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Short communication

Photo-induced activity of $BiFeO_3/TiO_2$ nanotube arrays derived from ultrasound-assisted successive ionic layer adsorption and reaction

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ABSTRACT

In this work, a facile strategy of ultrasound-assisted successive ionic layer adsorption and reaction was successfully employed to modify TiO_2 nanotube arrays with $BiFeO_3$ nanoparticles. An enhanced positive surface photovoltage was observed with the obtained $BiFeO_3/TiO_2$ nanotube arrays as well as a longer lifetime of charges separation state, as probed by transient photovoltage technique. The higher photocurrent density produced by $BiFeO_3/TiO_2$ nanotube arrays further indicated that $BiFeO_3$ nanoparticles contributed to photo conversion and promoted the generation of photo-induced charge carriers over TiO_2 nanotube arrays. Besides, the prepared $BiFeO_3/TiO_2$ electrode exhibited a much enhanced photoelectrocatalytic performance in removing methyl blue compared with bare TiO_2 nanotube arrays.

1. Introduction

Highly ordered, vertically oriented TiO_2 nanotube arrays (TiO_2-NTAs) have been extensively studied due to many promising applications in various areas, including hydrogen generation, photovoltaics, gas sensing, field emission, lithium anode materials and so on [1–4]. However, some of its practical applications are restricted owing to the wide band gap of TiO_2 and unfavorable recombination of photo-generated electrons and holes [5]. In order to break the two bottlenecks, sensitizing TiO_2 with narrow band gap semiconductor has been deemed as a promising method, which could widen the spectral region of photo response and meanwhile promote electron transfer from an excited small band-gap semiconductor into the conduction band of the attached TiO_2 [5–7].

$BiFeO_3$ is a typical perovskite material with rhombohedral structure and one kind of the multiferroic materials which exhibit both ferroelectricity and magnetic ordering at room temperature [8,9]. $BiFeO_3$ material has been regarded as a promising photo-catalyst due to its proper band gap (2.2–2.7 eV), which allows its visible light response [10–12]. In general, synthetic methods of $BiFeO_3$ materials include hydrothermal method, sol-gel, pulsed laser deposition, coprecipitation method, etc [10–15]. It has been observed that $BiFeO_3$ nanoparticles could exhibit higher photo-activity than the larger-sized particles [15,16]. However, $BiFeO_3$ nanoparticles in powder form is not favorable for most of practical applications including photocatalysis. Therefore, macroscopically shaped materials based on $BiFeO_3$-containing composites are highly desirable for various applications [17]. Successive ionic layer adsorption and reaction (SILAR) has recently emerged as a promising technique to obtain nanoparticles loaded TiO_2-NTAs, because its process is simple, safe, environmental friendly, low temperature and cost efficient [18,19]. To the best our knowledge, SILAR strategy has not been reported to prepare $BiFeO_3$ nanoparticles modified TiO_2-NTAs. As a follow-up work after our previous report [20], herein we successfully fabricated $BiFeO_3/TiO_2$-NTAs electrode through an ultrasound-assisted SILAR method followed by annealing. Beyond transient photovoltage (TPV) and photoelectrochemical (PEC) characterizations, the photoelectrocatalytic activity of the $BiFeO_3/TiO_2$-NTAs was further evaluated by degradation of methyl blue (MB) under visible light.

2. Materials and methods

All the chemicals and reagents were of analytical grade and used as received without further purification. Ti foils (0.5 mm thick, 99.7% purity, Beijing Academy of Steel Service, China) were cut into samples of size 20 mm × 40 mm. Ultrapure water was used for the preparation of all solutions and the rinse of Ti foils. The TiO_2-NTAs were synthesized by the anodic oxidation of a Ti foils

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according to the literature [7]. The detailed procedure is described in the supplementary material online.

$BiFeO_3$ nanoparticles were deposited onto both the outer and inner walls of TiO_2-NTAs by using an ultrasound-assisted SILAR approach. A typical procedure is described as follows. Firstly, TiO_2-NTAs electrode was sequentially immersed in two beakers containing 0.01 M $Bi(NO_3)_3{\cdot}5H_2O$ ethylene glycol solution and 0.01 M $Fe(NO_3)_3{\cdot}9H_2O$ DI water solution for 1 min, respectively, assisted by an ultrasonic process of 40 W. Between every two successive immersion steps, the samples were rinsed with ethanol adequately to remove excess ions. A desired loading amount of $BiFeO_3$ precursor could be obtained after five cycles of the above sequential ultrasonic immersion process. Finally, the obtained electrode was annealed at 500 °C for 2 h in a muffle furnace in the air with a ramp of 2 °C min^{-1}. Detailed information on characterizations and photoelectrochemical measurements is described in the supplementary material online.

In this study, we determined the best loading times by monitoring the variation of photocurrent density vs. bias potential curves. When photocurrent density of $BiFeO_3/TiO_2$-NTAs electrode came to a highest value, compared to TiO_2-NTAs electrode, such loading amount should be most desirable as the energy conversion efficiency approaches a highest level, and the corresponding loading times for producing the composite electrode was observed as five. Therefore, we chose five loading cycles as a best fabrication procedure, which led to a desired loading amount of $BiFeO_3$ onto the TiO_2-NTAs electrode.

3. Results and discussion

Fig. 1a shows the top-view scanning electron microscope (SEM) images of the TiO_2-NTAs. It can be seen that TiO_2-NTAs prepared through anodization exhibit a smooth top surface with an average nanotube diameter of about 90 nm and the wall thickness of about 20 nm. Fig. 1b shows the top- and side-view SEM images of TiO_2-NTAs after $BiFeO_3$ modification. It is obvious that the deposited $BiFeO_3$ nanoparticles are not only distributed on the top of TiO_2-NTAs but also surrounding the tube walls without blocking up the tube entrances. As a chemical deposition strategy, the operation procedure of SILAR method is technically simple and low cost. Impressively, $BiFeO_3$ particles can be uniformly loaded on the surface and internal tube walls of the TiO_2-NTAs electrode through the employed SILAR process. The energy dispersive X-ray (EDX) pattern in Fig. 1c reveals that the as-prepared sample contains Ti, O, Bi and Fe. Fig. 1d presents the X-ray diffraction (XRD) patterns of the TiO_2-NTAs and $BiFeO_3/TiO_2$-NTAs. The diffraction peaks at 35.2°, 38.5°, 40.3°, and 53.2° could be well indexed to the (100), (002), (101) and (102) crystalline planes of Ti metal (JCPDS No.05-0682) [7]. The peaks at 2θ value of 25.2° and 48.2° correspond to the (101) and (200) crystal facets of anatase phase of TiO_2 (JCPDS No.21-1272) [15]. After the deposition of $BiFeO_3$, only one weak peak at 32.1° appeared and it could be attributed to (110) planes of the hexagonal phase of $BiFeO_3$ (JCPDS No.86-1518) [20], probably due to the small loading amount of $BiFeO_3$.

Fig. 2a shows the UV–vis diffuse reflection spectra (DRS) of the as-prepared electrodes. It is observed that $BiFeO_3/TiO_2$-NTAs

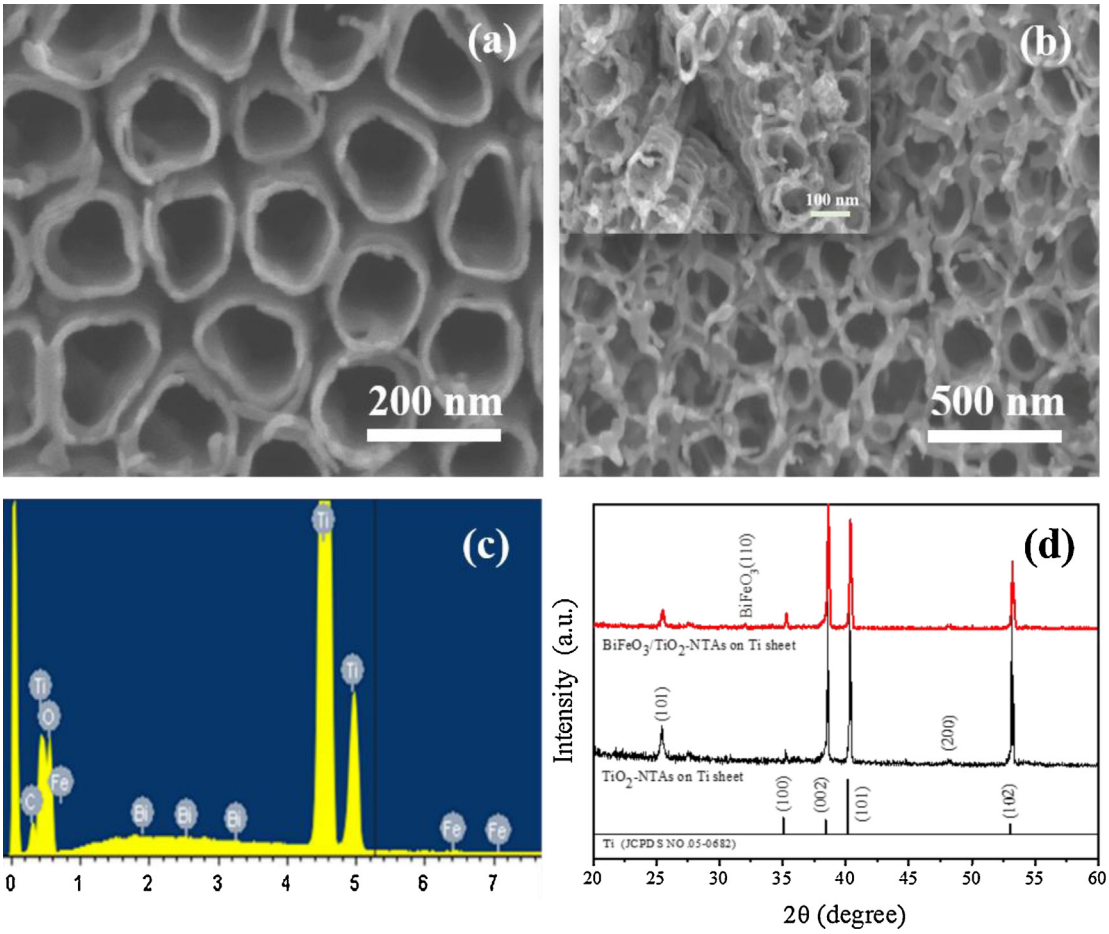

Fig. 1. Top-view SEM images of TiO_2-NTAs (a) and $BiFeO_3/TiO_2$-NTAs (b). Inset of (b) is a cross-sectional view of $BiFeO_3/TiO_2$-NTAs. (c) EDX pattern of $BiFeO_3/TiO_2$-NTAs. (d) XRD patterns of TiO_2-NTAs and $BiFeO_3/TiO_2$-NTAs grown on Ti sheet.