Research Article

Photoelectrochemical Properties of Porous Si/TiO₂ Nanowire Heterojunction Structure

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Received 25 April 2020; Accepted 8 June 2020; Published 1 July 2020

Guest Editor: Mingyi Zhang

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The porous silicon as substrate material was prepared by metal-assisted chemical etching (MACE) method. The TiO₂ nanowire cover layer on porous silicon was prepared by hydrothermal method. Thus, porous Si/TiO₂ nanowire heterostructure was obtained. The formation of the porous Si/TiO₂ nanowire heterostructure was confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results of diffuse reflection spectra (DRS) show that porous Si/TiO₂ nanowire has the highest antireflectivity among the four tested samples. Photoelectric catalysis (PEC) and photocurrent measurement show that the porous Si/TiO₂ nanowire heterostructure has higher photoelectric catalytic and photocurrent activity than the other samples under the simulated solar light and visible light irradiation. The results showed that the construction of the porous Si/TiO₂ nanowire heterostructure improved the photoelectrochemical properties, which is attributed to the heterogeneous effect and window effect.

1. Introduction

Energy source and environment have become an urgent problem for every country all over the world, and the utilization of clean and reproducible energy becomes the important task for us especially [1–5]. In order to overcome this problem, photocatalysis has been extensively studied by researchers [6–8]. The titanium dioxide (TiO₂) has been a promising catalysis since Fujishima and Honda reported [9]. And TiO₂ shows a significant power conversion efficiency, which can degrade a wide range of organic macromolecular pollutants in water [10]. Due to the excellent chemical, physical properties [11–15] and strong capability of light harvesting effects [16–19], the nanostructured TiO₂ may serve as an ideal heterojunction structure in photoelectric catalysis applications. However, TiO₂ cannot utilize the visible spectrum effectively and has the high band gap energy (3.2 eV), which limits the absorption of the visible light. Thus, the photocatalytic performance of the TiO₂ nanowires is affected [20].

Silicon as one of the most abundant elements is a narrow gap semiconductor [21, 22]. The optical band gap of the single-crystal silicon is about 1.12 eV [23], and the single-crystal silicon has a high utilization of sunlight. However, silicon can be easily oxidized in water due to its unique photoelectric and chemical properties in photodegradation [24]. Nanostructured silicon is a prospective material which can be used to construct various types of heterojunction structure with semiconductor. And the porous Si could generate photocurrent when it was illuminated [25]. But this photocurrent is unstable in aqueous electrolytes [26]. In the electrolyte without fluorine anion, oxides are formed on the surface of the porous silicon, and photocurrent would be shut off [27]. Therefore, the TiO₂ nanowires as a shield can protect porous Si from oxidation in the electrolyte.

Recently, Qu et al. [28] prepared porous silicon nanowires by the silver particle-assisted chemical etching method. The photocatalytic properties of porous silicon nanowires were studied, and the result shows that the porous silicon nanowires can utilize the entire spectral regime from UV to near IR range. Hwang et al. [29] studied the photoelectric

catalysis of n-SiNWs/TiO₂ nanowire heterojunction and p-SiNWs/TiO₂ nanowire heterojunction for aqueous phenol solution, and the results show that the n-SiNWs/TiO₂ nanowire heterojunction have higher photoelectric catalysis activity compared with the p-SiNWs/TiO₂ nanowire heterojunction due to the window effect. In addition, Shi et al. [30] studied the photocurrent density of the planar Si and Si electroless etched nanowire (EENW) coated by ALD TiO₂ thin film. The results showed that SiEENW/TiO₂ has higher photocurrent than the planar Si/TiO₂ due to lower reflectance and higher surface area.

Overall, the combination of nanostructured silicon and TiO₂ nanowires can improve the photoelectrochemical activity. In this paper, we prepared porous Si/TiO₂ nanowire heterostructure with a two-step method involving hydrothermal synthesis and metal-assisted etching. The photoelectrocatalytic and photocurrent activity of porous Si/TiO₂ nanowire heterostructure under simulated solar light and visible light irradiation were studied. Moreover, the photocurrent and photoelectrocatalytic mechanism of porous Si/TiO₂ nanowire heterostructure were also studied.

2. Experimental

2.1. Chemicals and Instrumentation. The chemicals used in this study are as follows: n-Si <111> wafer (ρ : 20~50 Ω cm, Shunsheng Electronics Science & Technology Group, Zhejiang, China); HF, absolute ethanol, 37 wt% HCl, isopropanol [(CH₃)₂CHOH], and 97 wt% H₂SO₄ (Beijing Chemical Works, China); 66 wt% HNO₃, Na₂SO₄, and 30 wt% H₂O₂ (Xilong Chemical Co., Ltd., China); AgNO₃ (Sinopharm Chemical Reagent Co., Ltd., China); methylene blue (MB, Tianjin Guangfu Fine Chemical Research Institute, China); tetrabutyl titanate [CH₃(CH₂)₃O]₄Ti (Tianjin Guangfu Fine Chemical Research Institute, China).

The surface morphology views of the samples were observed by SEM (SNE4500M, SEC Co., Ltd., Korea) with an accelerating voltage of 30 kV. The crystallographic structures of the samples were characterized by X-ray diffractometer (XRD, Ultima IV, Rigaku Co., Ltd., Japan). The diffuse reflectance spectra (DRS) were measured using the UV-Vis-NIR spectrophotometer (Cary 5000 UV-Vis-NIR, Agilent Technologies Inc.). The photocurrent measurement was measured by the electrochemical station (LK98C, Lanlike Instrument Corp, Tianjin, China). The Xe lamp (50 W, PLS-SXE300, Perfect light Instrument Corp, Beijing, China) was used as the simulated solar light irradiation. The concentration of dyes was analyzed by the UV-Vis spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd., China).

2.2. Preparation of the Porous Si/TiO₂ Nanowire Heterostructure. We followed the methods of Chen et al. for the preparation of the porous Si/TiO₂ nanowire heterostructure [31]. The porous Si was prepared based on the two-step metal-assisted chemical etching method. The cleaning process comprises following steps. Firstly, the Si wafers were put into solution (H₂SO₄: H₂O₂ = 3:1, v/v) for 20 min. Secondly, the Si wafers were dipped into the mixed solution

(H₂SO₄: H₂O₂ = 3:1, v/v) with ultrasonic bath at room temperature for 2 min (3 times). Then, the Si wafers were rinsed in the deionized water with ultrasonic bath for 2 min (3 times). Lastly, the Si wafers were dried in nitrogen flow at room temperature. Thus, the cleaned silicon wafer is obtained. The silver particles which act as catalysts assist the etching of silicon. Firstly, the silver nanoparticles (AgNPs) were deposited on the surface of the Si wafers in the plating solution (AgNO₃ = 0.01 M, HF = 4.65 M) at room temperature for 1 min. Secondly, the Si wafers covered by AgNPs were immersed in the etching solution (H₂O₂ = 0.05 M, HF = 4.65 M) for 35 min at 50°C. Then, the Si wafers were immersed in the mixed solution (HNO₃: H₂O = 2:1, v/v) for 2 h at room temperature. Lastly, the samples after the etching process were thoroughly rinsed several times in the deionized water and dried in nitrogen flow at room temperature, and the porous Si samples (area $\sim 1 \times 2$ cm²) were obtained.

The preparation of the porous Si/TiO₂ nanowire heterostructure involves the hydrothermal synthesis method. Firstly, porous Si samples were dipped in the mixture of tetrabutyl titanate (0.075 M) and isopropanol for 2 min. Second, the porous Si samples were rinsed in absolute ethanol for 1 min and dried in a nitrogen gas flow, repeat these steps for five times. Finally, the porous Si samples with seed layer of TiO₂ were annealed for 2 h at 500°C. On the other hand, the tetrabutyl titanate [CH₃(CH₂)₃O]₄Ti (2 ml) was added into the mixed solution (HCL = 80 ml, deionized water = 80 ml) under magnetic stirring. Then, the precursor solution was prepared. The porous Si samples with seed layer of TiO₂ and the above-mentioned precursor solution limited to 15 ml were transferred into the autoclaves and put into a blast drying oven for 6 h at 150°C. Next, the samples were washed with deionized water and dried in a nitrogen gas flow. Finally, the samples were annealed at 450°C for 30 min, and the porous Si/TiO₂ nanowire heterostructure was obtained. And the Si/TiO₂ nanowire heterostructure was also prepared by the above-mentioned process.

2.3. Photoelectrochemical Experiment. Photoelectrochemical measurements were carried out on a LK98C workstation. The simulated solar light irradiation was provided by a 300 W Xe lamp, and the simulated visible light irradiation was provided by a 300 W Xe lamp with a 420 nm cut-off filter. The porous Si/TiO₂ nanowire, the Si/TiO₂ nanowire, porous Si, and Si were used as working electrodes, respectively. The platinum foil and the silver chloride electrode acted as the counter electrode, and the reference electrode, respectively. The electrode was illuminated from the front side, and the exposed area was 2 cm²; the incident light intensity on electrode surface was 50 Mw/cm². The photocurrent measurements of all samples were performed in 0.01 M Na₂SO₄ solution under simulated solar light irradiation (visible light irradiation). Prior to catalytic experiment, the three-electrode was immersed in the dye for 20 min to obtain a good dispersion and establish absorption/desorption equilibrium between the organic molecules and the photoanode surface. The PEC activities of all samples were evaluated by monitoring the degradation of

FIGURE 1: XRD pattern of porous Si/TiO₂ nanowire heterostructure.

methylene blue (MB) solution (90 ml, MB = 6 mg/l, Na₂S O₄ = 0.01 M) under simulated solar light irradiation (visible light irradiation) and bias voltage at 1.5 V. At given time intervals for 10 min, the concentration of MB dye was measured by UV/Vis spectrophotometer (TU-1810) with detection wavelength of 665 nm.

3. Results and Discussion

Figure 1 shows the XRD patterns of the porous Si/TiO₂ nanowire heterostructure. The peaks at $2\theta = 23^\circ, 33^\circ, 37^\circ, 39^\circ, 54^\circ, 64^\circ$, and 71° (JCPDF No.02-0494) correspond to rutile phase TiO₂. There are slight traces of anatase TiO₂ diffraction peaks observed ($2\theta = 21^\circ$ and 47° ; JCPDF No. 02-0406). The result shows that the porous Si/TiO₂ nanowire heterostructure has been synthesized by the combination of metal-assisted chemical etching and hydrothermal synthesis.

Figure 2 shows the SEM images of the porous Si, Si/TiO₂ nanowire, and porous Si/TiO₂ nanowire heterostructure, respectively. Figure 2(a) shows that the macropores are uniformly distributed in porous Si due to the silicon anisotropic etching. Figure 2(b) shows that the TiO₂ nanowires on the surface of Si were compact and uniform. In Figure 2(c), it clearly shows that TiO₂ nanowires were grown on the macropore structure of the porous Si, and the length of the nanowires is ca 1 μm . The results are consistent with that of XRD.

The light absorption property of heterojunction is very important for its photoelectric property research. Figure 3 shows the DRS of Si wafer, porous Si, Si/TiO₂ nanowire, and porous Si/TiO₂ nanowire heterostructure, respectively. Compared with the absorption of Si wafer, the absorption of the porous Si is stronger. The porous Si owns a light trapping structure due to the gradient-index multilayer and macropores of porous Si [28], which results in the strong light absorption of the porous Si. The Si/TiO₂ nanowire and the porous Si/TiO₂ nanowire heterostructure show a stronger absorption from 300 to 400 nm, relative to

the Si wafer and the porous Si. This means that the TiO₂ nanowires have preponderant absorption ability in the utilization of UV light region. The porous Si/TiO₂ nanowire heterostructure shows a stronger absorption compared with that of the Si/TiO₂ nanowire, which is attributed to the utilization of the solar spectrum in both UV and visible spectral regions.

In order to understand the photoelectrochemical performance of the porous Si/TiO₂ nanowire heterostructure, photocurrent and photoelectric catalytic activity of different samples were measured. Figure 4 shows I-V curves of porous Si/TiO₂ nanowire heterostructure, Si/TiO₂ nanowire, porous Si, and Si wafer under the simulated solar light and visible light irradiation. The photocurrents of all samples increase with the increasing of bias potential under the simulated solar light (Vis+UV) and visible light (Vis) irradiation as shown in Figures 4(a) and 4(b), respectively. Obviously, the difference of dark current under the simulated solar light and the visible light irradiation is negligible. It is observed that the sequence of photocurrents under the simulated solar light and the visible light irradiation is porous Si/TiO₂ nanowire heterostructure > Si/TiO₂ nanowire > porous Si > Si wafer.

Due to the obvious difference of the photocurrent at a bias voltage 1.5 V (vs. Ag/AgCl), we chose the bias voltage 1.5 V to perform the photoelectric catalysis measurements. The photoelectric catalytic degradation efficiency (C/C_0) of porous Si/TiO₂ nanowire heterostructure, Si/TiO₂ nanowire, porous Si, and Si wafer for degradation of methylene blue (MB) under the simulated solar light (Vis+UV) and visible light (Vis) irradiation was shown in Figure 5, where C is the concentration of organic pollutants with different catalytic degradation time, and C_0 is the initial concentration of organic pollutant. We can clearly see that the Si wafer shows the lowest PEC activity that is almost no effect under the simulated solar light and the visible light irradiation. From Figure 5(a), it is observed that the sequence of PEC activities under the simulated solar light irradiation is porous Si/TiO₂

FIGURE 2: SEM of (a) porous Si, (b) Si/TiO₂ nanowire, and (c) porous Si/TiO₂ nanowire heterostructure.

FIGURE 3: DRS of Si, porous Si, Si/TiO₂ nanowire, and porous Si/TiO₂ nanowire heterostructure.

nanowire heterostructure>Si/TiO₂ nanowire>porous Si>Si wafer. The degradation efficiency of porous Si/TiO₂ nanowire heterostructure and Si/TiO₂ nanowire is much higher than that of porous Si and Si wafer under the simulated solar light irradiation. It means that the UV light can be utilized by the TiO₂ nanowires in porous Si/TiO₂ nanowire heterostructure and Si/TiO₂ nanowire. From Figure 5(b), it is observed that the sequence of PEC activities under the visible light is porous Si/TiO₂ nanowire heterostructure>Si/TiO₂ nanowire>porous Si>Si wafer. It is worth noting that the degradation efficiency of Si/TiO₂

nanowire is higher than the porous Si before 100 min. However, the degradation efficiency of the Si/TiO₂ nanowire and the porous Si tends to the same after 100 min. It means that the visible light can be utilized by the porous Si. Thus, porous Si/TiO₂ nanowire heterostructure shows the highest PEC activity under the simulated solar light and visible light irradiation. The results are consistent with that of photocurrent.

In order to analyze the performance of the porous Si/TiO₂ nanowire heterostructure, several experiments had been performed; all results showed that the porous Si/TiO₂ nanowire heterostructure had the highest photocurrent and PEC activity. We consider that the reasons might be as follows. Firstly, due to the window effect [32], the TiO₂ nanowires can utilize the UV light in the solar spectrum, and the porous Si can utilize the visible light in the solar spectrum as indicated by the DRS result in Figure 3. As a result, a more efficient utilization of the solar spectrum could be achieved, which improved the photocurrent and PEC activity of the porous Si/TiO₂ nanowire heterostructure. Secondly, due to the heterostructure effect, the separation efficiency of electron-hole pairs and the transmission efficiency of charge carriers have been increased by the construction of porous Si/TiO₂ nanowires heterostructure as shown in Figure 6. Under the simulated solar light irradiation, the UV spectral region can be utilized by the TiO₂ nanowires and the visible spectral region can be utilized by the porous Si, which leads to the producing of the electron-hole pairs. Holes in valence band of porous Si and electrons in conduction band of TiO₂ nanowire are recombined [29, 33, 34], which is harmful to the PEC

FIGURE 4: I-V curves of porous Si/TiO₂ nanowire heterostructure, Si/TiO₂ nanowire, porous Si, and Si wafer under the simulated (a) solar light and (b) visible light irradiation.

FIGURE 5: Photoelectric catalytic degradation efficiency (C/C_0) of porous Si/TiO₂ nanowire heterostructure, Si/TiO₂ nanowire, porous Si, and Si wafer for degradation of MB under the simulated (a) solar light and (b) visible light irradiation (bias potential is 1.5 V vs. Ag/AgCl).

activity as shown in Figure 6(a). Under the external bias potential and simulated solar light irradiation, the PEC process of the porous Si/TiO₂ nanowire heterostructure is shown in Figure 6(b). In PEC process, the electrons will flow from the conduction band of TiO₂ nanowires into the conduction band of the porous Si, and the holes will flow from the valence band of the porous Si into the valence band of TiO₂ nanowires through the interface. This leads to the high separation efficiency and transmission efficiency of electrons and holes in the porous Si/TiO₂ nanowire heterostructure. Thus, the heterostructure effect

leads to the high photocurrent and PEC activity of the porous Si/TiO₂ nanowire heterostructure.

4. Conclusions

The porous Si/TiO₂ nanowire heterostructure was successfully fabricated by the MACE combined hydrothermal synthesis method. The porous Si/TiO₂ nanowire heterostructure shows the strong absorption under simulated solar irradiation. The porous Si/TiO₂ nanowire heterostructure shows the highest photocurrent and PEC activity under

FIGURE 6: Schematic illustration of the PEC mechanism of the porous Si/TiO₂ nanowires heterostructure under the simulated solar light ((a) without and (b) with bias potential).

simulated solar irradiation, which is attributed to the window effect and the heterostructure effect. The result presented in this work indicates that the porous Si/TiO₂ heterostructure supplies a high efficiency in photoelectrocatalytic process, which may offer some useful guidance for many other important domains.

Data Availability

All the data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The work was supported by the National Natural Science Foundation of China (Grant/award number: 51502023), Education Department project of Jilin Province (Grant/award number: JJKH20190588KJ and JJKH20200777KJ), and Science and Technology Department project of Jilin Province (Grant/award no. 20200201077JC, 20180201033GX, and 20190302125GX).

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