One-step Preparation of Ag-loaded Bi₄Ti₃O₁₂ Nanofibers by Electrospinning and Their Photocatalytic Activity

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Introduction

The semiconductor photocatalysis holds great promise for confronting global energy and environmental problems. Bismuth titanate (Bi₄Ti₃O₁₂, BTO) as a novel kind of photocatalyst has attracted much attention because of its high catalytic activities. It is believed that the noble metal deposition can act as traps for photoinduced electrons, leading to the reduction of electron-hole recombination. One-dimensional (1D) semiconductor photocatalysts have aroused great concern because of high surface areas, porosities, remarkable transport characteristics of electrons and holes, and thus enhanced photocatalytic activities. Here we report for the first time the one-step synthesis of Ag-loaded Bi₄Ti₃O₁₂ nanofibers via simple electrospinning methods. In contrast to pure Bi₄Ti₃O₁₂ nanofibers, the as-fabricated Ag-loaded Bi₄Ti₃O₁₂ nanofibers show enhanced photocatalytic activities under visible-light and UV-light irradiation.

Experimental

The Ag-loaded Bi₄Ti₃O₁₂ nanofibers were prepared via a simple electrospinning process. In a typical procedure, the precursor solution for electrospinning was prepared by dissolving Bi(NO₃)₃·5H₂O (1.55 g), TBT (0.82 g), and Ag(NO₃)₃ (the samples are denoted as BTO, BTA-1, BTA-2, BTA-3, BTA-4, and BTA-5 with respect to 0, 0.01, 0.02, 0.05, 0.75, and 0.10 g of Ag(NO₃)₃ correspondingly) in DMF (20 mL) at room temperature according to the stoichiometric composition. After stirring for 30 min, 2.5 g of PVP was added into the mixture. This precursor solution was delivered into a plastic syringe equipped with a 20-gauge stainless steel needle. The metallic needle clamped with an electrode was connected to a variable high-voltage power supply, and a collector of an aluminum foil was as a grounded counter electrode. As a high voltage of 15 kV was applied, the composite nanofibers were formed. The as-collected electrospun fibers were dried at 80 °C in air for 6 h. Subsequently, the composite fibers were calcined at 600 °C in air for 30 min. Photocatalytic activities of the as-prepared samples were evaluated by the degradation of methylene orange (MO) under visible-light irradiation of a 500-W Xe lamp with a 420 nm cut-off filter and a 500-W high pressure Hg lamp at ambient temperature. The photocatalyst (80 mg) was dispersed uniformly into the reactor containing 80 mL of aqueous MO (30 ppm). At a certain time interval, 3 mL of the reaction solution was taken, centrifuged, and measured with a UV-vis spectrometer.

Results and discussion

Fig. 1a and 1b show the typical FESEM images of the products. Clearly, the surface of the precursor nanofibers was very smooth and these fibers were as long as several millimeters. The BTA-2 nanofibers shrink a little after annealing (Fig. 1b) and are composed of inter-linked nanoparticles of 50–80 nm in size. In a typical high-resolution TEM (HRTEM) image (Fig. 1c), clear lattice fringes with a space of 0.2 and 0.38 nm are assigned to the [002] planes of Ag and the [111] planes of orthorhombic Bi₄Ti₃O₁₂, respectively. This indicates that Ag particles are loaded on the Bi₄Ti₃O₁₂ nanofibers. The EDX of A, B, and C position also reveal the compositions of the interface between the Ag particle and Bi₄Ti₃O₁₂ nanofibers.

Fig. 2a shows the XRD pattern of the Ag-loaded Bi₄Ti₃O₁₂ nanofibers with different Ag contents. All the diffraction peaks for the Bi₄Ti₃O₁₂ nanofibers can be readily indexed to orthorhombic Bi₄Ti₃O₁₂ (JCPDS 35-0795) except the diffraction peak at 38 degree of Ag. Fig. 2b indicates that the binding energies correspond to metallic Ag and Ag oxide.

Fig. 3a and 3b show the change in MO concentration over the photocatalytic degradation reaction under visible-light irradiation. After the adsorption-desorption equilibrium, the BTA-2 sample shows a considerably higher photocatalytic activity. In summary, the Ag-loaded Bi₄Ti₃O₁₂ nanofibers with different Ag contents have been successfully fabricated for the first time through the electrospinning method. The Ag/ Bi₄Ti₃O₁₂ composite shows substantial improvement in the photocatalytic activity for the degradation of MO under visible-light and UV irradiation, resulting from Schottky barrier between Ag and Bi₄Ti₃O₁₂ contact regions and the surface plasmon resonance.

References