Full paper

Synthesis of WO₃@ZnWO₄@ZnO-ZnO hierarchical nanocactus arrays for efficient photoelectrochemical water splitting

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ABSTRACT

Hierarchical heterostructures with large surface areas and multiple interfaces as photoanode materials, are holding great promise for photoelectrochemical (PEC) water splitting toward efficient solar energy utilization. In this work, the cactus-like WO₃@ZnWO₄@ZnO-ZnO (i.e. W@WZ@Z-Z) arrays compromising the first-order W@WZ@Z core-shell nanosheets and the second-order ZnO nanosheets, have been fabricated by combining atomic layer deposition (ALD) technique and hydrothermal process. The modification of ZnO nanosheets on the surface of WO₃ and the simultaneous formation of ZnWO₄ in-between buffer layer have endowed the photoanode a drastic enhancement in both ultraviolet light absorption and charge separation via the favorable band alignment at the WO₃-ZnWO₄-ZnO interfaces. Particularly, the W@WZ@Z-Z nanocactus (NC) array photoanode with a 30 nm ZnO layer on WO₃ precisely controlled by ALD, exhibited around 3.8 times higher photocurrent density (~ 1.57 mA/cm²) at 1.23 V vs. RHE than pristine WO₃ photoanode (~ 0.41 mA/cm²), with little loss after long-term continuous illumination as well. Overall, the novel combination of WO₃ with ZnO and the ZnWO₄ buffer layer, and construction of hierarchical heterostructures, along with the resulted improvement in light absorption and charge separation which have been confirmed by spectroscopic characterizations and finite-difference time-domain simulation, suggest many exciting opportunities for further development of high-performance PEC devices for solar energy conversion.

1. Introduction

Photoelectrochemical (PEC) water splitting is widely considered to be a simple and low-cost approach for hydrogen generation from solar light and water, which is a promising energy conversion route toward a clean energy society [1–4]. Till now, various nanostructured semiconductor materials, such as WO₃ [5], TiO₂ [6] Fe₂O₃ [7] and BiVO₄ [8], have been intensively selected for fabrication into photoelectrodes for PEC water splitting. Recently, substantial efforts have been paid to the development of highly active and low-cost photoanodes for water oxidation, within which the doping of semiconductors and construction of hierarchically hybrid materials are the most important methods [9]. It is known that the PEC performance of photoelectrodes is closely related to their structures. As a result, semiconductor nanostructures with diversified morphologies, such as nanowires, nanobowls, nanoparticles and nanofibers, have been designed and synthesized toward photoanodes with enhanced PEC performance [10–13]. In particular, the hierarchically branched heterostructures with tunable three-dimensional (3D) morphologies have attracted considerable research interest as promising photoelectrode materials, due to the increased surface areas and multiple interfaces, superior charge transfer, and improved light harvesting capability than other simple and single-component structures [14]. For example, the hierarchical ZnO nanotree arrays with branches perpendicular to the parent rods have been selectively grown on conductive glass substrates, which demonstrated superior PEC water splitting performance [15,16]. However, single-component structures still suffer from its low quantum efficiency and poor photostability in PEC water splitting.
reaction. Therefore, tremendous effort has been focused on preparation of hybrid heterostructured photocatalysts due to their promoted charge separation of photogenerated electron-hole pairs due to favorable band alignment, the increased active surface areas and enhanced photo-stability [17,18]. For instance, Zhang et al. fabricated well aligned, tree-like heterostructures with multiple components (ZnO, TiO2, CuO) on FTO glass, which have been demonstrated as an efficient photoanode for hydrogen generation (0.8 μmol cm⁻² h⁻¹) in PEC cells at a low applied potential (0.3 V vs. RHE) [19]. Specifically, seed-mediated secondary hydrothermal growth has been considered to be a versatile approach for preparation of 3D branched nanostructures of hybrid semiconductors [20]. In this process, well controlled seed layer modification is the key step to prepare multi-component hierarchically branched nanostructures. Hence in this regard, atomic layer deposition (ALD) technique is gaining increased attention as an important approach for seed layer deposition due to its ability for precisely controlled thickness and uniformity of the deposited layer. For instance, 3D branched ZnO nanorods can be synthesized on a variety of substrates based on the ALD-dominated seed-mediated hydrothermal method [21–24].

Tungsten oxide (WO3) and tungstate materials (e.g. ZnWO4 [25], CuWO4 [26] and Bi2WO6 [27]), owing to their moderate band gaps, favorable hole diffusion lengths and superior electron-hole separation, have been regarded as attractive candidates for PEC energy conversion. Herein, for the first time we fabricated a large-scale array of 3D heterostructured hierarchical WO3@ZnWO4@ZnO-ZnO (i.e. W@WZ@Z-Z) nanocactus (NC) through a sequential process combining ALD of thickness-controlled ZnO seed layer on the surface of first-order WO3 nanosheets and the hydrothermal process for growth of second-order ZnO nanosheets on W@WZ@Z core-shell nanosheets. Coupling WO3 with ZnO has previously been confirmed as an appealing method to improve the PEC performance, due to the band alignment-induced efficient interfacial charge separation and the easy formation of ZnWO4 buffer layer at the interface [28]. As a result, significantly improved photocurrent density and stability of W@WZ@Z NC array photoanodes were demonstrated comparing to W@WZ@Z core-shell nanosheet photoanode. The W@WZ@Z-Z NC array photoanode with 30 nm ZnO ALD layer (i.e. W@30-WZ@Z-Z) displayed 3.8 times higher photocurrent density (~ 1.57 mA/cm²) than pure WO3 photoanode at 1.23 vs. RHE in Na2S-Na2SO3 solution (pH = 13.4). Meanwhile, the W@30-WZ@Z-Z NC array photoanode showed better photo-stability as well proved by a long-term successive water splitting reaction. Such a drastic improvement in PEC performance could be attributed to the synergistic effect of the hierarchical heterostructures including enlarged active surface areas, promoted ultraviolet light absorption and beneficial charge separation by the band alignment at the WO3-ZnWO4-ZnO interfaces, which have been revealed by both the spectroscopic characterization and finite-difference time-domain (FDTD) simulation, together suggesting many new possibilities for enhancing the PEC performance of WO3 and other semiconductor-based photoelectrodes.

2. Experimental section

2.1. Synthesis of WO3 nanosheet arrays

WO3 nanosheet arrays were synthesized via a modified hydrothermal method reported before. [9] Briefly, a seed solution containing 2.5 g of H2WO4 and 1.0 g of poly(vinyl alcohol) (PVA) in 34 mL of H2O2 (30 wt%) was spin-coated onto FTO substrates at 2500 rpm, followed by annealing at 500 °C in air for 2 h. Another H2WO4 solution was prepared by adding 5.0 g of H2WO4 and 68 mL of H2O2 (30 wt%) into 100 mL of H2O and stirred at 95 °C to dissolve. This H2WO4 solution was then diluted to 0.05 M for the hydrothermal process. Next, for preparing the hydrothermal precursor solution, 3 mL of the H2WO4 solution (0.05 M), 0.02 g of oxalic acid, 0.02 g of urea, 12.5 mL of acetonitrile and 0.5 mL of HCl (6.0 M) were added into a 50 mL beaker and stirred to clear. An FTIR glass substrate pre-coated with the WO3 seed solution was then placed into a 25 mL Teflon-lined stainless steel autoclave filled with as-prepared precursor solution, and kept at 180 °C for 2 h. Finally, the obtained sample was annealed at 500 °C in air for 2 h.

2.2. Synthesis of WO3@ZnWO4@ZnO core-shell nanosheet arrays

The WO3@ZnWO4@ZnO (i.e. W@WZ@Z) core-shell nanosheet arrays were prepared by deposition of a ZnO layer on as-obtained WO3 nanosheets by thermal ALD at 200 °C. Diethylylzinc (DEZ) and deionized (DI) water were used as the zinc (Zn) and oxidant sources, respectively. The WO3 nanosheets on FTO substrate were alternately exposed to DEZ and DI water in the reactor chamber using high-purity argon (Ar) as both the carrier gas and purge gas. For all samples, the deposition process in each cycle briefly consists of a 0.2 s pulse of DEZ, a 5 s purge, a 0.2 s pulse of DI water, and a 5 s purge. The different desired thicknesses were achieved by varying the number of thermal ALD cycles. Finally, the obtained samples were calcined in air at 450 °C for 2 min with 15 °C/min of the ramping rate in a rapid thermal process (RTP).

2.3. Synthesis of WO3@ZnWO4@ZnO-ZnO nanocactus array

The WO3@ZnWO4@ZnO nanocactus (i.e. W@WZ@Z-Z) NC arrays were further synthesized via a secondary hydrothermal growth process. Briefly, ZnO nanosheets were grown in an 80 mL Teflon-lined stainless steel autoclave. The aqueous solution of precursors was prepared by adding zinc nitrate hexahydrate (Zn(NO3)2·6H2O) and hexamethylenetetramine (C6H12N4) in an equimolar ratio of 25 mM. The as-obtained W@WZ@Z core-shell nanosheet arrays were then placed into the sealed autoclave, heated to and kept at 80 °C for 8 h. After the reaction, the W@WZ@Z-Z NC arrays were thoroughly washed with DI water and dried in high purity nitrogen.

2.4. Instruments and characterization

The ZnO layers were deposited in a BENEQ TFS-200 (Finland) ALD system. The thicknesses of the ZnO films deposited on Si substrates were measured by a Supra GES-5E spectroscopic ellipsometry system (Semilab, Hungary). Transmission electron microscope (TEM) characterization was carried out on a FEI Tecnai G2 F20 S-TWIN field-emission TEM (United States) with the acceleration voltage of 200 kV. Scanning electron microscope (SEM) images were recorded on a Zeiss field-emission SEM (Germany). Wide-angle X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance powder X-ray diffractometer (Germany) with Ni-filtered Cu-Kα radiation (40 kV, 40 mA, 1.5406 Å). X-ray photoelectron spectroscopy (XPS) measurement was conducted on a PHI 5000 VersaProbe system (United States) using an Mg-Kα X-ray source. The UV–visible steady-state diffuse reflectance spectra (DRS) of the samples were obtained on a JASCO V-670 spectrophotometer (Japan), and the Raman spectra were measured on a Renishaw inVia-reflex laser confocal Raman micro-spectrometer (United Kingdom) equipped with a Leica DM-2500 optical microscope (Germany).

2.5. Photoelectrochemical measurements

PEC performance of as-fabricated photoanodes was measured using a CHI 660D working station (CH Instrument, Inc.) in a three-electrode setup with the synthesized sample as the working electrode, a Pt wire as the counter electrode, a Ag/AgCl electrode as the reference electrode, and mixed aqueous solution of 0.35 M Na2S and 0.25 M Na2SO3 (pH = 13.4) as the electrolyte under the illumination of a 500 W Ushio Xe lamp (100 mW/cm²). The scan rate was 10 mV/s from negative to positive potentials for current density–potential (J–E) measurement. The electrolyte was stirred and purged with high-purity Ar gas for more...
than 20 min before each measurement. The 1000 s successive photocurrent density–time (i-t) curve measurement and electrochemical impedance spectra (EIS) measurement were both performed utilizing the same system at an applied potential of 1.23 V vs. RHE under illumination. EIS spectra were recorded at a frequency range of 10–100 kHz with an amplitude of 5 mV. The incident photon-to-current conversion efficiency (IPCE) profiles were measured by interposing a monochromator (715W15, Beijing 7-Star Optical Instruments Co., Beijing, China) between the Xe lamp and the PEC cell. The monochromatic light was passed through filter plates for different wavelengths with the bandwidth of 10 nm, and the monochromatic light power density was measured with a UV–visible irradiatometer (CEL-NP2000, Beijing Jin Yuan Science and Technology Co.) with an accuracy of 1 μW cm⁻². The recorded potentials vs. Ag/AgCl were converted to RHE scale according to the following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E^0_{\text{Ag/AgCl}}$, where $E_{\text{Ag/AgCl}}$ is the measured potential against the reference electrode (i.e. Ag/AgCl electrode) and $E^0_{\text{Ag/AgCl}}$ is equal to 0.1976 V at room temperature.

3. Results and discussion

Scheme 1 illustrates the synthetic protocol of the 3D hetero-hierarchical WO₃@ZnWO₄@ZnO-ZnO nanocactus (W@WZ@Z NC) arrays based on the ALD process and hydrothermal method (denoted as ALD-based hydrothermal). Well-aligned WO₃ nanosheets array was first grown on FTO glass via a modified hydrothermal process [9]. Scanning electron microscopy (SEM) images in Fig. S1 of the Supporting Information (SI) confirm that this film with a thickness of about 2.8 μm (Fig. S1a) is composed of vertically aligned WO₃ nanosheets with the thickness of about 23 nm (Fig. S1b). After that, these WO₃ nanosheets were coated conformably by amorphous ZnO layers with the thickness of about 30 nm through thermal ALD at 200 °C. After further annealing in the air, the easy diffusion of Zn²⁺ ions into WO₃ lattices led to the formation of a ZnWO₄ buffer layer at the interface between WO₃ and ZnO shells [25]. Therefore, the WO₃@ZnWO₄@ZnO core shell nanosheets array was obtained at this time, which is denoted as the sample W@30-WZ@Z in this paper. Fig. S1c-d shows the top-view SEM image of this W@30-WZ@Z core-shell nanosheets array. The thickness of a single nanosheet is estimated to be ~ 80 nm. A noticeable increase in the thickness of each nanosheet has been observed because of existence of the ZnO shell while the morphology of nanosheets remained essentially, confirming the uniform and conformal deposition process enabled by the ALD technique. Owing to the WO₃ nanosheets had been covered by the ZnO seed layer uniformly, the ZnO nanosheets were then successfully grown on the surface of the W@30-WZ@Z core-shell nanosheets via a secondary hydrothermal process. Fig. 1a shows the SEM images of the W@30-WZ@Z-Z NC arrays. After grafting of ZnO nanosheets via a secondary hydrothermal reaction, it could be clearly seen that the ZnO nanosheets have grown vertically on the surface of the W@30-WZ@Z-Z NC arrays after 8 h hydrothermal reaction. Inset in panel (a) shows the image of a cactus with the similar hierarchical morphology.
(74) than Zn (30), the core-shell structure could be identified by this distinct Z-contrast as well. Meanwhile, the elemental line scanning profiles also confirm that the elemental W can be detected in the core region due to the WO3 core layer. At the same time, it is obviously that the W element also can be detected at the interface of WO3 and ZnO layer due to the construction of ZnWO4. The O and Zn elements were detected in core, shell and branched ZnO regions while the concentration of Zn in the shell and branched ZnO regions seems much higher than the core region, which further verifies the well-defined hierarchically core-shell structures of the W@30-WZ@Z-Z NC arrays.

The crystal structures of the W@WZ@Z-Z NC array sample after annealing were determined by X-ray diffraction (XRD) analysis. As shown in Fig. 3a, it is clear that the diffraction peaks of pristine WO3 nanosheets could be well indexed to a monoclinic WO3 phase (PDF#43-1035) after subtracting the background of FTO glass. Compared to the WO3 nanosheets arrays, the W@30-WZ@Z core-shell nanosheets obtained after annealing in the air displayed new characteristic diffraction peaks which can be assigned to ZnWO4 (PDF#15-0774) and ZnO (PDF#36-1451) phase, respectively. Consequently, with ZnO nanosheets further grafting on the surface of W@WZ@Z nanosheets via secondary hydrothermal method, the intensity of the characteristic diffraction peaks of ZnO increase. Raman spectrum of pure WO3 nanosheets array exhibits three main scattering bands located at around 272, 712 and 808 cm⁻¹ respectively, which could be assigned to the active Raman scattering modes of monoclinic WO3 according to previous literature reports[5]. After coating ZnO seed layers on WO3 nanosheets accompanied by rapid thermal annealing, the Raman spectrum of the obtained W@30-WZ@Z-Z nanosheets displays extra characteristic scattering bands at 342, 407, and 906 cm⁻¹ which could be attributed to the newly generated ZnWO4 and ZnO components[29]. Further, with the W@WZ@Z-Z NC arrays, the RAMAN spectrum corresponding to the W@WZ@Z-Z samples demonstrates increased intensities of the Raman modes of ZnO since the ZnO nanosheets have been grafted on the surface of W@WZ@Z core-shell nanosheets successfully. Both the XRD and Raman results confirm the successful construction of a ZnWO4 buffer layer and hierarchically branched ZnO nanosheets in the W@30-WZ@Z-Z NC arrays.

Fig. S2a-c displays the XPS spectra of the samples W@30-WZ@Z and W@30-WZ@Z-Z NC. As shown in the full spectrum (Fig. S2a) of the W@WZ@Z-Z NC arrays, the detected Zn 2p, O1s peaks confirm the presence of Zn and O in the two samples. Since the sample W@30-WZ@Z-Z NC possesses a branched ZnO nanosheets as a shelter, the component W cannot be observed in the full spectra. As shown in the Fig. S2b, the W 4f spectrum of sample W@30-WZ@Z has two separate peaks, which is corresponding to the characteristic W 4f5/2 and W 4f7/2 peaks for W⁶⁺, respectively. The Zn 2p XPS spectra (Fig. S2c) of both samples show the similar characteristic Zn 2p3/2 and Zn 2p1/2 peaks centered at 1021 and 1044 eV, respectively, which are also identical with the typical values of ZnO. No significant change in the
electronic state of Zn in the W@30-WZ@Z and W@30-WZ@Z-Z NC was observed, which is consistent with the previous reports[25]. In order to investigate the growth process of the W@WZ@Z-Z NC arrays, the products synthesized with different reaction conditions have been observed by SEM systematically. First, by changing the cycle numbers of ALD process, a series of W@WZ@Z samples were fabricated and denoted as sample W@X-WZ@Z in this study, where X = 10, 30 and 40, representing the thickness of the ZnO shell layer controlled by different ALD cycle numbers of 50, 150, 200. As shown in SEM images of Fig. S3a-c, with the increase of the cycle numbers of ALD reaction, the overall thicknesses increase from 43 nm, 83–103 nm. The thickness of the seed layer is almost linearly dependent on the number of ALD cycles, with a nearly constant growth rate of 0.2 nm/cycle. Identical hydrothermal growth parameters were used for each sample. Specifically, for the W@10-WZ@Z and W@30-WZ@Z samples, after grafting of ZnO nanosheets via hydrothermal method, it is clear that the ZnO nanosheets had grown vertically on the surface of W@WZ@Z core-shell nanosheets successfully (Fig. S3d-e). Meanwhile, for the W@30-WZ@Z sample, the grafted ZnO nanosheets on the surface of W@WZ@Z nanosheets were obviously much lusher than the W@10-WZ@Z sample, suggesting the higher surface area as a result. However, further increase of the thickness of ZnO shell would result in an overall growth of the ZnO nanosheets, leading to the complete filling of the space between individual W@WZ@Z core-shell nanosheets and vanishing of the 3D hierarchical heterostructures (Fig. S3f), which would finally reduce the surface areas for contacting with the electrolyte. It is notable that the grafting densities of ZnO nanosheets can be adjusted by changing the retention time of the secondary hydrothermal reaction. As displayed in Fig. S4a, with affection of the ZnO seed layer and ZnWO4 buffer layer, small pieces of ZnO nanosheets would be grafted on the surface of the W@WZ@Z core-shell nanosheets after 2 h of the hydrothermal reaction. With increased reaction time, the grafted ZnO nanosheets became larger, and the grafting densities also experienced an obvious enhancement when the reaction time reached 8 h (Fig. S4b). At last, when the reaction time increased to 20 h, the ZnO nanosheets became too dense that they have almost filled the space between individual W@WZ@Z core-shell nanosheets completely (Fig. S4c), leading to the undesired decrease of active surface areas of the nanostructures. These results together indicate that the well-controlled seed layer modification of ZnO and formation of ZnWO4 buffer layer, accompanied with appropriate reaction time of the secondary hydrothermal reaction are three key factors for preparation of the hierarchically heterostructured W@WZ@Z-Z NC arrays. Based on the results, the growth mechanism of the second-order ZnO nanosheets could be described as follows[30]. First, hydroxide ions were provided by the two-step reaction of HMT.

\[
(CH_2)_6N_4 + 6 H_2O \rightarrow 6HCHO + 4 NH_3
\]

\[
NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)
\]

Second, the ZnO seed layers pre-deposited by thermal ALD process were dissolved in the form of \([Zn(OH)₄]^-\) by hydroxide reaction:

\[
ZnO + H_2O + 2 OH^- \rightarrow [Zn(OH)₄]^- \quad (3)
\]

Next, the branched second-order ZnO nanosheets in situ generated on the surface of the first-order WO₃@ZnWO₄@ZnO nanosheets. The
As the hydrothermal reaction proceeded, the growth of ZnO crystal tended to be elongated crystallization because the (0001) polar plane was energetically unfavorable and had a faster growth rate than other planes [31]. In this study, the XRD pattern of the deposited ZnO seed layer (Fig. 3a) displays the polycrystalline characteristics with comparable intensities of the (100), (002) and (101) diffraction peaks, instead of showing only one strong (002) diffraction peak [32,33]. The presence of the (100) and (101) peaks indicates that the ALD-ZnO seed layer on WO3 surface was not well orientated due to the formation of the (100) and (101) peaks. The (002) orientation is inhibited by the presence of W6+ ions, as well as the citrate ions. Thus, the ZnO nanosheets, instead of nanorods, were grafted in situ on the surface of WO3@ZnWO4@ZnO nanosheets. Then the size of the ZnO nanosheets gradually grew lager as the reaction time further increased.

To evaluate the PEC performance of these hierarchically branched core-shell nanosheets, the samples obtained before and after the second hydrothermal reaction with the pre-deposition of 30 nm-thick ZnO seed layers by thermal ALD have been fabricated into photoanodes with an exposed area of ~1 cm². The current densities of all samples were measured in an aqueous solution containing 0.35 M Na2S and 0.25 M Na2SO3 (pH = 13.4) under the irradiation of a 500 W Xe lamp (100 mW/cm²). Fig. 4a compares the linear sweep voltammetry (LSV) curves of pure WO3 nanosheets sample, W@30-W@Z sample and W@30-W/Z-Z NC sample in the range from −0.8 to 0.25 V vs. Ag/AgCl. The photocurrent density of pure WO3 reached 0.41 mA/cm² at an applied bias of 0.241 V vs. Ag/AgCl (i.e. 1.23 V vs. RHE), while W@W@Z core-shell nanosheet photoanode exhibited larger photocurrent densities of about 0.75 mA/cm², achieved by deposition of a ZnO shell and in-situ transformation to a ZnWO4 buffer layer. This remarkable increase in photocurrent density should be derived from the advantageous features of the well-defined W@W@Z core-shell heterostructures. The saturated photocurrent density of the W@30-W@Z-Z NC array sample further reached 1.57 mA/cm² at the same applied potential, which represents an almost 3.8 times increase compared with pure WO3 nanosheet photoanode, which could be ascribed to the various advantages offered by the unique W@30-W@Z-Z NC heterostructures, such as enhanced light harvesting by multiple light scattering, increased surface area for contact and reaction with electrolyte, and the construction of the favorable WO3-ZnWO4-ZnO heterojunctions. Moreover, Fig. 4b compares the LSV curves of W@W@Z-Z NC array samples obtained with ZnO seed layers of different thicknesses confined by ALD cycle numbers in the range from 0.85 to 0.25 vs. Ag/AgCl. The photocurrent densities of the W@10-W@Z-Z NC and W@40-W@Z-Z NC array samples reached 0.81 and 1.02 mA/cm², respectively, at an applied bias of 0.241 V vs. Ag/AgCl (i.e. 1.23 V vs. RHE) while the W@W@Z-Z NC array sample exhibits a larger photocurrent density of about 1.57 mA/cm² at the same potential, confirming that the thickness of the deposited ZnO seed layer can indeed influence the photoactivity of derived W@W@Z-Z NC array photoanodes. Overall, this higher photocurrent density displayed by the W@30-W@Z-Z NC array photoanode is attributed to the higher contact area due to the increased contacting surface area. At the same time, compared with the W@W@Z core-shell nanosheet array photoanode, the W@30-W@Z-Z NC array photoanode exhibits an increase of IPCE in the wavelength range between 350 and 440 nm. It might be attributed to the increased contact area, enhanced light capture ability and efficient charge separation/transfer arising from the multiple interfaces and heterojunctions contributed by the ZnWO4 buffer layer in the hierarchical W@30-W@Z-Z NC nanostructures. The chemical and structural stability of the W@30-W@Z-Z nanosheet array and W@30-W@Z-Z NC array photoanodes during PEC water splitting reactions were also investigated via a 1000 s continuous PEC water splitting experiment. As shown in the photocurrent density-time (I-t) curves of Fig. 4d, owing to the higher surface area and larger IPCE values, the W@30-W@Z-Z NC array photoanode shows a higher photocurrent density than the W@30-W@Z-Z nanosheet photoanode all the time. At the same time, after grafting ZnO nanosheets on the surface of the W@30-W@Z-Z core-shell nanosheets, the obtained W@30-W@Z-Z NC array photoanodes demonstrated substantially improved photoelectrochemical performance with less than 13% loss in the recorded photocurrent densities after the 1000 s successive PEC water splitting reaction.

In order to further understand the mechanisms behind the enhanced PEC performance of the W@30-W@Z-Z NC array sample, UV-visible diffuse reflectance spectroscopy (DRS) was employed to investigate the light-absorption properties of the samples, as presented in Fig. 5a. Obviously for the pure WO3 nanosheets, the absorption edge appears near 450 nm of wavelength which is consistent with the intrinsic bandgap absorption edge of WO3 (2.6 eV) [34]. After coating with ZnO shell, the light absorption spectra of the composite samples still closely resemble that of pure WO3 with an absorption onset at around 450 nm (~2.6 eV) and an improved absorption tail in ultraviolet band, which could be ascribed to the strong ultraviolet absorption of ZnO. Moreover, for the W@30-W@Z-Z NC array sample, the absorption in the ultraviolet band exhibits a significant increase compared with the W@30-W@Z-Z nanosheet array sample, which might be originated from the multiple scattering-induced absorption inside the hierarchically branched hetero-nanostructures of W@30-W@Z-Z NC array. In addition, the experiment results were verified by 2D finite difference time domain (FDTD) simulations, as shown in Fig. 5b. It is noted that the bending surface of the nanosheet is ignored in the simulation to simply the model (Fig. 5b). The thickness and height of the model for the nanosheets are roughly estimated from the SEM and TEM images shown above. The results clearly demonstrated that the electric field intensity of the W@30-W@Z-Z NC array architecture is larger than that of the W@30-W@Z-Z nanosheet array under 390 nm of ultraviolet light excitation, due to the light reflection and interference effect [35]. These simulation results are well agreement with the absorbance spectra, which suggesting much higher possibilities for excitation of charge carriers in W@30-W@Z-Z NC array, thus are very suitable to be used in PEC performance.

Furthermore, the interfacial charge transfer resistance between the photoanode and the electrolyte could be revealed by the diameter of the semicircle in the middle frequency region from the electrochemical impedance spectroscopy (EIS) Nyquist plots. As can be seen in Fig. 5c, a smaller interfacial charge transfer resistance between the W@30-W@Z-Z-Z NC array and the electrolyte was revealed than W@30-W@Z-Z nanosheet array, which could be ascribed to the increased contact surface area leading to the improved transport behavior of photogenerated holes. Based on the above-mentioned results, the enhanced PEC performance of the hierarchical W@30-W@Z-Z NC array photoanode would have benefited from both the enhanced light absorption ability and the increased contacting surface area. At the same time, to estimate the effective active area during the PEC reaction, we measured the electrochemically active surface area of the W@30-W@Z-Z and W@30-W@Z-Z NC array through electrical double-layer capacitance (EDLC) measurement in Na2S/Na2SO3 solution, since the double-layer capacitance (Cdl) is proportional to the electrochemically active surface area [36]. The cyclic voltammetry (CVs) were tracked in the range of −0.7 to +1.23 V vs. RHE.
to $-0.4$ V, where the current response should only refer to the charging of the double layer. The CV curves of $W@30-WZ@Z$ and $W@30-WZ@Z-Z$ NC array at various scan rates (3, 5, 6, 10, 20, 30, 40 and 50 mV/s) are shown in Fig. S6(a) and (b), respectively. As a result, the capacitance of the $W@30-WZ@Z-Z$ NC array (0.281 mF/cm$^2$) is higher than that of $W@30-WZ@Z$ array electrode (0.157 mF/cm$^2$), indicating the higher electrochemical active surface area of the $W@30-WZ@Z-Z$ NC array electrode, which is consistent with the EIS and SEM results.

In addition, the charge transfer pathway in these $W@30-WZ@Z-Z$ NC array photoanodes is proposed in Fig. 5d. It is clear that photogenerated electrons and holes could be transferred from one to the other semiconductor driven by the alignment of their conduction and valence band edge positions ($E_{CB}$ and $E_{VB}$). According to previous reports [28,34], the $E_{CB}$ and $E_{VB}$ values of $WO_3$ are 0.25 V and 3.3 V while the corresponding values of $ZnO$ are $-0.31$ V and 2.89 V, respectively. As has been discussed before, the $ZnWO_4$ buffer layer has formed at the interface between $WO_3$ and $ZnO$, the $E_{CB}$ and $E_{VB}$ values of $ZnWO_4$ are $-0.1$ V and 3.05 V, respectively. Under light illumination, the electrons would be excited upon irradiation from the valence band of $WO_3$, $ZnWO_4$ and $ZnO$ simultaneously to their own conduction band, leaving positive holes in the valence band. In this constitution, the photogenerated electrons of $ZnO$ would migrate to the $ZnWO_4$ buffer layer, then to the $WO_3$ core, transfer from $WO_3$ to FTO substrate efficiently via back contact, and finally reach the counter electrode of Pt. At the same time, the photogenerated holes have a higher probability of entering $ZnWO_4$ buffer layer and then travelling to the surface of $ZnO$ nanosheets due to the lower-lying valence states and thin thickness of the $ZnO$ nanosheets, and finally reacting with water molecules to generate oxygen gas on the photoanode. Such favorable charge transfer behavior enabled by the band alignment may lead to a remarkably inhibited charge recombination rate, and therefore higher photocurrent densities of the $W@WZ@Z$ nanosheet array and $W@WZ@Z-Z$ NC array photoanodes than pristine $WO_3$ photoanodes.

4. Conclusions

In summary, for the first time, we report a ALD-dominated seed-layer-mediated secondary hydrothermal strategy for the synthesis of hierarchically heterostructured $WO_3@ZnWO_4@ZnO-ZnO$ nanocactus (i.e. $W@WZ@Z-Z$ NC) arrays. The obtained $W@WZ@Z-Z$ NC arrays exhibit drastically increased active surface areas, multiple interfaces and light scattering centers, and thus improved ultraviolet light absorption and interfacial charge transfer and charge separation, which were revealed by finite-difference time-domain (FDTD) simulation, specific band alignment, and various optical and electrochemical spectroscopic characterizations. When the $W@WZ@Z-Z$ NC arrays were afterward fabricated into photoanodes, greatly improved photocurrent densities and photostability were demonstrated when comparing to $W@WZ@Z$ core-shell nanosheet and pure $WO_3$ nanosheet photoanodes. Specifically, the $W@WZ@Z-Z$ NC array photoanode with a $ZnO$ seed layer of $\sim 30$ nm deposited on $WO_3$ by ALD achieved around 3.8 times higher photocurrent density ($\sim 1.57$ mA/cm$^2$) than pure $WO_3$ nanosheet photoanode ($\sim 0.41$ mA/cm$^2$) at 1.23 V vs. RHE. In consideration of the versatility as well as facile but precise controllability of this ALD-mediated hydrothermal growth strategy for hierarchically hetero-nanostructured photoelectrode materials, and also the performance enhancement of the $WO_3$-based photoanodes for PEC water splitting regarding both the photocurrent density and the stability, it is
expected that such methodology could be spread for fabrication of a variety of hybrid metal oxide hierarchically heterostructured nanomaterials toward energy conversion, storage and many other applications.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Nos. 61376008, U1632121 and 51102048), MOST (No. 2016YFE010700), the State Key Laboratory of Luminescence and Applications (SKL-2016-16), the Science Foundation of State Key Laboratory of Silicon Materials (Grant no. SKL2015-01), and the Innovation Program of Shanghai Municipal Education Commission (14ZZ004). Besides, Q. Cao acknowledges the support of China Scholarship Council (No. 201506100018).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2017.09.053.

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