



ZnO nanowires coated stainless steel meshes as hierarchical photocatalysts for catalytic photodegradation of four kinds of organic pollutants



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ABSTRACT

ZnO nanostructures were grown on the stainless steel mesh substrates using an aqueous chemical growth method. The different additives (such as 1,3-diaminopropane and polyethyleneimine) can be used to control the morphology of ZnO nanostructures. ZnO nanowires exhibit very prominent green emission and weak UV emission from defect and band gap in the cathodoluminescence spectrum, respectively. The different morphology of ZnO nanostructures on the stainless steel mesh substrates can be used to irradiate UV light for the photocatalytic degradation of four kinds of organic pollutants, such as methylene blue, rhodamine 6G, methyl orange, and 4-nitrophenol. The ZnO nanowires can provide a higher surface-to-volume ratio and stronger defect emission, resulting in their highest photocatalytic performance in 10 W UV light irradiation. The ZnO nanowire arrays on the stainless steel mesh substrates provide a large-scale, facile, low-cost, high surface area, and high photocatalytic efficiency, which shall be of significant value for practical applications of the decomposition of environment pollutants and reusing of wastewater treatment.

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1. Introduction

Organic pollutants (such as organic dyes) have been widespread manufactured for using in the textile, industrial painting, food, plastics, cosmetics, and consumer electronic sectors [1,2]. Most of organic pollutants are non-biodegradability, toxicity, and potential carcinogenicity cause serious threat to the environment and human health [2,3]. Recently, there are several innovative technologies used to organic pollutants treatment, such as adsorption, filtration, sedimentation, and photocatalytic degradation [4], etc. Among them, photocatalytic degradation of organic pollutants is one of the most attractive technologies because it is complete mineralization, no waste disposal problem, low cost, mild temperature, and pressure conditions [5–7].

Photocatalytic degradation under light energy is utilized to excite the semiconductor material producing electron-hole pairs for the detoxification of organic pollutants or splitting water into hydrogen [8,9]. Semiconductor nanostructures are efficient

photocatalysts in comparison with semiconductor bulk materials [10,11]. Various semiconductor nanostructures have been used as photocatalysts to decompose organic pollutants, such as Bi₂O₃, CdS, Fe₂O₃, SiO₂, TiO₂, ZnO, ZnS, and other metal oxide etc [12–19]. It is relative difficult to find a stable and nontoxic semiconductor nanostructures with high photocatalytic activity for decomposed organic pollutants. TiO₂ and ZnO materials are extensively used as effective and nontoxic semiconductor photocatalysts for the degradation of organic pollutants [1,20,21]. Compared to TiO₂ nanostructures, ZnO nanostructures have attracted much attention due to their high quantum efficiency, excellent thermal and chemical stability, nontoxicity, abundance, and low cost, etc [22–25]. In addition, ZnO nanostructures are more suitable for photodegradation of organic pollutants in present of sunlight for practical use as a photocatalyst in wastewater treatment [21,26,27].

ZnO oxide (ZnO) is an important oxide material with a wide direct band-gap (3.37 eV), n-type semiconducting properties, large exciton binding energy (60 meV), has been extensively studied due to its potential applications in solar cells [28,29], sensors [30], photocatalysis [31–33], photonic crystals [34,35], light-emitting diodes [36,37], and piezoelectric nanogenerators [38–40]. The different kinds of ZnO nanostructures have been fabricated through

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various techniques, such as chemical vapor deposition (CVD) [41], physical vapor deposition (PVD) [42,43], molecular beam epitaxy (MBE) [44], pulsed laser deposition [45,46], thermal evaporation [47,48], and aqueous chemical growth (ACG) method [49–51]. Among them, ACG method is one of most important techniques attributed to its catalyst-free, template-free, low temperature, low cost, and low substrate selectivity [29,52–54]. There are a lot of methods used to control the morphology of ZnO nanostructures by an ACG process, such as reaction time, solution concentration, different pH values, and capping reagents [27,29,54,55]. The capping reagents have a remarkable ability to control the dimensions or shapes of ZnO nanostructures. In general, capping reagents may play two kinds of roles to grow the ZnO nanostructures in an ACG process [29]. One is absorbed onto the side surfaces of ZnO nanostructures and enhanced the vertical growth, such as hexamethylenetetramine (HMTA), ethylenediamine (EDA) [56], and polyethyleneimine (PEI) [57]. The other is capped onto the basal plane of ZnO nanostructures and induced lateral growth, such as citrate ions [51], ascorbic acid [27], and chloride [58]. PEI is a nonpolar polymer with a large amount of amino groups ($-\text{NH}_2$), which can be used to grow ZnO nanowires with long length by longer growth time [29]. However, there are no reports about the growth of ZnO nanowires on the stainless steel mesh substrates with longer than 10 μm by an ACG method for a short reaction time.

Hierarchical structures with high degree of order have improved physical or chemical properties rather than their single component [59]. Flexible stainless steel mesh has attracted wide interest due to their many properties, such as light weight, high flexibility, transparency, and low cost [60]. In addition, metal meshes can also provide larger substrate specific surface area for loading light-harvesting components relative to metal foils. Marbán et al. demonstrated that the stainless steel mesh-supported catalysts can be beneficial to oxidation of CO [61], decomposition of NO [62], and photodegradation of methylene blue under UV light irradiation [63]. Hsu et al. obtained that Ag doped ZnO nanorods were grown on the stainless steel mesh substrates can act as visible light driven hierarchical photocatalysts with high activity and stability [59]. Lu et al. reported that ZnO nanorods were prepared on the stainless steel mesh substrates by using a direct electrodeposition method for photocatalytic degradation of rhodamine B [64]. Jung et al. described the photocatalytic activity of flower-like CuO–ZnO heterostructured nanowires fabricated on a stainless steel mesh [65]. However, there are also no reports about the different one-dimensional ZnO nanostructures and mesh sizes for the photodegradation of four kinds of organic pollutants with high reusability.

The present work is used appropriate concentration of 1,3-diaminopropane (DAP) and PEI to grow longer ZnO nanowires on the stainless steel mesh substrates with ZnO seed film at the short reaction time. The ZnO nanowires exhibit weak UV emission from band gap and very strong green emission from defect in the cathodoluminescence spectrum. The stainless steel mesh substrates with ZnO nanowires have shown a structure-induced enhancement of photocatalytic performance by higher surface-to-volume ratio, which exhibit a much better photocatalytic property for the photodegradation of four kinds of organic pollutants in 10 W UV light irradiation. The ZnO nanowires on the stainless steel mesh substrates are expected to have excellent potential for surface-related applications.

2. Experimental

2.1. Synthesis

Silicon (001) wafers and stainless steel mesh substrates were

cleaned by ultrasonic vibrator and dipping in 95% ethanol for 10 min simultaneously to remove particles and organic pollutant from the surface of substrates. For silicon wafers, a thin film of zinc acetate was then coated on the substrate by spinning a layer of solution of 20 mM zinc acetate dihydrate (98%, Aldrich) in ethanol and repeating for 10 times. 10–20 nm thick ZnO seed film was produced after annealing at 350 °C in air for 20 min. For stainless steel mesh substrates, ZnO seed film was fabricated by dip coating a layer of solution of 20 mM zinc acetate dihydrate (98%, Aldrich) in ethanol and then heated the substrates at 80 °C for 3 min and 350 °C for 20 min. The ZnO nanorod arrays were grown by an ACG method in 100 mL aqueous solution containing 10 mM equimolar zinc nitrate dihydrate (98%, Aldrich) and hexamethylenetetramine (99%, Aldrich) (HMTA) each. The ZnO nanoneedle arrays were grown by an ACG method in 100 mL aqueous solution containing 10 mM equimolar zinc nitrate dihydrate and HMTA and 0.12 M 1,3-diaminopropane (98%, Alfa Aesar) (DAP). The ZnO nanowire arrays were grown by an ACG method in 100 mL aqueous solution containing 10 mM equimolar zinc nitrate dihydrate and HMTA and 0.12 M DAP with the addition of different concentrations of polyethyleneimine (average molecular weight 800 g/mol, Aldrich)(PEI). The substrates with ZnO seed film was pasted at the side of sealed bottle containing with above solution and heated to about $T = 90^\circ\text{C}$ for 2 h. The experimental conditions and morphologies are listed in Table S1.

2.2. Characterization

The morphology of nanostructures was examined with a field emission scanning electron microscope (FESEM) using a JEOL JSM-6700F SEM operating at 15 kV accelerating voltage. A JEOL-2010 transmission electron microscope (TEM) operating at 200 kV was utilized to identify phase and examine the microstructures. The crystalline phase of the ZnO nanostructures was determined using the X-ray powder diffraction method (Shimadzu XRD-6000, $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 0.1505\text{ nm}$)). The cathodoluminescence (CL) spectra were acquired with an electron probe microanalyzer (Shimadzu EPMA-1500) attached to a SEM. CL spectra were accumulated in a single shot mode within an exposure rate of 1 nm/s. All the CL spectra were taken at room temperature. The degradation of the different kinds of organic pollutants was used to evaluate the photocatalytic activity of ZnO nanostructures. The different kinds of organic pollutants were exposed to a 10 W UV lamp (254 nm). The concentrations, maximum absorption peaks, and pH values of different kinds of organic pollutants are listed in Table S2. For the photocatalytic activity evaluation, the concentration of photo-degraded organic pollutants was recorded by a Hitachi U-2900 UV–vis spectroscopy.

3. Results and discussion

3.1. Morphologies and crystal structures

Fig. 1a shows the cross-sectional SEM image of ZnO nanorod arrays on a silicon substrate with ZnO seed film. ZnO nanorod arrays were grown from equimolar (10 mM) zinc nitrate and HMTA by an ACG method at the growth temperature of 90 °C for 2 h. The average lengths and diameters of ZnO nanorod arrays are 1.8 μm and $47.5 \pm 5.6\text{ nm}$, respectively. The aspect ratio of ZnO nanorod arrays is about 37.9. The reaction solution is reacted under near neutral conditions ($\text{pH} = 6.93$). Fig. 1b shows the cross-sectional SEM image depicting the tapered ZnO nanorod arrays, herein called nanoneedle arrays were grown from equimolar (10 mM) zinc nitrate and HMTA and 0.12 M DAP by an ACG method at the growth temperature of 90 °C for 2 h. The average lengths and diameters of

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