Full Length Article

Fabrication and photoelectrochemical properties of silicon nanowires/g-C₃N₄ core/shell arrays

Zhen Chen⁠, Ge Ma⁠, Zhihong Chen⁠, Yongguang Zhang⁠, Zhe Zhang⁠, Jinwei Gao⁠, Qingguo Meng⁠, Mingzhe Yuan⁠, Xin Wang⁠, Jun-ming Liu⁠, Guofu Zhou

A Institute of Electronic Paper Displays, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou, Guangdong Province, China
b Shenyang Institute of Automation, Chinese Academy of Sciences, Shenyang 110870, China
c Institute of Advanced Materials, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou, Guangdong Province, China
d Research Institute for Energy Equipment Materials, Tianjin Key Laboratory of Materials Laminating Fabrication and Interface Control Technology, Hebei University of Technology, Tianjin 300130, China

ABSTRACT

A photoelectrochemical (PEC) cell made of metal-free carbon nitride (g-C₃N₄) @siliconnanowire(Si NW) arrays (denoted as Si NWs/g-C₃N₄) is presented in this work. The as-prepared photoelectrodes with different mass contents of g-C₃N₄ have been synthesized via a metal-catalyzed electroless etching (MCEE), liquid atomic layer deposition (LALD) and annealing methods. The amount of g-C₃N₄ on the Si NW arrays can be controlled by tuning the concentration of the cyanamide solution used in the LALD procedure. The dense and vertically aligned Si NWs/g-C₃N₄ core/shell nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). In comparison with FTO/g-C₃N₄ and Si NW samples, the Si NWs/g-C₃N₄ samples showed significantly enhanced photocurrents over the entire potential sweep range. Electrochemical impedance spectroscopy (EIS) was conducted to investigate the properties of the charge transfer process, and the results indicated that the enhanced PEC performance may be due to the increased photo-generated interfacial charge transfer between the Si NWs and g-C₃N₄. The photocurrent density reached 45 μA/cm² under 100 mW/cm² (AM 1.5 G) illumination at 0 V (vs. Pt) in neutral Na₂SO₄ solution (pH ~ 7.62). Finally, a systematical PEC mechanism of the Si NWs/g-C₃N₄ was proposed.

© 2016 Published by Elsevier B.V.

1. Introduction

Energy harvested directly from sunlight offers a promising approach to satisfy the increasing global energy demands and to resolve environmental issues caused by the overuse of fossil fuels. One of the most attractive options is the conversion of solar energy into chemical bonds, such as H₂, through a water splitting process with the help of semiconductor-based photocatalysts [1–4]. In the past decades, the traditional TiO₂ has been extensively investigated in the field of hydrogen production since Fujishima and Honda first demonstrated that water could be split into H₂ and O₂ on a TiO₂ electrode under light irradiation [5]. However, the relatively high band gap of TiO₂ (ca. 3.2 eV) leads to insufficient use of the solar spectrum (it can absorb less than 4% of the available solar energy), resulting in the low visible-light photocatalytic activity of TiO₂ [6]. Therefore, developing novel visible-light-responsive photocatalysts has become a hot topic in the photocatalysis field.

In recent years, special attention has been paid to graphite carbon nitride (g-C₃N₄), due to the relatively low band-gap (ca. 2.8 eV) and the appropriate positions of the conduction band (CB) and valence band (VB) for water reduction and oxidation, respectively [7–10]. Furthermore, g-C₃N₄ can be synthesized by the simple thermal condensation of low-cost nitrogen-rich precursors, such as urea, cyanamide, dicyandiamide, and melamine, among other precursors [11–14]. However, the photocatalytic activity of the as-obtained g-C₃N₄ is usually restricted by the relatively fast recombination of photo-generated electron–hole pairs [15]. Various strategies, such as morphology modification, elemental doping, and copolymerization are subsequently applied to improve
the photocatalytic performance of g-C3N4 [16–18]. More recently, combining g-C3N4 with other semiconductors, such as ZnO, TiO2, CulnS2, Bi2O3-I, InVO4, to form a photoelectrochemical (PEC) heterogeneous electrode for water splitting has been considered an effective way to improve its photocatalytic activity [19–25]. However, these photoelectrodes also suffer from insufficient absorption of solar energy and poor surface area, which may restrict their practical applications.

Silicon is a promising photoelectrode material for PEC applications because of its narrow band gap, enabling easily controllable electrical conductivity [26–28]. Compared to the bulk Si structure, Si NWs exhibit significantly enhanced light absorption and energy conversion efficiency due to their faster charge transport pathways, more efficient charge collection, higher contact area with the electrolyte and lower reflectivity [29–31]. Hence, constructing a heterojunction by coupling g-C3N4 and Si NWs may provide an alternative novel pathway to address the intrinsic drawbacks of g-C3N4-based photoelectrodes for PEC applications. To the best of our knowledge, there are no reported studies about Si NWs/g-C3N4 heterojunction PEC electrodes.

In the current work, we report a novel metal-free Si NWs/g-C3N4 core/shell PEC photoanode for water splitting prepared by simple metal-assisted etching, liquid atomic layer deposition (LALD) and annealing methods and characterized by TEM, SEM, XPS, DRSS, XRD. Under visible light irradiation, the Si NWs/g-C3N4 photoelectrodes exhibited noticeably enhanced PEC performance compared to FTO/g-C3N4 and Si NW photoelectrodes, which is attributed to the fast photo-generated charge transfer between the Si nanowires and g-C3N4. A systematic investigation of the effects of g-C3N4 thickness on photocurrent and the PEC mechanism was conducted. This work may provide a common and simple route along with an insight into designing and understanding an efficient wide spectral-response PEC photoelectrode for renewable energy applications.

2. Experimental

2.1. Synthesis of Si NW nanowires

N-type vertically aligned Si NW arrays were synthesized via metal-catalyzed electroless etching (MCEE) of the n-Si wafer substrate. A 2 cm × 2 cm phosphorous-doped n-type Si wafers piece (2–10 Ω/cm) was cleaned by water and acetone, and immersed in an oxidant solution containing H2SO4 (98%) and H2O2 (40%) (v/v = 3/1) for 60 min to remove organics entirely. The cleaned silicon wafer was then immediately immersed in an HF–AgNO3 solution in a sealed vessel to etch for 45 min and then immersed in the oxidant solution for over an hour to remove the residual Ag dendritic crystal on the wafer. The solution concentrations of HF and AgNO3 were kept at 49% (mass fraction) and 0.25 mol/L, respectively.

2.2. Synthesis of Si NWs/g-C3N4 core/shell nanowires

In a typical synthesis of the Si NWs/g-C3N4 nanowires, as shown in Scheme 1, Si NWs were used as the core, and a cyanamide solution with a certain mass concentration was used as the shell precursor. The Si NWs/g-C3N4 samples mentioned later were fabricated with cyanamide solutions with a mass concentration of 0.25, except where noted. Then, a piece of the Si NW nanowire sample was immersed in the cyanamide aqueous solution and left standing for 30 min. After being taken out, the treated Si NW sample was placed on planar glass and exposed to air for 12 h. Then, the Si NWs/cyanamide wafer was transferred to a vacuum tube furnace and maintained at 550 °C for 3 h.

2.3. Synthesis of FTO/g-C3N4 photoelectrode

To confirm the superiority of the core-shell nanowires, a FTO/g-C3N4 photoelectrode was prepared. Twenty milliliters of cyanamide aqueous solution was transferred to a crucible with a lid. Then, the crucible with the cyanamide solution was heated to 550 °C at a heating rate of 10 °C/min in a muffle furnace and then maintained at this temperature for 3 h. In total, 0.2 g of the as-prepared sample was suspended in 5 mL of ethanol, which was then ground for 4 h to form a slurry. The slurry was dip-coated on a 20 mm × 20 mm fluorine–tin oxide (FTO) glass electrode. The electrode was then annealed at 150 °C for 2 h at a heating rate of 5 °C/min.

2.4. Characterization

The crystalline structure of the Si NWs/g-C3N4 sample was characterized using a Shimadzu 7000S X-ray diffractometer (XRD) with Cu Kα radiation. The morphologies and nanowire sizes of the as-prepared samples and high-resolution images were studied with a field-emission (JEM 2100F) transmission electron microscope (TEM). EDX mapping analysis was carried out with the same TEM in STEM mode. Scanning electron microscopy (SEM) was performed using a Zeiss ULTRA 55 field-emission scanning electron microscope. The UV–vis diffuse reflection spectra were measured by a Shimadzu U-3010 Ultraviolet–vis spectrophotometer equipped with an integrating sphere using barium sulfate as the reference. Electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV) and amperometric i–t curve (AIT) measurements were conducted with an accurate electrochemical workstation (CHI 660E) in a two-electrode system using platinum wire as the counter electrode. X-ray photoelectron spectroscopy (XPS) data were obtained from a Thermo Scientific, Escalab250Xi X-ray photoelectron spectrometer.

2.5. PEC measurements

The PEC properties of the as-prepared samples were evaluated by a three-electrode electrochemical workstation (CHI 660 E, China). For the two-electrode system, we used the as-prepared Si NWs/g-C3N4 nanowires as the working electrode and a platinum wire as the counter electrode and reference electrode [32,33]. An aqueous solution containing 0.5 M Na2SO4 was used as the electrolyte. The pH value of 0.5 M Na2SO4 is approximately 7.62, which was measured by a pH meter (Hzaool PS-3C, with a precision of 0.01). A 300-W xenon lamp with a light intensity of 100 mW/cm2 (AM 1.5 G) acted as the light source. LSV was carried out at a scan rate of 50 mV/s from –1.5 to 1.5 V vs. Pt. 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

3.1. Characterization of composition and structure

The structures and morphologies of Si NWs and Si NWs/g-C3N4 core/shell arrays are observed by SEM and TEM. As shown in Fig. 1(a), the smooth Si NW arrays with diameters ranging from 70 to 300 nm are evenly and vertically arranged on the Si substrate. Moreover, from the view of the cross-section image of the Si NWs, the length of the single Si NWs is approximately 10 μm, controlled by adjusting the etching time. The surface of the Si NWs becomes rough after coating it with g-C3N4 by the LALD method, but the length of the Si NWs did not change, as indicated by the comparison of Fig. 1(a) and (b). The g-C3N4 is coated onto the surface of the
Si NWs uniformly to form the Si NWs/g-C$_3$N$_4$ core/shell structure, confirming the intimate interfacial contact between Si NWs and g-C$_3$N$_4$, as shown in Fig. 1(c). An HRTEM image of Si NW/g-C$_3$N$_4$ is shown in Fig. 1(d), which indicates that the thickness of the g-C$_3$N$_4$ shell is approximately 15 nm.

The elemental composition and chemical state of the as-prepared Si NWs/g-C$_3$N$_4$ sample are detected by XPS measurements, and the results are shown in Fig. 2. The Si NWs/g-C$_3$N$_4$ composites are composed of C, N, Si and O, which confirms the coexistence of Si NWs and g-C$_3$N$_4$ in the Si NWs/g-C$_3$N$_4$ composite. The typical high resolution XPS C 1s and N 1s spectra in different samples are also given in Fig. 2(b–c). The C 1s high-resolution spectrum shows two different peaks with binding energies of 284.8 and 289.4 eV. The sharp peak located at 284.8 eV is attributed to sp$^2$ hybridized carbons (C–C) and the peak located at 289.4 eV corresponds to C–(N)$_3$ bonds [34,35]. The N 1s high-resolution spectrum is decomposed into three peaks. The peak centered at 399.8 eV is attributable to the sp$^2$ N involved in the bridging nitrogen atoms.
of N–(C)$_3$, whereas the contribution at 398.5 eV corresponds to triazine rings [36]. The peak at 401.1 eV may be ascribed to the –NH$_2$ or =NH groups originating from the incomplete condensation of cyanamide [37]. The XRD spectra of the as-prepared Si NWs/g-C$_3$N$_4$, pure g-C$_3$N$_4$ and Si NW samples are shown in Fig. 2(d). As for the pure g-C$_3$N$_4$ sample, the two noteworthy diffraction peaks at 27.5° and 13.1° correspond to the (002) and (100) crystal planes [38]. All the peaks of the Si NWs show compliance with the rutile phase (JCPDS 35–1158), and the fact that no other impurity phase is detected indicates the good crystallinity of the Si NWs. No obvious diffraction peaks for g-C$_3$N$_4$ can be observed in the Si NWs/g-C$_3$N$_4$ core/shell arrays. Comparing the XRD pattern of Si NWs/g-C$_3$N$_4$ and the Si NWs, it can be concluded that the diffraction peaks at 38.5° and 44.7° of the Si NWs/g-C$_3$N$_4$ sample can be attributed to the (111) and (200) crystal planes of Si. This result might be ascribed to the fact that the amount of g-C$_3$N$_4$ was very small and well dispersed onto the surface of the Si NWs [20].

3.2. Photoelectrochemical performance

The photoelectrochemical properties of the Si NWs/g-C$_3$N$_4$, Si NWs, and FTO/g-C$_3$N$_4$ samples are evaluated via linear sweep voltammetry experiments. The corresponding current density–potential relations tested in the dark and under illumination are shown in Fig. 3(a). Under irradiation, all the prepared photoelectrodes exhibit an anode current. The Si NWs/g-C$_3$N$_4$ photoanode shows a higher photocurrent of approximately 0.316 mA/cm$^2$ at 1.0 V vs. Pt compared to that of Si nanowire and FTO/g-C$_3$N$_4$ photoanodes, which can be attributed to the formation of a heterojunction of the Si nanowire and g-C$_3$N$_4$, indicating that N-doping of the WO$_3$ coating is an efficient strategy to enhance the PEC performance of Si-based photoanodes. To investigate the effect of g-C$_3$N$_4$ thickness on the photocurrent density, cyanamide solutions with different mass concentrations were used to wet the sample of Si NWs. The linear sweep voltammetry (J–V) curves of the resulting samples with varying g-C$_3$N$_4$ shell thicknesses are shown in Fig. 3(b). When the mass concentration of cyanamide increases from 0.125 to 0.5, the current density increases. The optimal mass concentration is 0.25, corresponding to a 15 nm g-C$_3$N$_4$ shell thickness. When the mass concentration of cyanamide is larger than 0.25, the photocurrent of the Si NWs/g-C$_3$N$_4$ photoanode decreases drastically because the thicker g-C$_3$N$_4$ shell may decrease the light absorption of the Si core. The linear sweep voltammetry (LSV) measurement of the FTO/g-C$_3$N$_4$ samples was conducted to further demonstrate the positive effects of silicon nanowires. When g-C$_3$N$_4$ was deposited on FTO, an extremely weak photocurrent was obtained (as shown in the inset of Fig. 3(d)), indicating that the bulk g-C$_3$N$_4$ has a very low PEC performance. When g-C$_3$N$_4$ was deposited on the silicon nanowires structure, the photocurrent was significantly raised because of the increasing of light absorption and contact area. Fig. 3(c) shows the LSV curve with chopped AM 1.5 light of 100 mW/cm$^2$ intensity. A much higher transient photocurrent is observed compared to the steady-state photocurrent. This phenomenon may simply be ascribed to carrier recombination at the surface of g-C$_3$N$_4$. We also investigated the amperometric I–T curve of Si NWs/g-C$_3$N$_4$, Si NWs and FTO/g-C$_3$N$_4$ at 0 V vs. Pt under AM 1.5 light, as shown in Fig. 3(d). The Si NWs/g-C$_3$N$_4$ sample achieves a stable photocurrent density of 45 µA/cm$^2$, which is 2.5 times that of the Si NW sample and 562.5 times that of FTO/g-C$_3$N$_4$. This promotion of photocurrent density indicates that constructing a Si NWs/g-C$_3$N$_4$ core/shell heterojunction is an effective route to address the intrinsic drawbacks of g-C$_3$N$_4$-based photoanodes for PEC applications.

3.3. Optical absorption and charge transfer properties

The optical absorption of the Si NWs, FTO/g-C$_3$N$_4$ and Si NWs/g-C$_3$N$_4$ samples were investigated by UV–vis spectrophotometry, and
rent spectroscopy NWs/g-C₃N₄ samples was compared to the wavelengths and density of Si NWs/g-C₃N₄, Si NWs, and FTO/g-C₃N₄ just showed absorption of Si NWs/g-C₃N₄, Si NWs, and FTO/g-C₃N₄ photoanodes. There is no difference between the two photoanodes in terms of characteristic maximum frequency peaks. Since Si NWs/g-C₃N₄ and Si NWs have the same characteristic maximum frequency peaks, they exhibit similar carrier recombination kinetics. However, a relative high f_max measured in FTO/g-C₃N₄ electrode under the same conditions as Si NWs/g-C₃N₄ indicates the relatively short τ_e of electrons generated in FTO/g-C₃N₄. Thus, we can declare that the combination of Si NWs and g-C₃N₄ promotes carrier separation.

3.4. Mechanism analysis

The curves based on the Kubelka–Munk function versus the energy of light are shown in Fig. 6(a). The estimated band gap of g-C₃N₄ is approximately 2.79 eV. The VB XPS spectra of the pristine g-C₃N₄ are shown in Fig. 6(b). The VB of g-C₃N₄ is observed at ~1.88 eV, which is consistent with the previous result [40]. The VB edge of the Si NWs is ~−0.73 eV.

\[ E_{CB} = E_{VB} - E_g \]  

(1)

The CB of g-C₃N₄ and Si NWs can be calculated by the above equation, and the CB energies of g-C₃N₄ and Si NWs were determined to be ~−0.91 and ~−0.39 eV, respectively. On the basis of the results of all the measurements of the as–prepared samples, a possible mechanism for the performance improvement of photocatalytic activity of the Si NWs/g-C₃N₄ core/shell structure is proposed, as

Fig. 3. (a–c) Linear sweep J–V measurements under 100 mW cm⁻² of simulated sunlight illumination: (a) FTO/g-C₃N₄, Si NWs and Si NWs/g-C₃N₄ samples; (b) photocurrent density over g-C₃N₄-modified Si NWs with different cyanamide concentrations; (c) Si NWs/g-C₃N₄ array electrodes illuminated with chopped white light; and (d) amperometric I–t curves of FTO/g-C₃N₄, Si NWs and Si NWs/g-C₃N₄ samples at 0 V vs. Pt with 25 s light on/off cycles.

Fig. 4. UV–vis absorption spectra of the FTO/g-C₃N₄, Si NWs and Si NWs/g-C₃N₄ samples.
Fig. 5. EIS measurements of FTO/g-C$_3$N$_4$, Si NWs and Si NWs/g-C$_3$N$_4$ photoanodes under illumination: (a) Nyquist and (b) Bode phase plots.

Fig. 6. (a) UV–vis diffuse reflectance curves of the pristine g-C$_3$N$_4$; (b) XPS VB spectra of the pristine g-C$_3$N$_4$ and Si NWs.

Scheme 2. The proposed mechanism for the charge separation and transfer at the Si NWs/g-C$_3$N$_4$ heterojunction.

shown in Scheme 2. The CB potentials of the Si NWs are lower than those of g-C$_3$N$_4$, so the photo-generated electrons in the CB of g-C$_3$N$_4$ could transfer to the CB of the Si NWs. For the junction between n-Si and n-g-C$_3$N$_4$, the depletion region mostly lies in n-g-C$_3$N$_4$ because of the higher concentration of electron of the n-Si NWs (its low resistivity is approximately 2–10 $\Omega$ cm). The direction of the built-in electric field between the two semiconductors is from the n-Si to the g-C$_3$N$_4$. Under illumination, the electron–hole pairs generated in the depletion region (g-C$_3$N$_4$) increase the number of electrons in the conduction band (CB) of g-C$_3$N$_4$ as well as the Si NWs. Then, the electrons in the CB of g-C$_3$N$_4$ will drift to the n-Si NWs, which is beneficial for carrier separation on the surface of g-C$_3$N$_4$. The surviving abundant holes in the VB of g-C$_3$N$_4$ can oxidize water and produce O$_2$.

4. Conclusion

In conclusion, metal-free Si NWs/g-C$_3$N$_4$ heterojunction core/shell array photoelectrodes with different g-C$_3$N$_4$ mass contents have been fabricated. These photoelectrodes not only expand
the optical absorption range of the g-C3N4-based photoelectrodes but also significantly improve the PEC performance of bulk phase g-C3N4. The Si NW arrays have been proven to further accelerate the migration of charge carriers and improve the effective separation of the charges generated in g-C3N4. Conversely, the strong optical absorption performance of the Si NWs also contributes a critical role in the improvement of PEC performance. Meanwhile, the examined photocatalyst for neutral water splitting provides a promising prospect for overall splitting of water using metal-free materials. All the conclusions discussed above will provide convenient guidance for researchers studying the photoelectrochemical process.

Acknowledgments

The authors acknowledge the financial support from the National Natural Science Foundation of China (Grant Nos. 21406052, 51602111), Guangdong Province Grant Nos. 2014A030308013, 2014B090150055, 2015A030310196, 2015B050501010, 14KJ13, and the Pearl River S&T Nova Program of Guangzhou (201506040045), Guangdong Innovative Research Team Program (No. 2011D09), PCSIRT Project No. IRT13064.

References