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Preparation of amphiphilic TiO₂ Janus particles with highly enhanced photocatalytic activity

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ABSTRACT

Stearic-acid-modified TiO₂ (STA-TiO₂) particles were prepared via the impregnation approach and used as a precursor for preparing TiO₂ Janus particles. The morphology, structure, and properties of the TiO₂ Janus particles were characterized using Fourier-transform infrared spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, thermogravimetric analysis, fluorescence microscopy, high-resolution transmission electron microscopy, contact angle analysis, dynamic light scattering, biological microscopy, X-ray photoelectron spectroscopy, and electrochemical impedance spectroscopy measurements. The results show that TiO₂ Janus particles can be successfully prepared via toposelective surface modification. STA grafted on the surface of TiO₂ enhances its hydrophobicity, promotes charge separation, and improves its adsorption capacity for organic compounds. The TiO₂ Janus particles strongly adsorb on an oil-water interface to form a stable Pickering emulsion. The degradation rates of high-concentration kerosene and nitrobenzene wastewaters when the photocatalyst is pure TiO₂, STA-TiO₂, or TiO₂ Janus particles are discussed and compared. The degradation rates were determined using an ultraviolet-visible spectrophotometer. It was found that the Pickering emulsion stabilized by the TiO₂ Janus particles exhibited the best photocatalytic performance; these Janus particles show promising potential for catalytic application.

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1. Introduction

With the rapid development of industrial technology and the social economy, the problem of water pollution has become increasingly serious. In particular, accidents in the production, storage, transportation, and industrial maintenance of chemical raw materials and products cause a large amount of organic matter to enter water bodies, inflicting great harm on the natural environment [1–3]. In addition to their toxicity, these products constitute an insoluble liquid phase that floats on the surface of water, which results in a reduction in atmospheric oxygen transfer. Since the solubility of organic matter in water

is very low, its treatment is very difficult [4–6]. Particularly, in the case of organic matter leakage in large-scale seawater, there will be a small amount of pollutants that cannot be further removed via simple physical methods such as adsorption and extraction.

Photocatalytic oxidation has recently emerged as an environmentally friendly and highly efficient method for organic wastewater treatment [7–11]. However, its efficiency generally decreases greatly when the concentration of the contaminant on the surface of the photocatalyst becomes low. Consequently, it is expected that an improvement in the contact area between the organic matter and the photocatalyst will increase the pho-

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tocatalytic activity, and thereby enhance the efficiency of the process.

In recent years, numerous articles have been published describing the application of Pickering emulsions in photocatalysis technology [12,13]. Pickering emulsions were first discovered by Ramsden [14] and Pickering [15] about a century ago. The Pickering emulsion is a new interfacial catalysis technology [16–19] and it is an oil-water dispersion system formed by amphiphilic colloidal particles instead of traditional surfactants. Catalysts are adsorbed at the oil-water interface and constitute a myriad of microreactors for enhanced reaction, greatly improving the interfacial area between photocatalytic particles and organic pollutants. Nsib et al. [20,21] studied the degradation efficiency of organic wastewater in a Pickering emulsion system that was stabilized by modified TiO_2 , and achieved certain results. Wu et al. [22] studied the degradation of nitrobenzene (NB) wastewater by modified ZnO in a Pickering emulsion. The results demonstrated that the use of the Pickering emulsion stabilized by surface-modified ZnO nanoparticles provided an effective and novel method to enhance the photocatalytic degradation of the organic contaminant. However, for randomly modified particles, the distribution of the modifier on the surface of TiO_2 is random, which affects the stability of the Pickering emulsion.

Janus particles are anisotropic and multifunctional materials [23]. Janus particles have drawn a lot of scientific attention due to the many potential applications, such as stabilizations of emulsions [24–28], drug delivery [29–31], multifunctional magnetic asymmetric materials [32], electronic devices [33,34], bio-sensors, and catalytic degradation [35–38]. It has been reported that an emulsion prepared using Janus particles is more stable than that prepared using homogeneous particles, and therefore more suitable for solid emulsifiers [39,40].

In this study, TiO_2 was modified via the impregnation method [41] and TiO_2 Janus particles were prepared using toposselective surface modification. Then, a Pickering emulsion was prepared using the TiO_2 Janus particles as stabilizers, and water and kerosene (or NB) as the aqueous and oil phases, respectively; wastewater was degraded under illumination. This Pickering emulsion stabilized by TiO_2 Janus particles is expected to serve as an effective means to intensify the photocatalytic degradation of organic pollutants.

2. Experimental

2.1. Materials

Titanium dioxide (TiO_2) nanoparticles consisting of 71% anatase and 29% rutile (21 nm in diameter, P25) were provided by Degussa Co. (Germany). Stearic acid (STA), absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$), sodium hydroxide (NaOH), chloroform (CHCl_3), carbon tetrachloride (CCl_4), paraffin (fully refined, oil content <0.8%), kerosene, NB, *t*-BuOH (TBA), *p*-benzoquinone (BQ), ethylenediaminetetraacetic acid disodium salt (EDTA-Na_2), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), and sodium sulfate (Na_2SO_4) were purchased from Tianjin Guangfu Chemical Reagent Factory (China). All these chemicals were of reagent grade and were used without further purification. Deionized water was used for all the preparation and treatment processes.

2.2. Preparation

STA-modified TiO_2 was prepared via the impregnation method (Fig. 1(a)). The process was as follows. 10 g of STA and 210 mL of absolute ethanol were added into 500 mL 3-neck flasks. The 3-neck flasks were placed in a 20 °C constant-temperature water bath. The electric stirring device was turned on and the rotation speed was set to 600 rpm. When the STA was completely dissolved, 10 g of TiO_2 was added to the system. After 12 h, the reactant was quickly filtered, and the surface-modified TiO_2 (STA- TiO_2) nanoparticles were washed with chloroform five times to remove free STA and dried in vacuum at 20 °C. Finally, the obtained powder was ground to prepare fine particles.

The preparation process of the TiO_2 Janus particles was as follows. 20 g of paraffin was added into a 200 mL 3-neck flask, and the system was maintained at 70 °C to completely melt the paraffin. 5 g of STA- TiO_2 and 120 mL of deionized water were added to the flask, which was stirred constantly at 600 rpm. After 1 h, the system was cooled to room temperature to solidify the paraffin. Then, an NaOH solution was added to the system to remove the STA exposed to the aqueous phase. After a period of reaction, the solid paraffin droplets were washed several times with deionized water to remove excess NaOH. Finally, carbon tetrachloride was added to dissolve the paraffin,

Fig. 1. (a) Schematic illustration of preparation of TiO_2 modified with stearic acid via impregnation method; (b) Schematic illustration of preparation of TiO_2 Janus particles via toposselective surface modification.

and monodisperse Janus particles were obtained (Fig. 1(b)).

A Pickering emulsion was prepared using kerosene as the oil phase, deionized water as the water phase, solid particles (pure TiO_2 , STA- TiO_2 , or TiO_2 Janus particles) as the stabilizers, and a high-speed disperser as the emulsifying device. The specific preparation process is as follows. The oil and water phases at a 1:4 ratio were blended initially in a beaker, and then mixed with 2.5 wt% solid particles. Then, the high-speed homogenizer was switched on and the speed was adjusted to 2400 rpm. After mixing for 5 min, a Pickering emulsion was formed. Finally, the Pickering emulsion was stored and its stability was observed.

2.3. Characterization

The modifying effect of STA on the TiO_2 particles was characterized using a Perkin-Elmer Spectrum Two Fourier-transform infrared spectroscopy (FT-IR) instrument in the range 400–4000 cm^{-1} , with 40 scans of FT-IR curves. Powders of the TiO_2 , STA- TiO_2 , and TiO_2 Janus particles were pressed into pellets containing 0.1 mg of the material mixed with 10 mg of KBr. Contact angle measurements were performed on a JYC-1 contact angle goniometer. The TiO_2 , STA- TiO_2 , and TiO_2 Janus particles were prepared as pellets using a tableting machine. The optical absorption region of the TiO_2 , STA- TiO_2 and TiO_2 Janus particles was recorded using ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS; Agilent DRA-2500). Thermogravimetric (TG) analysis of the TiO_2 , STA- TiO_2 , and TiO_2 Janus particles was performed, using a NETZSCH STA449F3, in an alumina crucible heated from 50 to 800 °C with a heating rate of 5 °C/min, under a dynamic atmosphere of nitrogen. Fluorescence microscopy analysis of the TiO_2 Janus particles was performed using an Olympus BX61 fluorescence microscope. High-resolution transmission electron microscopy (HRTEM) micrographs were recorded using a JEM-2100 (JEOL Ltd., Japan) electron microscope and were used to observe the shape of the prepared particles, and to estimate the particle size. Dynamic light scattering measurements were carried out via noninvasive backscattering on a DSA 30 (KRÜSS GmbH, Germany) compact goniometer system. The morphology of the emulsion was determined using a Chongqing Optec BK300 biomicroscopy instrument. X-ray photoelectron spectroscopy (XPS) was conducted to determine the chemical states of the samples, using a Kratos Axis Ultra DLD photoelectron spectrometer.

2.4. Photocatalytic degradation experiments

The photocatalytic properties of the Pickering emulsion formed by the TiO_2 Janus particles were evaluated using the degradation of kerosene and NB wastewater under ultraviolet irradiation (double UV lamp, 18 W, 254 nm). In the experiment, the Pickering emulsion was prepared with 48 ml of deionized water, 12 ml of an oil phase (kerosene or NB), and 1.5 g of TiO_2 (STA- TiO_2 or TiO_2 Janus particles), in a high-speed disperser. The prepared emulsion was placed in the dark for 30 min to ensure adsorption-desorption equilibrium, and was then illu-

minated to start the photocatalytic degradation. At predetermined times, samples were collected and filtered. The concentration of kerosene and NB was measured using a Cary 5000 UV-Vis spectrophotometer. In addition, different scavengers were used to determine the main reactive species during the photocatalytic degradation of NB. In this work, TBA, BQ, EDTA- Na_2 , and $\text{K}_2\text{S}_2\text{O}_8$ acted as the scavengers for hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\cdot\text{O}_2^-$), holes (h^+), and electrons (e^-), respectively.

2.5. Electrochemical impedance spectroscopy (EIS) measurements

EIS measurements were carried out using a Metrohm Autolab (PGSTAT302N) electrochemical station with a three-electrode cell. The working electrode was prepared by coating a slurry of the sample on a cleaned glassy carbon electrode. The slurry was prepared by dispersing the powder sample (0.5 g) in absolute ethanol (2 mL). A Pt wire and Hg/HgCl_2 electrode (saturated KCl) were used as the counter and reference electrodes, respectively. The light sources were two 18-W UV lamps. The electrolyte was Na_2SO_4 solution (0.4 mol/L). The measurements were carried out 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.

2.6. Adsorption experiments

TiO_2 (5 mg), STA- TiO_2 (5 mg), or TiO_2 Janus particles (5 mg) were added to NB aqueous solutions (40 mL, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 mg/L). The suspensions were shaken in a sealed vessel at 25 °C for 12 h to achieve adsorption equilibrium. The concentrations of NB were measured using a Cary 5000 UV-Vis spectrophotometer.

3. Results and discussion

Fig. 2(a) shows the FT-IR spectra of pure TiO_2 , STA, STA- TiO_2 , and the TiO_2 Janus particles. The pure TiO_2 shows the deformation frequencies of -OH located at 3419 and 1636 cm^{-1} . The peak located at 1398 cm^{-1} is attributable to the stretching vibration of the Ti-OH bond, whereas the absorption peak at 668 cm^{-1} is characteristic of the Ti-O bond vibration [42]. In the STA spectrum, the peaks recorded at 2919 and 2846 cm^{-1} correspond to the symmetrical stretching vibration of the -CH₃ and -CH₂- groups, respectively. The stretching vibration of the -COOH group produced a strong absorption peak at 1709 cm^{-1} . The peak located at 1465 cm^{-1} is attributable to the in-plane bending vibration of the functional -OH group in STA [43]. The spectrum of STA- TiO_2 shows a new peak attributable to the -COOTi- group [20] (1709 cm^{-1}). The characteristic absorption peaks of STA appeared in the spectra of the STA- TiO_2 and TiO_2 Janus particles, indicating that STA had been successfully grafted onto the surface of TiO_2 . In addition, the intensity of the -OH absorption peaks at 3419 and 1636 cm^{-1} is much weaker than that of pure TiO_2 , but the peaks still exist, indicating that the modification does not consume all the hydroxyl species,

Fig. 2. FTIR (a), UV-Vis (b), and TG (c) curves of the samples.

and that the alkali can regenerate the hydroxyl groups, which proves that the modified TiO_2 particles still have strong oxidation ability.

Fig. 2(b) shows the UV-Vis DRS results of the pure TiO_2 , STA- TiO_2 , and TiO_2 Janus particles. It shows that pure TiO_2 particles exhibit high absorption at 200–400 nm (consistent with the literature [44]), but almost no absorption in the visible light region at 400–800 nm. In contrast, the maximum absorption of the STA- TiO_2 and TiO_2 Janus particles is more than 400 nm. It is evident that STA modification results in a significant red shift of the absorption band of TiO_2 nanoparticles and expands the absorption range of the photocatalyst to the visible region. The doped dose of STA adsorbed on the TiO_2 surface was deduced from TG analysis of TiO_2 , STA, STA- TiO_2 , and the TiO_2 Janus particles, as shown in Fig. 2(c). The TG curve of pure TiO_2 indicates thermal stability up to 800 °C, for which the loss of mass is negligible (1.1%); this may be due to the degree of humidity. On the contrary, the TG curve of pure STA presents a single stage of thermal decomposition in the temperature range of 200–300 °C, wherein the loss of mass is complete. The thermal decomposition temperature of the STA- TiO_2 and TiO_2 Janus particles is in the range 296–419 °C and the temperature starting point obviously lags behind that of STA. This indicates that STA forms stable chemical bonds on the surface of TiO_2 , and it needs to overcome a certain energy barrier to decompose. In addition, the amounts of STA grafted on the STA- TiO_2 and TiO_2 Janus particles were about 14.72% and 11.80%, respectively.

The amphiphilic nature of the TiO_2 Janus particles was confirmed via fluorescence microscopy. Since the Janus particles (40 nm) cannot be seen clearly under a microscope, TiO_2 with a particle size of 2.23 μm was prepared via the hydrothermal method and toposelective surface modification was used to prepare micron-sized TiO_2 Janus particles. The TiO_2 Janus particles were tagged with the fluorescent dye fluorescein isothiocyanate (FITC), which attached to the OH groups present on the hydrophilic half of the Janus particles through its isothiocyanate groups [45]. The reaction mechanism of the attachment of FITC to the TiO_2 Janus particles is shown in Fig. 3(a). Fig. 3(c) shows a fluorescence micrograph of the TiO_2 Janus particles (Fig. 3(b) is an illustration of the fluorescence image) with half the particles illuminated due to the presence of FITC and the other half showing slight fluorescence, which is without FITC, because of the multiple reflections and scattering of the light

emitted by the fluorophores on the edges of the transparent modifier. This not only confirms the characteristics of the TiO_2 Janus particles but also proves that the OH groups with strong oxidation property are reinstated upon NaOH addition; this can be applied to wastewater treatment.

To investigate the morphology and microstructure, HRTEM images of the TiO_2 Janus particles were recorded (Fig. 4(a)). The lattice fringe with an interplanar spacing of 0.34 nm was perfectly equal to the lattice constant of the (101) crystal plane of anatase-phase TiO_2 . Furthermore, the layer fringe of STA could be visually identified. This result confirmed that STA was successfully grafted onto the surface of TiO_2 . The HRTEM images also indicate that the average particle size of the TiO_2 Janus particles is about 40 nm. Elemental mapping EDS analysis (Fig. 4(b)) of the TiO_2 Janus particles clearly shows the uniform

Fig. 3. (a) Mechanism of attachment of fluorescein isothiocyanate onto TiO_2 Janus particles; (b) schematic representation of various surface views of TiO_2 Janus particles, wherein (i), (ii), and (iii) designate the side view, the view with OH groups facing up, and the view with STA groups facing up, respectively; (c) fluorescence image of TiO_2 Janus microparticles.

Fig. 4. HRTEM image (a) and EDS mapping (b) of TiO_2 Janus particles.

distribution of C elements on one side of the TiO_2 particles. This indicates that STA is asymmetrically distributed on the TiO_2 particle surfaces, thus confirming the Janus structure of TiO_2/STA .

The chemical states and elemental composition of the TiO_2 Janus particles were investigated using XPS. Fig. 5(a) shows the Ti 2p XPS spectra. There are two peaks at binding energies of 459.2 and 464.9 eV, which correspond to the signals of $\text{Ti}^{4+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$ [46]. The high-resolution XPS spectrum of O 1s is shown in Fig. 5(b). The O 1s peak consisted of three components at 532.3, 533.9, and 535.1 eV, which are attributable to crystal lattice oxygen (Ti-O), carboxyl group oxygen (COO-), and hydroxyl group oxygen (-OH), respectively [42]. The C 1s spectrum shows three fitted peaks at 285.1, 286.5, and 288.1

eV. The main peak located at 286.5 eV can be assigned to C-O-Ti. The peaks located at 285.1 and 288.1 eV can be ascribed to C-C and O=C-O, respectively. These results further confirm that STA is successfully grafted onto the surface of TiO_2 .

The water contact angle is often used to characterize the surface hydrophilicity of a photocatalyst [47]. Furthermore, the contact angle can be used to determine the ability of particles to contact with organic matter, and the stability of the formed Pickering emulsion [19,48]. Fig. 6(a), Fig. 6(b), and Fig. 6(c) show that the water/air contact angle is about 14.6° for pure TiO_2 , 96.1° for STA- TiO_2 , and 72.9° for the TiO_2 Janus particles. The results show that pure TiO_2 has strong hydrophilicity due to a large amount of -OH groups. After modification, the hydrophobicity of STA- TiO_2 significantly improved, mainly because the -COOH groups of STA reacted with the -OH groups on the surface of the TiO_2 , and a large number of C-H long-chains were grafted onto the surface, thereby reducing its hydrophilicity. Some of the STA on the Janus particles was washed away by NaOH, and the hydrophobicity decreased slightly.

Pickering emulsions were prepared using the TiO_2 , STA- TiO_2 , and TiO_2 Janus particles as the emulsifiers, and the sizes of the emulsion drops were measured (Fig. 6(a)–(c)). Pure TiO_2 particles cannot form a stable Pickering emulsion, and the

Fig. 5. Ti 2p (a), O 1s (b), and C 1s (c) core-level XPS spectra of TiO_2 Janus particles.

Fig. 6. Particle size distributions, water contact angles, and emulsion morphologies of TiO_2 (a), STA- TiO_2 (b), and TiO_2 Janus particles (c). Dispersion behavior of pure TiO_2 (d), STA- TiO_2 (e), and TiO_2 Janus particles (f) in kerosene-water mixture.

Fig. 7. Picture of emulsions, and amount of Janus particles in 2 wt% (a), 2.5 wt% (b), 3 wt% (c), and 3.5 wt% (d) solutions.

system exhibits obvious stratification after stirring is stopped. Compared with that prepared using pure TiO_2 , the emulsion prepared using STA- TiO_2 has better stability, more uniform mixing, and a smaller size of the emulsion droplets. However, if it is kept for a few minutes, stratification occurs. The average drop size of the Pickering emulsion made from the TiO_2 Janus particles is only 81.32 nm; it can be observed under a microscope to be very fine and uniform. It is vital that the emulsion remains in a stable state after being stored for 15 days, except for a small amount of solid particles at the bottom. The emulsions prepared with low-hydrophobicity STA- TiO_2 particles are more stable than those prepared with high-hydrophobicity particles. This is mainly due to the amphiphilicity of the Janus particles. To further confirm the amphiphilicity, the dispersion behavior of the TiO_2 Janus particles in a kerosene-water mixture was studied and compared with that of TiO_2 and STA- TiO_2 . Being immiscible liquids, kerosene and water separate into two different layers upon mixing. When pure TiO_2 particles were added to this mixture, they dispersed into the water phase, whereas when STA- TiO_2 particles were added to the mixture, they moved into the kerosene phase, as shown in Fig. 6(d) and Fig. 6(e), respectively. In contrast, the TiO_2 Janus particles arranged themselves at the interface of kerosene and water, as shown in Fig. 6(f), confirming their amphiphilic nature.

The optimum amount of Janus particles required to stabilize the Pickering emulsion was studied by observing the changes in the emulsion after storage for 72 h at room temperature (the ratio of kerosene to water was 1:4); the results are shown in Fig. 7. It is obvious that the Pickering emulsion shown in Fig. 7(b) was the most stable, whereas the mixtures shown in Fig.

Fig. 8. Adsorption capacity of samples for NB at different concentrations.

7(c) and Fig. 7(d) are not emulsions, and have obvious solid particles.

The NB adsorption capacity of the TiO_2 , STA- TiO_2 , and TiO_2 Janus particles was studied, as represented in Fig. 8. STA- TiO_2 has a high adsorption capacity for NB, and its adsorption saturation capacity is about twice that of pure TiO_2 . This is due to the large number of C-H long-chains grafted onto the surface of the modified particles, which increase the hydrophobicity of the modified particles, thereby resulting in enhanced adsorption of NB. Compared with those of STA- TiO_2 , the hydrophobicity of the TiO_2 Janus particles decreases and the adsorption capacity for NB is slightly lower. In general, the adsorption capacity of the TiO_2 Janus particles for NB is greater than that of pure TiO_2 , accelerating the migration rate of NB to the surface of the photocatalyst, and thereby improving the degradation efficiency of NB.

Fig. 9(a) and Fig. 9(b) show the effects of three different systems on the kerosene and NB degradation rates, respectively. The concentrations of kerosene and NB decrease after the photocatalytic tests. However, this decrease is small in the emulsion stabilized by TiO_2 particles. This is due to the weakness of the contact area between the contaminants and the TiO_2 photocatalyst. The photodegradation rate is significantly higher in the emulsion stabilized by the STA- TiO_2 particles. This is mainly attributable to the fact that STA improves the hydrophobicity of TiO_2 , enabling the catalyst to fully contact the contaminants and thereby improving the degradation efficiency.

Fig. 9. Photocatalytic degradation of kerosene (a) and NB (b) in different systems; (c) reusability of TiO_2 Janus particles for degradation of NB under ultraviolet irradiation.

However, the stability of the system is not satisfactory. When the TiO_2 Janus particles were used as the catalysts to degrade organic pollutants, the catalysts were arranged at the interface of the organics and water, which not only improved the catalyst contact with the pollutants but also stabilized the oil-water system to the maximum extent. The degradation rates of kerosene and NB were 89% and 98.9%, respectively, after 120 min irradiation. The stability of photocatalysts is crucially important for their application [46]. To evaluate the photostability of the TiO_2 Janus particles, cycling experiments for the photocatalytic degradation of NB were conducted, as shown in Fig. 9(c). The results show that the TiO_2 Janus particles are stable under ultraviolet irradiation and maintain excellent photocatalytic activity; self-degradation takes place less readily.

To determine the main active species involved in the degradation process, and the possible photodegradation mechanism, four scavengers were used to investigate the reactive species in the photocatalytic reaction [50]. For this, TBA, BQ, EDTA- Na_2 , and $\text{K}_2\text{S}_2\text{O}_8$ were employed to scavenge the $\cdot\text{OH}$, $\cdot\text{O}_2^-$, h^+ , and e^- , respectively. As shown in Fig. 10, in the presence of different scavengers, the corresponding photocatalytic efficiency is partly restrained. The degradation of NB is slightly inhibited by the addition of $\text{K}_2\text{S}_2\text{O}_8$, implying that e^- are not the main active species responsible for the decomposition of NB. However, when TBA, BQ, or EDTA- Na_2 was added into the reaction solution, the photocatalytic activity of the TiO_2 Janus particles was remarkably lowered. Surprisingly, the degradation efficiency of NB decreased to 51% in the presence of TBA. These results clearly demonstrate that the $\cdot\text{OH}$ radicals are the main active species and played a dominant role in NB degradation under ultraviolet irradiation. This is basically consistent with the photocatalytic mechanism of pure TiO_2 . The main reason for the efficient degradation of organic matter by the TiO_2 Janus particles is the increase in their hydrophobicity, which improves the interfacial contact area between the catalyst particles and organic pollutants, and strengthens the rate of hydroxyl radical migration to the surface of the organic pollutants, thereby significantly enhancing the photocatalytic efficiency.

An EIS test was employed to study the impact of STA on the

Fig. 10. Photocatalytic activity of TiO_2 Janus particles toward the degradation of NB in the presence of different scavengers.

Fig. 11. EIS plots for TiO_2 , STA- TiO_2 , and TiO_2 Janus particle electrodes.

charge separation in TiO_2 . Fig. 11 shows the EIS curves of TiO_2 , STA- TiO_2 , and TiO_2 Janus particle photocathodes measured in 0.4 mol/l Na_2SO_4 under ultraviolet irradiation. The charge transfer resistance, which is the resistance to electron transfer from the electrode to the electrolyte, directly correlates with the semicircle diameter at high frequencies [51]. The STA- TiO_2 and TiO_2 Janus particle photocathodes exhibited a smaller EIS curve diameter compared with that of the TiO_2 photocathode. This indicates that resistance to electron transfer through the solid/liquid interface is lower for the STA- TiO_2 and TiO_2 Janus particles. This would result in fewer possibilities for charge recombination and a higher efficiency of reactive species generation and pollutant degradation.

A possible photocatalytic mechanism of the TiO_2 Janus particles, based on the characterization results described above, is presented in Fig. 12. Under ultraviolet irradiation, photons excite e^- from the VB of TiO_2 to the CB, producing photo-generated e^- and h^+ pairs. The photogenerated h^+ oxidize adsorbed water molecules to produce $\cdot\text{OH}$ radicals for the photodegradation of NB, and a fraction of h^+ directly attack the NB adsorbed on the surface. Simultaneously, e^- are transferred to adsorbed oxygen molecules and produce $\cdot\text{O}_2^-$ species. The adsorbed NB can also be attacked by the $\cdot\text{O}_2^-$ radicals.

4. Conclusions

TiO_2 Janus particles were prepared via toposselective surface modification. The results show that stable chemical bonds formed between STA and the TiO_2 surface. The STA groups

Fig. 12. Schematic illustration of NB degradation mechanism over TiO_2 Janus particles.

enhanced the hydrophobicity of the Janus particles and facilitated the separation of photogenerated electron-hole pairs. The Pickering emulsion prepared using the Janus particles as the emulsifier remained stable after 72 h. When the Pickering emulsion was used for photocatalytic degradation, the organic oil phase showed a high degradation efficiency. This was mainly attributed to the fact that the TiO₂ Janus particles were both emulsifiers and photocatalysts, which greatly increased the contact area between the organic compounds and these catalysts. The ·OH reactive species were demonstrated to be the major reactive species in the photodegradation process of NB over the TiO₂ Janus particles.

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Graphical Abstract

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Preparation of amphiphilic TiO₂ Janus particles with highly enhanced photocatalytic activity

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TiO₂ Janus particles were successfully prepared via toposelective surface modification. The particles adsorbed stably on the interface between pollutants and water, greatly improving the photodegradation efficiency of organic wastewater.

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具有高光催化活性的两亲性TiO₂ Janus粒子的制备

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摘要: 随着工业技术和社会经济的快速发展, 水污染问题日益严重. 尤其是化工原料和产品在生产、储存和运输过程中发生的事故, 造成大量有机物进入水体, 对自然环境造成极大危害. 特别是在海洋中发生大规模的泄漏事故时, 通过简单的物理方法如吸附、萃取等能够回收大部分资源, 但在水体中仍有高浓度的污染物以油滴的形式存在, 难以进一步去除. 二氧化钛光催化技术在处理高浓度、难降解有机废水方面具有独特优势, 但由于其强亲水性导致与污染物接触面积受限, 降解效率不高. Pickering乳液是一种界面催化新技术, 是由具有两亲性的胶体粒子代替传统表面活性剂形成的油水分散体系, 固体粒子吸附在油/水界面, 提高了固液接触面积, 由此构成了无数个强化反应的微反应器. 本文将光催化技术与Pickering乳液优势结合, 实现催化剂与有机物界面面积的最大化, 从而提高降解效率. 首先采用拓扑选择表面改性法用硬脂酸改性二氧化钛制备Janus粒子, 在此基础上用制得的二氧化钛Janus粒子构筑Pickering乳液光催化降解体系, 研究其对有机废水的降解效率.

FM和HRTEM表征结果显示, 硬脂酸均匀分布在TiO₂的一侧, 符合Janus粒子的结构特征. 与纯TiO₂相比, TiO₂ Janus粒子的接触角从14.6°增大到72.9°, 具备一定的亲水亲油性, 可以有效润湿油性有机物, 说明TiO₂ Janus粒子可以构筑稳定的Pickering乳液光催化体系. 乳液稳定性实验表明, 以TiO₂ Janus粒子为乳化剂的乳液稳定时间长达15 d, 明显优于TiO₂和STA-TiO₂. 降解高浓度煤油废水和硝基苯废水的实验表明, 与纯TiO₂和STA-TiO₂相比, TiO₂ Janus粒子的光催化效率有明显提高, 紫外灯辐照120 min后, 硝基苯的降解率达到98.9%, 约是纯TiO₂的2倍, STA-TiO₂的1.3倍, 煤油的降解率也达到89%. 采用叔丁醇、对苯醌、乙二胺四乙酸二钠和过硫酸钾作为捕获剂对TiO₂ Janus粒子的光催化机理进行了研究. 结果表明, 羟基自由基在硝基苯降解过程中起主要作用, 光生空穴和超氧自由基起次要作用. TiO₂ Janus粒子能够高效降解有机物归因于粒子的亲油性提高, 增大了催化剂粒子与有机污染物的界面接触面积, 强化了羟基自由基迁移到有机污染物表面的速率, 从而显著提高了光催化效率.

关键词: 二氧化钛; Pickering乳液; 纳米颗粒; 光催化; 降解

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