



Full Length Article

High-quality ZnO inverse opals and related heterostructures as photocatalysts produced by atomic layer deposition



Jie Long, Ming Fu*, Caixia Li, Cuifeng Sun, Dawei He, Yongsheng Wang

Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing, PR China

ARTICLE INFO

Keywords:

Photonic crystals
Colloidal template
Zinc oxide
Atomic layer deposition
Heterostructures
Photocatalysis

ABSTRACT

ZnO with various nanostructures is widely investigated for high photoelectrochemical (PEC) catalysis performances due to its abundant and inert semiconducting properties with elevated electronic mobility and variable morphologies. Because the solar energy conversion efficiencies could possibly be further enhanced by the introduction of nanophotonic structures with larger surface ratios, high-quality ZnO inverse opals (IOs) were achieved by ALD method using O₃ as the oxidant. The intrinsic UV emission peaks and PEC currents of ZnO IOs produced by O₃ atomic layer deposition (ALD) method were much improved when compared to those made by H₂O ALD and electrodeposition. ALD at higher temperatures (240 °C) can further enhance the crystalline quality and PEC performances. The optimal ALD thickness and filling fraction obtained by controlling ALD cycles, as well as the optimal photonic stop band position obtained by colloidal crystals with different sphere diameters were also discussed. It was found that conformally coated samples with TiO₂ protection layers by ALD method using titanium tetrachloride as a precursor enhanced the photochemical stability of ZnO IOs. The photocorrosion was further reduced by inserting ALD Al₂O₃ inside the TiO₂ protection layers. Heterostructured photonic crystals with double-layer IO structures with different pore periodicities were also developed for enhancing the PEC performances.

1. Introduction

Among recent renewable energy technologies, the conversion of solar energy to chemical energy is considered promising for applications in solving the energy crisis, global warming, and environmental pollution. In this respect, the photoelectrochemical (PEC) splitting of water into hydrogen and oxygen using direct sunlight is an ideal approach for renewable methods by integrating solar energy collection and water electrolysis into single semiconductor photoelectrodes [1]. Metal oxide semiconductors are widely studied as photo-electrolyzers for H₂ production due to their appropriate bandgap and flat band potential, as well as their low-cost, moderate electrical resistance, and good scalability for production purposes [2–4]. Among them, titanium TiO₂ [5–12] is considered as a pioneering model material due to its abundance, steady in aqueous solutions, and strong photocatalytic activity under UV–visible irradiation [13].

Zinc oxide (ZnO) is another abundant and inert semiconducting material with photocatalytic performances and bandgap/band-edge positions that are similar to TiO₂ [3]. In addition, crystalline ZnO has elevated electronic mobilities ranked to respectively 205 ~ 300 and 1000 cm² V⁻¹ s⁻¹ for bulks and nanowires, at room temperature. These

values are higher than most semiconducting metal oxides, including SnO₂ and TiO₂. These unique characteristics made ZnO advantageous for PEC water splitting as it provides a fast electron delivery and low recombination of the photo-generated carriers [14,15]. On the other hand, the wide band gap in ZnO (3.37 eV at 368 nm) limits the amount of the absorbed solar light. However, ZnO can be alloyed with other semiconductors with similar lattice structure like GaN or InN to yield significantly reduced band gaps [16–18]. ZnO can also uniformly grow at low temperatures (≤ 500 °C) on both crystalline (e.g. ZnO, sapphires Al₂O₃, Si) and noncrystalline (e.g. glass, plastic) substrates with larger areas. In addition, ZnO of diverse nanostructured electrodes with large surface-to-volume ratios could readily be formed to provide much more active sites for catalytic reactions if compared to traditional electrodes [19–21]. A number of ZnO nanostructures have been synthesized by different methods, including nanoclusters [22,23], nanowires [24–26], nanotube [27–29], nanobelt [26], nanofilms [28,30], and nanosheets [31]. Most of the studies have been focused on typical quasi-one-dimensional ZnO nanomaterials with nanorods, nanowires, and two-dimensional nanobelts structures applied as photocatalysts. Common catalytic ZnO nanowires have average diameters of few tens of nanometers and length of 1 μm, with packing densities of

* Corresponding author.

E-mail address: mfu@bjtu.edu.cn (M. Fu).

$2 \sim 3 \times 10^{10} \text{ cm}^{-2}$ [25]. This provides a great surface area for photocatalytic reactions and short traveling distances for the photo-generated carriers to reach the surface of the nanostructures. ZnO nanostructures such as nanowires can also perform behaviors including waveguide, Fabry–Pérot modes [32] and show photonic advantage of orthogonalized light absorption and charge transfer [33,34]. However, the major contributions are still induced from the electronic and photoelectronic advantages of these materials. Possibly, the solar energy conversion performance could further be enhanced when light absorption is improved by modifying the photonic density state by means of different microstructures. The development of materials using metal-based plasmonic nanoparticles [35] and periodic basic photonic morphologies [36] are among commonly used technologies for photonic modulations.

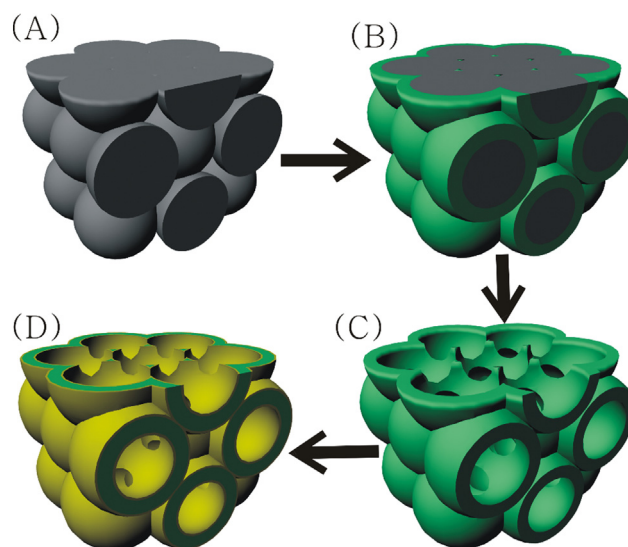
In this study, aperiodic macroporous structures of photonic crystals made of high-quality ZnO, ZnO inverse opals (ZnO IOs), were examined. The slow light propagation [1,37] near the stop band and multiple scattering effect [36] in IO photonic crystals are possible routes for improving light harvesting. The resulting continuous porous channels have further increased the specific area of reactions and facilitated the transfer of reactant molecules [38–40]. IO structures fabricated using polystyrene (PS) microsphere templates have been studied as conventional ZnO electrodes. Numerous synthetic methods have been developed to prepare ZnO IOs, including electrochemical deposition [31], chemical vapor deposition (CVD) [41], and sol-gel [42,43] methods. However, most of these procedures yield unsatisfactory crystalline quality, a key predictive factor in the photocatalytic performances. Actually, a better crystallinity of ZnO can be obtained by electrochemical deposition [31], but it is not suitable for the formation of ZnO microstructures inside three-dimensional templates. On the other hand, the atomic layer deposition (ALD) method [44,45] is used as a scalable layer-by-layer synthesis process due to its numerous advantages, including its ability to conformally coat 3D structures, uniformly coat large surfaces, flexible deposition at low temperatures, and controlled thickness even at the angstrom scale. However, the crystalline quality of currently reported ZnO IOs by ALD methods is still overall poor as using H_2O as oxidant. Ozone (O_3) has higher activity and may produce oxide films with lower concentrations of impurities when compared to the films grown with H_2O [46–48]. But the thermal ALD using O_3 is not employed for ZnO IOs till now. In this account, an enhanced ALD method for formation of ZnO IOs with high quality and good photocatalytic performance was investigated.

One of the major drawback of ZnO lies in its low photo-corrosion resistance in aqueous media under ultraviolet illumination [44,45,49–51]. However, the high aspect ratio of the 3D porous structures make it more difficult for the anti photo-corrosion for ZnO IOs. Therefore, this study was also focused on demonstrating the anti-photo corrosion performance of ZnO IOs using a highly conformal coating of TiO_2 or alternative $\text{Al}_2\text{O}_3/\text{TiO}_2$ layers formed by ALD for water splitting. Hetero-structure photonic crystals of ZnO IOs formed using different colloidal templates of monodispersed spheres of various diameters were also developed as photoanodes.

2. Experimental

2.1. Synthesis of TiO_2 coated ZnO-IO

The general route used to prepare ZnO IO films with the conformal TiO_2 protecting layer was illustrated in Scheme 1. The colloidal crystal templates were fabricated using monodispersed polystyrene colloidal spheres using the self-assembly route based on vertical deposition method on indium tin oxide (ITO) covered glass shown in Scheme 1(a). Firstly, the clean ITO glasses were put vertically in a 10 mL water solution containing 0.25% colloidal spheres with diameters of 155 nm, 197 nm, 238 nm, and 302 nm. The apparatus was then placed in an incubator at 55°C for about 4 ~ 5 days, and close-packed 3D colloidal crystals were obtained on ITO glass substrates. Hetero-structured



Scheme 1. Fabrication of ZnO-IO conformally coated by multi-step ALD deposition: (a) self-assembled colloidal crystal template, (b) ALD-deposited ZnO on prepared opal template, (c) ZnO-IO after removing the template by calcination, and (d) TiO_2 coated ZnO-IO by further ALD deposition.

colloidal templates were then formed during the next vertical deposition process. It will be noted that conformal ALD ZnO coatings were required for template immobilization before next vertical deposition process.

As shown in Scheme 1(b), ultrathin ZnO layers were deposited on the prepared colloidal crystal templates using a thermal ALD system (TALD-150, Wayes-Vac, China), with diethylzinc $\text{Zn}(\text{C}_2\text{H}_5)_2$ (DEZ) ($T_{\text{precursor}} = \text{room temperature}$), H_2O ($T_{\text{precursor}} = \text{room temperature}$) or O_3 ($T_{\text{precursor}} = \text{room temperature}$) were employed as Zn and O precursors. The prepared samples were ZnO(H_2O) and ZnO(O_3) for ALD ZnO with different oxide precursors. The oxide precursors (H_2O or O_3) were first pulsed for 0.03 s, held in the chamber for 4 s, purged with nitrogen for 60 s, and finally evacuated for 20 s. The zinc precursor (DEZ) was pulsed for 0.06 s, held in the chamber for 4 s, purged with nitrogen for 60 s, and then evacuated for 20 s.

The ALD was carried out at 85°C and between 160 and 240°C when H_2O and O_3 were used as oxide precursors, respectively. As shown in Scheme 1(c), the direct run of the ALD process in N cycles followed by removal of the template yielded ZnO(H_2O)-IO samples, named as ZnO (H_2O , N)-IO- DIAMETER (where N is a positive integer, DIAMETER is the number of the diameter of the monodispersed colloidal spheres in nanometer).

Due to the fragile nature of the polystyrene templates, which would deform at temperatures higher than 95°C , thinner ALD ZnO (H_2O , 40c) were deposited as a skeleton for further ALD process of ZnO using O_3 . The ALD process of ZnO(O_3) was performed at $160\text{--}240^\circ\text{C}$ after ZnO (H_2O , 40c)-IO platforms were fabricated. The colloidal templates were removed when ALD-related ZnO was annealed in air at 400°C for 30 min using a ramp rate of $10^\circ\text{C min}^{-1}$ until the oven was cooled down to room temperature. The growth thickness per cycle (GPC) were measured using a stylus profiler (XP-2, AMBIOS TECHNOLOGY). The O_3 gas was produced by an XM-DS1600 ozone generator and dried using a drying tower of calcium chloride.

As shown in Scheme 1(d), the TiO_2 or Al_2O_3 protection layers were conformally deposited on the prepared ZnO IOs using titanium tetrachloride/trimethylaluminum as titanium precursors and H_2O as the oxidant ($T_{\text{precursor}} = \text{room temperature}$, $T_{\text{substrate}} = 80^\circ\text{C}$), respectively. The oxidant precursor was pulsed for 0.03 s, held in the chamber for 4 s, purged with nitrogen for 60 s, and then evacuated for 20 s. On the other hand, the titanium/aluminum precursor was pulsed for 0.06/0.03 s. Different cycles of ALD TiO_2 or $\text{TiO}_2/\text{Al}_2\text{O}_3$ alternative layers were

Download English Version:

<https://daneshyari.com/en/article/7833190>

Download Persian Version:

<https://daneshyari.com/article/7833190>

[Daneshyari.com](https://daneshyari.com)