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Porous nanosheet-based hierarchical zinc oxide aggregations grown on compacted stainless steel meshes: Enhanced flexible dye-sensitized solar cells and photocatalytic activity

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ABSTRACT

Porous nanosheet-based hierarchical ZnO aggregations are prepared on compacted stainless steel meshes (CSSMs) using a facile precursor template method. The coverage density and morphology of the film are controlled by the concentration of alkaline in the precursor solution. Relative to the traditional planar substrate, CSSMs with multi-layered structure have larger surface area and higher porosity to capture more light from all directions. The three-dimensional (3D) hierarchical ZnO aggregations assembled by porous nanosheets could take both the advantages of nanosheets and micrometer-sized assemblies. As expected, combining the virtues of ZnO aggregations and CSSMs, the ZnO aggregations/CSSMs structure exhibit the significantly improved conversion efficiency as photoelectrode of flexible dye-sensitized solar cells and photocatalytic performance in the photodegradation of pollutants with a better recyclability. Furthermore, our work would offer idea for the growth of complex 3D hierarchical micro-/nanoarchitecture on the high curvature surface of the substrates.

1. Introduction

Synthesis of wide-band gap oxide semiconductors with controllable sizes and shapes on various substrates have great appeal because of the enormous requirements of practical applications in function devices [1,2]. Compared to the traditional rigid fluorine-doped tin oxide (FTO) glass, the flexible substrates such as plastic and polymer substrates [3,4], metal foils [5,6], carbon fibers [7], graphene foam [8] and the stainless steel meshes (SSMs) [9–11] are lighter and softer, which can be convenient for transportation and used in more complex environments [12]. And among of these materials, the SSMs are conductive, low-cost, what is important is that they are resistant to corrosion, heat and fatigue compared to plastic and polymer substrates. Meanwhile, relative to metal foils, SSMs can be introduced light irradiation from all directions for the capture of more incident photons [10]. So, the SSMs were introduced into flexible dye-sensitized solar cells' (F-DSSCs) working electrode [9,13,14]. However, with the existence of spaces between the warp and the woof of SSMs, there is no doubt that the efficient surface area would decrease, resulting in a reduction in efficiency of corresponding devices (Supplementary Fig. S1a).

Zinc oxide (ZnO) is generally recognized as one of the most versatile functional oxides for practical applications in the transforming solar energy into electricity [15,16] and photocatalytic degradation of pollutants in air and water [17,18], owing to its lower cost, non-toxicity, attractively catalytic and electronic properties. Amounts of theoretical and experimental researches have concluded that the efficiency of ZnO-based dye-sensitized solar cells (DSSCs) and photocatalyst dependent on not only the surface area and crystallinity, but also the mesoporosity and morphology [15–19]. So, much low-dimensional ZnO prepared on the flexible substrates served as the photoelectrodes of F-DSSCs [20,21] and also photocatalyst to degrade pollutant, which was easy to recycle from photocatalytic reactions solution and avoid secondary pollution [10]. In recent years, a massive effort has been spent to the fabrication of 3D hierarchical micro-/nanoarchitectures ZnO assembled by low-dimensional nanostructured building blocks [22]. On the one hand, low-dimensional nanostructured

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building blocks, such as nanowires or nanosheets, can provide the high surface area and direct electrical pathways for the collection of photogenerated electrons to reduce the charge recombination [23]; On the other hand, hierarchical aggregates with micrometer-sized can function as light scatters to increase the light-harvesting capability [24,25]. Therefore, hierarchical architectures showed superior photoelectric and photocatalytic properties to those of the building blocks [26,27]. However, so far, hierarchical architectures were synthetised merely on the flexible flat plate substrates with low curvature surface for F-DSSCs, such as metal foils [28]. A method of effective growth of such 3D hierarchical structures on weaved metal wires is still an issue because such complicated construction is hard to grow on high curvature surface.

Here we introduce compacted stainless steel meshes (CSSMs) as a substrate, which were prepared by pressuring multichip SSMs under high pressure. Compared to the traditional SSMs, CSSMs have larger efficient surface area and higher porosity to capture more light from all directions (Supplementary Fig. S2). A facile hydrothermal precursor template method was developed for synthesis of 3D hierarchical ZnO aggregations on the CSSMs. The coverage density and morphology of the films were controlled by the concentration of alkaline in the precursor solution. The as-prepared ZnO aggregations were built by many interlaced porous nanosheets with thickness of ~15 nm. In comparison with ZnO aggregations grown the traditional SSMs and ZnO nanowires grown on CSSMs, the as-prepared structure obtained a nearly 25.0%, 52.2% improvement in the F-DSSCs and 74.9%, 171.1% improvement in photocatalytic degradation of Rhodamine B (RhB) under UV light irradiation with a better recyclability, respectively. Furthermore, our work would offer idea for the growth of complex 3D hierarchical micro-/nanoarchitectures on the high curvature surface of the substrates.

2. Experimental

2.1. Fabrication of ZnO nanostructures

The compacted stainless steel mesh (4 cm × 2 cm) was cleaned ultrasonically in the sequence of acetone, ethanol for 20 min. Porous nanosheet-based hierarchical ZnO aggregations grown on the CSSMs were fabricated using precursor template method. The dense ZnO seed layer (DSL) solution was the ethanol solution of Zn $(CH_3COO)_2{\cdot}2H_2O$ and NaOH 0.1 g of $Zn(CH_3COO)_2{\cdot}2H_2O$ was added into a set of 100 mL NaOH alcohol solution (1 mM, 2 mM, 3 mM) with ultrasonic vibrating for 10 min, respectively. The cleansed CSSMs was dipped in the DSL solution for 1 min, taken out, dried by ultrared rays, and then sintered at 350 °C for 10 min. The above process was repeated three times. The corresponding samples were labelled as P1, P2 and P3, respectively. 0.33 g of Zn $(CH_3COO)_2{\cdot}2H_2O$ and 0.21 g of hexamethylenetetramine (HMT, $C_6H_{12}N_4$) were dissolved in 30 mL deionized water and transferred to a 50 mL Teflon–lined autoclave. The DSL-coated CSSMs were obliquely immersed into the resulting solution. The sealed autoclave was treated at 100 °C for 3 h, the CSSMs was took out and rinsed with deionized water. Finally, the as-prepared samples were calcined at 500 °C for half an hour. By contrast, the sample without DSL was labelled as "without DSL". Hierarchical ZnO grown on the traditional stainless steel meshes were synthesized under the same preparing conditions of P2 and labelled as P4.

ZnO nanowires grown on the CSSMs were prepared by a precursor template method and labelled as ZnO-NW. The DSL solution was 5 mM ethanol solution of $Zn(NO_3)_2{\cdot}6H_2O$. The hydrothermal reaction solution was prepared by dissolving 4.5 mmol of $Zn(NO_3)_2{\cdot}6H_2O$ and 1.5 mmol of $C_6H_{12}N_4$ into 30 mL H_2O. Other experimental operation and conditions were unchanged.

2.2. Characterizations

The morphology images were recorded via the scanning electron microscopy (SEM, FEI NOVA NanoSEM230, USA) and the transmission electron microscopy (TEM, JEOL 3010, Japan). For TEM samples, hierarchical ZnO was detached from the CSSMs by ultrasonic treatment in ethanol. The X-ray diffraction (XRD) data were collected by X-ray diffractometer with Cu-Kα radiation at 200 mA and 40 kV. Shimadzu UV-2550 UV–vis spectrometer was used to investigate the diffuse reflectance spectrum and optical absorption of powder. Intensity-modulated photocurrent/photovoltage spectra (IMPS/IMVS) were examined on the electrochemical 30 workstation (Zahner, Zennium). The incident-photon-to-current conversion efficiency (IPCE) spectra were performed using PEC-S20 (Peccell Technology). The photocurrent–voltage measurements (*J-V*) were performed under a sunlight simulator with an active area of 0.132 cm^2 (Oriel 92251A-1000, AM 1.5 globe, 100 mW cm^{-2}).

2.3. Preparation of the electrode

The loaded meshes were soaked in N719 ethanol solution for 1 hr at room temperature. Here a platinum plate was used as counter electrode. 50 mM LiI, 30 mM I2, 1.0 M 1-*Butyl*-3-methylimidazolium iodide (BMIMI) and 0.5 M tert-butylpyridine in a mixed solvent of acetonitrile and valeronitrile (v/v, 85:15) was applied as electrolyte. The dye-coated electrode was sandwiched together with counter electrode. The electrolyte was introduced into the gap of the two electrodes.

2.4. Photocatalytic activity test

An initial concentration of 1.0×10^{-5} M Rhodamine B (RhB) aqueous was used to investigate the photocatalytic activity of the prepared samples. All the samples with the same irradiation areas were immersed in 100 mL of RhB solution for 24 hrs to ensure an established adsorption/desorption equilibrium. Then, 5 mL of RhB solutions was collected and marked as the base concentration C_0. The remaining RhB solution was exposed to a 500W xenon lamp with a current of 20 A (80 mW cm^{-2}) and AM 1.5 G solar simulator (100 mW cm^{-2}) at room temperature, respectively. The distance between the light source and sample was 10 cm. In the following 75 min, 5 mL of solution was extracted out every 15 min, whose

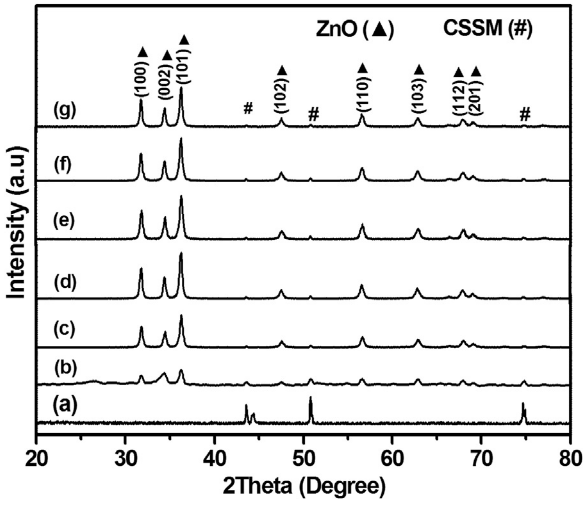

Fig. 1. XRD patterns of (a) the compacted stainless steel mesh (b) without DSL, (c) P1, (d) P2, (e) P3, (f) P4 and (g) ZnO-NW.