Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Fabrication and photocatalytic performance of one-dimensional Ag_3PO_4 sensitized $SrTiO_3$ nanowire

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ARTICLE INFO

Keywords:
Nanowire
Heterojunction
Visible light photocatalysis
Recycle

ABSTRACT

The 1D Ag_3PO_4 sensitized $SrTiO_3$ nanowires are prepared by simple route of electrospinning-in situ deposition technique. The results of the thermogravimetry (TG), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive Spectrometer (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and UV–Visible diffuse reflectance spectroscopy (UV–Vis) indicate that the Ag_3PO_4 nanoparticles has been deposited on the surface of the $SrTiO_3$ nanowires successfully. Experimental results showed that compared with pure $SrTiO_3$, the as-prepared 1D Ag_3PO_4 sensitized $SrTiO_3$ nanowires exhibit obvious enhancement of photocatalytic performance and stability. Especially, the $Ag_3PO_4/SrTiO_3$ (3AS sample) had a satisfactory photocatalytic activity for degrading methylene blue (MB) more than 98% under visible light irradiation. As to pure $SrTiO_3$ and Ag_3PO_4, only 9.8% and 49% of MB was decomposed after 35 min irradiation respectively. Furthermore, the mechanism of the enhancing photocatalytic activity could be ascribed to the nano-heterojunction of the $Ag_3PO_4/SrTiO_3$, the visible light response of the Ag_3PO_4, and the 1D structure of the nanowires.

1. Introduction

Water pollution, as a significant issue in environmental pollution, has attracted more and more attentions of the researchers. In the past few decades, series of methods have been attempted, especially the semiconductor photocatalyst [1–3], with the low-cost, easy preparation and recycle stability, has attracted lots of interest and been reported substantially in the treatment of water pollution [4–6]. Among these, the strontium titanate ($SrTiO_3$), as a typical perovskite structure semiconductor, exhibits excellent photocatalytic activities of the photodegradation of organic pollutants and water splitting with the well heat resistance, thermal stability and anti-photocorrosion [7–11]. However, with the band gap of 3.2 eV, the perovskite $SrTiO_3$ could only responds to ultraviolet light(accounts for the 3–5% of the solar spectrum) [12–14], and which restrict the application in visible light photocatalysis. Therefore, expanding the visible light response would be an efficient way to optimize the photocatalysis of the $SrTiO_3$, and have been reported by lots of literatures, such as doping, surface modification, etc. Particularly the heterojunction sensitized modification, with the easy preparation, is widely reported in previous works, such as NiS/g-$C_3N_4/SrTiO_3$ [15], $SrTiO_3/CeO_2$ [16], $SrTiO_3/TiO_2$ [17], etc. There, the Ag_3PO_4 (2.4 eV), with the wonderful quantum yield efficiency of about 90% is considered as a superior visible light driven photocatalyst [18–20]. However, due to the high cost and low photostability, the pure Ag_3PO_4 could be hardly applied in practical water purification [21–25]. Nevertheless, as the modification materials, the Ag_3PO_4 would be a commendable choice. With the narrower band gap, the Ag_3PO_4 could act as the sensitizer to increase the visible light efficiency, and the heterojunction could separate the photon-generated carrier more efficiently. Both above are the advantages for the photocatalysis, and similar works have been reported, such as Ag_3PO_4/TiO_2 [26,27], Ag_3PO_4/CeO_2 [28,29], Ag_3PO_4/ZnO [30,31], TiO_2/Ag_3PO_4/graphene [32,33], which have shown better photocatalytic activity and high photostability than single phase Ag_3PO_4. In addition, extra Ag^0 nanoparticles that degraded from Ag_3PO_4 would cover on the surface of the Ag_3PO_4 and act as an ideal conductor to transfer the light-generated electron [34]. What's more, the Ag^0 could act as the quenching center to prevent the degradation of Ag_3PO_4 for improving the stability of the photocatalyst. All above are the advantages for the modification of the Ag_3PO_4, and have been researchered by previous literatures [35].

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https://doi.org/10.1016/j.ceramint.2018.07.049
Received 18 June 2018; Received in revised form 1 July 2018; Accepted 5 July 2018

Besides, $SrTiO_3/Ag_3PO_4$ composite photocatalyst which was built by introducing $SrTiO_3$ spherical nanoparticles to Ag_3PO_4 polyhedron has been reported to be an excellent photocatalyst for O_2 evolution from aqueous solution under visible light irradiation [36], and it has also been reported that 3DOM-$SrTiO_3/Ag/Ag_3PO_4$ photocatalysts prepared by using polymer colloidal crystals as templates has good photocatalytic activity in the treatment of organic contaminants [37]. There, the introducing of the Ag_3PO_4 into the system of the 1D-$SrTiO_3$ nanowires would be an ideal method.

On the other hand, the morphology would be another important factor for the photocatalysis, that the large specific surface area could provide abundant reactive sites to improve the photocatalysis, and have been explored by lots of groups, such as $SrTiO_3$ nanoparticles [38] and $SrTiO_3$ nanotubes [39]. Especially the nanowires, prepared by the electrospinning technology with low cost and easy preparation, is considered as an excellent method, that the 1D nanowires could provide large specific surface area for the reaction and remarkable aisles for the transfer of the photon-generated electrons, both are beneficial for improving the photocatalystic performance, and have been reported by series of works, such as ZnO nanowires [40] and WO_3 nanowires [41], above researches would enlighten the inspiration for the design of the photocatalyst.

In this paper, the 1D Ag_3PO_4 sensitized $SrTiO_3$ nanowires have been fabricated via simple electrospinning-in situ precipitation technique. The as-prepared samples exhibit an obvious enhancement of photocatalytic activity under visible light irradiation than the unmodified samples. Then the mechanism of the enhancement are studied.

2. Experimental procedure

2.1. Materials

Silver nitrate (99.8% purity), N, N-Dimethylformamide (DMF, 99.5% purity), Tetra butyl titanate (TBT, 99.0% purity), Strontium acetate (99.97% purity) were supplied by Aladdin Chemical Co. Ltd. Glacial acetic acid (99.5% purity), Sodium phosphate (98% purity), Polyvinylpyrrolidone (PVP, M_W = 1300,000) were obtained from Shanghai Macklin Biochemical Co. Ltd.

2.2. Preparation of 1D Ag_3PO_4 sensitized $SrTiO_3$ nanowires

The 1D Ag_3PO_4 sensitized $SrTiO_3$ nanowires was prepared by simple electrospinning-in situ precipitation method. Firstly, the precursor solution was prepared by dissolving 2 g PVP into 8 mL DMF and 2 mL glacial acetic acid. After stirring 24 h, 2 g of TBT was added to the precursor solution with a magnetic stirrer for 12 h. Further, a certain amount of strontium acetate was added into above mixture slowly and stirred until the solution was transparent. Then the prepared sol-gels were loaded into a glass syringe,(diameter of needle, 0.5 mm, rate, 0.7 mL/h, KDS-200, KD Scientific, United States). The working voltage was 17 kV (Model: ES40P-10W, Gamma HighVoltage, United States), the distance was 16 cm, the humidity was maintained at = 30%, and the ambient temperature was 25 °C. The non-woven nanofiber webs were consequently obtained at the collector and dried in an oven at 80 °C for 4 h, and then were calcined at 700 °C in air (5 °C/min) for 3 h to obtain 1D-$SrTiO_3$ nanowires. Secondly, 50 mg of the electrospun 1D-$SrTiO_3$ nanowires was placed in a beaker containing 30 mL of $AgNO_3$(0.006 M) solution, with the magnetic stirring, 30 mL of Na_3PO_4(0.002 M) was added into the beaker for precipitating completely. Then the 1D Ag_3PO_4 sensitized $SrTiO_3$ nanowires were obtained by drying the residual solution at 80 °C. The same as the above precipitation, repeated for 1 times, 2 times, 3 times, 4 times and 5 times were labeled as 1AS, 2AS, 3AS, 4AS and 5AS. What's more, the pure 1D-$SrTiO_3$ nanowires and Ag_3PO_4 nanoparticles were prepared for contrast.

2.3. Characterization

Thermal analysis of the non-woven nanofiber webs (unsintered) by TGA (20–800 °C, 5 °C/min, air) was performed to identify the evaporation, decomposition and phase crystallization during pyrolysis. Crystallinities of samples were analyzed by Bruker/D8-advance with Cu Kα radiation (λ = 1.518 Å) at the scanning rate of 0.2 s/step in the range of 20–70°. The surface morphology of the as-prepared samples was characterized by the field-emission scanning electron microscope (FESEM, Hitachi S-4800) equipped with Energy-dispersive X-ray spectroscopy (EDS), and the crystalline structure was observed by a transmission electron microscope (TEM, JEM-2100, 200 kV). X-ray photoelectron spectroscopy (XPS) was carried out to determine the chemical states of all the elements on a VGESCALABMKII X-ray photoelectron spectrometer. The binding energies obtained in the XPS analysis were corrected by the C1s to 284.60 eV. The absorption spectra were recorded by a UV–Visible pectrophotometer (U-3900Hitachi). The photoluminescence emission spectra (PL) were recorded with an excitation wavelength of 332 nm by a Hitachi F-7100 fluorescence spectrophotometer at room temperature.

2.4. Photocatalytic activity test

In this experiment, 30 mg photocatalyst was filled into 50 mL Methylene Blue (MB, 10 mg/L) solution under the irradiation of visible light (PHILIPS, 200 W, λ ≥ 420 nm). Before turning on the light, the solution was continuously kept in dark with magnetic stirring for 30 min to reach an adsorption–desorption equilibrium. At given intervals (t = 5 min) of irradiation, the samples of the reaction solution (3 mL) were taken out, centrifuged and analyzed. The concentrations of the remnant dye were measured by a UV–Vis absorption spectrophotometer at a maximum absorption wavelength of λ = 662 nm.

3. Results and discussion

The thermogravimetric analysis (TGA) of theunsintered as-spun PVP/$Ti(oBu)_4/Sr(C_2H_3O_2)_2$ non-woven nanofiber webs are performed to guide the process of the thermal treatment (Fig. 1a). The result indicates that the presence of four remarkable phases of weight loss: (1) within the range of 20–120°C, the weight loss could be ascribed to the adsorption of water, (2) within the range of 120–300°C, the weight loss of moisture could be attributed to chemicals employed and extend all over the preparation procedure, (3) within the range of 300–700 °C, the weight loss could be ascribed to the thermal decomposition of the polymer(PVP) and organic matter(DMF, HAc,etc) [42], (4) After the temperature rising to 700°C, no evident weight loss could be observed, which indicates that the perovskite phase $SrTiO_3$ nanowires have formed.

Fig. 1b is the XRD of the 1D Ag_3PO_4 sensitized $SrTiO_3$ nanowires, including the pure $SrTiO_3$ and Ag_3PO_4 (Fig. 1b). It is clear that the characteristic diffraction peaks at 2θ = 32.5°, 40.0°, 46.5°and 57.9° could be indexed to the (110), (111), (200), and (211) crystal planesof the perovskite phase $SrTiO_3$ structure (JCPDS No. 84–0443), and corresponds to the TGA (Fig. 1a). With the introducing of the Ag_3PO_4, the new characteristic diffraction peaks of 2θ = 20.9°, 29.7°, 33.3°, 36.6°, 47.8, 52.7°, 55.0°, and 61.6° could be observed, which are ascribed to the (110), (200), (210), (211), (310), (222), (320) and (400) planes of the Ag_3PO_4 structure (JCPDS No.06–0505), respectively, No other impurities diffraction peaks are discovered (Fig. 1b). All above result shows that the Ag_3PO_4 sensitized $SrTiO_3$ heterojunction with higher crystallinity are successfully prepared (Fig. 1b), which would be conducive to promote the photon-generated carrier separating to increasing the photocatalytic efficiency. Additionally, it could be observed that the characteristic diffraction peaks of Ag_3PO_4 increase with the deposition times, which indicates that the Ag_3PO_4 nanoparticles have been introduced successfully by the deposition.