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Amplified visible light photocatalytic activity of mesoporous TiO_2/ZnPc hybrid by cascade Mie light scattering

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ABSTRACT

We synthesize the anatase TiO_2/zinc phthalocyanine (ZnPc) hybrids in various sizes (245–1188 nm) and examine the visible light photocatalytic activity of TiO_2/ZnPc hybrids, in conjunction with their Mie light scattering ability. Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy show that ZnPc molecules are well-incorporated and dispersed on the surface of the TiO_2, instead of being aggregates. From the field-emission scanning electron microscopy, dynamic light scattering, and nitrogen adsorption–desorption analysis, we confirm the formation of spherical TiO_2/ZnPc hybrids in various sizes (245, 548, 798, 1188 nm in diameter), the large specific surface areas (up to 223.76 m^2/g), and the mesoporous structures. The mesoporous TiO_2/ZnPc hybrids show excellent photocatalytic efficiency (up to 89.93% after 90 min) toward the degradation of methylene blue under visible light irradiation, which is about 2 times of that of simple nanoparticular P25/ZnPc. Among the mesoporous TiO_2/ZnPc hybrids, the hybrid with a size of 548 nm (P123–TiO_2/ZnPc) exhibits the highest photocatalytic activity. The highest activity observed on P123–TiO_2/ZnPc may be attributed to its efficient cascade Mie scattering effect under visible light irradiation.

1. Introduction

Environmental pollutants in water and air pose a serious threat to the public health and safety, and much effort has been directed toward solving these problems. From the point of green technology, photosensitive semiconducting materials are promising to be environmentally friendly and economically practicable catalysts, due to their nontoxicity and low cost [1–3]. Titanium dioxide (TiO_2) is of particular interest, because TiO_2 has been proven to be the benchmark of photosensitive semiconducting material with an effective degradability against organic contaminants, a long-term chemical stability, and a good photostability without toxicity [4–9]. Unfortunately, pure TiO_2 can only be excited under ultraviolet (UV) irradiation, owing to its wide band gap (e.g. 3.2 eV for anatase and 3.0 eV for rutile), and thereby no visible light response is obtained [10,11]. Such a photosensitive characteristic of pure TiO_2 is quite ineffective, because UV radiation accounts for less than 5% of all natural sunlight and *c.a.* 43% of solar spectral energy is contained in the visible light.

To improve the utilization of solar light in practical photocatalytic applications, the development of TiO_2 photocatalysts responsive to visible light is highly desirable. Many strategies have been developed to extend the absorption spectra of TiO_2 to the visible light region, including doping with non-metal elements [12–16], loading with noble metals [17–23], dye sensitization [24–26], and combining TiO_2 with other semiconductors [27–29]. Among them, a dye photosensitization is an inexpensive and efficient method to extend the absorption spectra of TiO_2 into the visible light region [24–26]. Indeed, this type of reaction has been exploited in the dye sensitized solar cells [30–33].

Zinc phthalocyanine (ZnPc) is highly stable metal complex acting as a visible light absorption dye [34–40], and has potential application in optical switching [41], solar cell [42], and photocatalyst [35]. It is known that the incorporation of zinc phthalocyanine in a TiO_2 can effectively extend the absorption spectra of TiO_2 into the visible light region. In general, dye sensitization of TiO_2 photocatalytic cycle consists of four steps: (i) photo sensitization of TiO_2 proceeded by the initial excitation of the dye;

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(ii) electron injection into the TiO_2 conduction band; (iii) migration of excited electrons to the surface of TiO_2; (iv) reaction of excited electrons with the adsorbed electron acceptors. Since the first step for the photocatalysis is a light excitation process, an efficient utilization of the incident light is an effective way to improve photocatalytic activity. Particularly, when the size of the particles is similar to the wavelength of the incident light, the Mie scattering occurs. Such a comparable size of particles can promote light scattering, resulting in the improvement of light utilization and further enhancement of photocatalytic activity [43–47]. Indeed, Mie scattering effect has been applied in the dye-sensitized solar cells previously. However, there are few studies that observed the light scattering effect on dye sensitized TiO_2 for the application of photocatalyst to solve the environmental problems.

Here, we prepared the spherical TiO_2 with the mesoporous framework to increase the specific surface area and to improve the incorporation efficiency of ZnPc, which can further enhance the visible light photocatalytic activity. The mesoporous TiO_2/ZnPc hybrids were synthesized with the varied size to investigate the effect of Mie scattering on the photocatalytic activity of TiO_2/ZnPc hybrid. We showed that the scattering efficiency of the incident visible light is dependent on the diameter of ZnPc-incorporated mesoporous TiO_2 spheres. When the size of TiO_2/ZnPc hybrid was comparable to the wavelength of incident visible light, the mesoporous TiO_2/ZnPc exhibited the highest photocatalytic decomposition activity due to the cascade Mie scattering effect. The enhanced photocatalytic activity of mesoporous TiO_2/ZnPc by Mie scattering makes it tremendously attractive for applications ranging from water purification to hydrogen generation. In addition, the simplicity of the current process to produce mesoporous TiO_2/ZnPc makes it attractive for large-scale production.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide (TTIP, $Ti(OPr^i)_4$), Pluronic L121 (L121, $EO_5PO_{70}EO_5$), Pluronic P123 (P123, $EO_{20}PO_{70}EO_{20}$), Pluronic F68 (F68, $EO_{75}PO_{30}EO_{75}$), Pluronic F127 (F127, $EO_{108}PO_{70}EO_{108}$), 2,4-pentanedione (acetylacetone, AcAc), sulfuric acid, dimethyl sulfoxide, zinc phthalocyanine (ZnPc), poly(ethylene glycol) (PEG, average MW = 10,000), and poly(ethylene oxide) (PEO, average MW = 100,000) were purchased from Sigma–Aldrich. They were used in the received form without further purification. Water used in all syntheses was distilled and deionized.

2.2. Preparation of ZnPc incorporated TiO_2 spheres

The TiO_2 spheres were synthesized with sol–gel method by using triblock copolymer surfactants (L121, P123, F68, and F127 for samples L121–TiO_2, P123–TiO_2, F68–TiO_2, and F127–TiO_2, respectively) in aqueous solution. The general procedure was as follows. First, 1.0 mmol of the surfactant was dissolved in 100 mL of deionized water. The mixture (pH 7.09) was stirred vigorously at 50 °C to produce a transparent solution. After the surfactant was dissolved sufficiently, 1.5 g of sulfuric acid was added to the aqueous surfactant solution (pH 0.76). TTIP (7.84 g) was mixed with AcAc (2.76 g) in a separate beaker and dropped into the aqueous surfactant solution (pH 0.89) with vigorous stirring for 1 h at 50 °C. Light yellow powders formed within several minutes. The resulting materials were treated hydrothermally at 90 °C for 12 h. The solids in the solutions were filtered out, dried in air, and ground to fine powders. To remove the organic residue including surfactants and increase crystallinity of TiO_2, the materials were calcined at 500 °C at a rate of 1 °C/min in air.

ZnPc incorporated TiO_2 (TiO_2/ZnPc) was prepared according to the previous procedure [48]. To prepare TiO_2/ZnPc, ZnPc (12 μmol) was dissolved in dimethyl sulfoxide (30 mL). A TiO_2 sample (one of L121–TiO_2, P123–TiO_2, F68–TiO_2, or F127–TiO_2, 2 g) was added to this solution. The resulting suspensions were magnetically stirred at room temperature for 10 h. The catalysts were collected by removing solvent under vacuum and were dried at 60 °C for 12 h. The products were denoted L121–TiO_2/ZnPc, P123–TiO_2/ZnPc, F68–TiO_2/ZnPc, or F127–TiO_2/ZnPc, respectively.

2.3. Preparation of TiO_2/ZnPc films

The TiO_2/ZnPc films used for photocatalytic test were prepared via a doctor-blade method. The weight content of the TiO_2/ZnPc spheres in the water-based suspension was 40 wt%. The pastes were prepared by admixing the 10 g of suspension with 0.12 g of PEG and 0.12 g of PEO. The resulting pastes were doctor-bladed onto glass slides. In order to further improve the connectivity among TiO_2/ZnPc spheres, the coated films were then pressed. The typical pressure was at 12 MPa with plates preheated to 120 °C for 10 min. Teflon plates were inserted between the films and the plate, to prevent the films from sticking to the plate. The films were then heated at 170 °C for 30 min in air. The thickness of the films were measured using an α-step profiler. The thicknesses of the films were in the 17.2–17.7 μm range and were uniform (the largest variation being approximately 0.2 μm for all samples).

2.4. Characterization

Fourier-transform infrared (FT–IR) spectra of the samples pelletized with KBr powder were collected over the range of 4000 to 400 cm^{-1} with a spectral resolution of 4 cm^{-1} by using a Thermo Scientific Nicolet iS10 IR spectrophotometer. The X-ray diffraction patterns of the nanoparticles in the TiO_2/ZnPc spheres were collected at room temperature, by using a MAC/Sci MXP 18XHF-22SRA diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 1.541 Å, 50 kV, and 100 mA) as the X-ray source. Data acquisition was performed over the 2θ angular range 20°–80° with a scanning speed of 5°/min. XPS was performed on a Kratos AXIS photoelectron spectrometer, with a background pressure of approximately 1×10^{-9} Torr, by using Mg Kα X-rays as the excitation source (1253.6 eV). All binding energies were calibrated by assuming that the binding energy of the C 1s peak at 284.6 eV. The morphologies of the materials were examined using a JEOL JSM-6330F FE-SEM under an applied voltage of 3.0 kV. The average particle sizes of the TiO_2/ZnPc spheres were determined using a DLS method with a Photal DLS-7000 spectrophotometer equipped with a Photal GC-1000 digital autocorrelator (Otsuka Electronics Co., Ltd.). In this procedure, the wavelength (λ) of the argon laser was 488 nm. The scattering angle was 90° with respect to the incident beam. All samples were finely ground and dispersed in deionized water. The intensity-average and number-average particle size distributions were analyzed by using the conventional CONTIN algorithm to estimate the diameters of the particles. The specific surface areas and pore size distributions of the materials were characterized by analyzing the N_2 adsorption and desorption isotherms obtained at 77 K with a Micromeritics ASAP 2000. All samples were degassed at 200 °C and 10^{-6} Torr for 10 h prior to measurements. The surface areas were calculated with the Brunauer–Emmett–Teller (BET) equation. Pore-size distributions were determined from the adsorption and desorption branches, by using the Barrett–Joyner–Halenda (BJH) formula. The specific surface areas and average pore sizes of the samples were calculated with Micromeritics Density Functional Theory (DFT) Plus software package.