聚苯胺类/n-Si(111)单晶硅复合电极：制备与光电性质

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摘要：在过氧化月桂酰作用下,于 n-Si(111)型单晶硅表面上分别嫁接苯胺及烷基取代苯胺,进而实现晶体硅表面上聚苯胺和烷基取代聚苯胺的原位聚合,制备得到了系列聚苯胺(或烷基取代聚苯胺)/n-Si(111)单晶硅复合电极。此外,对上述合成电极表面苯胺链进行磺化,得到系列磺酸基化的单晶硅复合电极。电化学研究结果显示,聚苯胺直接嫁接于晶体硅表面所得到的复合电极光电转化效率最高,苯胺聚合链通过碳碳双键桥连于单晶硅表面所得到复合电极的光电转化效率高于通过碳碳单键桥连得到的复合电极,但其光电转化效率低于苯胺聚合链直接桥连于晶体硅表面而得到的复合电极。另外发现,苯环磺酸基化有利于提高复合电极的光电转化效率。

关键词：半导体；表面化学；薄膜；合成设计；电化学

Photoelectrode of Polyanilines/n-Si(111) Crystalline: Preparation and Photoelectric Property

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Abstract: The self-assembled monolayers (SAMs) of aniline and alkyl substituted anilines grafted on n-Si(111) crystalline surface were prepared in the presence of lauroyl peroxide, and the photoelectrodes of polyanilines/n-Si(111) crystalline were prepared based on polymerizations between the SAMs and anilines. Additionally, the polyanilines with sulfonic acid group (SPANI) substituted n-Si(111) crystalline photoelectrodes were prepared via the above samples to fabricate SPANI/n-Si(111) electrodes (Si-SPANIs). Electrochemical studies indicate that the electrode based on 4-bromoaniline (Si-PANI) is better than that of 4-ethynylaniline (Si-C=C-PANI), and the electrode from 4-vinylaniline (Si-C-C-PANI) is the poorest. In addition, anion ring substitution is important in promoting photoelectric conversion of the electrodes. An electrode with high photocurrent density of 15.4 mA·cm^{-2} and photoelectric transformation efficiency of 13% was obtained.

Key words: semiconductors; surface chemistry; thin films; synthesis design; electrochemistry

0 Introduction

The solar energy is the most promising energy due to its basal and inexhaustible properties in the future. Photovoltaic (PV) technology is regarded as the most important one in application of solar energy, and silicon crystalline plays a key role in this area[1]. Positive-negative junctions (PN-j) in inner structure of intermingled silicon crystalline will accelerate oriental movement between electrons and holes after the

silicon absorbs solar energy, but the dangling bonds Si-O-Si on silicon surface will diminish output of photoelectrons. Several methods, including surface coverage with Pt nanoparticles on hydrogenated silicon or surface grafted with organic compounds, are used to eliminate the dangling bonds. Unsaturated organic compounds were firstly grafted on Si-H surface in 1993[2]. Our group has reported the surface modification on n-Si (111) crystalline with aliphatic carboxylic acid and aliphatic sulfonic acid to prepare photoelectrodes[3].

Conjugated conducting polymers (CCP), such as polyaniline (PANI), are emphasized due to their special electronic, optical properties[4-5], soft mechanical and redox properties[6], and these materials are possibly applied in redox reactions[7-8], supercapacitor[9], electro-rheology[10], bacterial luminescence[11], organic photoel-ectric[12] and electrochemical sensor[13]. In this paper, photoelectrodes of Si-C=C-PANI (polyaniline is grafted by -C=C- bonds on n-Si (111) crystalline surface), Si-C-C-PANI (polyaniline grafted is by -C-C- bonds on n-Si(111) crystalline surface), Si-PANI (polyaniline is grafted on n-Si (111) crystalline surface), Si-C=C-SPANI (sulfonic acid group substituted polyaniline is grafted by -C=C- bonds on n-Si (111) crystalline surface), Si-C-C-SPANI (sulfonic acid group substituted polyaniline is grafted by -C-C- bonds on n-Si(111) crystalline surface) and Si-SPANI (sulfonic acid group substituted polyaniline is grafted on n-Si (111) crystalline surface) were prepared by fabricating polyaniline (PANI) and polyanilines with sulfonic acid group substitued (SPANI) onto surface of n-Si(111) crystalline, and their photoelectric properties were examined. Structural, morphological, and photoelectric properties of the electrodes were studied by X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and cyclic voltammetry (CV). Results indicate that the photocurrent density and open circuit photovoltage of the electrode with conjugated structure grafted are larger than that of the electrode with unconjugated bonds grafted. Existence of sulfuric groups connected to benzene promotes PV properties of the electrodes greatly.

1 Experimental

1.1 Materials

n-Si (111) crystalline with thickness of (515 ± 35) μm and resistivity about $1\sim5$ $\Omega\cdot cm^{-1}$ was purchased from General Research Institute for Nonferrous Metals of Beijing (GRINM). All cleaning and etching reagents were from Beijing Chemical Regent Company without any purification before use. 4-ethynylaniline (>99.0%, analytical reagent) and 4-vinylaniline (>98.5%, analytical reagent) were purchased from Sigma-Aldrich Company Ltd. Lauroyl peroxide (>97.0%, analytical reagent) was obtained from Alfa Aesar. 4-bromoaniline (>98.0%, analytical reagent), aniline (≥99.5%, analytical reagent), N-methyl-pyrrolidone (>99.0%, analytical reagent), ammonium persulfate (≥98.0%, analytical reagent), hydrosulfite of sodium (≥99.0%, analytical reagent) and liquid bromine (>99.0%, analytical reagent) were all supplied by Beijing Chemical Reagent Company.

Deionized water was used in all experiments, and all reactions were protected by nitrogen gas.

1.2 Preparation of photoelectrodes

Surface hydrogenated n-Si (111) crystalline was prepared according to the reference[14].

Formation of the SAMs on n-Si (111) crystal surface: The hydrogenated n-Si (111) crystal wafers (1.0 cm×1.0 cm) were placed in a Schlenk tube filled with 4-ethynylaniline (or 4-vinylaniline, deoxygenated and dehydrated) and lauroyl peroxide in toluene solution according to a mass ratio of 25:1 (w/w)[2,15], and the mixture was refluxed for 4 h. Finally the wafers were taken out and rinsed with dichloromethane several times, dried under vacuum and kept in nitrogen gas.

SAM of 4-bromoaniline grafted on n-Si (111) crystal surface was prepared as follows. The hydrogenated n-Si (111) crystal wafer was immersed into a solution of Br$_2$ in CCl$_4$ for a few minutes to get surface bromated silicon wafer, and the bromated silicon wafers was then placed into a dried toluene solution containing Grignard reagent of aniline, which was prepared from 4-bromoaniline and Mg in dry

toluene. Monolayer of n-Si (111)/aniline was obtained after the mixture was refluxed for several minutes under the protection of nitrogen gas.

　　Preparation of sulfonated electrodes PANIs/n-Si (111): The electrodes of PANIs/n-Si (111) and their sulfonated products were prepared according to the reference [16]. Firstly, SAMs on silicon wafers were dipped into 20 mL of HCl solution (1.0 mol·L^{-1}) containing aniline (0.2 mol·L^{-1}). 5.0 mL of ammonium peroxydisulfate solution (0.2 mol·L^{-1}) was then added to the stirred mixture at 0~5 ℃. Finally, the silicon wafers were taken out and rinsed with HCl (0.5 mol· L^{-1}) for several times, immersed in NaOH solution(0.1

mol·L^{-1}) for 2 h, N-methyl-pyrrolidone for 48 h and HCl (1.0 mol·L^{-1}) for 10 h at room temperature, respectively.

　　Some of the above products were immersed in liquid bromine for two weeks to ensure bromination of PANIs/n-Si (111) completely[17]. Afterward, the brominated SAMs were immersed in NaHSO$_3$ saturated solution and refluxed for 12 h[18], and SPANIs/n-Si (111) electrodes were then obtained.

　　Sulfonated aniline/n-Si(111) wafers were prepared in the same way except polymerization. The above reactions are shown in Scheme 1.
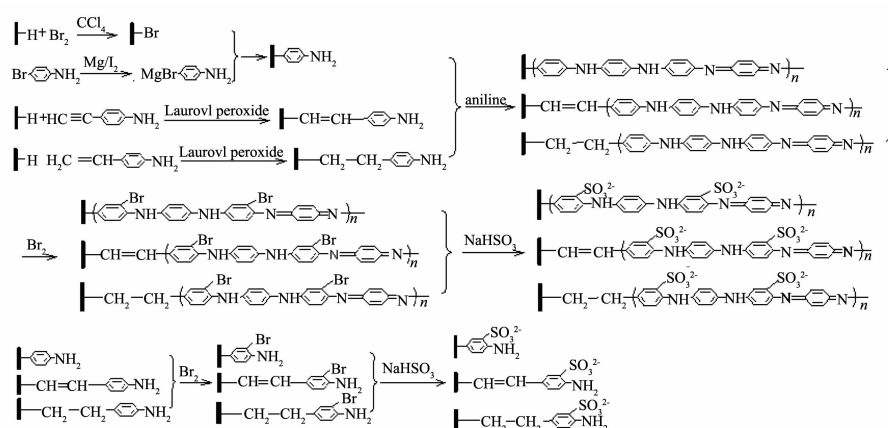
Scheme 1　　Formation of PANI/n-Si(111) electrode, SPANI/n-Si(111) electrode and SAM of sulfonated aniline/n-Si(111) wafer

1.3　Characterizations

　　X-ray photoelectron spectroscopic (XPS) analysis was performed on Shimadzu ESCA-1000 spectrometers (Japan) with Mg Kα X-ray source (1 253.6 eV) and the energy resolution was set to 0.05 eV, and all the binding energies were referenced to C1s at 284.5 eV. Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded using a Bruker Vector-22 Fourier transform spectrometer (made in Germany) in the range 4000 to 400 cm^{-1} with 2 cm^{-1} resolution. Scanning Electron Microscopy (SEM) images were recorded on a Shimadzu SS-550 microscope(made in Japan) at 15 keV.

　　Ohmic contacts were made on the rear side of the modified n-silicon wafer with indium-gallium alloy. The modified n-Si (111) wafer was placed in a Teflon holder (effective area: 0.25 cm^2) and used in photoelectrochemical measurements. A platinum plate

was used as the counter-electrode, and an aqueous solution of 7.6 mol·L^{-1} HI/0.05 mol·L^{-1} I$_2$ was used as the redox electrolyte. An AM 1.5 G 100 mW·cm^{-2} solar simulator (WXS-85H, Wacom) was used as light source. Mott-Schottky plots were obtained with a potentiostat and a potential programmer (a solartron 1 260 impedance analyzer combined with a solartron 1 287 potentiostat). The potential of the n-Si (111) wafer was measured with respect to the counter-electrode. Deionized water and reagent-grade chemicals were used for all the experiments.

2　Results and discussion

　　Binding energies (BEs) of C1s and Si2p of the samples are shown in Fig.1 and Fig.2, respectively. After fitted in gauss software, BEs of C1s in C-Si, C-C, C=C and C-N bonds are found at 283.8, 284.3,
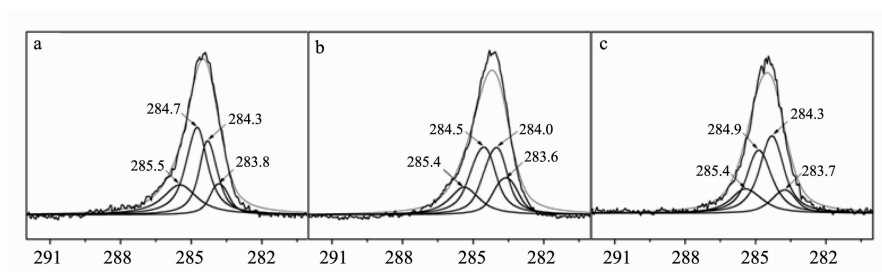
Fig.1　XPS spectra of C1*s* on the surface of n-Si(111) crystal modified with 4-bromoaniline (a), 4-ethynylaniline (b) and 4-vinylaniline (c)

284.7 and 285.5 eV in Fig.1a in 4-bromoaniline grafted sample [19-22], respectively. Similar results are obtained in 4-vinylaniline (Fig.1b) and 4-ethynylaniline (Fig.1c) grafted products. Appearance of C-Si states indicates that the graft is successful. The above results are also proved by BEs of Si2*p*. BEs of Si2*p* in Si-C bonds are at 102.1, 101.8 and 101.8 eV in the three modifications (Fig.2)[23-24]. Some unmodified Si-H bonds are oxidized in the experiments, which can be found from BEs of Si2*p* at 103.0, 103.1 and 102.8 eV in the figure. A weak peak at 101.4 eV attributed to BE of Si2*p* in Si-Br bond[25] in Fig.2a indicates some bonds of Si-Br remain in Grignard reaction due to the steric hindrance effect. Calculation gives that the average grafting ratio of the three organic compounds on silicon surface are 5.8%, 5.4% and 7.7% (S_{Si-C}/S_{Si-Si}, S is the peak area in XPS spectra), respectively.
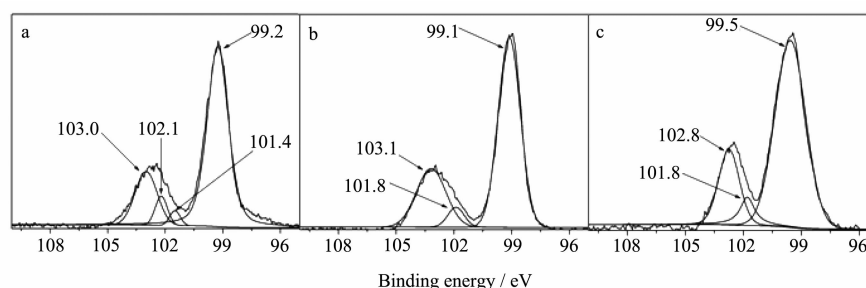

Fig.2　XPS spectra of Si2*p* on the surface of n-Si(111) crystal modified with 4-bromoaniline (a), 4-ethynylaniline (b) and 4-vinylaniline (c)

Infrared absorptions of Si-C stretching around 650 cm^{-1} in Fig.3 give another evidence of the graft[26-28].

Polyanilines (PANIs) are formed based on polymerization between SAMs and aniline on the surface of n-Si (111) wafers. XPS analysis to Si-PANI from SAM of 4-bromoanilines graft indicates that the BE of C1*s* in C=N bond at 286.5 eV (Fig.4a), proving the success of polymerization. Flat surface are found to the SAMs, for the thin organic monolayer, in their SEM images (from Fig.5a to 5c). But some wormlike aggregations with diameter about 10 to 15 nm are found after the polymerization (shown in Figs.5d to 5f). The aggregations are considered coming from polyanilines [29].

Increasing in density of surface negative charge distribution is an important factor in enhancing photoelectric conversion effect to an electrode. SO_3^{2-} is
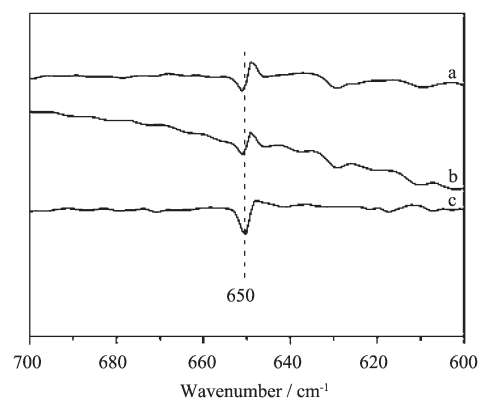

Fig.3　ATR-IR spectra of n-Si(111) crystal modified with 4-bromoaniline (a), 4-ethynylaniline (b)and 4-vinylaniline (c)
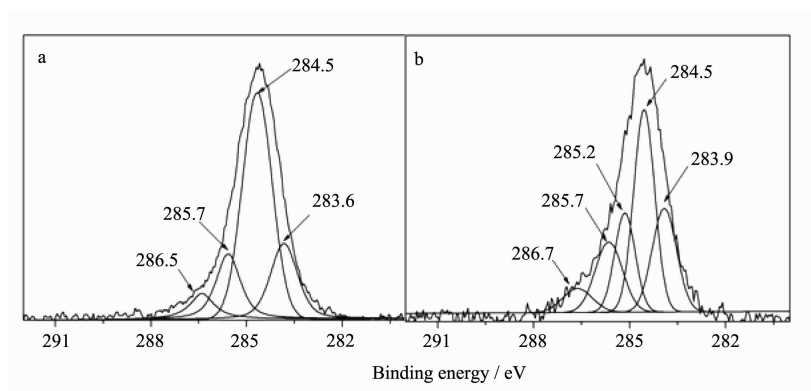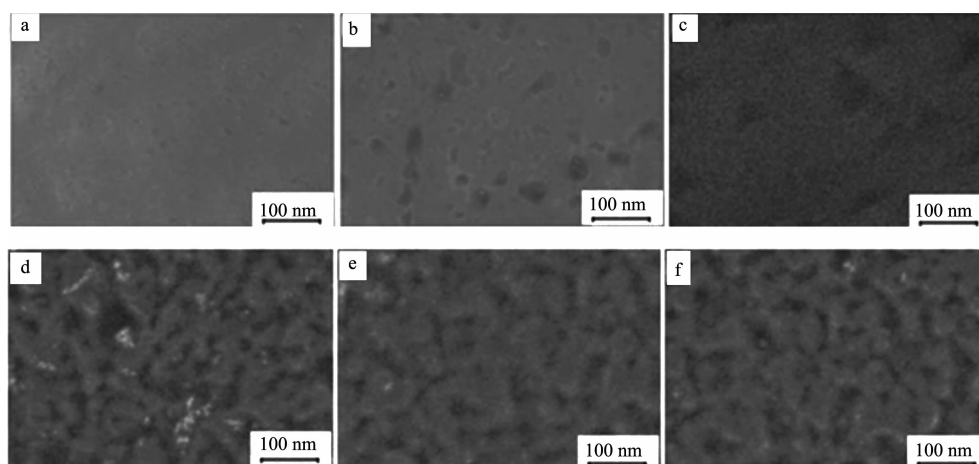
Fig.4　XPS spectra of C1*s* on the surface of Si-PANI(a) and Si-SPANI (b)

a and d arefrom SAM of 4-bromoaniline; b and eare from SAM of 4-ethynylaniline; c and f are from SAM of 4-vinylaniline

Fig.5　SEM images of the composite electrodes before and after polyaniline formation on n-Si(111) crystalline surface

connected on benzene rings in PANI/n-Si (111). A BE state of C1*s* relating to C-S bond is found at 285.2 eV (Fig.4b) in Si-SPANI[30], proving that the sulfonated polyaniline on the wafer is successful.

ATR-IR spectra of Si-SPANI, Si-C=C-SPANI and Si-C-C-SPANI electrodes are shown in Fig.6. Absorptions from N-H, C-H, N=Q=N (Q: quinine), N-B-N (B: benzene), Si-O-Si, Si-C and SO_3^{2-} are found at about 3 750, 2 995, 1 630, 1 523, 1 021, 650 and 590 cm^{-1}, respectively. Absorption of C=C in Fig.6b is overlapped by the absorption of N=Q=N and N-B-N.

Cyclic voltammetry curves of the electrodes are shown in Fig.7 when 7.6 mol·L^{-1} HI/0.05 mol·L^{-1} I$_2$ solution is used as redox electrolyte. Photocurrent density of the electrode grafted by aniline only is about 2.1 mA·cm^{-2} at an open circuit photovoltage (V_{oc}) of −0.64 V. When aniline structures are bridged

by C=C and C-C bonds, photocurrent densities of the electrodes are 1.6 and 0.4 mA·cm^{-2}, with V_{oc} corresponding to −0.57 and −0.45 V, respectively. After the SAMs are sulfonated, the photocurrent densities of electrodes are about 3.2, 2.1 and 0.5 mA·
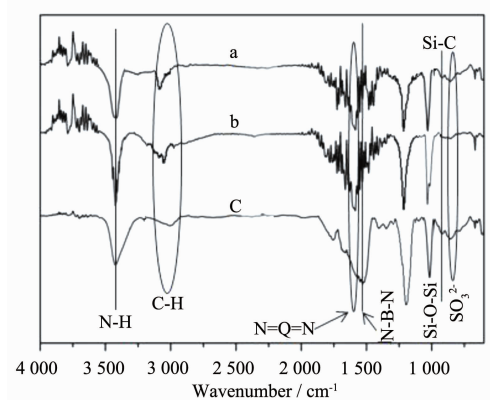

Fig.6　ATR-IR spectra of the Si-SPANI (a), Si-C=C-SPANI (b) and Si-C-C-SPANI (c)electrodes
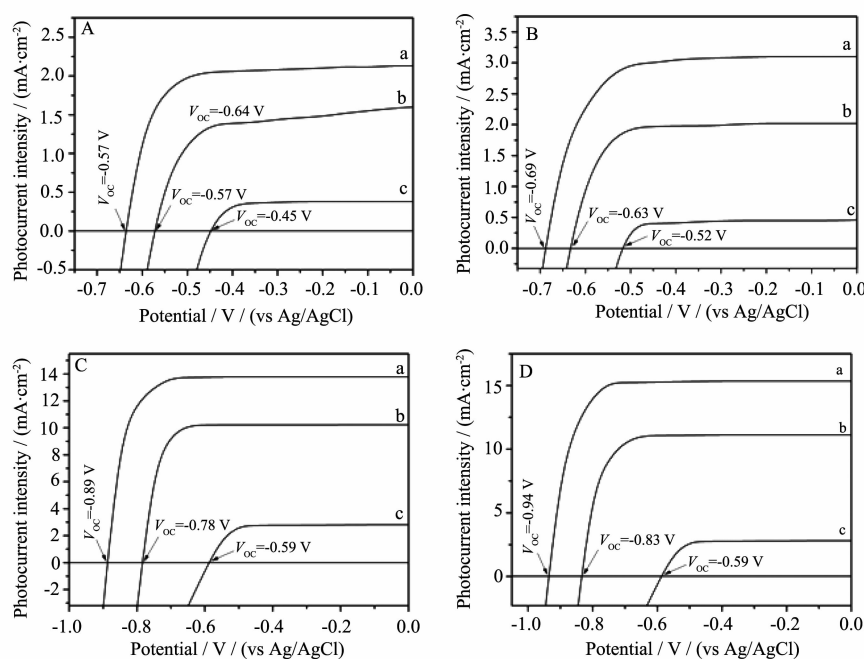
Fig.7 CV curves of the composite electrodes. A: for n-Si(111) crystalline modified with 4-bromoaniline (a), 4-ethynylaniline (b) and 4-vinylaniline (c) before polymerization; B: for sulfonated composite electrodes from A; C: for composite electrodes after polyaniline is formed on silicon surface and D: for sulfonated composite electrodes from C

cm^{-2}, with V_{oc} corresponding to −0.69, −0.63 and −0.52 V, respectively. These results indicate the influence of different grafting forms of anilines on the wafers on photoelectric properties. Much larger photocurrent density and more negative V_{oc} of the SAMs can be obtained when conjugate structure is introduced, and existence of negative charge in SAMs strengthens the above two parameters.

Electrons in semiconductor can be possibly output via benzene rings or conjugate structure after the modified wafers are illuminated by solar light while aniline molecules are grafted directly or by C=C bridge. On the contrary, if the bridging bond between aniline structure and silicon is -C-C-, output of excited electrons from the semiconductor will be halted and the electronic output efficiency becomes poor. Negative charge on silicon surfaces and recombination rate between electrons and holes are key influencing factors in the photovoltaic system. In this work, I$^-$ is oxidized and H$^+$ is reduced on the composite electrode surface, negative charge of the connected organic groups would promote the redox

reaction. More negative charge covered on the electrode, more photoelectric transformation efficiency will be obtained. A potential drop coming from an electric double layer induced a V_{oc} shift to the negative is shown in Scheme 2, and the working model of the composite electrodes in HI/I$_2$ solution are
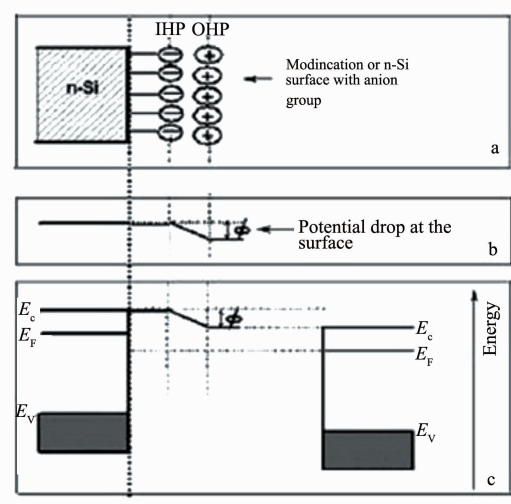
Scheme 2 Energy level diagram for n-Si(111)electrode surface-modified with sulfonated polyaniline, in contact with an electrolyte solution
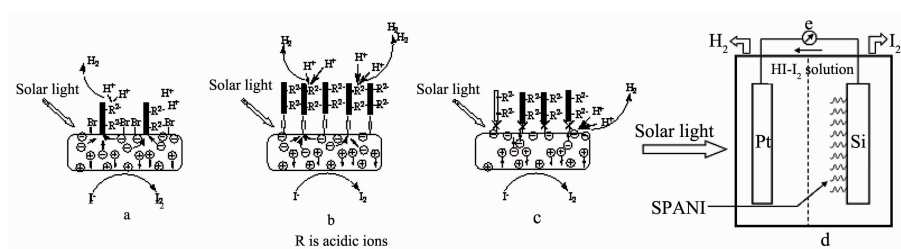
Scheme 3　Working model of the composite electrodes. a: Si-SPANI; b: Si-C=C-SPANI; c: Si-C-C-SPANI and d: a total model of the electrodes

demonstrated in Scheme 3.

When polyaniline is formed on silicon surfaces, output of the electronic in silicon conductor will be more efficient. Fig.7C and 7D show the cyclic voltammogram of PANIs/n-Si (111) and SPANIs/n-Si (111) electrodes. Photocurrent densities of Si-PANI, Si-C=C-PANI and Si-C-C-PANI electrodes are 13.8, 10.3 and 2.8 mA·cm^{-2}, with V_{oc} corresponding to −0.89, −0.78 and −0.59 V, respectively. After PANIs/n-Si(111) are sulfonated, photocurrent densities of the electrodes Si-SPANI, Si-C=C-SPANI and Si-C-C-SPANI are 15.4, 11.1 and 2.8 mA·cm^{-2}, with V_{oc} corresponding to −0.94, −0.83 and −0.59 V, respectively. It strongly supports the result of SAMs grafted on silicon surface. The above data are listed in Table 1 and Table 2. Maximum photoelectric transformation efficiencies of the composite electrodes Si-SPANI, Si-C=C-SPANI and Si-C-C-SPANI are calculated as 13.3%, 8.3% and 1.5%.

Table 1　Photocurrent densities of the composite electrodes before and after sulfonation

mA·cm^{-2}

	Unsulfonated[a]	Sulfonated[a]	Unsulfonated[b]	Sulfonated[b]
Modified with 4-bromoaniline	2.1	3.2	13.8	15.4
Modified with 4-ethynylaniline	1.6	2.1	10.3	11.1
Modified with 4-vinylaniline	0.4	0.5	2.8	2.8

[a] Photocurrent density was obtained from the sample with self-assembled monolayer before polymerized

[b] Photocurrent density was obtained from the sample with self-assembled monolayer after polymerized

Table 2　Data of the open circuit photovoltages of the composite electrodes before and after sulfonated

V

	Unsulfonated[a]	Sulfonated[a]	Unsulfonated[b]	Sulfonated[b]
Modified with 4-bromoaniline	−0.64	−0.69	−0.89	−0.94
Modified with 4-ethynylaniline	−0.57	−0.63	−0.78	−0.83
Modified with 4-vinylaniline	−0.45	−0.52	−0.59	−0.59

[a] Photocurrent density was obtained from the sample with self-assembled monolayer before polymerized

[b] Photocurrent density was obtained from the sample with self-assembled monolayer after polymerized

3　Conclusions

In this work, a series of composite photoelectrodes were prepared based on grafting 4-vinylaniline, 4-ethynylaniline and 4-bromoaniline on n-Si (111) crystalline surface and the surface polymerizations between the SAMs and aniline, and the electrodes were sulfonated to introduce SO_3^{2-} groups on benzene rings to obtain the electrodes of SPANIs/n-Si(111). Photoelectrochemical studies reveal that the open circuit photovoltages of SPANIs/n-Si (111) are more negative and the photocurrent densities have large promotion after -SO_3^{2-} groups are introduced. A larger photocurrent density of 15.4 mA·cm^{-2}, a more negative photovoltage of −0.94 V and a larger photoelectric transformation efficiency of 13.3%

are obtained to the composite electrode Si-SPANI.

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