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Fabrication and photoelectrochemical performance of Ag/AgBr sensitized TiO_2 nanotube arrays for environmental and energy applications

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ABSTRACT

The TiO_2 nanotube arrays (TiO_2 NTs) sensitized by Ag-AgBr nanoparticles were prepared with different alkali (sodium hydroxide, urea and methenamine) as mineralizers by a hydrothermal method, and the TiO_2 NTs/Ag-AgBr photoelectrode showed high visible light absorption, transient photocurrent and photoelectrocatalytic (PEC) performances. The results indicated that TiO_2 NTs/Ag-AgBr (SH) photoelectrode showed the high visible light photocurrent density of 5.86 mA/cm^2, photovoltage of −0.31 V/cm^2 and PEC removal efficiency for MO (71.97%), RhB (59.88%), MB (80.76%) and Cr(VI) (52.24%), respectively. The high PEC property could be attributed to the high activities of solar absorption and electron separation. The excellent photoelectrochemical property of TiO_2 NTs/Ag-AgBr would induce the novel photoelectrode promising applications in solar cells and wastewater treatment.

1. Introduction

In recent years, the energy crisis and environmental pollution cause the intense attention of scientist, and they are seeking for a novel material to solve the obstacles [1–5]. The photocatalytic properties for water splitting to produce hydrogen and oxidative decomposition of organic wastewater are recognized to be an effective strategy since the discovery of water photolysis by TiO_2 photoelectrode by Fujishima and Honda [6] in 1972. Because of the high chemical and physical stability and super high photocatalytic activity, TiO_2 causes intense attention using as photocatalysts and photoelectrodes. However, the discommodiousness of the recycling limits applications of TiO_2 powders. TiO_2 nanotube arrays (TiO_2 NTs) are the two-dimensional films prepared by the anodization of Ti foils. The regular tubular structures have the advantagements of high length-diameter ratio and specific surface area, which provide excellent electron percolation channel for vectorial charge transportation along tubes [7–9]. Except for the effective electron transfer, the massive electron generation is also the prerequisites of high photoelectrochemical properties. The TiO_2 NTs could only absorb UV light due to the inherent large band gap (3.2 eV), and so the sensitization by semiconductors with narrow band gaps is an effective method to improve the visible light response of TiO_2 NTs. Previous investigation indicated that AgBr nanoparticles with energy band gap of 2.45 eV were attractive photosensitizers because of the high visible light response and photochemical stability [10,11]. Li [12] investigated the photoelectrochemical performance of TiO_2 NTs sensitized by AgBr, and the TiO_2 NTs/AgBr photoelectrode showed a high activity for MO photodegradation. Hou and his colleagues [13] also observed the high PEC properties of TiO_2 NTs by the deposition of AgBr nanoparticles. Moreover, the investigation indicated that the co-sensitization of semiconductors and noble metals would synchronously enhance the solar absorption and charge carrier transfer. The hybrid sensitizers of semiconductors and metals on TiO_2 NTs significantly attracted intense interest in the application of photoelectric conversion and wastewater treatment [14–17]. For example, Xue [18] successfully synthesized the Ag–AgBr/TiO_2 plasmonic nanotube heterojunction photocatalyst, and the reason of enhanced photocatalytic activity could be ascribed to the high light harvesting and electron transfer capability. Cheng [19] prepared TiO_2 NTs/AgBr-Ag by the simple precipitation method, and the sample possessed superior physicochemical properties. Our group [20] also successfully prepared AgBr-Ag microspheres on the surface of TiO_2 NTs via the successive ion layer adsorption and reaction followed by UV irradiation, the TiO_2 NTs/AgBr-Ag photoelectrodes showed excellent visible light photocurrent and PEC degradation of pollutants. However, the two-step preparation progress of AgBr-Ag co-sensitizers makes against the effective connection and formation of AgBr-Ag heterojunction, and which may reduce the photoelectrochemical performances. Fortunately, the one-pot hydrothermal preparation of AgBr-Ag co-

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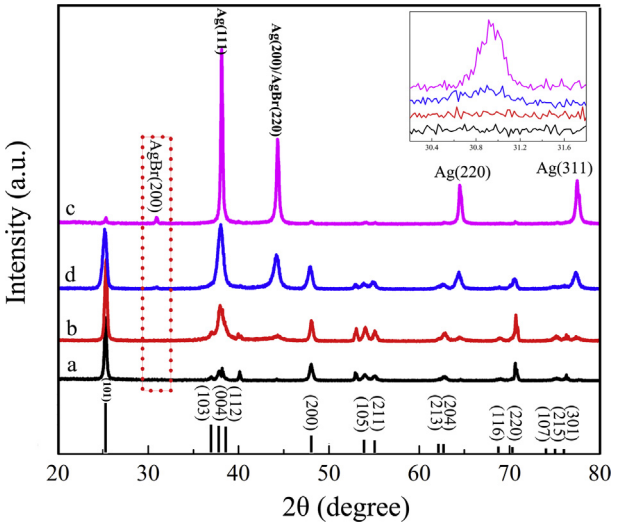

Fig. 1. The XRD patterns of (a) TiO_2 NTs, (b) TiO_2 NTs/Ag (U), (c) TiO_2 NTs/Ag-AgBr (SH) and (d) TiO_2 NTs/Ag (MA).

sensitizers possesses the advantagements of simple preparation progress, close interface connection and high crystallinity without annealing [21–23]. Despite the investigations reported thus far in previous studies, noteworthily, up to now, there have still been very limited systematic studies on the solvothermal preparation of AgBr-Ag on the surface of TiO_2 NTs and the corresponding photoelectrochemical properties of TiO_2 NTs/AgBr-Ag photoelectrodes. In this paper, Ag-AgBr nanospheres were deposited on the surface of TiO_2 NTs by a hydrothermal method by addition of NaOH as the mineralizer. The as-prepared TiO_2 NTs/AgBr-Ag photoelectrode displayed uniform deposition of AgBr-Ag nanospheres into nanotubes, showed excellent visible light response, photoelectric conversion and PEC removal of dyes and Cr(VI). The novel photoelectrode would open up extensive applications of solar cells and photocatalysts.

2. Experimental

2.1. The preparation of TiO_2 NTs/AgBr-Ag photoelectrodes

The TiO_2 NTs on the surface of Ti foils were prepared by a two-step anodization method, and the detailed preparation progress was described in our previous research [24]. The deposition of Ag-AgBr on the surface of TiO_2 NTs was carried out by the hydrothermal method, and the detailed progress was described as follows: Firstly, 1 mmol of $AgNO_3$ and 0.1 g of cetyltrimethyl ammonium bromide were dissolved into 30 mL of deionized water, and then 0.1 mmol of alkali (urea, sodium hydroxide or methenamine) was added into the mixed solution under magnetic stirring to be transparent. The solution was transferred into a 50-mL Teflon-lined autoclave and heated at 160 °C in an oven for 14 h. After the cooling to room temperature, the sample was taken out and cleaned in ethanol for 3 times. For the comparation, the samples prepared by the addition of urea, sodium hydroxide and methenamine were marked as TiO_2 NTs/Ag (U), TiO_2 NTs/Ag-AgBr (SH) and TiO_2 NTs/Ag (MA), respectively.

2.2. Characterization

The phase and morphology of the as-prepared samples were characterized by XRD (Siemens D-5000, Germany) and SEM (FEI SU8010, Japan). The optical response was measured by UV–Vis-NIR diffuse reflectance spectrum (SolidSpec-3700DUV, Japan). The photoelectrochemical performances of visible light transient photocurrent, current-voltage (*I-V*) curves, open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and carrier concentration (N_D) were measured in a photocell with three electrodes. The PEC removal properties of organic dyes (MO, RhB and MB) and Cr(VI) were characterized under solar irradiation. The detailed characterization progress of photoelectric conversion and PEC pollutant removal was reported in our previous research [25].

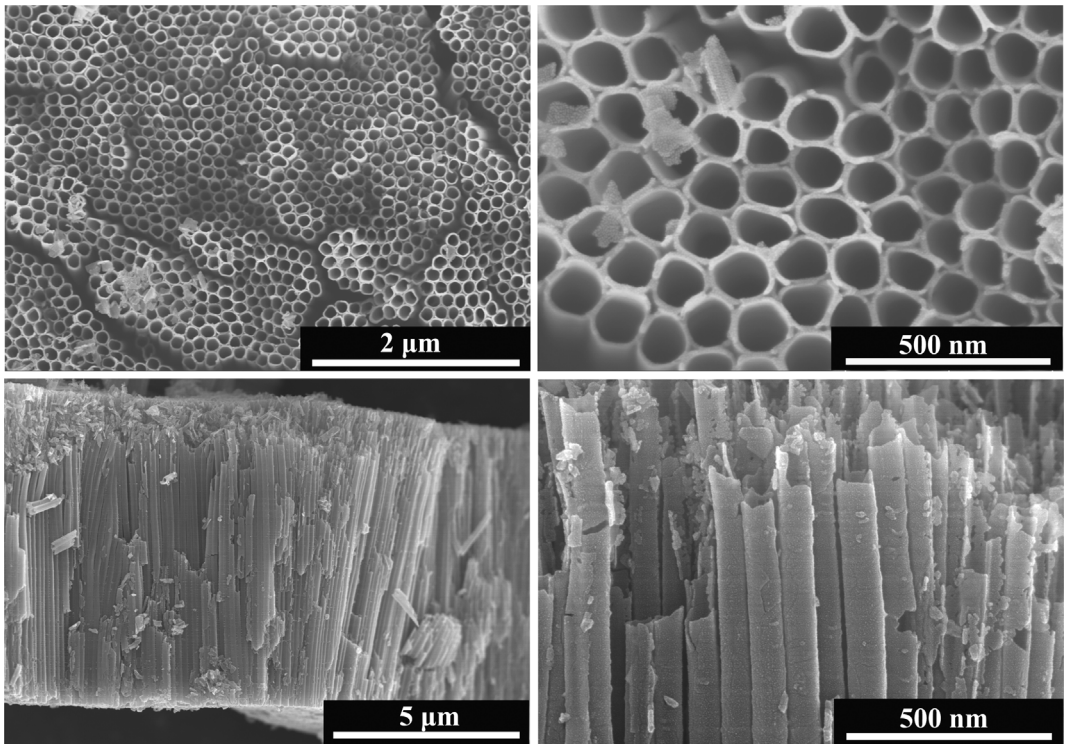

Fig. 2. The SEM images of TiO_2 NTs.