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Iodine-modified nanocrystalline titania for photo-catalytic antibacterial application under visible light illumination

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ABSTRACT

Iodine-modified TiO_2 nanocrystallites (denoted as I-TiO_2) were synthesized by a combination of sol-gel process (TiO_2 sol) and solvothermal method in the presence of HI solution. Their photocatalytic and anti-bactericidal activities were systematically investigated under visible light irradiation. The results showed that the iodine modifier existed in the form of I_2 is responsible for the visible light response. Moreover, the I_2 significantly enhanced the antibacterial activity under visible light and was stable during the photocatalytic process. In addition, an interesting post-illumination catalytic memory of I-TiO_2 that continues to inhibit the growth of *Escherichia coli* in dark was also observed after the visible light was shut off.

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1. Introduction

Despite TiO_2 has been extensively used in environmental and clean energy fields due to its highly active, low toxicity, chemical stability, biocompatibility and inexpensiveness [1–10], using TiO_2 particles as antibacterial agent in biomedical applications has received considerable attention because of its long-acting antibacterial properties under UV light illumination [11–13]. The antibacterial effect of TiO_2 was first applied in biomedical application by Cai in the immortal HeLa cell lines [1].

However, TiO_2 and some TiO_2-based photocatalyst can only be excited by UV light [6,14–16], which greatly limits its biomedical application under visible-light or normal room light illumination. Search for high efficient antibacterial photocatalyst under visible light (VL) has been an intensively pursued topic in the field of photocatalysis research. Generally, two major approaches have been frequently employed to fabricate visible-light-driven (VLD) photocatalyst. One is to purposely fabricate new forms of VLD photocatalyst, such as Cu_2O/SiC [17], $LaVO_4$/g-C_3N_4 [18], $(Ag_{0.75}Sr_{0.25})(Nb_{0.75}Ti_{0.25})O_3$ [19], $C_3N_3S_3$ [20], and N-Modified $BiWO_6$ [21], etc. Another is to modify TiO_2 with elements such as C, N, S, F, B, Fe, Bi and I [2,15,22–34], to extend the light absorption spectrum of TiO_2 from the UV to VL region. Among these nonmetal impurities, iodine-modified TiO_2 nanocrystallites have been received more attention because iodine-doping not only alters the surface charge and bulk band gap of TiO_2, which causes the photo-response of TiO_2 to enlarge from UV to VL region, but also sufficiently reduces the recombination of photogenerated electron–hole(e^-–h^+) by trapping the photogenerated electrons [35–44]. I-modified TiO_2 has been reported enhance visible-light photocatalytic activities in the degradation of organic pollutant such as methyl orange [45], 4-CP [13], phenol [46], acetone [39] and RhB [47]. However, there are little reports about the antibacterial activity of iodine-modified TiO_2 nanocrystallites under visible light and the stability of iodine-modified TiO_2 during the photocatalytic process has not been well demonstrated. In addition, no experimental evidence has been given on the post-illumination catalytic memory of iodine-modified TiO_2 in dark, a characteristic that has great importance in the practical applications [48–50].

In this work, iodine-modified TiO_2 nanocrystallites samples with different amount iodine were prepared by a combination of sol–gel process (TiO_2 sol) and solvothermal method. The antibacterial activity and stability of iodine-modified TiO_2 were valued by antibacterial of *Escherichia coli* and photocatalytic degradation of RhB under VL for multiple cycle tests. The chemical states of iodine-modified TiO_2 before and after photocatalytic reaction were characterized by XPS. By further detecting the generation of •O2− and OH species, the plausible mechanism of photocatalytic antibacterial activity and the post-illumination catalytic memory of iodine-modified TiO_2 in dark are discussed. It is hoped that our work helps better understanding of the role of the iodine-modifier in the photocatalytic antibacterial activity of TiO_2, and also provides

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a method to obtain highly visible photoactive and antibacterial photocatalysts.

2. Experimental

2.1. Catalyst preparation

2.1.1. Materials and Reagents

RhB ($C_{28}H_{31}C_lN_2O_3$) was purchased from Beijing Chemical Reagents Company. The bacterial cells were cultured in nutrient broth (BioLife, Milano, Italy) solution at 37 °C for 18 h and immediately diluted. The concentration of cell density is 10^7 cfu (colony forming unit)/ml. TiO_2 sol (Research Institute of Photocatalysis, State Key Laboratory Breeding Base, Fuzhou University, Fuzhou, China) was used as the Ti source. Hydroiodic acid (HI, ≧45%, Sinopharm Chemical Reagent Co., Ltd., Shanghai) was used as the iodine source. Furfural (The morning chemical reagent factory in Tianjin) was used as template. All these reagents were of analytical grade and used as received. Millipore water with a resistivity of 18.2 MΩ was used throughout the study. All of used glass apparatuses were washed with millipore water, and then autoclaved at 121 °C for 15 min.

2.1.2. Synthesis of TiO_2

50 mL of titanium oxide sol and 25 mL of furfural (65–68%) were mixed and stirred at room temperature for 4 h. Then the color of TiO_2 sol changes from blue to brown. The brown solution was transferred to a Teflon-lined autoclave and reacted at 160 °C for 12 h, after that time a black resin was formed. Finally, the black resin was heated at 450 °C in air for 36 h to remove furfural and a white cotton-like product was obtained. In this work, the furfural acts as template agent to inhibit agglomeration of TiO_2 at 450 °C and enlarge the surface area of TiO_2.To compare, TiO_2 powder was prepared by the same method as above only without adding furfural.

2.1.3. Synthesis of iodine-modified TiO_2 (I-TiO_2)

Iodine-modified TiO_2 was prepared as follows: first, different amounts of hydroiodic acid were dissolved in 25 mL absolute ethanol. The TiO_2-iodine suspension was obtained by mixing TiO_2 and the above hydroiodic acid solution with the molar ratios of HI to TiO_2 of 0.4, 0.8, 1.6, respectively. After stirring at room temperature for 4 h, the three suspensions were transferred into Teflon-lined autoclave to solvothermal treatment at 160 °C for 12 h. Finally, the obtained suspensions were filtered and the resultant powders were washed with distilled water and then dried at 80 °C for 12 h to get iodine-modified TiO_2 powders. For ease of presentation, the corresponding samples were labeled as 0.4I-TiO_2, 0.8I-TiO_2, and 1.6I-TiO_2, respectively.

2.2. Characterizations

The crystal structure was analyzed by X-ray diffraction (XRD) on a DMAX-2400 (Rigaku, Japan, Cu Kα, λ = 0.15406 nm) radiation at 56 kV and 182 mA with a secondary graphite crystal monochromator. The morphologies were observed by a scanning electron microscopy (SEM, HITACHI S-4700) and high-resolution transmission electron microscopy (HRTEM). HRTEM analysis was performed on a JEOL 2200FS (JP) microscope, with a field emission gun, operated at 300 kV and equipped with energy-dispersive X-ray (EDX) analyzer (Oxford Instruments, Abingdon, U.K.). Samples were prepared by suspending and sonicating the powders in isopropyl alcohol and then placing sonicating evaporating a drop of the suspension on a carbon-coated copper grid. The surface area, pore textures, and size distributions were characterized on a Micromeritics ASAP 2020 system by the N_2 adsorption–desorption experiment. Pore diameter and volumes were calculated from the desorption branch of the Barret–Joyner–Halenda (BJH) model. The optical absorption properties were evaluated on Carry 500 UV/vis/NIR spectrometer that equipped with an integrated sphere attachment using $BaSO_4$ as the reference. The X-ray photoelectron spectroscopy (XPS) measurements of the samples were carried out on a ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 3.0×10^{-10} mbar with monochromatic Al Kα radiation (E = 1486.2 eV). To detect the generation of activated species, spin-trapping electron spin resonance (ESR) measurements were conducted on a Bruker model A300 spectrometer. Transient photocurrent characterization was conducted on a ZENNIUM electrochemical workstation (Zahner, Germany) with a standard three-electrode system under visible light irradiation. The prepared samples served as the working electrode with an active area of ca. 0.25 cm^2. The counter and reference electrodes were Pt plate and Ag/AgCl electrode and 0.2 M Na_2SO_4 (pH 6.8) was used as electrolyte.

2.3. Visible-light-driven photodegradation/antibacterial activity

The photocatalytic activity of the prepared samples was evaluated by measuring the photocatalytic degradation of RhB and phenol. In order to evaluate the VL induced photocatalytic activity, 50 mg powers were put into a pyrex glass reactor and 80 mL RhB (10 ppm) was added. A 300 W Xe lamp was used with cut-off filter to provide visible light (≥420 nm). Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to establish the adsorption–desorption equilibrium. At given irradiation time intervals, 4 mL of the solution were taken out and centrifuged, then analyzed on the UV–vis spectrometer (Cary 500). The final efficiency was calculated by the following equation:

$$E_t(\%) = (1 - C_t/C_0) \times 100\%,$$

where C_0 and C_t stand for the concentration of reactants at initial and at a certain irradiation time, respectively.

The antibacterial activity was estimated by killing of *E. coli* under visible light irradiation. 5 mL of *E. coli* suspension (1.0×10^7 cfu/mL) and 45 mL of a phosphate buffer solution were pipetted into a container and 50 mg catalyst powers were added. At given irradiation time intervals, 0.5 mL of the solution were taken out and centrifuged, and spread on freshly prepared agar plates, and incubated at 37 °C for 48 h, then, the number of viable cells in terms of colony-forming units was counted.

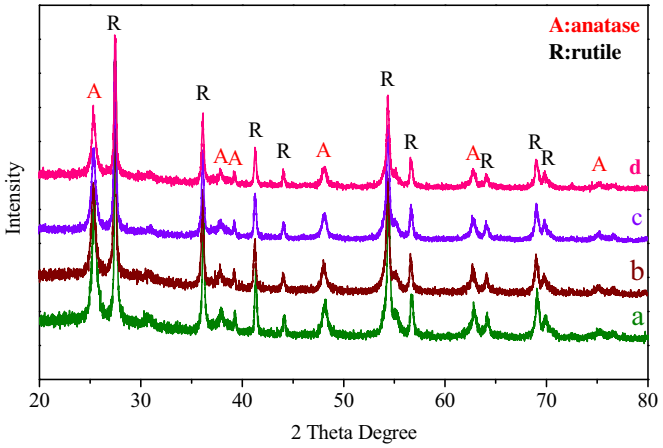

Fig. 1. XRD patterns of (a) TiO_2, (b) 0.4I-TiO_2, (c) 0.8I-TiO_2, (d) 1.6I-TiO_2.

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