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Short Communication

# Enhanced photoactivities of $TiO_2$ particles induced by bio-inspired micro-nanoscale substrate

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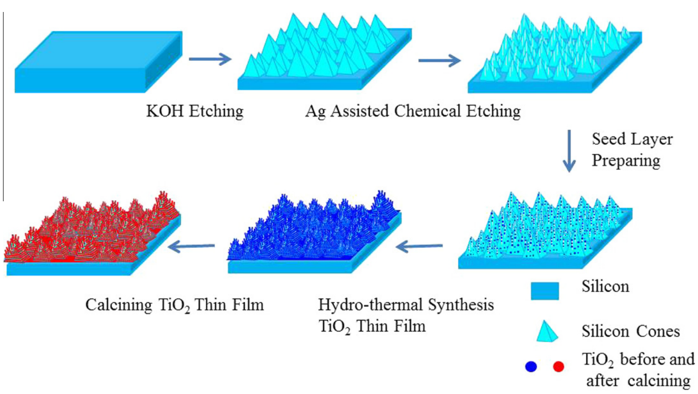
## GRAPHICAL ABSTRACT

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## ABSTRACT

A silicon substrate with bio-inspired micro-nanoscale structure has been fabricated by wet etching, which is used as $TiO_2$ particles supporting substrate and makes them recovery more easily. It has been shown that the structure facilitates $TiO_2$ with large surface area and suppresses light reflection more effectively, which results in a high photocatalytic performance. The photocatalytic and stable performance has been applied on degrading methyl orange (MO).



## 1. Introduction

Photocatalysis is a promising technology for the conversion of solar energy into chemical energy in an environmentally friendly way [1–4]. To date, a wide variety of semiconductors have been studied as photocatalysts such as $TiO_2$ [5], $WO_3$ [6], CdS [7], $SrTiO_3$ [8], $C_3N_4$ [9] and metal–organic framework (MOF) based materials [10]. Since 1972, Fujishima and Honda successfully used $TiO_2$ as electrode to split water, $TiO_2$ has drawn much attention due to its high photoreactivity, good stability with time, low cost, and environmentally friendly nature [11,12].

However, one limitation of $TiO_2$-based particles is its 3.2 eV bandgap, which allows only UV light to be absorbed. To harvest more incident light and improve solar energy conversion efficiency, much effort has been done in both physical and chemical ways. In physical ways, researchers have revealed that well-designed nanostructures can trap photons and force them to

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propagate more effectively through $TiO_2$, which results in more efficient light absorption, such as multi-reflection effect in semi-hollow $TiO_2$ spheres and slow-light effect in period $TiO_2$ photonic crystals [13,14]. The utilization of localized surface enhanced plasmon resonance (LSPR) enables $TiO_2$ to absorb visible light [15,16]. In chemical ways, doping could narrow the bandgap of $TiO_2$, which is responsible for the red-shifted and increases light-absorption [17]. Introducing disorder on the surface of nanophase $TiO_2$ by hydrogenation (called "black $TiO_2$") can create stable mid-gap states, which drastically makes light absorption shifted from the UV region to the near-infrared [18]. Another crucial limitation of the $TiO_2$-based particles is recovery and reusability [19]. During the photocatalytic degradation process, $TiO_2$ particles may undergo coagulation due to the instability of the nanosized particles, which will hamper the light incidence on the active centers and consequently reduce its catalytic activity [20]. The intense effort has been devoted to loading $TiO_2$ on different supports in order to increase the illuminated specific catalyst area and light adsorption capacity [21].

In this paper, we fabricate $TiO_2$ nanoparticles on a silicon substrate with bio-inspired micro-nanoscale structures, which is used to suppress light reflection and enhance the light absorption of $TiO_2$. $TiO_2$ nanoparticles are connected to the structures by a seed layer and then synthesized by a hydro-thermal method. The photocatalysis performance of $TiO_2$ has been applied on degrading MO.

## 2. Results and discussion

Since the corneas of nocturnal-moth eyes were found to have antireflective properties, periodic sub-wavelength architectures, called the antireflective structures, have a graded transition of refractive index, enabling minimal reflection over a broad range of wavelengths and angles of incidence [22]. Inspired by the marriage of eyes of moths, a silicon substrate with micro-nanoscale structure has been fabricated by wet etching in this paper, which has the antireflective properties and been used as $TiO_2$ particles supporting substrate. The fabrication procedure of $TiO_2$ on bio-inspired micro-nanoscale silicon structures has been shown in Fig. 1. Firstly, pyramidal structures are fabricated on the silicon surface by anisotropic etching in KOH solution. Then, silver nanoparticles (about 100 nm in diameter) were electroless deposited on the micrometer-sized pyramidal surfaces. Bio-inspired micro-nanoscale structure is generated after a silver catalytic etching step. Secondly, a seed layer is prepared by immersing the substrates into titanium tetrachloride, followed by rinsing with deionized water. Finally, $TiO_2$ particles are synthesized on substrates by a hydro-thermal method and calcined at 500 °C for 2 h.

Photocatalytic redox reactions take place on the surface of $TiO_2$ particles, which means that more surface area offers more redox reaction place. Surface area of $TiO_2$ depends on the size of particle and micro structure surface. Fig. 2 shows a set of scanning electron microscope (SEM) images of $TiO_2$ particles on different substrates. From the images in Fig. 2, we can see that the size of the particles is almost the same. But the redox reaction surface area is gradually increasing with different structures from Fig. 2b–d. This is mainly because more complexity morphology can allow more $TiO_2$ particles growing on its profile. Hence, the good photocatalytic performance on bio-inspired micro-nanoscale structure could be attributed to the more complexity morphology [23].

The X-ray diffraction (XRD) patterns of $TiO_2$ particles on different substrates are shown in Fig. 3. The crystalline diffraction peaks of bare silicon substrate is shown at $2\theta = 54°$. All of the other diffraction peaks match well with the crystal structure of the anatase $TiO_2$ phase [24]. Moreover, it can be seen that, with more complexity structure fabricated, the XRD peak intensities of anatase become steadily stronger. Even another two anatase diffraction peak (004) and (200) appears when $TiO_2$ is fabricated on bio-inspired micro-nanoscale silicon substrate.

The antireflective property is characterized by the reflection measurement shown in Fig. 3. The diffuse reflectivity measurements indicate that up to 32% of the incident light is reflected on the bare silicon wafer (see black line in Fig. 4). After a thin film $TiO_2$ layer grown on the bare silicon substrate, only 7% of the incident light is reflected at the wave length 260 nm (see red line in Fig. 4). However, the reflective light gradient rises with wave length increasing. This is because $TiO_2$ thin film acts as an intermediate coating utilized to suppress undesired Fresnel reflection at the short wavelength [25]. For longer wave length, the coating layer doesn't work anymore, so the incident light reflectance is as the same as bare silicon. According to effective medium theory, the antireflectance is better on silicon substrate with pyramidal structure than bare silicon, and much better on silicon substrate with micro-nanoscale structure. The antireflective properties could be obtained without any difference after $TiO_2$ thin film grew on the structures as shown in Fig. 4. (The blue line is corresponding to $TiO_2$–p-Si. The pink line is corresponding to $TiO_2$–m-Si.) The antireflective properties of $TiO_2$–m-Si have been supressed much more than $TiO_2$–p-Si at UV wave length from 250 nm to 400 nm, which could result in more efficient UV light absorption. This result matches well with the degradation of MO in Fig. 5.

The evolution of the degradation processes with and without the assistance of the micro-nanoscale structures has been com-

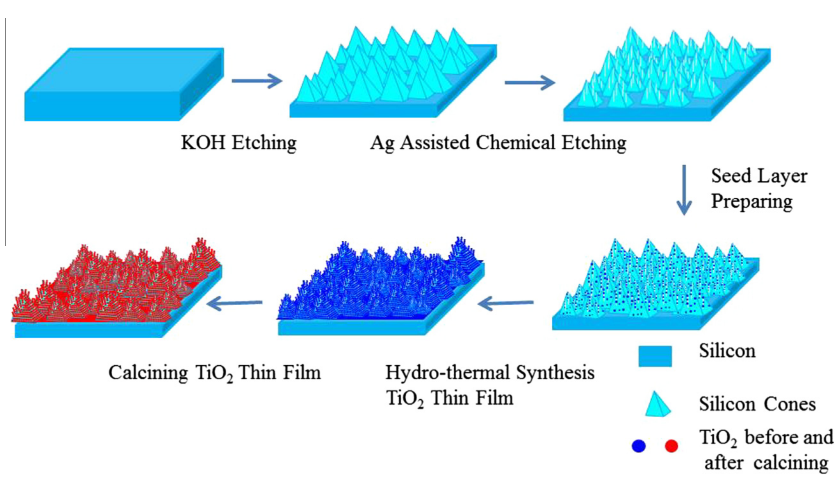


**Fig. 1.** Schematic representation of the fabrication process of $TiO_2$ particles on bio-inspired micro–nanoscale silicon substrate.