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Research paper

Morphology effect of honeycomb-like inverse opal for efficient photocatalytic water disinfection and photodegradation of organic pollutant

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A B S T R A C T

Morphology is crucial component to achieve high photon utilization efficiency and efficient photocatalytic activity. In this work, novel honeycomb-like inverse opals were fabricated by a simple sol-gel method combined with a self-assembly polystyrene (PS) opal as template. The obtained materials exhibit unique 3D ordered porous structure with center-to-center distance of about 200 nm, which lead to periodic modulations of light propagation and strengthen light absorption of materials. Photocatalytic activity of TiO_2 with morphology of honeycomb and bulk, with or without doping Mg^{2+} was comparatively investigated by disinfection of bacteria and photodegradation of organic pollutant. Morphology evolution of TiO_2 from bulk to honeycomb would increase specific surface area and strengthen light adsorption, which could largely strengthen photocatalytic activity of honeycomb-like TiO_2. After Mg^{2+} is doped, it was found that Mg-TiO_2 systems exhibited much higher activity than their counterpart due to decreased band gap. In this way, water disinfection of 100% inactivation of bacteria was achieved under visible light. Highly reactive h^+ and $^{\bullet}O_2{}^-$ were found to be major reactive species and a possible mechanism was reasonably proposed.

1. Introduction

In recent years, microbial contamination has drawn widespread attention due to health of human beings is always threatened and millions of serious illness and even death are caused by pathogenic microbes every year [1–3]. Solar energy is a renewable energy sources and can be applied for water purification. However, solar disinfection of drinking water mostly depends on ultraviolet (UV) light, which occupies about 5% of the solar spectrum and this leads to a slow purification speed. Rapid and energy-efficient water disinfection techniques are urgently needed to solve these global challenges. Photocatalytic disinfection of bacteria, an economical, efficient and environmentally friendly inactivation method, can effectively purify drinking water which is vitally important for public health [4,5]. As the most promising photocatalyst, titanium dioxide (TiO_2) has been widely investigated owing to its cheapness, high oxidative power and excellent chemical inertness [6–9]. Unfortunately, photocatalytic activity of TiO_2 suffers from limitation owing to its wide band gap (E_g = 3.2 eV), which is active only under UV light, about 5% of the solar spectrum [10–12], while the residual 48% and 47% of solar spectrum are made up of visible light and near-infrared light, respectively [13]. Therefore, modification of TiO_2 materials that can utilize visible light for water disinfection and organic pollutant degradation, is highly desirable.

Among the numerous modified method, ion doping and shape control could be two effective strategies [14–16]. Previous studies have revealed that doping metal elements into TiO_2 is an effective way to strengthen photocatalytic activity [16–18]. Doped photocatalysts may introduce a new impurity energy level between conduction band (CB) and valence band (VB) and decrease band gap. Therefore, a photon with lower energy can excite electrons from defect state to CB and extend absorption band to visible range. On the other side, a main focus in fabricating semiconductor samples is to precisely control structure of material [18,19]. It is generally acknowledged that morphology is closely related to light harvesting performance and activity site number as well as the accessibility to active sites [20]. Three-dimensionally ordered macroporous

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(3DOM) inverse opal (IO) structure as one of the photonic crystals (PCs) for light harvesting via slow photon enhancement has drawn considerable attention [21,22]. This framework has been reported to strengthen light absorption and improve their photocatalytic activity as well [8]. 3DOM inverse opal have periodic modulations of light propagation in the structures, thus restricting light with certain energies to propagate through materials along a particular crystallographic direction and leading to a stop-band reflection (also called photonic band gap) owing to coherent Bragg diffraction [23]. The stop-band reflection frequencies depend on periodicity and dielectric contrast of PCs. At the wavelengths corresponding to edges of these stop-bands, photons propagate with strongly reduced group velocity and hence are called 'slow photons'. The slow photons can be applied to strengthen light absorption of photocatalysts when photon energy matches irradiation wavelength resulting in formation of a large number of electron-hole pairs. This possible improvement opens an alternative and attractive route to enhance photocatalytic activity [24].

Morphology-controlled synthesis of materials with perfect physical or chemical performances is still challenging for photocatalysis. Herein, honeycomb-like TiO_2 IO and Mg doped TiO_2 (Mg-TiO_2) IO were firstly fabricated through a simple sol-gel method combining with PS as sacrificial template. The obtained samples are 3D ordered porous framework with center-to-center distance of about 200 nm. By contrast with bulk TiO_2, a large enhancement in photocatalytic disinfection of bacteria and photodegradation of organic dye is observed for honeycomb-like IO structure under visible light irradiation. After Mg^{2+} is doped, it is found that Mg-TiO_2 systems exhibit much higher activity than their counterparts. In this way, water disinfection of 100% inactivation of bacteria was achieved under visible light.

2. Experimental

2.1. Synthesis of PS latex spheres and PS opal template

A surfactant-free emulsion polymerization reaction was used to prepare colloidal spheres (Fig. 1a–f). 13.5 g of styrene and 0.7 g of polyvinylpyrrolidone were added to 100 mL of distilled water in a three-necked bottle and then stirred at room temperature for 15 min. After that, 0.3 g of potassium persulfate as an initiator was introduced into the above hybrid solution. The reaction mixture was deoxygenated by bubbling N_2 through it at room temperature for 30 min and then heated at 70 °C for 24 h. Finally, milk white solution with suspended PS spheres was obtained.

PS opal templates were fabricated using a vertical deposition process by assembling monodispersed PS latex spheres onto a glass substrate at 45 °C for several days. Then opal templates were put into drying oven at 70 °C for 1 h to improve connection between neighboring PS spheres (Fig. 1a and b).

2.2. Synthesis of honeycomb-like Mg-TiO_2 samples with different amounts of Mg

10 mL butyl titanate, 10 mL absolute ethanol, 1 mL nitric acid and 0.05 g of $Mg(NO_3)_2$ were mixed with vigorous stir for 1 h to form a transparent solution. The obtained PS opal was dipped in TiO_2 precursor solution for 30 min through capillary force and then dried at room temperature for 1 h (Fig. 1c and d). Sintering was carried out in a tube furnace by slowly improving temperature (1 °C/min) up to 550 °C for 3 h (Fig. 1e and f). Bulk TiO_2 and Mg-TiO_2 were fabricated without PS opal as template. Honeycomb-like Mg-TiO_2 samples with different amounts of Mg (0.3%Mg-TiO_2, 1.0%Mg-TiO_2, 3.0%Mg-TiO_2, 5.0%Mg-TiO_2, 10.0%Mg-TiO_2) were also synthesized by adjusting amounts of Mg.

2.3. Photocatalytic disinfection experiment

Photocatalytic activity of as-prepared samples was investigated by disinfection of bacteria under a 300 W Xe lamp equipped with a UV cutoff filter (>420 nm). Staphylococcus aureus was selected as typical bacteria for photocatalytic disinfection experiments. Bacterial cells were cultured in LB broth at 37 °C to obtain a cell count of approximate 10^9 colony forming units (CFU)/mL. 20 mg of catalyst was dispersed in 30 mL bacteria suspension solution. 1 mL of sample was taken out then immediately spread on nutrient agar plates and incubated at 37 °C for 24 h to determine the number of viable cells.

2.4. Photocatalytic degradation experiment

Photocatalytic performance of as-prepared samples was investigated by degrading of Rhodamine B (RhB) under a Xe lamp equipped with a UV cutoff filter ($\lambda > 420$ nm). Prior to irradiation, 30 mg of catalyst was dispersed in RhB solution (100 mL, 5 mg/L) under magnetic stir for 30 min to guarantee adsorption-desorption equilibrium between photocatalysts and RhB. During irradiation, 5 mL of susp ension was taken out and centrifugated at intervals of 30 min. Concentrations of dye were calculated by UV–vis absorption using a TU-1901 spectrophotometer.

3. Results and discussion

3.1. Morphology characteristics

Morphology of four catalysts is presented in Fig. 1g–l. As can be observed in 1 g, TiO_2 shows irregular bulk structure and the size of bulks ranges from 60 to 70 μm. While microstructure of TiO_2 IO obtained through sacrifice template method is quite different. Fig. 1i and j present SEM images of three-dimensional PS colloidal crystal template, which arranges as multilayer PS microspheres, and the array between layers is arranged orderly, as well as tightly. In order to determine optimal calcination temperature for removal of colloidal crystal template, TG-DTA curves are examined. As shown in Fig. S1, three obvious weight losses can be seen in temperature range of room temperature to 280 °C, 280–410 °C and 410–520 °C, all of them are exothermic. In TG curve, PS colloidal crystal can be cleared away at about 520 °C, thus calcination temperature is selected at 550 °C. After annealing, IOs replica of ordered array spheres is formed. In Figs. 1k and S2a-b, the obtained catalysts exhibit honeycomb-like structure, which has unique 3D ordered porous framework with center-to-center distance of about 200 nm. This inverse opal structure has periodic modulations of light propagation, which would strengthen light absorption of materials and further improve their photocatalytic activity. Besides, the size of honeycomb ranges from 6 to 10 μm, much smaller than that (60–70 μm) of bulk samples. Small crystallite size can result in a large surface area with many active sites, which could facilitate organic pollutant access, adsorption and decomposition. Therefore, honeycomb-like TiO_2 is expected to exhibit outstanding photocatalytic performance. When Mg^{2+} is introduced, it is clearly seen that Mg dopant could not significantly affect morphology of Mg-TiO_2 (Figs. 1k and S2c-d). Besides, SEM images of Mg-doped TiO_2 IOPCs with different Mg contents were also investigated. As shown in Fig. S3, honeycomb-like morphology is also maintained for samples with high Mg content.

3.2. Crystal structure analysis

Phase structure of as-prepared samples was analyzed by XRD patterns. In Fig. 2a and c, it can be observed that good crystal is obtained for TiO_2 bulk and TiO_2 honeycomb, diffraction peaks