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Facile fabrication and photocatalytic properties of ZnO nanorods/ZnSe nanosheets heterostructure

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ABSTRACT

The ZnO nanorods/ZnSe nanosheets heterostructure had been successfully fabricated by the spin coating method. The evolution of the structural, optical and photocatalytic properties of the samples with different spin coating times was comprehensively investigated. The X-ray diffraction (XRD) patterns showed that the relative intensities of ZnSe peaks increased gradually with the increase of spin coating times, but the ZnO peaks were relatively suppressed, which had a good agreement with the results of Raman spectra. The scanning electron microscope (SEM) and transmission electron micrograph (TEM) images further confirmed that the ZnSe nanosheets (NSs) had been successfully assembled on the top surfaces of the ZnO nanorods (NRs) and in the upper parts of the gaps between the rods. At room temperature, the ZnO/ZnSe heterostructures exhibited a relatively suppressed UV emission together with a dramatically enhanced deep-level emission. In addition, the heterostructures exhibited remarkable photocatalytic activities. The type-II staggered band alignment and defects formed at the ZnO/ZnSe interfaces should be the key factors for improved photocatalytic performance, and the probable photocatalytic mechanism was discussed in detail.

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1. Introduction

In recent years, semiconductor-based photocatalyst as an effective candidate for purifying contaminants has attracted intense interest with the increase of environmental pollution worldwide [1–4]. It is well-known that zinc oxide (ZnO) is an useful semiconductor nanomaterial for photocatalysis [5–7]. As an important II–VI group semiconductor, ZnO with a direct band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [8], which is appropriate for a variety of applications related to photoelectronic, photovoltaic, photocatalysis and others. In contrast to a single phase semiconductor, a heterostructured semiconductor is beneficial to the improved photocatalytic performance due to its synergistic effects such as enhanced light harvesting, improved photostability, efficient charge separation and accelerated electron–hole transfer via heterojunction [9–12]. Zinc selenide (ZnSe) is an ideal choice for fabricating ZnO-based heterostructures because its band gap (2.67 eV) is narrower than that of ZnO, and it is good compatible with ZnO [13–17]. What's more, ZnSe displays the environmental friendly properties.

Over the past few years, research on heterostructures has covered from the symmetric core/shell quantum dots [18] to anisotropic dumbbell-like [19], nanobelts [13], nanocables [12,20], nanobarbells [21], nanowires [14–16], and so on. Many researchers have also concentrated on the preparation of heterostructures with greater complexity, such as tetrapods [22], multipods [23], and hyperbranched heterostructures [24], which may introduce many new opportunities for enhancing the functionality. But the study of the nanorods/nanosheets heterostructures is still quite rare.

So far, a variety of techniques have been employed for the synthesis of ZnO/ZnSe heterostructures, such as chemical vapor deposition (CVD) [15], chemical transformation [25], pulsed laser deposition (PLD) [26] and successive ionic layer adsorption and reaction [27]. But most of these methods generally required harsh conditions, such as complex processes, high temperature, long reaction times, and also needed highly expensive and sophisticated equipments, which determined that they were not suitable for large-scale production with a relatively low cost. Consequently, the methods that may be feasible, easily controllable, and easily repeatable are urgently needed.

In this paper, we presented a facile method to prepare ZnO nanorods (NRs)/ZnSe nanosheets (NSs) heterostructure. Firstly, we prepared the ZnO NRs arrays, and then the solution of the ZnSe NSs was spin coated onto the substrate of the ZnO NRs for different times. The effects of the spin coating times on the structure, optical property, and photocatalytic activity of heterostructure were investigated. Particularly, the heterostructures exhibited excellent photocatalytic properties, which were very promising for the removal of organic pollutants from wastewater. The fabrication procedure and photocatalysis mechanism of the ZnO/ZnSe heterostructures were systematically illuminated.

2. Experimental

All the chemical reagents used in the experiments were of analytical grade (purchased from Sinopharm Chemical Reagent Co., Ltd), and used without further purification. Distilled water was made in analytical laboratory.

2.1. Preparation of ZnO nanorods (NRs) (Ref. [28])

ZnO NRs were grown on indium tin oxides (ITO) substrates by a two step CBD method, i.e., a substrate treatment prior to the CBD growth, details of the sample preparation can be found elsewhere in our previous work [28]. Firstly, the pretreatment of the substrates, by coating the substrate for several times with a 10 mM solution of zinc acetate dihydrate ($Zn(OOCCH_3)_2 \cdot 2H_2O$, 99.9% purity) dissolved in pure ethanol. This solution was coated four times onto ITO substrate by a spin coater (Laurell WS-400-8TFW-Full) at the rate of 2000 rpm for 30 s, and then the ITO substrate with a seed layer was annealed at 300 °C for 1 h. Subsequently, the CBD growth, the 0.1 M aqueous solutions of zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 99.9% purity] and 0.1 M aqueous solutions of methenamine ($C_6H_{12}N_4$, 99.9% purity) were first prepared and mixed together. The pretreated ITO substrates were immersed