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Preparation of homogeneous nitrogen-doped mesoporous TiO_2 spheres with enhanced visible-light photocatalysis

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ABSTRACT

A series of mesoporous TiO_2 spheres of nanosized crystals with high monodispersity and dimensional homogeneity are synthesized by a simple reflux method. In order to improve the visible light response and to further narrow the band bap of TiO_2 sphere, nitrogen is used as the dopant in a hydrothermal method. Different from the traditional nitrogen doping in TiO_2 solid sphere, the nitrogen is uniformly distributed from bulk to the surface of mesoporous TiO_2 sphere, which is beneficial to the generation of the successive energy bands inside the TiO_2 band gap. Interestingly, the XPS results indicate that the nitrogen doping concentration could reach 1.31% (only 0.17% for nitrogen doped solid TiO_2 sphere), owing to the homogeneous doping in the mesoporous TiO_2 spheres. The nitrogen doped TiO_2 spheres exhibit such excellent characteristics as high specific area, relatively small particle size, pure anatase phase and excellent UV–vis absorption capacity in the range of 400–800 nm, which are all beneficial to the photodegradation of Rhodamine B under the visible light irradiation. The high photocatalytic activity could be ascribed to the homogeneous nitrogen doping on the deep adjustment of energy band of TiO_2 sphere from the bulk to the surface.

1. Introduction

Titanium dioxide (TiO_2) has been known as one of the most promising photocatalytic materials and attracted much attention due to its good stability, nontoxicity, high efficiency and low cost [1–3]. However, TiO_2 with the wide band gap ($E_g = 3.2$ eV) can only absorb the near-UV light ($\lambda < 380$ nm)[4], which greatly limits its practical applications. In order to overcome this shortcoming, the appropriate modifications such as non-metal doping and metal doping are essential for TiO_2 to make maximum use of the visible-light region of sun. In the past few years, plenty of researches have been reported that doping TiO_2 with non-metal elements, such as carbon, boron, fluorine and nitrogen demonstrated enhanced visible light photocatalytic activities [5–8]. Among them, nitrogen doping has been proved to be a simple and effective method to attain visible-light photocatalysis [9]. However, most of studies on nitrogen doped TiO_2 considered that the nitrogen doping is only a surface or sub-surface modification and difficult to narrow the band gap in the bulk of TiO_2, thus, it could only improve the visible light absorption in the range of 400–600 nm. It is really difficult to achieve the absorption in the wider region of 400–800 nm only by the heterogeneous nitrogen doping.

In addition to focus on the improvement of visible light absorption, more and more researchers paid attention to the modification of microstructure of TiO_2, such as the TiO_2 with mesoporous structure. Both high specific surface area and porous frameworks are important characteristics of mesoporous TiO_2, which may exhibit large pore volume or large pore diameter [10] and are beneficial to such applications as photocatalytic activity or electrochemical activity. For example, Hao et al. [11] prepared mesoporous titania powders with a bicrystalline (anatase and brookite) framework by a modified sol–gel method. The as-prepared sample showed high photocatalytic activity to degrade Rhodamine B (RhB), which was attributed to the porous structure and large surface area. In addition, Zhou et al. [12] synthesized anatase TiO_2 with mesoporous structure by a unique hydrothermal process, applied in Lithium-based storage devices as an electrode material. Due to its large active surface area, the sample would allow for the use of high electrochemical reaction rates and is of great importance in battery applications.

Therefore, we can make out that the formation of mesoporous structure could improve the performance of TiO_2. Beyond that, the changing of morphology of TiO_2 is also an effective means to

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adjust the characteristics of TiO_2 [13,14]. There are various TiO_2 nanostructures reported, like nanotubes [15], nanoparticles (NPs) [16], nanowires [17], nanosheets [18] and so on. Particularly, three-dimensional (3D) TiO_2 sphere has attracted great interest because of its wide applications in photocatalysis and energy conversion [19,20]. However, the general TiO_2 powder or TiO_2 sphere still faces such difficulties as aggregation, uncontrolled size and low uniformity and so on. For example, Grosso et al. [21] adopted a one-step method combined with sol–gel chemistry to prepare nanocrystalline transition metal oxide spheres with controlled multi-scale porosity. It can be observed from TEM images that the TiO_2 spheres have poor dispersibility and the sizes are messy, which greatly limit their wide applications. The irregular morphology and lower surface area of powder TiO_2 always lead to the heterogeneous and low doping concentration of impurities in the bulk of TiO_2.

Apart from the physical improvements, hitherto, some researches about mesoporous TiO_2 spheres with nitrogen doping have been reported. Wu et al. [22] prepared visible-light-responsive nitrogen doped TiO_2 hollow spheres by acid-catalyzed hydrolysis using carbon spheres as a hard template and urea as a nitrogen source. Jung et al.[23] synthesized spherical pure anatase TiO_2 spheres with a mesoporous structure and high surface area of 116.5 m^2/g by a simple urea-assisted hydrothermal process. The sample was applied as dye-sensitized solar-cell electrodes and achieved 7.54% of conversion efficiency. However, the nanoparticles prepared above tended to be huddled together and presented irregular shapes, so the nitrogen sources are really difficult to enter into the bulk of TiO_2 spheres. Thus in order to improve the photocatalytic activity of TiO_2, these issues should be addressed wisely and need an appropriate strategy.

Above all, it will be of great significance to have perfect control over the physical or chemical properties if the morphology and chemical composition of the porous material with a nanometre scale could be manipulated well. Therefore, in this work, a series of mesoporous TiO_2 spheres with high monodispersity and dimensional homogeneity are synthesized. Owing to the unique spherical structure consisted of nanocrystals, uniform pore size distribution and high surface area, further nitrogen doping modification can achieve a homogeneous doping and produce uniform and high concentration of nitrogen, which is expected to narrow the band gap of TiO_2 sphere from bulk to surface and enhance the photocatalytic activity of TiO_2 under the visible light irradiation for the degradation of RhB.

2. Experimental

2.1. Preparation of mesoporous titanium dioxide spheres

Mesoporous TiO_2 spheres were synthesized via a modified sol–gel method with polyvinylpyrrolidone (PVP) as dispersant and $Ti(SO_4)_2$ as Ti precursor. Besides, dodecyltrimethylammonium bromide (CTAB) was added as a sort of soft template or pore-forming agent. In a typical process, 2 g of $Ti(SO_4)_2$ or 2 g of PVP with 0.4 g of CTAB was dissolved into a mixture of certain amount of n-propanol and deionized water, respectively. The obtained two solutions were blended together and stirred for 15 min at room temperature. Subsequently, the transparent mixture was heated to 70 °C and kept for another 2 h. After it cooled to the ambient temperature naturally, the precipitates were collected through vacuum filtering, and washed for several times with deionized water and ethanol, then dried overnight at 80 °C. Up to this step, the obtained sample was marked as TiO_2 precursor. Finally, the precursor was calcined at 400 °C for 2 h with a heating rate of 1 °C/min to be mesoporous TiO_2 spheres, denoted as m-TiO_2.

By contrast, the pure TiO_2 solid sphere as control sample was achieved in the absence of CTAB and denoted as p-TiO_2.

2.2. Preparation of nitrogen doped mesoporous titanium dioxide spheres

To prepare nitrogen doped mesoporous TiO_2 spheres, ammonia was adopted as the nitrogen source in a hydrothermal process. The detailed procedure was as follows: 0.2 g of TiO_2 precursor was added into a mixture of 8 mL deionized water and 12 mL of ethanol in a cylindrical vessel. Then a certain amount of ammonia was put into the suspension under stirring and the mixture was stirred for 2 h to get a uniform solution. Subsequently, the mixed solution was transferred into a 50 mL Teflon-lined autoclave and kept at 180 °C for 12 h. The product was centrifugated, washed and dried at 80 °C. The final sample was obtained via calcination at 400 °C for 2 h with a 1 °C/min heating rate. The sample of nitrogen doped mesoporous TiO_2 sphere was marked as n-N-TiO_2 where n represents the mole ratio of ammonia to TiO_2, chosen as 2, 1, 0.8, 0.5, 0.2, 0.

By contrast, the solid p-TiO_2 sphere was treated by a same method to prepare the nitrogen doped solid TiO_2 sphere, which was denoted as N-p-TiO_2.

2.3. Characterization

The morphologies were characterized by transmission electron microscopy (TEM, JEM2000EX) and scanning electron microscopy (SEM, JEOL JSM-6360 LV). X-ray diffraction (XRD) measurements were carried with Rigaku Ultima IV (Cu Kα radiation, $\lambda = 1.5406$ Å) in the range of 10–80° (2θ). The instrument, a Perkin-Elmer PHI 5000C ESCA system with Al Kα radiation, was adopted to acquire the data of X-ray photoelectron spectroscopy (XPS). The shift of the binding energy was referred to the C1s level at 284.6 eV as an internal standard. The room-temperature Raman analysis of samples was performed using a inVia Reflex Raman spectrometer with 524.5 nm laser excitation. The X-band electron paramagnetic resonance (EPR) spectra of samples were collected at liquid nitrogen temperature using Bruker EMX-8/2.7 spectrometer. The Brunauer–Emmett–Teller (BET) surface areas of the prepared samples were obtained from N_2 adsorption–desorption isotherms at liquid nitrogen temperature using a Micromeritics ASAP 2020 system. UV–vis absorption spectra were obtained using a scan UV–vis spectrophotometer (Varian Cary 500) equipped with an integrating sphere assembly, while $BaSO_4$ was used as reference.

2.4. Measurement of photocatalytic activity

The photocatalytic activity was evaluated by analyzing the degradation of Rhodamine B (RhB) (10 mg/L) under visible light irradiation. And a 1000 W tungsten halogen lamp equipped with a UV cut-off filter ($\lambda > 420$ nm) was used as a visible light source in the home made photo-reactor, having a wooden box fitted with a quartz jacket containing a water circulation facility to maintain the temperature below 40 °C. 50 mg of as-prepared sample was added into 50 mL of RhB solution in a 100 mL quartz tube and carried out ultrasonic for 1 min. Subsequently, the suspension was stirred in the dark for 1 h to obtain the adsorption–desorption equilibrium on the surface of the catalyst. At given time intervals, about 5 mL of the dispersion was sampled and centrifuged. The filtrates were analyzed by recording variations in the absorption in UV–vis spectra of RhB, using a UV–vis spectrophotometer.

3. Results and discussion

The formation process of nitrogen doped mesoporous TiO_2 spheres can be explained through the schematic illustration shown