Solar Energy 174 (2018) 770–779

Contents lists available at ScienceDirect

Solar Energy

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

Ag-induced synthesis of three dimensionally ordered macroporous anatase/rutile homojunction for solar light-driven Z-scheme photocatalysis

Yuanyuan Zhang[a], Lili Wang[a], Shuguang Yu[a], Haiyan Jiang[a], Yuliang Yun[b], Yuwei Sun[c], Jinsheng Shi[a,*]

[a] *Department of Chemistry and Pharmaceutical Science, Qingdao Agricultural University, PR China*
[b] *Department of Mechanic and Electronic Engineering, Qingdao Agricultural University, PR China*
[c] *Department of Animation and Media, Qingdao Agricultural University, PR China*

ARTICLE INFO

Keywords:
Anatase/rutile homojunction
Ag-induction
Z-scheme mechanism
3DOM structure

ABSTRACT

Z-scheme composites are considered as desirable photocatalysts. However, most of them are heterostructure and Z-scheme homojunction have been rarely reported. In this paper, for the first time, Z-scheme anatase/rutile homojunction was obtained by Ag nanoparticles (NPs) induction. Polystyrene spheres modified by Ag NPs were used as sacrificial templates to prepare three dimensionally ordered macroporous (3DOM) anatase. Incredibly, Ag NPs could induce the formation of rutile from anatase and anatase/rutile homojunction was created. High-resolution transmission electron microscopy clearly revealed the structure of anatase-Ag-rutile. Both experimental and theoretical evidences were utilized to study the induction of Ag NPs. Compared to commercial P25 and control samples, anatase-Ag-rutile composites exhibited obviously enhanced photocatalytic hydrogen evolution and disinfection under simulated solar light. The enhanced photocatalytic activities could be mainly attributed to the Z-scheme electron migration mechanism in ternary composites, which was confirmed via active species trapping experiment, electron spin resonance spectra and surface redox reactions.

1. Introduction

Energy crisis and environmental pollution are two challenging problems for human beings in the 21st century, which has become a great threat to human survival and social development (Liu et al., 2016; Jiang et al., 2016; Wang et al., 2017; Jin et al., 2017; Zhao et al., 2018). Solar-driven photocatalysis is widely used to settle these global matters due to its high efficiency, low cost and environmental friendliness (Li et al., 2017; Cruz-Ortiz et al., 2017). As we know, a wide light-response range, efficient charge separation and strong redox property are vital characters for ideal photocatalysts (Liu et al., 2017; Cao et al., 2016). However, it is difficult for a single semiconductor catalyst to satisfy all these merits (Yuan et al., 2017; Panneri et al., 2016; Zhang et al., 2018). Construction of all-solid-state artificial Z-scheme photocatalytic system is an effective method because this system could not only improve additional light absorption and realize spatial charge separation, but also retain strong redox abilities of electrons and holes (Yuan et al., 2017; Zeng et al., 2017; Yang et al., 2017). For example, Hong et al. (2016) built direct Z-scheme V_2O_5/g-C_3N_4 heterojunction by in-situ method, with which the photocatalytic elimination efficiency of organic pollutants was obviously enhanced under visible light irradiation (Hong et al., 2016). Yu et al. (2017) synthesized Z-scheme g-C_3N_4/WO_3 composite to enhance the efficiency of hydrogen evolution (Yu et al., 2017). In addition, noble metal nanoparticles (NPs) are usually used as electron mediators to broaden light response range and facilitate charge migration in Z-scheme composites (Yang et al., 2018). Although these catalysts exhibited excellent photocatalytic activity, no consideration was given to whether the constituents are homogeneous or not. It was generally accepted that order morphology might have a good effect on their abilities to capture light and the increase of activity site numbers, as well as the accessibility to active sites (Toumazatou et al., 2017; Chai et al., 2015).

According to the reported papers, most of Z-scheme catalysts are heterojunction composites. However, design and construction of such systems are closely related to energy band configurations, crystal structures and surface/interfacial performances of constitutive components, which makes it difficult to fabricate in synthesis progress (Yang et al., 2017; Pan et al., 2016). Recently, homojunction, built by same semiconductor materials with different crystal phases, semiconductor types or exposing facets, has attracted considerable attentions. Compared with heterojunction fabricated from different components, homojunction presents a great many advantages in the above-

---

* Corresponding author at: Qingdao Agricultural University, Department of Chemistry and Pharmaceutical Science, Chengyang District, Qingdao, PR China.
E-mail address: jsshiqn@aliyun.com (J. Shi).

https://doi.org/10.1016/j.solener.2018.09.041
Received 31 July 2018; Received in revised form 10 September 2018; Accepted 15 September 2018

mentioned aspects. Besides, homojunction could produce an internal field between the two components for inhibiting recombination of photogenerated charge carriers and accelerating their migration across the interface (Zhou et al., 2017; Zhang et al., 2017; Lyu et al., 2017). For instance, Wang et al. (2012) fabricated α-Ga_2O_3/β-Ga_2O_3 homojunction to accelerate photoinduced charge separation and migration across the α-β phase interface and enhance photocatalytic overall water splitting (Wang et al., 2012). The {1 0 1}/{0 0 1} facets co-exposed TiO_2 material could obviously strengthen photocatalytic activity in the process of CO_2 reduction into CH_4 (Yu et al., 2014). Pan et al. (2016) constructed a type-II TiO_2 p-n homojunction; which could enhance charge separation through band bending and be used for photoelectrochemical and photocatalytic hydrogen evolution (Pan et al., 2016). Up to now, the reported homojunction composites have been categorized as type-II according to charge carriers migration route, which considerably weaken the redox potentials of electrons and holes and lower photocatalytic activity (Huang et al., 2017; Wei et al., 2017; Lian et al., 2017). It is worth noting that Z-scheme homojunction materials have been rarely reported so far.

In this work, for the first time, Ag-induced Z-scheme anatase/rutile homojunction with 3DOM structure was designed and synthesized. As an open interconnected porous structure, 3DOM samples could periodically control light propagation then increase light absorption, which provide an alternative and attractive way to strengthen photocatalytic activity (Zalfani et al., 2017). High-resolution transmission electron microscopy (HR-TEM) clearly revealed the structure of anatase-Ag-rutile (A-Ag-R). In addition, Z-scheme electron migration in anatase-Ag-rutile was determined via active species trapping experiment, electron spin resonance (ESR) spectra and surface redox reactions. This work provides a new insight into constructing efficient Z-scheme homojunction for photocatalysis.

2. Experimental section

2.1. Synthesis of Ag-modified PS colloidal spheres

Ag-decorated polystyrene (PS) latex spheres with diameter of 200 nm were prepared by a surfactant-free emulsion polymerization method (Fig. 1a and b). Typically, 13.5 g of styrene (St), a certain amount of $AgNO_3$ and 0.7 g of polyvinylpyrrolidone (PVP) were added into a four-necked bottle containing 100 mL of deionized water. After stirring for 30 min, 0.3 g of potassium persulfate ($K_2S_2O_8$) as an initiator was introduced into the above-mentioned mixture with vigorous stirring. The reaction hybrid solution was deoxygenated by bubbling N_2 for 30 min, then heated at 70 °C for 24 h under UV light illumination. Finally, milk white solution with suspended PS spheres was obtained.

2.2. Synthesis of Ag-modified PS opal template

Ag-decorated PS opal template was prepared through vertical deposition process by assembling monodispersed PS colloidal spheres onto glass substrate at 45 °C for several days (Fig. 1c). Then opal template dried at 70 °C for 2 h to enhance connection between these neighboring PS spheres (Fig. 1d).

2.3. Synthesis of Ag-induced anatase-rutile homojunction

10 mL tetrabutyl titanate (TBOT), 10 mL absolute ethanol and 1 mL nitric acid were mixed with magnetic stirring for 1 h to form a transparent solution. Subsequently, the obtained PS opal was immersed into the above solution for 1 h and then dried at room temperature for 2 h (Fig. 1e and f). The final sample was obtained by calcination in a tube furnace with slowly increasing temperature (1 °C/min) up to 600 °C for 3 h (Fig. 1g and h). Control samples were also fabricated via the same procedures with different synthesis conditions: PS + $AgNO_3$ + UV irradiation + TBOT (marked as A-Ag-R), PS + TBOT (marked as Cs-1), PS + $AgNO_3$ + TBOT (marked as Cs-2), TBOT + $AgNO_3$ + UV irradiation (marked as Cs-3), only TBOT (marked as Cs-4), $AgNO_3$ + TBOT (marked as Cs-5). Meanwhile, A-Ag-R composites with different Ag contents were also synthesized.

3. Results and discussion

3.1. Crystal structure and surface chemical composition

Phase structures of as-prepared samples were depicted in Fig. 2. The as-prepared A-Ag-R composite presents similar diffraction pattern with P25, implying the co-existence of anatase and rutile. The main peaks at

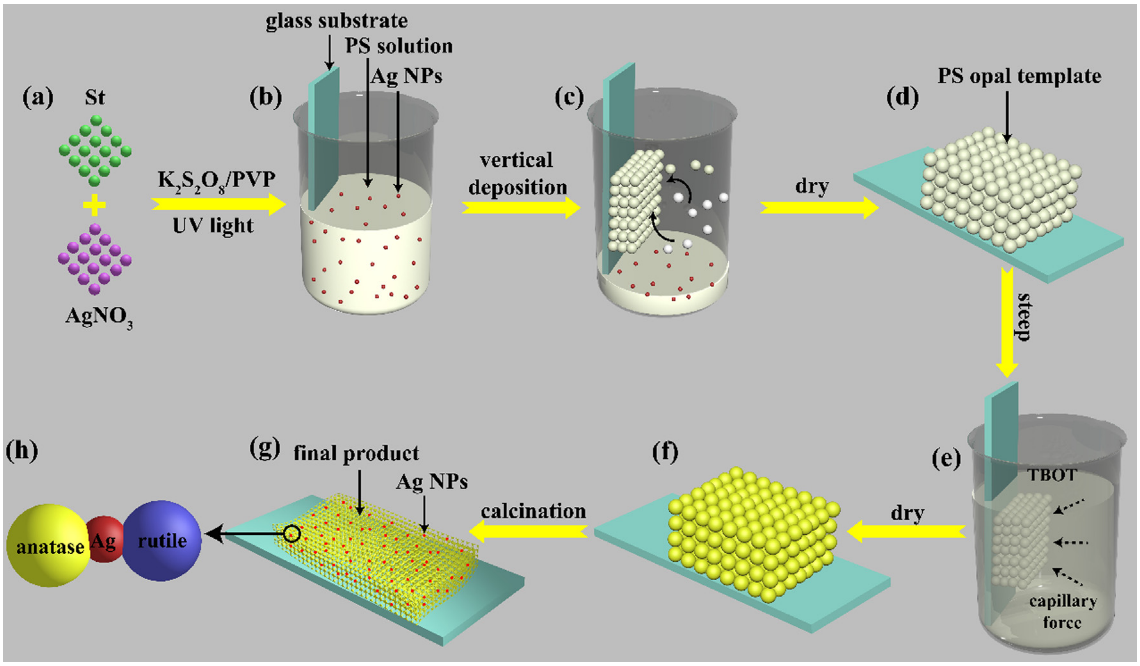

Fig. 1. Controlled fabrication process for A-Ag-R composite.