



Surface plasmon resonance of gold nanocrystals coupled with slow-photon-effect of biomorphic TiO₂ photonic crystals for enhanced photocatalysis under visible-light



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ABSTRACT

The slow photon effect in a photonic crystal (PC) can lead to delay and storage of light in the PC and has an immense potential for improving solar-to-energy efficiency. A series of biomorphic TiO₂ photonic crystal (TiO₂-BMPC) structures are fabricated through a sol-gel method by using butterfly wings as templates, and subsequently gold nanoparticles (Au NPs) with an average size of about 9 nm are deposited *in situ* into the TiO₂-BMPC. Varying structural characteristics of the PCs by choosing different butterfly wings, the slow photon region of the photonic band gap could be purposely tuned to overlap with strong localized surface plasmon resonance (SPR) region of the Au NPs. The matching slow photon of the TiO₂-BMPC templated from the butterfly wings of *Euploea mulciber* intensifies the SPR responses (central at 550 nm) of the Au NPs. Consequently, the visible-light harvesting capability of the Au/TiO₂-BMPC is significantly improved due to this unique biomorphic architecture. As a result, the designed photocatalyst exhibits a photocatalytic activity that is several time higher than conventional Au/TiO₂-P25 material, as illustrated by the example of the photocatalytic decomposition of methyl orange (MO) under visible-light illumination.

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1. Introduction

Photolysis of organic contaminants is one of the most promising strategies for solving environmental problems. Among many photocatalysts developed to date, titanium dioxide (TiO₂) has been considered as the most suitable candidate for photocatalysis, thanks to its remarkable nontoxicity, photostability, and low cost [1]. However, due to its large band gap (i.e., 3.2 eV for anatase and 3.0 eV for rutile), pure TiO₂ can only be active in the ultraviolet (UV) that accounts for only ~4% of the entire solar spectrum, and thus has low solar-to-energy efficiency [2,3]. Therefore, great efforts have been done to expand the TiO₂ optical absorption spectrum into the visible region [4], accounting for about 43% of the total energy, including doping TiO₂ with metallic or non-metallic elements [5], and sensitizing TiO₂ with a second photoactive component [6], such as dyes [7], or quantum dots of narrow-band-gap semiconductor

[8]. Although these approaches can partly improve the photocatalysis efficiency of TiO₂, their effectiveness are sometimes limited by either limited contribution of TiO₂ or much reduced electron-hole separation.

Recently, a strategy for enhancing the visible-light photo activity of TiO₂ by the surface plasmon resonance (SPR) of some noble metals, especially gold (Au), have been attracting much attention [9,10]. Under visible-light illumination, SPR induces light absorption and subsequent transfer of hot electrons from noble-metal nanocrystals to the conduction band of the semiconductors in contact [11]. However, the photocatalysis efficiency in visible region still remain unsatisfactory, because the SPR intensity is not enough and mainly relies on noble metals, receiving no assistance from TiO₂ matrix due to its little capability of light harvesting under visible-light [12,13].

Photonic crystal (PC) structure is composed of periodically repeating regions of high and low dielectric constant, which can affect electromagnetic wave propagation by defining photonic-stop-band (PGB) [14]. Slow photons (i.e., photons that propagate with a reduced group velocity) could be observed in a PC at a frequency near the PGB edge due to the strong interaction of light with the periodic dielectric structure [15]. On the other hand, the SPR of plasmonic metal nanostructures usually exhibit a strong

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optical absorption at a specific wavelength related to their size, composition and shape [11]. Thus, significant improvement on light harvesting in visible region will be achieved in TiO₂ PC coupled with plasmonic noble metal nanocrystals in condition that SPR wavelength overlaps with the slow photon wavelength. As a consequence, several Au/TiO₂-PC composite systems have been developed for photolysis of organic molecules and solar water splitting. Dinh et al. fabricated three dimensional ordered assembly of thin-shell Au/TiO₂ hollow nanospheres (Au/TiO₂-3DHNSs), which exhibited a good performance on photocatalytic degradation of isopropanol under visible-light illumination [16]. Zhang et al. reported improved photoelectrochemical water splitting efficiency in the visible-light region in Au/TiO₂-PC system [17]. In these successful examples, the PC structures investigated are exclusively of inverse opal type. Although these photonic structures can be tuned during the fabrication process [18], it sometimes remains little room for improving upon existing band-gap sizes, due to their single structures with few tunable parameters [19]. Moreover, there are highly strict requirements for sizes or shapes of the materials during the whole synthesis process [14].

In fact, biological systems in nature offer an astonishing variety of species with PC structures [20,21]. In contrast to the inverse opal PC that can be described by strict symmetry and is extremely sensitive to structural disorder that often degrading performance, biological photonic structures are less ordered in a certain extent but still possess multiple structural colors, which indicates a higher tolerance of structure defect and thus less strict demand on structure when fabricating the materials [22]. These advantages of biological photonic structures offer a new way in photonic structure research [23]. In recent years, our group have systematically investigated the fabrications of biomorphic structures that templated from natural species and their applications in light-driven energy conversion and storage [13,24–35]. However, coupling biomorphic PC-based materials with plasmonic nanostructures to synergistically enhance photocatalysis efficiency under visible-light has never been tried before. The strategy, if proven workable, would not only enhance the photocatalysis performance of Au/TiO₂, but also enrich the investigated system for visible-light-driven photolysis by coupling plasmonic nanostructures with PC-based materials.

Herein, we report on a novel Au/TiO₂-BMPC nanostructured photocatalyst that is templated from a butterfly wing called *Euploea mulciber* by a sol-gel method. The slow photon region of the TiO₂-BMPC is purposely tuned to overlap with strong localized surface plasmon resonance (SPR) region of *in situ* deposited Au NPs. The visible-light harvesting capability of the Au/TiO₂-BMPC is significantly improved due to this unique biomorphic architecture. The photocatalytic activity of obtained Au/TiO₂-BMPC is also investigated by degradation of methyl orange (MO).

2. Experimental

2.1. Synthesis of TiO₂-BMPC

The butterfly wings used in this work are fore wings of *E. mulciber*, *Thaumantis diores* and *Kallima inachus* butterflies, which were purchased from a butterfly garden in Shanghai. The fore wings were immersed thoroughly into anhydrous ethanol for 10 min and dried in air for half an hour. Then the wings were pretreated with 8% NaOH for 1.5 h at a constant temperature of 50 °C. Titanium sulfate (40 g) was dissolved in the ethanol/water system (50 ml) with volume ratio of 3:2. An appropriate amount of nonionic surfactant Triton X100 (2 ml) was also added to this solution. Then the mixture was stirred at 60 °C for 1 h to obtain the Ti-precursor solution [27]. The pretreated butterfly wings were dipped thoroughly into the Ti-precursor solution and maintained at constant 60 °C for 14 h.

Then the immersed wings were rinsed by anhydrous ethanol for 3 times and dried for 2 h at 50 °C. Finally, the dried wings were calcined in air at 500 °C to remove the organic template and crystallize TiO₂. The obtained sample was denoted as TiO₂-BMPC.

2.2. Synthesis of Au/TiO₂-BMPC

A solution of 10 ml HAuCl₄ (24.3 mM) was added into 200 ml H₂O, and the pH of the solution was adjusted to 6.0 with NaOH aqueous solution. The obtained TiO₂-BMPC samples were re-dispersed in the solution. In order to let Au particles fully deposit, the resulting mixture was stewed for 12 h and then stirred for 1 h at 70 °C. After that, the mixture was centrifuged with the speed of 3000 rpm for 10 min to separate the precipitate from the solution, and was washed with distilled water for 3 times. After being dried at 50 °C for 1 h, the precipitate was calcined at 400 °C for 2 h with the rate of 1 °C min⁻¹ per minute. The final sample was denoted as Au/TiO₂-BMPC.

2.3. Characterizations

X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker-AXS instrument with Cu K α radiation ($\lambda = 0.15406$ nm). Field emission scanning electron microscopy (FESEM) images were obtained on a FEI Sirion 200 field-emission scanning electron microscope. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) images were obtained on a JEOL JEM-2100F TEM. The specific surface area and pore-size distribution were evaluated by nitrogen adsorption analyzer at -196 °C. X-ray photoelectron spectroscopy (XPS) measurements carried out on a Thermo ESCALAB spectrometer with monochromatized Al K α X-rays ($h\nu = 1486.6$ eV) at a pass energy of 20 eV. The UV-vis spectra were recorded on an Olympus BX43 microscope coupled with NOVA spectrometer and ARM analyzer device (Shanghai Fuxiang Inc.). A small piece of aluminium mirror was used as a reference plane to calibrate the 100% reflectance and 0% reflectance.

2.4. Photocatalytic degradation of methyl orange (MO)

The photocatalytic degradation of methyl orange (MO) activity was assessed in an aqueous solution using a water-cooled quartz triangle conical flask. The as-prepared samples (20 mg) was dispersed in 20 ml of 10 mg/l MO aqueous solution, under magnetic stirring in the dark for 0.5 h to establish an adsorption-desorption equilibrium of MO on the surface of the material. The reaction system was then subject to visible light irradiation by a 300 W Xe lamp ($\lambda > 420$ nm). A series of aqueous solution samples were collected at every 40 min. These sample solutions were centrifuged and then the supernatants were tested using a 25 Lambda UV-vis spectrometer to get the absorption spectra. The extent of degradation is calculated as $D_e = (C_0 - C)/C_0 \times 100\%$. Here, C_0 is the initial concentration and C is the concentration after degradation time t .

3. Results and discussion

3.1. Characterization of TiO₂-BMPC and contrast samples

As shown in Fig. 1a, the wings of *E. mulciber* are about 6–8 cm in length, and the fore wings appear blue, which is identified as structural color resulting from periodic structures. The blue forewings consist of many scales of 100 μ m in length and 50 μ m in width (Fig. 1b). The fine structure of each blue scale is shown in Fig. 1c. The periodic region includes longitudinal ridges arrays on the scale. Between the parallel aligned ridges, there are horizontal struts that

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