HA. The degradation rate constants for phenol increased to $(0.0104 \pm 0.0001) \text{ min}^{-1}$ at a HA concentration of 20 mg/L, about four times that in the absence of HA. This can be ascribed to the sensitizing effect of HA, which can absorb light below 500 nm and inject excited electrons into TiO₂ to produce ROS. Even in the absence of TiO₂ or other semiconductors, ROS can be produced by illuminating a HA solution [43,45], and the presence of electron donors such as hydroxyaromatic compounds accelerate the generation of $\text{O}_2^{\cdot-}$ [42]. This explains why a 17% ($\pm 0.5\%$) decrease in the amount of phenol was achieved in the presence of 20 mg/L HA alone after irradiation for 120 min. The VL degradation rate of phenol on TiO₂ (Fig. 1(b)) increased with increasing HA concentration. However, the improvement lessened with increasing HA concentration from 20 to 40 mg/L. This can be ascribed to an inhibitory effect of HA and the saturation of occupied adsorption sites.

The Nf-TiO₂ and P-TiO₂ samples slightly changed the VL activity in phenol degradation compared to that of unmodified TiO₂ (Fig. 1(a)). The phosphate and Nafion loadings were also investigated (Fig. S1). The results indicate that the catalysts with 50 mg Nafion/g TiO₂ and 2 mmol/L phosphate had the best VL activities. However, the effects of both loadings on the photocatalytic performance of TiO₂ were low. HA strongly inhibited the VL degradation of phenol on P-TiO₂, with an R value of 0.51, which is much less than 1. This contradicts previous reports that under UV irradiation HA facilitated charge transfer and enhanced phenol degradation on phosphate-modified TiO₂ [32]. This indicates that the mechanism of phenol photocatalytic degradation depends on the light source. The phosphate in the solution did not inhibit sensitization of degradation of phenol by HA alone (Fig. S2). However, HA (20 mg/L) significantly increased the VL degradation rates of phenol on Nf-TiO₂. The reaction rate constant increased from $(0.003 \pm 0.001) \text{ min}^{-1}$ in the absence of HA to $(0.025 \pm 0.003) \text{ min}^{-1}$ in the presence of

Fig. 1. (a) Phenol photocatalytic degradation on various photocatalysts in absence or presence of HA (20 mg/L); effect of HA concentration on phenol degradation on (b) TiO_2 or (c) Nf-TiO_2 ([phenol] = 10 mg/L; initial pH 3.0; $\lambda > 420$ nm); (d) photocurrent responses of TiO_2 and modified TiO_2 film electrodes in absence or presence of HA ($\lambda > 420$ nm).

20 mg/L HA. The factor R is 7.8, which is much larger than that for pristine TiO_2 ($R = 4.0$ at 20 mg/L HA). Moreover, the phenol removal efficiency was 96% ($\pm 0.3\%$) after VL irradiation for 120 min. The results of control tests performed at an initial pH of 6.0 suggest that the trends in the effect of HA were similar for Nf-TiO_2 and P-TiO_2 under acidic and neutral conditions (Fig. S3). However, the phenol degradation rate decreased when the HA concentration was increased to 40 mg/L (Fig. 1(c)). This can be attributed to a concurrent inhibitory effect.

Enhancement of the VL activity of Nf-TiO_2 by HA modification was confirmed by photocurrent measurements. The current-time curves for electrodes with various on-off cycles of intermittent irradiation are shown in Fig. 1(d). The inset in the figure shows that the photocurrent signal was negligible for all the electrodes in the absence of HA; this is consistent with the large band gap of TiO_2 (~ 3.2 eV). For the P-TiO_2 electrode in the presence of HA, the photocurrents were also low, less than $1 \mu\text{A}/\text{cm}^2$. Sensitization by HA induced a significant photocurrent for TiO_2 ($90 \mu\text{A}/\text{cm}^2$), and an even higher photocurrent for Nf-TiO_2 ($117 \mu\text{A}/\text{cm}^2$). The better photocurrent response by Nf-TiO_2 indicates enhanced photoelectron generation and mobilization, which is consistent with a higher activity in phenol degradation under VL irradiation.

XPS was used to prove the presence of phosphate and Nafion on P-TiO_2 and Nf-TiO_2 . The P/Ti and F/Ti ratios at the TiO_2

surface were 0.05 and 1.3, respectively. For P-TiO_2 , the asymmetric $2p$ spectrum (Fig. 2(a)) can be fitted by two peaks, at 132.8 and 133.7 eV. These can be assigned to monodentate coordination between surface Ti sites and PO_4^{3-} , with P in the pentavalent state [35]. For F-TiO_2 , the band centered at 688.8 eV (Fig. 2(b)) is assigned to the F signal from Nafion molecules [27]. The presence of adsorbed Nafion is confirmed by a peak at 535.4 eV in the $1s$ spectrum (Fig. S4), which corresponds to oxygen in the sulfonic acid group.

One possible explanation for the differing effects of HA on the VL activities of P-TiO_2 and Nf-TiO_2 in phenol degradation and the photocurrent responses is that the amounts of HA adsorbed are different. An increase or decrease in HA adsorption would strengthen or weaken the favorable sensitizing effect of HA. The adsorption of HA on various catalysts was investigated; the results are shown in Fig. 3. The time to reach adsorption balance for Nf-TiO_2 was about 40 min (Fig. 3(a)), slightly longer than those for TiO_2 and P-TiO_2 (less than 10 min). However, the equilibrium concentrations of HA on P-TiO_2 and Nf-TiO_2 were similar (Fig. 3(b)). The adsorption capacities at an initial concentration of 20 mg/L HA were (30.2 ± 1.4) and (29.9 ± 0.1) mg/g for P-TiO_2 and Nf-TiO_2 , respectively; these are slightly lower than that for TiO_2 (33.9 ± 0.1) mg/g. The adsorption of HA on the oxide surface involves electrostatic interactions, ligand exchange, hydrophobic interactions, entropic effects, hydrogen

Fig. 2. P 2p (a) and F 1s (b) core-level XPS spectra for phosphate- and Nafion-modified TiO₂.

Fig. 3. Adsorption of HA on TiO₂, P-TiO₂, and Nf-TiO₂. (a) Time dependence of HA adsorption (initial [HA] = 20 mg/L); and (b) equilibrium adsorption capacity at various initial HA concentrations (initial pH = 3.0).

bonding, and cation bridging [53,54]. The modified TiO₂ materials both had negative zeta potentials at the studied pH (Fig. S5), indicating similar electrostatic interactions between HA and the modified TiO₂. However, phosphate modification would increase the hydrophilicity of the TiO₂ surface and strengthen adsorption via ligand exchange or cation bridging. Nafion modification of TiO₂ would enhance the hydrophobicity and improve hydrophobic interactions with HA. Both modified TiO₂ materials therefore had adsorption capacities similar to that of pristine TiO₂ at a low initial HA concentration. At higher initial concentrations of HA, the adsorption capacity of TiO₂ was much higher than those of P-TiO₂ and Nf-TiO₂. However, the amount of HA adsorbed on Nf-TiO₂ was always lower than that on P-TiO₂, which indicates that the poor sensitizing effect of HA on P-TiO₂ cannot be ascribed to blockage of HA adsorption by surface-modifying phosphate anions, and the better photocatalytic activity of Nf-TiO₂ is irrelevant in terms of adsorption.

Three chemicals, namely FFA, BQ, and IPA, were used as scavengers for singlet oxygen, superoxide, and hydroxyl radicals, respectively. Because phenol degradation in the P-TiO₂/HA suspension was poor, the effects of scavengers on phenol degradation in TiO₂/HA and Nf-TiO₂/HA suspensions were investigated. Fig. 4 shows that addition of BQ significantly decreased the phenol degradation efficiencies of both the TiO₂ and Nf-TiO₂ systems, suggesting that superoxide radicals are

the main ROS in HA-sensitized TiO₂ photocatalysis. The mechanism can be described by the sequential one-electron reactions shown in Eqs. (1)–(4). Under VL irradiation, electrons are generated by excitation of HA (Eq. (1)) and transferred to TiO₂ (Eq. (2)). The electrons are then scavenged by oxygen, producing superoxide radicals (Eq. (3)) and then H₂O₂ (Eq. (4)). Recombination can also take place when electrons are trapped by positively charged HA radicals (Eq. (5)). Unlike UV irradiation, which can induce band gap excitation of electrons and produce holes that are strong enough oxidants to produce ·OH, the active species produced by VL irradiation of sensitized TiO₂ originate exclusively from electron transfer, and superoxide radicals are the dominant ROS for organic degradation.

EPR spectroscopy was used to confirm the production of O₂^{•−} in the illuminated suspensions. Fig. 5(a) shows that six characteristic peaks from DMPO–O₂^{•−} spin adducts were clearly

Fig. 4. Effects of scavengers on VL degradation of phenol in presence of 20 mg/L HA on TiO_2 (a) and Nf-TiO_2 (b) ([phenol] = 10 mg/L; initial pH = 3.0; $\lambda > 420$ nm).

Fig. 5. (a) Ambient-temperature EPR spectra of $\text{DMPO-O}_2^{\bullet-}$ in illuminated suspensions with 20 mg/L HA; (b) photocatalytic generation of H_2O_2 in TiO_2/HA , $\text{Nf-TiO}_2/\text{HA}$, and $\text{P-TiO}_2/\text{HA}$ suspensions under VL irradiation ([HA]₀ = 20 mg/L, initial pH = 3.0).

observed for the TiO_2/HA and $\text{Nf-TiO}_2/\text{HA}$ suspensions; however, no signal was detected for $\text{P-TiO}_2/\text{HA}$, which indicates the absence of $\text{O}_2^{\bullet-}$ in the $\text{P-TiO}_2/\text{HA}$ suspension. Because $\text{O}_2^{\bullet-}$ is the photochemical precursor of H_2O_2 and accumulation of H_2O_2 formed as an intermediate is always observed in photocatalysis, the concentrations of H_2O_2 in different photocatalytic systems were monitored using the DPD–POD method to further investigate the effect of HA sensitization of modified TiO_2 . The concentration of H_2O_2 was negligible in the illuminated $\text{P-TiO}_2/\text{HA}$ suspension, but was significant in the other two suspensions (Fig. 5(b)). After VL irradiation for 120 min, the concentration of H_2O_2 had increased to 93 and 99 $\mu\text{mol/L}$ for the TiO_2/HA and $\text{Nf-TiO}_2/\text{HA}$ suspensions, respectively. The amount of H_2O_2 in the $\text{P-TiO}_2/\text{HA}$ suspension was almost negligible, indicating low production of $\text{O}_2^{\bullet-}$, in agreement with the EPR analysis. The results suggest that P-TiO_2 enabled the ORR to proceed via a direct four-electron pathway (Eq. (6)). This can be rationalized by assuming that the HA molecules and anchored phosphate anions served as proton relays to provide adequate localized protons for proton-coupled electron transfer in a multi-electron ORR [55]. Although singlet oxygen could be generated through energy transfer processes (Eqs. (7) and (8)), its contribution to organic degradation is limited because of its low quantum yield under VL irradiation and relatively

weak oxidation power. The poor VL activity of $\text{P-TiO}_2/\text{HA}$ in phenol degradation and the light-source-dependent effect of HA on P-TiO_2 photocatalysis can therefore be explained.

The production of a significant amount of H_2O_2 in the illuminated $\text{Nf-TiO}_2/\text{HA}$ suspension indicates that ORR on this catalyst followed the single-electron pathway. Moreover, the phenol degradation activity of $\text{Nf-TiO}_2/\text{HA}$ was better than that of TiO_2/HA , although less HA was adsorbed on Nf-TiO_2 than on TiO_2 . The improved electron transfer efficiency was investigated by measuring the conductivities of the catalysts. Fig. 6(a) shows Mott–Schottky curves for the three electrodes. For n-type semiconductors such as TiO_2 , the relationship between the depletion layer capacitance (C_{sc}) and applied bias (E) can be described by Eq. (9),

$$1/C_{sc}^2 = 2(E - E_{FB} - kT/e)/(\epsilon_0\epsilon_r N_D A^2) \quad (9)$$

wherein e is the electronic charge, ϵ_0 is the permittivity of a vacuum, ϵ_r is the dielectric constant of TiO_2 , A is the contact area of the electrode in the electrolyte, E_{FB} is the flat-band potential of the semiconductor, and N_D is the carrier (electrons for n-type) density. The term kT/e can be ignored because of its low value. The E_{FB} and N_D of the semiconductor can be obtained from the slope and intercept, respectively, of the fitted curves. The fitted equations in Fig. 6(a) show that the estimated E_{FB}

Fig. 6. Mott-Schottky (a) and EIS (b) plots for TiO_2 , P-TiO_2 , and Nf-TiO_2 electrodes.

potentials for TiO_2 , Nf-TiO_2 , and P-TiO_2 were -0.54 , -0.85 , and -0.36 V, respectively, vs the normal hydrogen electrode at $\text{pH} = 7$. Nafion modification led to clear cathodic shifts of the energy band positions, whereas phosphate modification had the opposite effect on energy band shifts. Electron transfer is expected to be facilitated when the semiconductor has more cathodic conduction band positions. The N_D values can be compared based on the curve slopes. P-TiO_2 had the lowest N_D value, about 62.4% of that for TiO_2 , and Nf-TiO_2 had the highest N_D , about 62% higher than that for TiO_2 . The increased N_D for Nf-TiO_2 improves the electron mobility and reduces electron resistance; this is supported by the EIS results (Fig. 6(b)). Nyquist plots for TiO_2 and the modified TiO_2 materials were obtained at 0.2 V vs the standard calomel electrode. The charge transfer resistance (R_{ct}), which is the resistance to electron transfer from the electrode to the electrolyte, directly correlates with the semicircle diameter at high frequencies. The EIS plots show that the Nf-TiO_2 electrode had the lowest R_{ct} and P-TiO_2 had the highest R_{ct} . This indicates that resistance to electron transfer through the solid/liquid interface was lowest for the Nf-TiO_2 . This would result in fewer possibilities for charge recombination and higher efficiency of ROS generation and pollutant degradation.

4. Conclusions

In this study, the sensitizing effects of HA on P-TiO_2 and Nf-TiO_2 were investigated. The results indicate the following. (1) Sensitization by HA was negligible for P-TiO_2 , and active species such as superoxide radicals were not observed in the illuminated suspension; this can be ascribed to a possible direct four-electron ORR. (2) Sensitization by HA was strong for Nf-TiO_2 ; the reaction rate constant for phenol degradation in the presence of 20 mg/L HA was 7.8 times that in the absence of HA; this can be attributed to a cathodic shift of the flat-band potential, increased electron density, and decreased resistance between TiO_2 and the electrolyte after modification with Nafion. The results of the present work suggest that phosphate modification could be used to reduce the photochemical activity of TiO_2 nanoparticles in water containing NOM, and the VL activity of sensitized TiO_2 can be further improved by tuning

the semiconductor properties through surface modification.

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Graphical Abstract

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Humic acid-mediated visible-light degradation of phenol on phosphate-modified and Nafion-modified TiO₂ surfacesLonghui Zheng, Xiaojuan Yu, Mingce Long*, Qilin Li
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Sensitization by humic acid was weaker for phosphate-modified TiO₂ than for Nafion-modified TiO₂. This is ascribed to an altered oxygen reduction pathway in the former case, and facilitated charge transfer in the latter case.

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磷酸根和Nafion修饰TiO₂表面腐植酸调控的可见光催化降解苯酚性能郑龙辉^a, 于晓娟^a, 龙明策^{a,b,*}, 李琪琳^c^a上海交通大学环境科学与工程学院, 上海200240, 中国^b上海交通大学薄膜与微细技术教育部重点实验室, 上海200240, 中国^c莱斯大学土木与环境工程系, 德克萨斯休斯敦77005, 美国

摘要: 光催化水处理技术有望成为一种有效去除水中难降解有机污染物的方法。尽管人们已经研制了大量的新型光催化剂, 但在环境应用中纳米TiO₂仍是最受欢迎的催化剂。由于光催化反应在表面发生, 反应动力学主要取决于TiO₂的表面性质, 因此, 表面修饰是调控TiO₂光催化反应的重要手段, 其中Nafion和磷酸根表面修饰TiO₂简单可行。Nafion修饰可以通过

离子交换吸附富集阳离子底物提高光催化降解效率;而磷酸根修饰则可以增强对弱吸附底物的降解活性.另一方面,水中共存的天然有机物(NOM)例如腐植酸(HA)将抑制 TiO_2 光催化降解目标污染物的活性,同时又将通过光敏化诱导可见光催化性能.因此,研究如何调控NOM对光催化反应的影响将有助于光催化水处理技术的工程应用.本文以HA作为代表性的NOM,研究了磷酸根和Nafion两种不同修饰方法对HA敏化 TiO_2 性能的影响规律.

可见光降解苯酚的实验结果表明,HA的敏化可以提高 TiO_2 可见光降解苯酚的效率.磷酸根修饰 TiO_2 抑制了HA的敏化作用,而Nafion修饰则增强了HA的敏化作用并提高可见光降解苯酚的活性.当HA浓度为20 mg/L时,Nafion修饰 TiO_2 降解10 mg/L苯酚的反应速率常数由 $(0.003 \pm 0.001) \text{ min}^{-1}$ 提高至 $(0.025 \pm 0.003) \text{ min}^{-1}$.表面修饰引起的反应活性差异不能归因于HA的吸附容量的变化,因为吸附实验表明在光催化反应条件下,两种表面修饰的 TiO_2 对HA的吸附容量并无显著差异.添加不同的自由基捕获剂发现,HA敏化 TiO_2 及Nafion修饰 TiO_2 降解苯酚的主要活性物质为超氧自由基,而磷酸根修饰 TiO_2 的光催化反应中并没有超氧自由基.通过检测超氧自由基的电子自旋共振信号进一步证实了这一点.测试发现,光催化反应中Nafion修饰 TiO_2 产生的 H_2O_2 增加,而磷酸根修饰的几乎不产生 H_2O_2 ,说明可能发生了四电子的氧还原反应.莫特-肖特基曲线(Mott-Schottky)的测试结果表明,Nafion修饰 TiO_2 的平带电位从 -0.54 V 负移到 -0.85 V ,多数载流子电子的密度提高了62%.电化学阻抗结果显示,Nafion修饰 TiO_2 具有较小的界面电子迁移阻抗.这些变化有利于提高电子迁移速率,抑制复合并增加超氧自由基的生成,从而提高光催化性能.因此对 TiO_2 进行恰当的表面修饰,将有助于强化HA的敏化作用,并提高可见光催化降解目标有机污染物的活性.

关键词: 二氧化钛; 腐植酸; Nafion; 磷酸根; 表面修饰

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