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Abstract
We report the first demonstration of a high-efficiency photoelectrochemical (PEC) water splitting reaction using a novel Si NWs/WO3 core/shell photoanode prepared by a mild and inexpensive metal-catalyzed electroless etching process followed by dip-coating, airing and annealing methods. The dense and vertically aligned Si NWs/WO3 core/shell nanostructure were characterized by scanning electron microscopy, transmission electron microscopy and x-ray diffraction. In comparison to planar n-Si, Si NWs and planar Si/WO3, the Si NWs/WO3 samples showed significantly enhanced photocurrent over the entire potential sweep range. More significantly, the Si NWs/WO3 samples have an exceptionally low photocurrent onset potential of −0.6393 V versus reversible hydrogen electrode (RHE), indicating very efficient charge separation and charge transportation processes. The as-prepared electrode also has a photocurrent density of 2.7 mA cm−2 at 0.6107 V versus RHE in 0.5 M Na2SO4 solution under simulated solar light irradiation (100 mW cm−2 from 300 W Xenon lamp coupled with an AM 1.5 G filter). An optimal solar-to-hydrogen efficiency of about 1.9% was achieved at 0.2676 V versus RHE. Electrochemical impedance spectroscopy was conducted to investigate the properties of the charge transfer process, and the results indicated that the enhanced PEC performance may due to the increased charge separation. The x-ray photoelectron spectroscopy measurements indicated the chemical composition of the Si NWs/WO3 nanostructure. Our work has provided an efficient strategy to improve the energy conversion efficiency and photocurrent of water splitting materials.

Keywords: water splitting, photoelectrochemical cells, SiNWs/WO3 core/shell nanostructures

(Some figures may appear in colour only in the online journal)

Supplementary material for this article is available online

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1. Introduction

Since Fujishima and Honda first demonstrated that water could be split into H₂ and O₂ on the TiO₂ electrode in a photoelectrochemical (PEC) cell under light illumination [1], the PEC water splitting process on semiconducting materials has received increasing attention, due to its potential as one of the clean, low-cost, and environmentally friendly strategies to solve the energy crisis [2, 3]. Until now, a variety of nanostructured metal oxides, such as TiO₂ [4], ZnO [5], Fe₂O₃ [6], and WO₃ [7–13] have been investigated as photoanodes for the PEC hydrogen generation.

Among these semiconducting materials, tungsten trioxide (WO₃) is a promising photoanode material because of its nontoxicity, chemical stability, high electron mobility and positive valence band position [14]. Despite the promising features of WO₃, the conversion efficiency of the reported WO₃ photoanodes is still far below its theoretical maximum conversion efficiency (6.3%) [15], thus limiting its applications. In order to enhance the conversion efficiency of WO₃ photoanodes, various strategies such as morphology modification and heterojunction have been employed to increase the PEC performance by improving the charge transport properties [16, 17]. Unfortunately, these strategies have not been able to sufficiently address the major inherent drawback of WO₃ (large band gap Eg ≥ 2.6 eV) [18], which largely limits its absorbance and photocatalytic activity. Considerable efforts have been made to expand the spectral response of WO₃, such as elemental doping (e.g., C, In, and N) [19–21] and sensitizing with narrow band gap semiconductors (e.g., CdS, PbS, and Bi₂S₃) [22–24]. Therefore, developing WO₃-based nanostructured heterojunction photoanodes with superior light absorbance property can greatly promote its application in the PEC water splitting process.

Silicon is potentially an excellent photoelectrode material because it possesses a narrow band gap enabling the absorption of energy from solar radiation ranging from ultraviolet to visible light [25, 26]. Furthermore, one-dimensional silicon nanowires (Si NWs) exhibit better behavior in the PEC water splitting process compared with bulk Si, since they have faster charge transport pathways, more efficient charge collection, higher contact area with the electrolyte and stability because it is rapidly oxidized in aqueous solutions [27, 28]. However, the Si nanowires photoanode is catalytically inactive and has poor chemical absorption of energy from solar radiation ranging from ultraviolet to visible light. Therefore, developing WO₃-based nanostructured heterojunction photoanodes with superior light absorbance property can greatly promote its application in the PEC water splitting process.

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In this present work, we report a high-efficiency PEC Si NWs/WO₃ core/shell photoanode, prepared by a simple sequence of metal-assisted etching, dip-coating, air-drying and annealing methods for the first time. The Si NWs/WO₃ core/shell photoanode was fully characterized and its various PEC properties were evaluated and compared against those of planar Si, planar Si/WO₃, Si NWs samples. To the best of our knowledge, there is no report until now focusing on highly efficient Si NWs/WO₃ core/shell photoanode. Finally, its excellent activity in the PEC process was attributed to the synergistic effects of Si nanowire and WO₃, as shown in figures 1(a) and (b). The detailed results are presented in the following sections.

2. Experimental

2.1. Synthesis of Si NWs/WO₃ nanoarrays

The Si NWs/WO₃ core/shell nano-arrays were synthesized by a simple metal-assisted etching, dip-coating and annealing methods, as shown in figure 1(c). In a typical process, The Si NWs were prepared by a mild metal-assisted chemical etching method using a typical procedure [40–42]. First, the Si NWs were immersed into HF solution (1 ml of HF solution (49%), diluted in 50 ml of deionized water), and then washed several times by deionized water. Then dip-coating and annealing processes were conducted to forming WO₃ shell. In details, a certain quantity of ammonium tungstate (APT) was dissolved in a solution consisting of 5 ml 40% H₂O₂ and 15 ml deionized water to form a homogenous APT aqueous solution. Then, 30 μl of the APT aqueous solution was poured onto the cleaned and wetted Si NWs, and dried in air naturally. Then, the dried Si NWs/APT was annealed for 3 h at 550 °C at the heating rate of 10 °C min⁻¹ in a vacuum tube furnace to form the Si nanowire/WO₃ core/shell. The thickness of WO₃ shell can be controlled by pouring different concentrations of APT aqueous solution. It should be note that the vacuum annealing process will convert APT shell to WO₃ without any change in morphology.

2.2. Characterization

X-ray diffraction (XRD) measurements of the film and powders were performed on an x-ray diffractometer (D/max-2550, Japan). The morphologies of the samples were studied by a scanning electron microscope (SEM, ZEISS ULTRA 55), and energy-dispersive spectroscopy (EDS) was performed using...
an EDS device from Oxford Instruments. The samples microstructures were analyzed by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (JEM 2100F, field emission electron microscope). X-ray photoelectron spectra were done by XPS (Thermo Scientific, Escalab250Xi).

2.3. Measurement of PEC properties

The PEC measurements were performed in a custom-made electrochemical cell with a 1.0 cm² quartz window using a CHI660E electrochemical workstation (CHI instrument) with an Ag/AgCl reference electrode and platinum wire coil as the counter electrode. A 300 W Xenon lamp was used to provide AM 1.5 illumination (100 mW cm⁻²) in each experiment. The electrolyte used was 0.5 M Na₂SO₄ aqueous solution (The pH value of 0.5 M Na₂SO₄ is about 7.02, which was measured by a pH meter). All the samples were assembled into the as-mentioned electrochemical cell with only a quartz window exposed to the Xe lamp. An indium–gallium alloy (99.99%, Sigma-Aldrich) was applied to the back-side of Si substrate enabling ohmic contact. In linear sweep voltammetry measurements, the scan rate was set at 50 mV s⁻¹ from −1.5 to 1.5 V versus Ag/AgCl. Electrochemical impedance spectra (EIS) were measured using the same workstation under an open-circuit condition with the frequency ranging from 0.05 Hz to 100 kHz.

3. Results and discussion

The linear sweep voltammetry (J–V) curves of the as-prepared photoanodes measured under illumination are shown in figure 2(a). It can be clearly found that the photocurrent densities of Si NWs sample is less than 0.5 mA cm⁻² and the planar Si photoanode shows a much lower photocurrent density at about 1.0 V versus RHE. The significantly enhanced photocurrent density of the Si NWs photoanode was due to the larger specific surface area, less light reflection, and more efficient charge transport in the Si NWs.

When planar Si and Si NWs were coated by WO₃ layer via dip-coating and annealing methods, the onset potentials of planar Si and Si NWs shifted towards negative potentials. At 0.6107 V versus RHE, both the planar Si and Si NWs photoanodes show enhanced photocurrent density with WO₃, indicating that the WO₃ coating is an efficient strategy to enhance the PEC performance of Si-based photoanodes. Furthermore, the onset potential and photocurrent density of Si NWs/WO₃ core/shell photoanodes was as high as −0.6393 V versus Ag/AgCl and 2.7 mA cm⁻² at 0.6107 V versus RHE, respectively, indicating that the Si NWs/WO₃ core/shell photoanodes possessed better photo-induced charge generation, separation, and heterojunction.

On the other hand, the remarkable negatively shifted onset potential suggests a larger accumulation of electrons and decreased charge recombination in the heterojunction. In order to investigate the effect of WO₃ thickness on the photocurrent
density, APT solutions with different concentrations were used to wet the Si NWs sample. The linear sweep voltammetry (J–V) curves of the resulting samples with varying WO$_3$ shell thicknesses are shown in figure 2(b). When the mass of APT increases from 1 to 4 g, the current density first increases and then drastically decreases. This is likely because the greater thickness of the WO$_3$ shell lowers the absorbance of Si NWs and the photo-generated electrons must travel longer distances to the interface to recombine with holes generated by Si NWs. Figure 2(c) shows the linear sweep voltammetry curve with chopped AM 1.5 light of 100 mW cm$^{-2}$ intensity. From −0.75 to 0 V, there is negligible difference between the photocurrent and dark current, but when the potential becomes a positive value, the photocurrent becomes much higher than the dark current, indicating favorable photoanode activity. Figures 2(d)–(f) shows the

Figure 2. (a)–(c) Linear sweep J–V measurements using a three-electrode setup under 100 mW cm$^{-2}$ simulated sunlight illumination in 0.5 M Na$_2$SO$_4$ neutral aqueous solution: (a) planar Si, Si NWs, planar Si/WO$_3$, Si NWs/WO$_3$ electrodes. (b) Si NWs/ WO$_3$ nanowire arrays electrodes obtained by different concentrations of precursor (1 g, 2 g, 3 g, 4 g ammonium tungstate dissolved in 15 ml DIW and 5 ml 40% H$_2$O$_2$ ) Wetting. (c) Si NWs/WO$_3$ nanowire arrays electrodes illuminated with chopped white light. (d) and (e) Showing the STH (solar-to-photoelectron) efficiency of planar Si, Si NWs, planar Si/WO$_3$, Si NWs/WO$_3$ electrodes at different applied bias. (f) The calculated optimal conversion efficiencies as a function of the mass of APT.

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STH conversion efficiency (\(\eta\)) calculated by the following equation [43–45]: 

\[
\eta = J_p (1.23 - |V|) / I_0,
\]

where, \(J_p\) is the photocurrent density, \(V\) is the applied potential versus RHE, and \(I_0\) is the power density of incident light. It should be noted that all the PEC tests are conducted by using Ag/AgCl reference electrode and the measured potential versus RHE and the SiO \(_x\) substrate, and then they agglomerated when they were coated with WO\(_3\) layer. Although the WO\(_3\) shell coated the Si NWs uniform as shown in figures 3(b) and S2, there are many area in the interior of the Si NWs cluster which could not be covered by APT since the high density of the Si NWs and the nature of the dip-coating process. These areas allow the formation of SiO \(_x\) when the Si NWs/WO\(_3\) electrode was added a positive bias versus RHE and the SiO \(_x\) is a layer with a very low conductivity, so the photocurrent of Si NWs/WO\(_3\) decreased rapidly.

Figures 3(a), (b) displays the cross-sectional views of n-Si NWs arrays and n-Si NWs/WO\(_3\) core/shell, respectively. It can be clearly seen that the Si NWs grew vertically on the Si substrate, and then they agglomerated when they were coated with WO\(_3\) layer. It should be noted that there still are interspaces between the Si NWs/WO\(_3\) core/shell nanostructures (shown in figure 3(c)), which benefit the light absorption and improve the contact surface between electrode and electrolyte, leading to higher efficiency of the photocatalytic reaction. The length of Si NWs is about 7.8 \(\mu\)m, and the fundamental morphology of the Si NWs did not change when they were coated with the WO\(_3\) shell. The WO\(_3\) shell is thin enough so that more photo-generated holes from inside the core can reach the interfaces of semiconductor and electrolyte for better performance in the water splitting reaction. The diameter of a single Si NWs/WO\(_3\) core/shell is about 200 nm and the entire surface of Si NWs was evenly covered with the WO\(_3\) layer with good interfacial contact (as shown in figure 3(d)). Furthermore the morphologies of Si NWs/WO\(_3\) samples with different thickness were investigate by SEM as shown in figure S2. The lattice fringe of WO\(_3\) and silicon is clearly shown in figure 3(e). This HRTEM image also clearly reveals the lattice plane with 0.35 mA cm\(^{-2}\). This phenomenon could be attribute to the formation of SiO \(_x\) layer. Although the WO\(_3\) shell coated the Si NWs uniform as shown in figures 3(b) and S2, there are many area in the interior of the Si NWs cluster which could not be covered by APT since the high density of the Si NWs and the nature of the dip-coating process. These areas allow the formation of SiO \(_x\) when the Si NWs/WO\(_3\) electrode was added a positive bias versus RHE and the SiO \(_x\) is a layer with a very low conductivity, so the photocurrent of Si NWs/WO\(_3\) decreased rapidly.

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spacings of 0.376 nm, corresponding to the (200) plane of WO₃, which indicates that the WO₃ shell has good crystallinity. The insert electron diffraction (SAED) map of selected area also provides clear evidence of the polycrystalline nature of the WO₃ shell. EDX analysis confirmed the presence of W, O, and Si elements (figure 3(f)). The above results indicate that the heterogeneous photoelectrodes were formed as desired by the dip-coating and annealing methods.

XRD spectrum of the as-prepared WO₃ powder sample and Si NWs/WO₃ with different thickness of WO₃ nanoshell are shown in figure 4(a). It can be seen that there are several significant peaks for cubic WO₃ in WO₃ powder, attributed to the diffractions from (200), (220), (222), (400) and (420) planes [JCPDS, 46-1096]. Comparing to pure WO₃ powder, the intensity of every peaks of WO₃ in different Si NWs/WO₃ samples are lower. The possible cause of this problem may be that the thickness of the WO₃ is too thin and as a result the intensity of peaks increased with the quality of APT in precursor increasing. The peak intensity of Si NWs at 38.4° and 44.6° have been shown in different Si NWs/WO₃ samples and they decrease with the thickness of WO₃ shell increasing. This may be due to the shielding by the WO₃ layer. The reflectivity spectra of the planar Si, Si NWs, planar Si/WO₃ and Si NWs/WO₃ core/shell electrodes are shown in figure 4(b). It can be seen from the spectra that Si NWs and Si NWs/WO₃ show drastically reduced reflectance compared to the planar Si and planar Si/WO₃ samples, indicating its superior anti-reflection properties. This is possibly caused by the strong light trapping and scattering behavior of Si NWs. It should be noted that there is a slight decrease in the reflectance observed after the deposition of WO₃ onto Si NWs. This is attributed to the rough surface of WO₃ shell which also has enhanced light trapping. Furthermore, the excellent broadband light-trapping ability is of great importance for efficient solar energy conversion.

X-ray photoelectron spectroscopy (XPS) measurements were conducted to determine the surface electronic states and chemical composition of the nanocomposites of the prepared Si NWs/WO₃ nanowires. Figure 5 shows the high resolution XPS spectra of so called Si NWs/WO₃. The characteristic peaks of W, O and Si elements in the 0–1200 eV binding energy range can be seen in figure 5(a). The presence of Si, W, O and C elements further confirms the high purity of the products. In figure 5(b), the peaks at 35.5, 37.6 and 42 eV binding energies correspond to W4f7/2, W4f5/2 and W5p3/2, respectively. A careful study shows that the weak peaks at 34.5 and 36.6 eV corresponding to low oxidation state of W, indicating the possible absence of O in WO₃. The peak at 532.5 eV can be attributed to O atoms in WO₃, as shown in figure 5(c) [45]. The peaks with binding energies of 530.5 and 531.5 eV are attributed to O in SiOₓ/Si and water molecules adsorbed on the surface of the film [46, 47]. The peaks of Si2p have shown in figure 5(d) and the peak at 99.4 and 103.3 eV banding energies corresponding to the Si/SiOₓ [48]. Combined with the SEM, TEM, XRD and XPS results, it can be assuredly concluded that the Si NWs/WO₃ nanowires were successfully obtained by a simple MCEE, dip-coating and annealing procedure.

Electrochemical impedance spectroscopy (EIS) has been carried out to investigate the properties of the charge transfer process in PEC. The EIS measurements were conducted at 0 V (versus Ag/AgCl) under irradiation covering a frequency interval of 0.05 Hz–100 MHz. Figure 6(a) shows the Nyquist plots of Si NWs/WO₃, planar Si/WO₃, Si NWs, and planar Si electrodes. The solid lines represent the experimental data. In typical three electrode experiments, the equivalent circuit (shown in the inset of figure 6(a)) consists of two parts [49]: (i) the series resistance (Rₛ) of the pure electrolyte, circuit wire and contact resistance between work electrode and wire; (ii) the charge transfer impedance at the electrolyte–semiconductor interface which is a parallel connection between a resistance (Rₛ) and a constant phase element (CPEₛ). For Si NWs/WO₃ and planar Si/WO₃ electrodes, there is another charge transfer impedance at the Si–WO₃ interface, which consists of parallel installed resistance (Rₛ) and constant phase element (CPEₛ). The arc radius of the planar Si wafer, Si NWs, planar Si/WO₃,
and Si NWs/WO3 samples are gradually decreased (shown in figure 6(a)). A smaller arc radius indicates faster charge transfer and more effective separation of the photogenerated electron–hole pairs. The Si NWs/WO3 sample shows the smallest arc radius in the low frequency range, suggesting that it has superior charge transfer and charge separation due to the formation of the heterojunction. In the Bode phase plots shown in figure 6(b), the Si NWs/WO3 sample correspondingly has the lowest characteristic peak frequency below 0.1 Hz, indicating the longest electron lifetimes. Bode plots in figure 6(b) exhibit the efficient electron lifetime in planar Si, Si NWs, planar Si/WO3 and Si NWs/WO3 samples. The lifetime (τe) of electron can be calculated by τe = 1/(2πfmax) and the fmax is the frequency at which the frequency peak appears in the Bode plot [13]. The values of the maximum characteristic frequencies are decreased gradually and vary from the Si NWs (10–100 Hz) to the planar Si (1–10 Hz), indicate the τe of Si NWs is shorter than that of planar Si. The possible reason may be the
nanostructure leading to the recombination of generated hole-electron pair. Comparing to the maximum characteristic frequency of Si NWs (10–100 Hz), the maximum characteristic frequency of Si NWs/WO3 is below 0.10 Hz represent the longer lifetime of generated electron in Si NWs/WO3.

4. Conclusions

In conclusion, we have presented a facile method for the preparation of Si NWs/WO3 core/shell photoanodes for application in PEC water splitting for the first time. The as-prepared NWs/WO3 core/shell photoanodes showed a remarkable photocurrent density of 2.7 mA cm⁻² at 0.6107 V versus RHE and onset potential of −0.6393 V under solar light irradiation. It is believed that the deposition of WO3 nanoshells on the surface of Si NWs can enhance the separation rate of the photo-generated holes, and further improve the separation of electron–hole pairs. Moreover, light absorption of the core/shell photoanode is also enhanced due to the complementary absorption of Si NWs and WO3 in different regions of the solar spectrum. The above characteristics of the Si NWs/WO3 core/shell photoanode contribute to its enhanced water splitting performance, as evidenced by a cathodic shift in the photocurrent onset potential. Overall, the results of this work provide a new approach to development of improved PEC materials.

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