Applied Surface Science 466 (2019) 515–524

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Carbon quantum dots sensitized $ZnSn(OH)_6$ for visible light-driven photocatalytic water purification

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ARTICLE INFO

Keywords:
Carbon quantum dots
$ZnSn(OH)_6$
Up-conversion
Efficient charge separation
Photocatalytic water purification

ABSTRACT

In this study, carbon quantum dots (CQDs) decorated $ZnSn(OH)_6$ (ZSH) micro-spheres with uniform solid, hollow and yolk-shell structures were successfully synthesized by an etching-second growth strategy and facile hydrothermal method. Compared with pure ZSH, ZSH@CQDs composites exhibited obviously enhanced photocatalytic activities for both degradation of organic pollutant and disinfection of *staphylococcus aureus*. In CQDs decorated composites, ZSH@CQDs with yolk-shell structure presented 70.4% of RhB degradation efficiency under visible light irradiation within 8 h, which was about 10 times higher than that of ZSH samples. ZSH@CQDs with yolk-shell structure also manifested the best photocatalytic inactivation performance under visible light illumination, which could achieve water purification of 100% bacteria disinfection within 16 h. The enhanced photocatalytic activities might be attributed to the unique up-conversion property of CQDs, as well as its efficient charge separation, and a possible mechanism was reasonably proposed. This work could provide a new perspective to design efficient CQDs decorated photocatalysts for water purification.

1. Introduction

With the fast development of industrialization, environmental problems especially wastewater contamination has caused widespread concern because its great threat to aquatic life, human survival and social development [1–3]. Millions of serious diseases even death is caused by them every year [4]. Therefore, rapid and efficient water purification methods are explored to address this global trouble. Photocatalysis, as an efficient, low cost and environmentally friendly strategy, has been one of the promising candidates in comparison with traditional purification methods [5,6]. Based on the reported papers, $ZnSn(OH)_6$ (ZSH), as one of the perovskite materials, has drawn great public attention in photocatalysis [1–4]. Compared with traditional catalysts such as TiO_2 and ZnO, ZSH presents much higher photocatalytic activities in organic pollutants degradation, hydrogen evolution and CO_2 reduction due to its abundant surface OH^- groups, which could utilize photoinduced holes to form highly active $^{\cdot}OH$ radicals. Unfortunately, the band gap of ZSH is about 4.0 eV, largely inhibited its photocatalytic activity because only ultraviolet (UV) can be utilized by ZSH [1,5]. As is well known, UV light only accounts for 5% of solar energy, while the residual 48% and 47% are composed of visible light and near-infrared light, respectively [6,7], which are not well utilized for ZSH-based photocatalysis.

Morphology control is an important way to realize high photon utilization efficiency and efficient photocatalytic activity. According to the reported studies, materials with yolk-shell structure displayed strengthened photocatalytic activity owing to their multi-reflections of light, organic adsorption and porous characteristics [8,9]. These catalysts with higher stability and light adsorption efficiency present remarkable ability in comparison with their conventional hollow and solid counterparts in photocatalytic activity [10]. For example, Sun et al. synthesized Zn_2SnO_4/SnO_2 composites with different morphologies and the result suggested that sample with yolk-shell structure presented higher photocatalytic activity in comparison with other catalysts [8].

In recent years, carbon-based materials, such as carbon nanotubes, activated carbon and graphene, are widely used to support samples for various applications in nanomedicine, bioimaging, as well as photocatalysis [11,12]. As we know, carbon quantum dots (CQDs), as a newly developed carbon-based zero-dimensional nanomaterial, have aroused

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https://doi.org/10.1016/j.apsusc.2018.10.087
Received 30 June 2018; Received in revised form 25 September 2018; Accepted 9 October 2018
Available online 10 October 2018

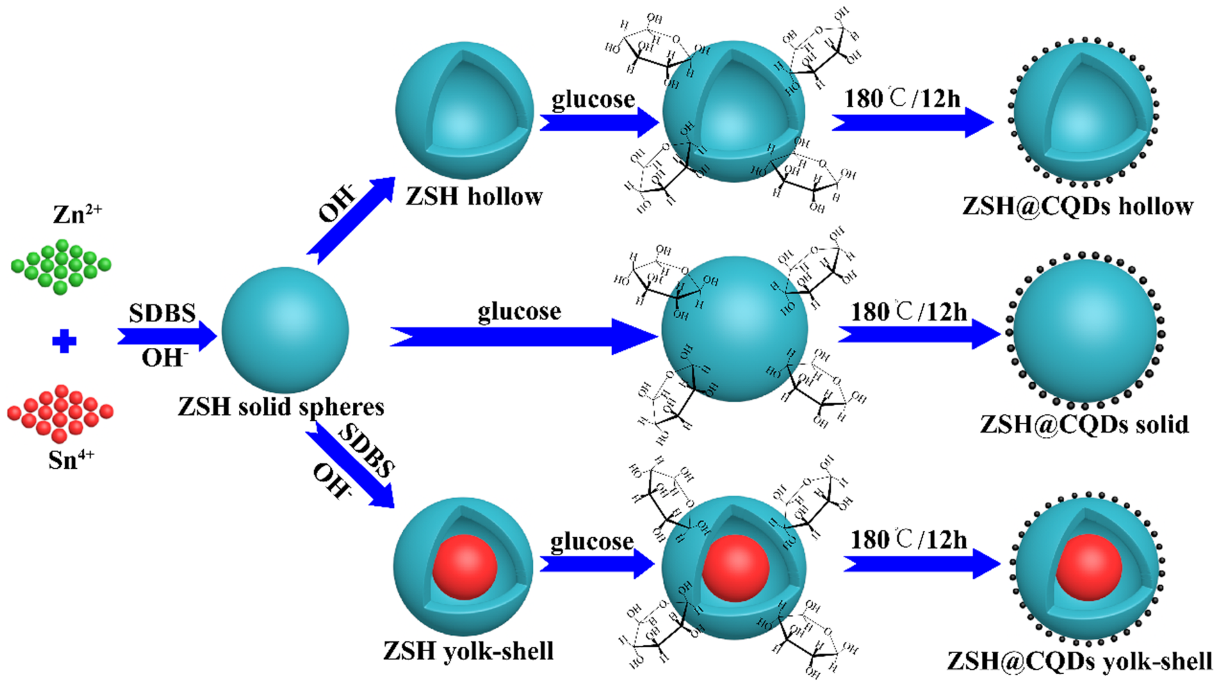

Fig. 1. Controlled fabrication process for three morphologies of ZSH@CQDs composites.

widespread attention owing to their unique properties including tunable photoluminescence (PL) emissions, low toxicity, high aqueous solubility, high chemical stability, environmental friendliness and excellent electrical conductivity [13,14]. Particularly, CQDs could act as outstanding spectral harvesters and converters, in which contradiction between light absorption and redox reaction dynamics of numerous UV and visible responsive photocatalysts could be realized [15,16]. This result might be attributed to ability of CQDs, which present a wide range of up-conversion absorption and a large cross-section of PL emission spectra, speeding up energy bandgap matching of a large number of catalysts [17,18]. In addition, CQDs could also suppress recombination of photogenerated charge carriers by capturing photogenerated electrons, thereby prolonging their lifetimes [19,20].

Herein, uniform solid, hollow and yolk-shell ZSH were successfully fabricated by a facile solvothermal method and etching-second growth strategy. CQDs was selected to sensitize ZSH. Compared with pure ZSH, ZSH@CQDs composites exhibited obviously enhanced photocatalytic activities for both degradation of organic pollutant and disinfection of *staphylococcus aureus*. The enhanced photocatalytic activity could be attributed to the unique up-conversion PL properties of CQDs, as well as efficient charge separation.

2. Experimental section

2.1. Fabrication of ZSH@CQDs composites

ZSH with three different morphologies were prepared according to the reported paper [8] and the specific procedures were shown in Supporting Information. ZSH@CQDs composites were fabricated through a facile hydrothermal method (see Fig. 1). Typically, 200 mg of as-prepared ZSH dispersed into 80 mL deionized water by ultrasound. After 30 min, 720 mg glucose as carbon source and 70 mg ascorbic acid as acid catalyst were introduced and stirred for 1 h. Then the mixtures were poured into 100 mL Teflon-lined stainless steel autoclaves and kept at 180 °C for 12 h. The obtained gray precipitates were collected and washed several times with deionized water and ethanol. Finally, samples were dried at vacuum oven for 12 h.

Pure CQDs was also synthesized by the same method only using glucose and ascorbic acid.

2.2. Photocatalytic experiments

2.2.1. Photocatalytic disinfection experiment

Photocatalytic inactivation of bacteria was investigated under a 300 W Xe lamp equipped with a UV cutoff filter (> 420 nm). *Staphylococcus aureus* was selected as typical bacteria. Firstly, *staphylococcus aureus* was cultured in LB broth at 37 °C to realize a cell count of approximate 10^7 colony forming units (CFU)/mL. 80 mg obtained sample was introduced into 30 mL bacteria suspension solution. 1 mL solution was taken out at intervals of 0.5 h then immediately spread on nutrient agar plates and incubated at 37 °C for 24 h to examine the number of viable cells.

2.2.2. Photocatalytic degradation experiment

Photodegradation experiment was also carried out by removing of RhB dye under visible light. Prior to irradiation, 50 mg of catalyst was dispersed in an aqueous solution of RhB (100 mL, 0.01 mM) with magnetic stirring for 30 min in dark condition. During irradiation, 5 mL of suspension was taken and centrifugated at intervals of 30 min. Concentrations of dye were determined by UV–vis spectrophotometer (TU-1901).

3. Results and discussion

3.1. Morphology and microstructure analysis

Morphology and microstructure of synthesized samples are investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In Fig. 2a, as-prepared ZSH spheres are uniform and their mean size is about 1.3 μm. Besides, their surfaces are