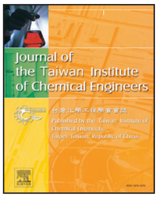
Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–9

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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



In situ formation of Ag/ZnO heterostructure arrays during synergistic photocatalytic process for SERS and photocatalysis

Yangsi Liu[a,b,*], Wei Gao[b], Chao Zhang[c], Lin Zhang[c], Yunxia Zhi[c]

[a] *Beijing Guyue New Materials Research Institute, Beijing University of Technology, Beijing 100124, PR China*
[b] *Department of Chemicals and Materials Engineering, The University of Auckland, PB 92019, Auckland 1142, New Zealand*
[c] *Material and Industrial Technology Research Institute Beijing, Beijing 102402, PR China*

ARTICLE INFO

Article history:
Received 8 January 2018
Revised 16 April 2018
Accepted 17 April 2018
Available online xxx

Keywords:
Ag/ZnO heterostructure
In situ formation
Photoreduction
Photooxidation
Photocatalytic kinetics
SERS

ABSTRACT

ZnO nanorod arrays were used to oxidize rhodamine B (RhB) and reduce Ag^+ ions simultaneously under UV or visible light. The photocatalytic kinetics of RhB degradation followed a pseudo-first order with two steps, and during the synergistic photocatalysis process, Ag/ZnO heterostructural nanocomposites were generated in situ based on ZnO nanorod arrays. The Ag/ZnO heterostructure arrays were composed of Ag nanosheets with (111) plane on the basis of ZnO nanorods. The growth process of Ag nanosheets experienced a similar two-stage manner as the degradation kinetics of RhB, indicating that the change in apparent rate constants for RhB degradation was ascribed to the variation of photoinduced electrons and holes. The microstructure, composition, chemical states, and UV–visible light adsorption of reclaimed Ag/ZnO heterostructure arrays were investigated; their multifunctional applications on surface enhanced Raman scattering and photocatalytic activity under UV or simulated solar light were also discussed.

1. Introduction

Water pollution brought about by industrial development causes severe threats to the environment and human health, which is one of problems needing resolution in modern society [1]. Semiconducting oxide photocatalysts have been considered as green materials for wastewater remediation, by which pollutants can be transformed into harmless substances [2]. This method is based on the reactive properties of reductive (electrons) and oxidative (holes) species generated by semiconductors. Reduction by electrons takes place concurrently with oxidation by holes [3]. ZnO, one of the most popular photocatalysts, has a rich family of nanostructures with abundant configurations for nanotechnology [4,5], and their nanostructures can be easily produced in immobilized states for convenient recycling [6]. However, the photocatalytic activities of semiconductors are often restricted by the rapid recombination of electrons and holes [7].

Considerable efforts have been made to address the aforementioned problem. Coupling of semiconductors with other semiconductors, or noble metals to form heterojunctions can improve the photocatalytic activities by reinforcing the separation of electron-hole pairs [7–10]. By adding electron or hole scavengers, the recombination of photogenerated charge carriers can be suppressed as the scavengers could consume corresponding charge carriers and allow rest ones to undergo the redox reactions [11]. When metal ions with reduction potentials coexist with organic species, the efficiency of photocatalysts increases as the photocatalytic oxidation and reduction may occur simultaneously, arresting the recombination of electron-hole pairs [12].

Researches have been focused on these concomitant photocatalytic systems since industrial wastewaters are often compound pollutions containing both organic matters and heavy metal ions [13,14]. Enhanced photocatalytic removal of co-existent Cr(VI) and 4-chlorophenol was obtained in binary systems by anatase/titania nanosheet composites [1]. The presence of $AgNO_3$ can enhance the photocatalytic activity of Bi_2WO_6 toward various organic dyes [15]. Ag^+ ions often exist in electroplating, mining, photographic and jeweler treatment process [16], thus the accumulation of noble metals in industrial wastes is of great environmental concern, and also represents significant losses in raw materials [17].

Given the above review, we propose to reinforce the photocatalytic activity of ZnO by employing Ag^+ ions. We applied ZnO nanorod arrays as the photocatalysts and took advantages of their portable state for convenient recovery. During the RhB photocatalytic degradation process, Ag/ZnO heterostructure arrays were formed in situ via the photocatalytic reduction of Ag^+ to Ag on ZnO nanorods. The reclaimed noble metal/semiconductor nanocomposites showed new features, especially the surface plas-

---

* Corresponding author at: Beijing Guyue New Materials Research Institute, Beijing University of Technology, Beijing 100124, PR China.
E-mail addresses: liuyangsi@bjut.edu.cn, yliu403@aucklanduni.ac.nz (Y. Liu).

https://doi.org/10.1016/j.jtice.2018.04.020
1876-1070/

Please cite this article as: Y. Liu et al., In situ formation of Ag/ZnO heterostructure arrays during synergistic photocatalytic process for SERS and photocatalysis, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.04.020

mon resonance (SPR), and they can be reused in surface enhanced Raman scattering (SERS) and photocatalytic activity.

2. Experimental

2.1. Simultaneous photocatalytic oxidation and reduction

The simultaneous photocatalytic reduction of Ag^+ ions and oxidation of organic dye were conducted by ZnO nanorod arrays, which were synthesized as reported in [6]. An aqueous solution containing 25 mM zinc nitrate ($Zn(NO_3)_2{\bullet}6H_2O$, 98%) and hexamethylenetetramine ($C_6H_{12}N_4$, 99%) in an equal molar ratio was prepared. The aqueous solution was then transferred into a sealable glass jar in which glass substrates with ZnO seed layers were held face-down. The whole set was put into an oven at 95 °C for 4 h, then samples were rinsed and dried.

The ZnO nanorod arrays (25 mm × 20 mm) were immersed into 5 ml mixed solutions with 0.05 M silver nitrate ($AgNO_3$) and 2.5 mgL^{-1} rhodamine B (RhB) and they were kept in dark for 30 min to establish an adsorption/desorption equilibrium of Ag^+ and RhB. The whole set was then exposed to different light sources, such as two 8 W germicidal lamps ($\lambda = 254$ nm UV), two 8 W ultraviolet lamps ($\lambda = 365$ nm UV), and one 40 W filament lamp bulb (visible light). Under UV light (254 nm or 365 nm), the experiment was conducted until the color of mixed solution became almost transparent; under visible light, the irradiation was last for 5 h and stopped, even though the solution was still light pink. The concentration of RhB versus irradiation time was measured by a UV–vis spectrometer (Presee TU1901). The intensity of absorption band peak (553 nm) was recorded.

2.2. Sample characterization

After the synergistic photocatalysis experiments, the morphology and microstructure of reclaimed samples were characterized by a scanning electron microscope (SEM, Hitachi S-3400 N), a scanning transmission electron microscope (STEM, Hitachi SU9000) and a high resolution transmission electron microscope (HRTEM, FEI Tecnai G^2 F20, 200 kV). Their elemental compositions were analyzed with energy dispersive spectroscopy (EDS) equipped on SEM; and the crystal structures were identified by X-ray diffraction (XRD, Bruker D8 Advance). The X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) was employed to study chemical states of surface elements. The UV–Visible absorption spectra were recorded on a Presee TU1901 UV–vis spectrometer.

2.3. SERS performance

RhB was used as the probe molecule to evaluate the molecular sensing performance of reclaimed samples. After cleaning by DI water and ethanol for several times, Ag/ZnO heterostructure arrays were dipped in diluted RhB aqueous solution (10^{-6} M) for 2 h and then dried at 60 °C for 1 h. The SERS spectra were recorded with a Raman spectrometer (LabRAM HR Evolution), using a 532 nm laser beam.

2.4. Photocatalytic activity

The reclaimed Ag/ZnO heterostructure arrays can be also used as new photocatalysts after clean and dried. Their photocatalytic activities were evaluated by degrading pure RhB solution without Ag^+ ions. The Ag/ZnO samples were immersed into RhB solutions (5 ml, 2.5 mgL^{-1}) and kept in dark for 30 min, and then they were exposed to 365 nm UV light or simulated solar light (AM 1.5, 500 w 7-SS1003A, SOFN Instruments). The degradation rate of RhB was measured as the way described in Section 2.1.

3. Results and discussion

3.1. Simultaneous photocatalytic oxidation and reduction

Fig. 1a displays the degradation rate of RhB by ZnO nanorod arrays with Ag^+ under different irradiation conditions. About 89.2% RhB is degraded after 45 min by 254 nm UV light and 87.0% RhB is removed under 365 nm UV light for 3 h, while there is 39.1% RhB remaining after 5 h under visible light. Without Ag^+, the degradation rate of RhB is quite low, since RhB still remains for 28.6%, 57% and 89.2% after 4 h under 254 nm UV, 365 nm UV and visible light, respectively (Supporting Information, Fig. S1). It is clear that Ag^+ ions remarkably increase the photocatalytic efficiency of ZnO.

During the photocatalytic process of ZnO under UV light, the photogenerated electrons could be accepted by surface-absorbed O_2 molecules or the dissolved oxygen, but this action is slower than the transfer of electrons to Ag^+ ions and the reduction to metallic Ag [16]. Meanwhile, the photogenerated holes can oxidize hydroxyl anions or H_2O molecules to hydroxyl radicals, which is a powerful oxidant and can decompose RhB molecules. The holes can also act as oxidants and directly participate in the RhB decomposition [18].

The role of holes was verified by adding ethanol, the hole scavenger [8], in the mixed solution. The identical ZnO nanorod arrays were used as photocatalysts toward the solution including $AgNO_3$, RhB and ethanol (45: 45: 10, volume ratio) under 365 nm UV light. Since a part of holes were captured by ethanol and cannot react with RhB molecules, the degradation rate of RhB worsens obviously (Fig. S2). It means the holes play a vital role for RhB photodegradation.

The kinetics of RhB photocatalytic degradation were studied in the Langmuir-Hinshelwood model [6,19] and the $\ln(C_0/C)$ as a function of irradiation time is plotted in Fig. 1b–d, where the slope of fitting equations is the apparent rate constant. To give the best fitting, two straight lines are needed for each sample. The dual linear relations indicate that the RhB photodegradation follows a pseudo-first order with two steps. For all irradiation conditions, the apparent rate constant in the first step (K1) is larger than that in the second step (K2). K1 is 5.86, 4.58 and 2.32 times bigger than K2 under 254 nm UV, 365 nm UV and visible light, respectively. The twofold kinetics must be related to the transfer and action of photoinduced electrons and holes during the synergistic photocatalysis process (a detailed discussion is given in Section 3.4).

3.2. Morphology of reclaimed photocatalysts

The color of ZnO nanoarrays was changing from light white to black during the simultaneous photocatalytic oxidation and reduction, and we assumed that Ag nanostructures were combining with ZnO nanorods in this process. The resultant Ag/ZnO nanocomposite samples were named after the light condition when they were formed. They are AgZnO254, AgZnO365 and AgZnOvis for the nanocomposites made by UV light (254 nm or 365 nm) and visible light, respectively.

The morphology of Ag/ZnO nanocomposites is shown in Fig. 2a–c. All of them are composed of many irregular nanosheets on the top of ZnO nanorod arrays. Some of the nanosheets are deposited on ZnO nanorod surfaces and many of them are erected to form random oriented arrays above the ZnO basis. The size of these nanosheets decreases with increasing density from AgZnO254, AgZnO365, to AgZnOvis (Fig. S3). Same major elements, Zn, O, Ag and Si from glass substrates, are detected for all samples (Fig. 2d).

The STEM images in Fig. 3a–c show that Ag nanosheets are originated from the top surfaces of ZnO nanorods with uneven and bent surfaces. They are 30–40 nm in thickness and assembled by many Ag nanograins (Fig. 3b). The schematic illustration of the in

Please cite this article as: Y. Liu et al., In situ formation of Ag/ZnO heterostructure arrays during synergistic photocatalytic process for SERS and photocatalysis, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.04.020