



Hydrothermal growth of nanorod arrays and in situ conversion to nanotube arrays for highly efficient Ag-sensitized photocatalyst



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ABSTRACT

TiO₂ nanorod arrays (NRAs) were hydrothermally grown on transparent fluorine-doped tin oxide (FTO) substrates, and were converted into nanotubes (NTAs) by hydrothermally in situ etching. Ag nanoparticles (NPLs) were sensitized on the NRAs and NTAs by a simple photodeposition approach (products were denoted as Ag-TiO₂ NRAs and NTAs). The Ag-TiO₂ NTAs samples possessed a large specific surface area (116 m² g⁻¹) with Ag NPLs homogeneously dispersed among the TiO₂ NTAs. The Ag-TiO₂ NTAs exhibited significantly enhanced photocatalytic activities (98.8%) in degradation of methyl orange (MO) compared to Ag-TiO₂ NRAs (92.6%), TiO₂ NTAs (86.2%), and NRAs (81.7%). The enhanced photocatalytic activities can be attributed to the large specific surface area of TiO₂ NTAs and strong surface plasmon resonance (SPR) of Ag NPLs. In addition, Ag-TiO₂ NTAs showed easy recovery feature in the recovery process and high durability in the recycling test, which was expected to be an efficient and practical photocatalyst used for waste water treatment.

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1. Introduction

Titanium dioxide (TiO₂) nanoarrays have attracted great interest due to their unique optical and electronic properties, which can be applied in water splitting [1], optical sensors [2], solar cells [3], and other applications [4–7]. However, the large band gap of TiO₂ (3.2 eV) and its high recombination rate limit the photoresponse spectral range and the practical efficiency of TiO₂ as a photocatalyst. Various attempts, such as metal doping [8], nonmetal doping [9], and surface modification with semiconductors [10], have been proposed to circumvent these problems. Sensitizing TiO₂ nanoarrays with noble metals was found to be the most effective way to improve the photocatalytic efficiency. During this process, photo-generated electrons migrate to the metals nanoparticles, and the nanoparticles become effective capture traps for photo-generated electrons, in return suppressing the recombination of electrons and holes [11].

In addition, the surface plasmon resonance (SPR) of noble metals is able to absorb visible light, in which increase the

utilization ratio of solar energy [12]. Although many metals have been proposed for this purpose, silver (Ag) remains a primary choice due to its relatively high stability against oxidation and significantly lower cost compared with other noble metals [13–15]. Ag sensitization together with the unique advantages of nanoarrays may synergistically enhance the photocatalytic activity of TiO₂ photocatalysts. As a consequence, some studies have investigated combining TiO₂ and Ag. Recently, Bodson et al., prepared P-Ag-codoped TiO₂, in which the enhanced photoactivity was obtained under visible light [16]. Yang et al. showed that Ag-modified TiO₂ nanosheet can achieve enhanced photoelectrochemical properties compared to bare TiO₂ [17]. In addition, Zhang et al. reported hierarchical nanoarchitecture of Ag/CuO/TiO₂ nanotube array, which exhibited excellent stability and reliability for degradation of organic pollutant [18]. It is generally agreed that the photocatalytic efficiency of films consisting of Ag/TiO₂ heterostructures is higher than that of bare TiO₂ films.

Common methods for TiO₂ synthesis include the Sol-gel method, chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD), and template assisted routes [19]. The hydrothermal synthesis method is a low temperature method that produces nanorod arrays with good dispersibility, small

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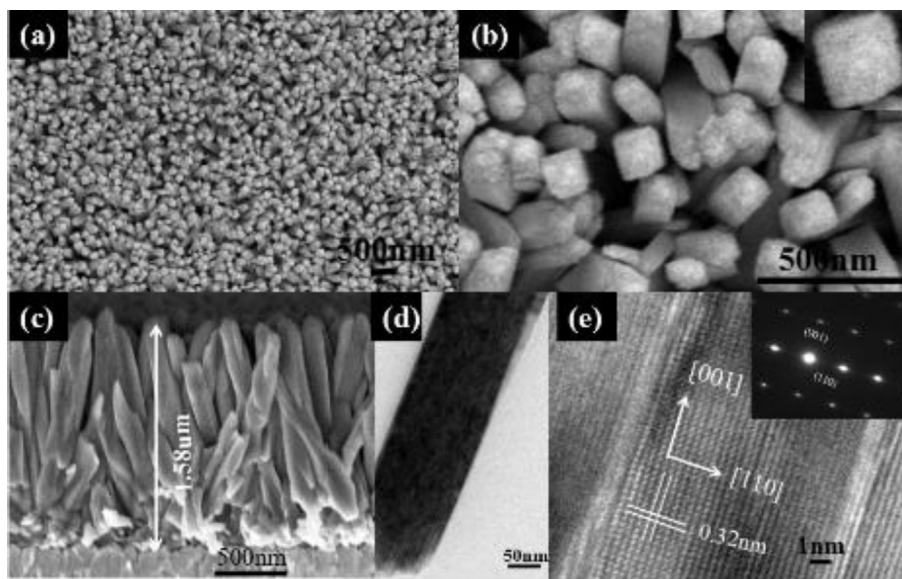


Fig. 1. SEM and TEM images of TiO₂ NRAs. (a) low- and (b) higher magnification SEM images (inset is close observation of a typical TiO₂ NRAs), (c) cross-sectional view SEM image, (d) TEM and (e) HRTEM images (inset is the SAED pattern).

particle size and uniform distribution [20,21]. The in situ transformation of inorganic crystal shape and composition has been widely studied by material scientists as an effective synthetic means to obtain a variety of crystalline materials [22,23]. The majority of the reported crystal transformation approaches is based on sacrificial mechanisms [24,25]. These sacrificial approaches are achieved by removing certain structural components of the precursor material structures [26]. Crystal growth is known to be strongly influenced by the surrounding chemical environment, particularly the environment at the growing crystal surface and interface. The Cl⁻ ion in the hydrothermal solutions has been shown to restrict the growth of (110) faces of TiO₂ nanorod arrays while promoting the growth along the [001] direction [27–29]. Therefore, the crystal structure transformation of TiO₂ from nanorod to nanotube arrays can be realized by selectively etching the core, while remaining the sidewall of (110) face via an in situ sacrificial mechanism with hydrochloric acid under hydrothermal conditions. Ag nanoparticles may be loaded on the surface of TiO₂ by several different techniques, including radio frequency (RF) sputtering [30], electrostatic force directed assembly (ESFDA) [31], and hydrothermal methods [32]. Nevertheless, through these methods, since most Ag nanoparticles were located on the surface of TiO₂, the surface area of TiO₂ exposed to illumination, as well as the interface between Ag and TiO₂ were reduced. A more effective strategy would be to produce Ag-TiO₂ nanostructures directly through photodeposition. The density of Ag nanoparticles can be easily controlled by adjusting the concentrations of Ag and deposition times [33].

In this paper, the growth and in situ transformation of TiO₂ nanorod and nanotube arrays were evaluated under hydrochloric acid hydrothermal conditions. Ag nanoparticles were further sensitized on TiO₂ nanorod and nanotube arrays by a photodeposition approach. The structure, morphology and crystallinity of the nanorod arrays were adjusted by varying the content of hydrochloric acid in hydrothermal process. The formation mechanism of the TiO₂ nanotube arrays was investigated and the photocatalytic activities of the Ag nanoparticles sensitized TiO₂ nanorod and nanotube arrays (Ag-TiO₂ NRAs and NTAs) were evaluated by measuring the degradation of methyl orange (MO) aqueous solution under UV irradiation. In addition, the recovery and recycling

features of photocatalysts were also evaluated. Experimental results showed that the novel Ag-TiO₂ NTAs exhibited enhanced optical and photocatalytic properties. From the results, it can be concluded that the Ag-NTAs nanostructure developed in our work provides a new platform for the design of highly efficient photocatalysts.

2. Experimental

2.1. Materials

Titanium butoxide (C₁₆H₃₆O₄Ti, CP, 99.9%) and silver nitrate (AgNO₃, AR, 99.8%) were purchased from Aladdin Reagent Company. Hydrochloric acid (HCl, AR, 36.0–38.0%) was obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. Fluorine doped tin oxide (FTO) coated glass (TEC-8, LOF, 20 mm × 40 mm) substrates were cleaned in an ultrasonicator sequentially with a washing powder solution, acetone, alcohol and deionized water (DIW) for 30 min. The

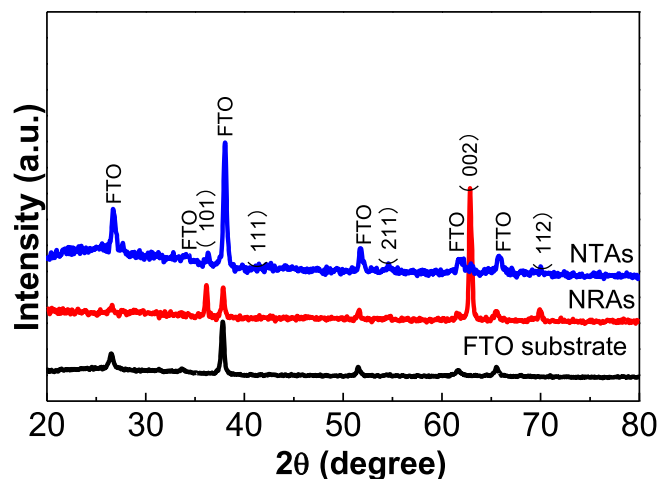


Fig. 2. XRD pattern of TiO₂ NRAs and NTAs.

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