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Probing significant light absorption enhancement of titania inverse opal films for highly exalted photocatalytic degradation of dye pollutants

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ABSTRACT

The continuous titania inverse opal (TiO_2-IO) films have been prepared by sol–gel infiltration method and calcined at different temperatures. The morphologies of the TiO_2 inverse opal films remain unchanged under high temperature treatment. XRD patterns reveal an anatase crystalline phase between 550 and 900 °C and a mixture of anatase and rutile phase at 1000 °C. Comparing with the mesoporous TiO_2 films obtained under the same conditions, all the TiO_2 inverse opal films demonstrate a highly enhanced photocatalytic activity in photodegradation of rhodamine B (RhB) as dye pollutant model in aqueous solution. In spite of the fact that the TiO_2 inverse opal films with open macroporous structures and possible light scattering effect of the wavelengths can result in the higher photocatalytic activity in the degradation of the dye pollutant, the phenomenon of the slow photon occurring in the TiO_2 inverse opal photonic crystals can explain the extraordinary enhancement of the photocatalytic activity. In consequence, the TiO_2-IO-700, TiO_2-IO-550 and TiO_2-IO-800 films show the best photocatalytic performance mainly due to the slow photon effect at the light incident angle at 0°, 20° and 45°, respectively, a direct proof of light absorption enhancement due to the slow photon effect. The slow photon effect in TiO_2 inverse opals to enhance light absorption and further to enhance photocatalysis is very important for further potential applications in solar cells and other processes linked to the light absorption.

1. Introduction

During the last decades, TiO_2 has been expected to be the most promising photocatalyst in environmental applications, such as the photodegradation of organic pollutants and the purification of water and air [1–3]. To achieve high photodegradation efficiency of the pollutants, various methods have been carried out to improve the activity of TiO_2 by controlling the morphologies [4], doping anions and cations [5], modification of surface with metals and graphene [6–8] and exposing high surface energy facets [9,10]. TiO_2 aerosol [11–13], meso/nanoporous TiO_2 [14–16] and photonic materials [17–20] have also been used for efficient photodegradation of organic pollutants due to the good mass transport and high surface area.

For the photocatalytic process, it is well known that when a photon with energy of $h\nu$ matches or exceeds the band gap energy (E_g) of the semiconductor, an electron is excited from the valence band to the conduction band, leaving a hole behind. These charge carriers migrate to the surface and react with the chemicals adsorbed on the surface to decompose these chemicals. Generally, the photocatalytic activity of a semiconductor is mainly determined by three factors: the light absorption properties; the light excited charges (electron–hole pairs) transport rate and the electron–hole recombination rates on the surface [1–3]. As mentioned above, a lot of works have been reported on accelerating the electron–hole separation and transport to enhance the photocatalytic activity [21–24]. Most of the previous works on light absorption focused on broadening the absorption of TiO_2 to visible light [25–28]. Another possible way to reinforce the light absorption property, however less explored, is the increase of the path length of light to improve the photocatalytic efficiency, a structure effect other than

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chemical composition effect. Several studies show that the hierarchically macro-mesoporous TiO_2 structures exhibit an important light harvesting effect of the macrochannels allowing light waves to penetrate deeper inside the photocatalyst [29–32]. For example, the efficiency of dye-sensitized solar cells can be improved by increasing the path length of light on these macro-mesoporous structures [33]. Recently, the macroporous TiO_2 inverse opals (TiO_2-IO) have been intensively studied in photocatalysis since this kind of structure can provide easy mass transportation and high surface area because of the hierarchical porous structure resulting in enhanced photocatalytic activity [31,32,38]. However one of the most important properties of macroporous inverse opal materials is less explored. In fact, these structures are photonic crystal structures having a periodic dielectric contrast and can provide an immense potential to increase the path length of light [34–38]. The feature of the photonic crystals (PCs) can allow to modulate the light propagation in the structures. In the length scale of the wavelength of light, light with certain energies is forbidden to propagate in the PCs because of coherent Bragg diffraction. This leads to stop-band reflection (also called photonic band gap, PBG) and the reflected energies (wavelength) depend on the periodic and dielectric contrast of the photonic crystals. At the frequency edges of the stop bands, photons propagate with strongly reduced group velocity in solid matter leading to the slow photon appearance. The slow photons can be observed at the edges (red and blue edges) of any stop band. The frequencies of slow photons can be thus varied depending on the edges frequencies (both at red and blue edges) of the stop bands of the photonic crystal. The location of stop bands, in consequence, the location of the red and blue edges depends on the photonic crystal structures when the chemical composition of two phases forming the photonic crystal structures is defined. This light reflectance and slow photons are generated by a structure effect. With the same chemical composition, by changing the air sphere diameter, the stop band position can be modulated. However, whether these slow photons can be used to enhance the light absorption or not depending on a specific condition: the wavelength of slow photons (at red or blue edge) overlaps with the electronic excitation wavelength (electronic band gap frequency) of semiconducting materials and the applied irradiation light wavelength. When these three wavelengths fall at the same wavelength zone, i.e. the condition cited above is satisfied, an enhancement of the light absorption by these slow photons can be expected and these slow photons will excite electrons of semiconducting materials from valence band to conduction band with the generation of a large number of electron–hole pairs resulting in an enhanced photocatalytic activity [34–38]. If the above condition is not satisfied, i.e. only two of three wavelengths coincide no slow photon enhanced light absorption effect can be observed. For example, if the red or blue edge wavelength of stop band coincides with the irradiation wavelength zone, however the electron excitation wavelength (electron excitation band gap) is located at a different wavelength, no photon at red and blue edges can be used to excite the electron. The occurrence of slow photon effect depend thus also on the irradiation wavelength and electronic band gap of materials. The irradiation wavelength can be easily adjusted following the position of red and blue edges and electronic band gap of materials. The stop band can be tuned by the variation of materials and also by changing the incident angle.

Although the materials containing an inverse opal structure have been previously and largely used in the photocatalysis by different research groups [32], the photocatalysis enhancement is often attributed to porous structure of materials. The slow photon concept in photonic crystals (inverse opals) to enhance light absorption and further to enhance photocatalysis is rarely explored although some papers claimed slow photon effect. Only few papers demonstrated the slow photon effect in photocatalysis enhancement [34]. The application of slow photon concept is a great challenge.

At present, the most typical method in preparation of TiO_2-IO films is based on a three step method: deposition of opals on a substrate by the self-assembly of submicrospheres (silica or polymeric) from a colloidal suspension; then filtration of titanium precursor into the interstitial spaces of the opal; finally removal of the colloidal crystal template by solvent extraction or calcination [39–41]. Although many achievements have been obtained for the TiO_2-IO films preparation, there are seldom reports on the effect of thermal treatment temperatures on the photocatalytic activity of the TiO_2-IO films. Furthermore, it will be interesting to investigate how the slow photon effect happens and influences the photocatalytic activity. In addition, the slow photon effect has been proved only in gas phase photocatalysis, the reaction performed in aqueous solution can render the modulation of slow photon effect more difficult due to the fact that the slow photon effect can become weaker in aqueous environment because of the lower refraction index contrast between TiO_2 wall and the aqueous-filled voids. However, for environmental remediation using photocatalytic technology, the processes occur very often in aqueous solution. Thus how to benefit the slow photon effect of photonic crystals is of great challenge in aqueous environment. Herein, we report the photocatalytic activity of titania inverse opal films calcined at different temperatures in the photodegradation of rhodamine B (RhB) in aqueous solution and correlated with the photonic properties of TiO_2-IO films. An evident slow photon effect on enhancement of the photocatalytic activity has been noted with the light incident angle change.

2. Experimental

2.1. Fabrication of TiO_2-IO films

The TiO_2-IO films were prepared based on the previous work with a slight modification [41]. Briefly, 8 mL of styrene (previously washed 3 times with 2 M NaOH aqueous solution to remove the inhibitor) and 120 mL of water were heated to 70 °C under N_2 atmosphere. $K_2S_2O_8$ (0.07 g) was added to initiate the reaction which was stopped after 3 h by cooling down the container. The polystyrene (PS) spheres opals were obtained on a 4 cm^2 quartz slide (20 mm × 20 mm × 1 mm) by the vertical deposition. The solution was prepared by mixing 100 μL of titanium (IV) isopropoxide (TTIP) in mixture of 10.0 mL anhydrous ethanol and 2 μL hydrochloric acid and then was stirred for 5 min for a fully dispersion of titanium isopropoxide. One droplet of the solution was carefully deposited on the middle of the PS opal. The template was then exposed to air and dried at room temperature for 12 h. The infiltration process was repeated three times in order to increase the filling of the voids. The resulting TiO_2/PS composites were then calcined in air at 300 °C with a ramp rate of 2 °C/min. This temperature was maintained for 2 h and then subsequently raised to 550, 700, 800, 900 or 1000 °C at 2 °C/min, respectively. After 3 h, the thermal treatment process was stop and the oven was cooled down to room temperature. The quartz substrates covered by the TiO_2 inverse opal were characterized. The mesoporous TiO_2 films were prepared by dropping the titanium isopropoxide, ethanol and hydrochloric acid solution on the quartz slide with the same procedure described above.

2.2. Photocatalytic activity measurement

The photocatalytic activities of the TiO_2-IO films and mesoporous TiO_2 films were evaluated by the degradation of a model pollutant basic RhB. The samples were placed at the bottom of a beaker filled with 1×10^{-5} M RhB aqueous solution