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Probing photon localization effect between titania and photonic crystals on enhanced photocatalytic activity of titania film

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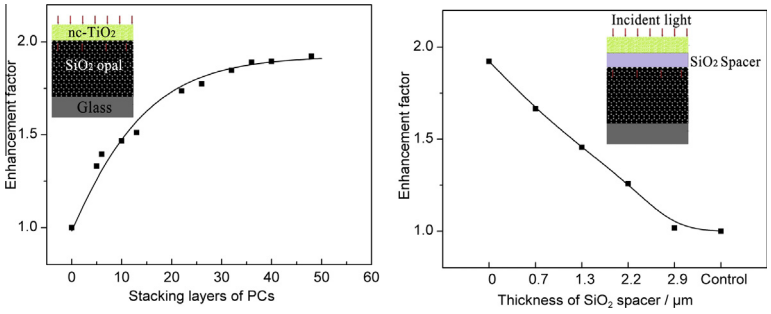
HIGHLIGHTS

- SiO_2 opal instead of inverse opal was applied for its tunable structure parameters.
- TiO_2/SiO_2 opal composite membrane shows improved photocatalytic activity.
- The photocatalytic enhancement factor increased with the SiO_2 opal periodicity.
- The distance between TiO_2 and SiO_2 opal was tuned by thickness of SiO_2 spacer.
- The optimum periodicity and effective confining distance are obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

A systematic study on the photon localization of photonic-crystals (PCs) was conducted with respect to its PCs periodicity and its spatial distribution using the photo-degradation of acetaldehyde on nc-TiO_2/SiO_2 PCs composite films as the probe reaction. The periodicity of SiO_2 PCs layer was tuned by the concentration of silica suspension in vertical deposition. The spatial distribution of photon localization was studied by inserting a SiO_2 spacer with various thicknesses between the SiO_2 PCs and nanocrystalline TiO_2 (nc-TiO_2). It was shown that the photocatalytic enhancement factor increased with the SiO_2 PCs periodicity, indicating that, the more the periodicity of the PCs, the stronger the effect of its photon localization. However, when the PCs periodicity was more than 35, the enhancement factor tends asymptotically to a stationary value. In addition, the photocatalytic activity decreased with the gap distance between the nc-TiO_2 catalytic layer and the PCs layer (i.e. the thickness of the SiO_2 spacer), and when the gap distance is larger than 2.9 μm, the PCs layer cannot enhance the photoactivity of the nc-TiO_2 any longer. The effect of the photon localization of PCs can exist outside the PCs, and weakens with the distance away from the surface of the PCs. This work can offer guidance for the fabrication and application of PCs-based photocatalysts.

1. Introduction

TiO_2 has been regarded as a most useful photocatalytic material due to its high stability and efficiency, low toxicity, low price and availability [1–5]. However, the wide electronic band-gap (EBG = 3.2 eV) of anatase TiO_2 limits its utilization in ultraviolet

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light with wavelength less than 387 nm which occupies just 5% of sunlight [6]. Extensive efforts have been made to enhance the energy harvesting efficiency of TiO_2 [7].

Ever since the concept of photonic crystals (PCs) was proposed by John [8] and Yablonovitch [9], PCs have attracted great interest in wide fields [10,11]. Recently, some studies have shown that the light harvest can be greatly improved when PCs are introduced in photocatalyst and photovoltaic cells.

Since Mallouk and co-workers [12,13] reported a 26% increase of photocurrent by coupling a TiO_2 inverse opal (a kind of PCs) with a dye-sensitized TiO_2 solar cells for the first time, an increasing interest is focused upon the improved solar energy conversion through introducing a PCs in silicon [14–18] or dye-sensitized solar cells (DSSC) [19–21]. It has been demonstrated experimentally [20,22–24] and theoretically [19] that the improved solar energy conversion was ascribed to the enhancement of light harvesting efficiency resulting from the dielectric mirror effect of PCs at frequencies of photonic band gap (PBG) [19–21] and the partial localization of resonant photons within the electrode layer. For the thick inverse opal, usually above 4 μm, would result in the low transparency, long charge transport across the solar cells, and therefore a reduction in open-circuit photovoltage in real operation conditions, some researchers prepared the PCs-based solar cells with the PCs-periodicity less than 20 [25–30]. However the decrease of the periodicity of the PCs will strongly reduce the Bragg reflection intensity of PCs [19,31], and therefore lower the light harvesting enhancement. So it is essential to investigate the optimum PCs periodicity. In this case, the PCs achieves strong enough Bragg reflection while the periodicity is as few as possible. But, by now the research about the effect of PCs periodicity on photon localization was mainly theoretical analysis [24,32].

Besides the PCs periodicity, the confine distance of photon localization in nc-TiO_2 layer is also responsible for the light-harvesting enhancement. However, the various thickness of nc-TiO_2 electrode in previous literatures puts an obstacle on the study of photon localization effect. On the one hand, the nc-TiO_2 layer was mostly up to 3 μm thick, some even to 7.5 μm thick [20], as the number of localized modes within the PBG of PCs rises as the thickness of nc-TiO_2 electrode increases [19]. On the other hand, the thickness of nc-TiO_2 electrode coupled with the PCs was only a few hundreds of nanometers in some works [19,21] to make the best use of the light harvesting enhancement of the PCs owing to a higher light transmission when the incident light first pass through the thinner nc-TiO_2 electrode [26,32]. So far, there is not a systematic study on the effective confining distance of photon localization between nc-TiO_2 and PCs.

The enhanced photocatalytic performance of nc-TiO_2 structured in inverse opal was firstly reported by Ozin research group [33]. Afterwards, a great deal of effort is made to further improve the photocatalytic performance of TiO_2 inverse opal [34–50]. Our research group has constructed a composite membrane by coupling a SnO_2 inverse opal to a nc-TiO_2 layer [51] and systematically studied the effect of PBG on the photocatalytic activity of the composite membrane [52]. And it is known that the PCs periodicity is the key to the photon localization effect of PCs [31,53,54]. However the higher performance can be achieved by structured TiO_2 in inverse opal, the preparation of inverse opal PCs is complex and their structure parameters are hard to control. Therefore no study, to our best knowledge was reported dealing with the effect of PCs photon localization with respect to its PCs periodicity and its spatial distribution. Our work is not to pursue higher performance, but to make a systematic and comprehensive investigation of photon localization effect from PCs on photocatalytic enhancement and to provide guidance for the application of PCs.

The objective of this work is twofold. The first is to demonstrate the effect of PCs periodicity on the intensity of localized photon between the PCs layer and nc-TiO_2 coating layer, and as a result, on the enhancement of photocatalytic activity. The second is to investigate the spatial distribution of the photon localization. Because the structure parameters of opal PCs are well tunable relative to inverse opal PCs and the SiO_2 is photochemically inert, almost transparent in the EBG of TiO_2, SiO_2 opal PCs were used in this work. The PBG of the SiO_2 PCs was designed to match the EBG of anatase TiO_2.

To address the first objective, we prepared nc-TiO_2/SiO_2-PCs composite films through coating an nc-TiO_2 layer on SiO_2 opal PCs with different PCs periodicity and then test their photocatalytic performance. To address the second objective, a SiO_2 spacer with various thicknesses was embedded to produce a different gap distance between the PCs layer and the nc-TiO_2 layer.

2. Experimental

2.1. Materials

Tetraethoxysilane (99%), Ethanol (>99.5%), methanol (>99.5%), hydrochloric acid (36–38%), sulfuric acid (98%), nitric acid (65–68%), acetic acid (99.5%), hydrogen peroxide (>30%), ammonium hydroxide (26–28 wt%), acetaldehyde (40%), and polyethylene glycol 2000 were purchased from the Beijing Chemical Factory, China. Titanium isopropoxide were purchased from Aldrich. Ludox AS-40 silica gel was purchased from Du Pont, with SiO_2 content of 41.8%, SiO_2 average diameter of 31.62 nm, and relative standard deviation of diameter of 15% determined by transmission electron microscopy. All chemicals were of analytical grade. Tetraethoxysilane was freshly distilled before use and other chemicals were used without further purification. Double-distilled water was used in all the experiments. Glass slides ($75 \times 25 \times 1$ mm) were cleaved into four pieces along the long sides and used as substrates. Prior to use, the glass slides were soaked in a Piranha cleaning solution overnight (a Piranha solution containing 30% hydrogen peroxide and 70% sulfuric acid (volume fraction)), then sonicated for 30 min in water and for 30 min in ethanol in an ultrasonic bath of 40 kHz and 600 W. After that, the substrates were rinsed with water, and then dried in air.

2.2. Preparation of SiO_2 opal layer

The SiO_2 microspheres were synthesized by the seed particle growth method using Ludox AS-40 silica gel as seeds, as reported in detail previously [55]. A typical process was as follows: one methanol solution containing tetraethoxysilane (TEOS) and another methanol solution containing ammonium hydroxide and water were simultaneously dropped into the methanol solution containing water, ammonia and seeds at 35 °C and under stirring condition at 200 rpm. After the SiO_2 seeds grew to desired size, stop adding the reagents, and recover the monodisperse SiO_2 microspheres (the grown SiO_2 seeds) through centrifugation. The microspheres diameter was measured to be 188 nm with the polydispersity below 0.5% with an equipment of Malvern Zetasizer Nano Series.

SiO_2 opal layer was fabricated via vertical deposition technique developed by Jiang et al. [53], because of its ease controllability. First the silica microspheres were dispersed into ethanol and put into a cylindrical vial, the height and the diameter of which were 160 mm and 20 mm respectively. Then a clean glass slide ($18 \times 25 \times 1$ mm) was vertically immersed into the cylindrical vial. The vial was kept at 46 °C in a temperature-controlled oven for 4 days. The SiO_2 microspheres in the suspension deposited on the vertical slide to form a SiO_2 opal layer as ethanol evaporated. The thickness of the SiO_2 opal layer can be controlled by changing