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A Detailed Study on Working Mechanism of Heteropoly Acid Modified TiO$_2$ Photoanode for Efficient Dye-Sensitized Solar Cells

Yanxia Jiang, a Yulin Yang, *a Liangsheng Qiang, a Ruiqing Fan, *a Liang Li, a Tengling Ye, a Yong, Na, a Yan Shi, a Tianzhu, Luan b

*aDepartment of Chemistry, Harbin Institute of Technology, Harbin, 150001, P. R. China.

bThe First Affiliated Hospital of Harbin Medical University, Harbin, 150001, P. R. China.

To whom the correspondence should be addressed.

Prof. Yulin Yang and Prof. Ruiqing Fan
Department of Chemistry
Harbin Institute of Technology, Harbin 150001, P. R. China
Fax: +86-451-86418270
E-mail: ylyang@hit.edu.cn and fanruiqing@hit.edu.cn
A novel heteropolyacid (HPA) \( \text{K}_6\text{SiW}_{11}\text{O}_{39}\text{Ni(H}_2\text{O})\cdot\text{xH}_2\text{O} \) modified \( \text{TiO}_2 \) has been successfully synthesized and introduced into the photoanode of dye-sensitized solar cells (DSSCs). The performance of the cell with the HPA-modified photoanode (\( \text{SiW}_{11}\text{Ni/TiO}_2 \)), mixed with P25 powder in the ratio of 2:8 is better than the cell with a pristine P25 photoanode. An increase of 31% in the photocurrent and 22% improvement in the conversion efficiency are obtained. The effect of the heteropolyacid was well studied by UV–vis spectroscopy, spectro-electrochemical spectroscopy, dark current, intensity-modulated photocurrent spectroscopy and intensity-modulated photovoltage spectroscopy, open-circuit voltage decay and electrochemical impedance spectra. The results show that the interfacial layer modified by \( \text{SiW}_{11}\text{Ni} \) can enhance the electrons injection, transport, and then retard the recombination of electrons, which results in a longer electrons lifetime. What’s more, the introduction of \( \text{SiW}_{11}\text{Ni} \) can simultaneously broaden the absorption to the visible region, eventually leading to an efficient increase in energy conversion efficiency.
Introduction

The dye-sensitized solar cells (DSSCs) developed by Grätzel have been widely studied by researchers due to their low cost, high efficiency and easy fabrication.\textsuperscript{1-4} The typical device structure of DSSCs is composed of a dye-sensitized semiconductor photoanode, an electrolyte with a redox couple, and a counter electrode.\textsuperscript{5}

Semiconductor photoanode is one of the key factors that affect the final device performance because it relates directly to the light absorption and electrons transport in DSSCs. TiO$_2$ is the most common photoanodes used in DSSCs. To develop more efficient TiO$_2$ photoanodes, many studies have been done and they mainly concentrated on enhancing the photoabsorption, tuning the energy level, the charge transport and retarding the charge recombination.\textsuperscript{6-12}

Polyoxometalates (POMs), a class of inorganic anionic clusters, have been widely applied in medicine, magnetism, nonlinear optics, and catalysis because of their versatile properties.\textsuperscript{13-19} Recently, POMs have been introduced into DSSCs to modify photoanodes. Chen et al. developed a H$_3$PW$_{12}$O$_{40}$-based TiO$_2$ photoanode and they found that H$_3$PW$_{12}$O$_{40}$-based TiO$_2$ photoanode can accelerate electrons transfer and retard recombination, eventually leading to a 19% increase in photocurrent.\textsuperscript{20} Xu et al. prepared multilayer film photoanodes consisting of TiO$_2$ nanoparticles, gold nanoparticles (Au) and Dawson-type polyoxometalate K$_6$P$_2$W$_{18}$O$_{62}$ by the layer-by-layer self-assembly method, and poly(styrenesulfonate) (PSS) was used as a film forming auxiliary material. They found that K$_6$P$_2$W$_{18}$O$_{62}$ could also retard charge pair recombination and enhanced the photovoltaic performance of DSSC with an efficiency of 0.014%.\textsuperscript{21} These pioneering studies indicate that POMs are promising candidates to modify the photoanode in DSSCs and to enhance the cell performance.

In this work, we synthesized a novel kind of SiW$_{11}$Ni modified TiO$_2$ semiconductor (SiW$_{11}$Ni/TiO$_2$). By mixing SiW$_{11}$Ni/TiO$_2$ with P25 in different mass ratio (2:8, 3:7, 4:6, 1:1) and applying them as photoanodes in DSSCs, the performance of the cells was enhanced dramatically compared to the pristine P25 cell. A 31% and 22% of improvement in the photocurrent and efficiency was obtained for
the DSSC using SiW\textsubscript{11}Ni/TiO\textsubscript{2}:P25=2:8 as the photoanode. Comparing to the
pioneering studies, SiW\textsubscript{11}Ni modified TiO\textsubscript{2} as a photoanode has a better performance
on the absorption of visible light and power conversion efficiency. We have studied
the working mechanism for SiW\textsubscript{11}Ni/TiO\textsubscript{2} in DSSCs in detail. The light absorption,
electrons injection, electrons transport, charge recombination and the physical
processes of enhancing the efficiency of electron transfer behavior of the SiW\textsubscript{11}Ni
modified TiO\textsubscript{2} were well studied by UV–vis spectroscopy, spectro-electrochemical
spectroscopy, dark current, intensity-modulated photocurrent spectroscopy (IMPS)
and intensity-modulated photovoltage spectroscopy (IMVS), open-circuit voltage
decay (OCVD), and electrochemical impedance spectra (EIS) respectively. A working
mechanism of SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25 photoanode for efficient DSSCs has been proposed.

**Experimental section**

**Synthesis of SiW\textsubscript{11}Ni and SiW\textsubscript{11}Ni/TiO\textsubscript{2}**

SiW\textsubscript{11}Ni was synthesized using similar method as discussed in the literature.\textsuperscript{22}
According to FT-IR spectrum shown in (Fig. S1a, ESI), the characteristic stretching
vibrations for SiW\textsubscript{11}Ni were observed at 953 cm\textsuperscript{-1} (W-O\textsubscript{a}), 908 cm\textsuperscript{-1} (Si-O\textsubscript{a}), 790 cm\textsuperscript{-1}
(W-O\textsubscript{b}-W) and 704 cm\textsuperscript{-1} (W-O\textsubscript{c}-W), respectively.\textsuperscript{23} The same peak at 527 cm\textsuperscript{-1}
confirmed the Keggin structure of SiW\textsubscript{11}Ni as reported in the literature.\textsuperscript{24} Fig. S1b
(ESI) shows the TG curve of SiW\textsubscript{11}Ni and a high thermal stability can be observed.

TiO\textsubscript{2} was modified with SiW\textsubscript{11}Ni through a hydrothermal method. 0.5 mL HNO\textsubscript{3}
was diluted into 60mL deionized water in flask. 10mL titanium tetraisopropoxide was
slowly added with stirred vigorously. Then 0.1 g SiW\textsubscript{11}Ni was added and a flaky
white precipitate could be obtained. This solution with vigorous stirring was kept
around 98 °C for 3 hours, the white precipitate would be re-dissolved and produce an
opaque solution. The opaque solution was transferred into a 25 mL Teflon-lined
stainless steel autoclave and maintained in an electric oven at 200 °C for 24 hours.
After natural cooling to room temperature, it was centrifuged and washed
thoroughly with deionized water and absolute ethanol. After dried at 100 °C in
vacuum, the precipitate was calcined at 450 °C for 30 minutes and then cooled to
room temperature. Finally SiW_{11}Ni modified TiO\textsubscript{2} powders were obtained. Fig. S2a (ESI) shows the high resolution XPS spectra of Ti 2p. Ti 2p3/2 and Ti 2p1/2 are situated at 458.9 and 464.7 eV for pristine TiO\textsubscript{2}. After modifying, both of them shifted toward lower binding energy of about 0.2 eV. This slight change of Ti 2p peaks and 5.8 eV between Ti 2p3/2 and Ti 2p1/2 indicates they are Ti\textsuperscript{4+}. Similar shift was previously attributed to the change of the local chemical environment of Ti ions influenced by SiW_{11}Ni incorporation and to the formation of Ti\cdots\text{O} bonds on the surface of TiO\textsubscript{2}. So, Ti 2p will shift to lower binding energy, and the peaks become slightly broader.\textsuperscript{25} Fig. S2b (ESI) displays the O 1s spectra comparison SiW_{11}Ni/TiO\textsubscript{2} and pristine TiO\textsubscript{2} samples. The O 1s region of the pristine TiO\textsubscript{2} is located at 530.2 eV, while the peak of SiW_{11}Ni/TiO\textsubscript{2} centered at 530.0 eV, further confirming the presence of Ti\cdots\text{O} weak interaction. The slight shift of these peaks can be attributed to the hydrothermal conditions, which can reduce the number of defects and impurities in TiO\textsubscript{2}.

**Preparation of Photoanodes and Cell Assembly Photoanode**

All photoanodes were fabricated using a screen printing method. There are two kinds of samples for photoanodes: photoanode SiW_{11}Ni/TiO\textsubscript{2} blended with TiO\textsubscript{2} nanoparticles (commercial Degussa P25 nanoparticles, which consists of about 20 % rutile and 80 % anatase and a particle size of about 25 nm) in a weight ratio of 2:8 and pristine TiO\textsubscript{2} paste without modified for comparison. Ethyl cellulose and α-terpineol were used as a binder to disperse the mixed powers while ethanol was used as dispersant. Then the ethanol was removed using rotary evaporation. The resulting slurry was screened-printed onto F-doped SnO\textsubscript{2}-coated conductive glass plate (FTO, 90% transmittance in the visible region, 15 Ω cm\textsuperscript{-2}) and sintered at 450 °C for 15 min. The photoanode film with thickness of 8 µm and active area 0.16 cm\textsuperscript{2} was covered on the FTO substrate by using the screen printing method to create 4 mm × 4 mm electrodes. Fig. S3 (ESI) shows the images of pristine TiO\textsubscript{2} and SiW_{11}Ni/TiO\textsubscript{2}. After modifying with SiW_{11}Ni, we can see some big blocks among TiO\textsubscript{2} particles.

The SiW_{11}Ni/TiO\textsubscript{2}-P25 and pristine TiO\textsubscript{2} (P25) photoanodes were then immersed in absolute ethanol solution containing 0.3 mM N719 (Solaronix SA, Switzerland) and kept at room temperature for 24 hours. The sandwich-type solar cell was
assembled by placing a platinum-coated conductive glass as counter electrode on the
N719 dye-sensitized photo-anode, a drop of liquid electrolyte with 0.5 M LiI, 0.05 M
I₂, 0.1 M TBP (4-tert-butylpyridine) was added to fill the void between two electrodes
and clipping together as open cells for measurement.

**Characterization**

Scanning electrons microscope (SEM) micrograph was analyzed by FEI Company
Helios Nanolab 600i focused ion electrons double beam SEM. Fourier transform
(FT)-IR spectra were measured on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer
with samples prepared as KBr pellet. Thermogravimetric (TG) analyses were
performed on Perkin-Elmer STA 6000 Simultaneous Thermal Analyzer with a heating
rate of 10 °C/min in flowing nitrogen atmosphere. UV-vis spectra were recorded by a
UV-2250 spectrophotometer (Shimadzu, Japan). A custom jacketed three electrodes
electrochemical cell was incorporated into an Agilent Technologies Cary 60 UV-vis
spectrophotometer such that the mesoporous TiO₂ film was positioned normal to the
optical path. The photocurrent-photovoltage (J−V) curves were recorded by CHI660D
electrochemical analyzer. The light intensity of AM1.5 global sunlight from a filtered
500 W xenon lamp (CHF-XM500, Changtuo, China with an AM1.5 global filter from
Newport) was calibrated by a standard Si solar cell (calibrated at National Institute of
Metrology, P. R. China). EIS and OCVD were recorded by CHI660D Electrochemical
Analyzer (Chenhua, China) and the applied forward bias was generally −0.8 V while
IMPS-IMVS were obtained by applied voltage under an illumination with different
light intensities from 30 to 150 W·m⁻². A 300 W Xe lamp was used for incident
photon-to-current quantum conversion efficiency (IPCE) measurements, a
monochromator (Newport 74125) with sorting filters focused on a spot with
additional optics. The current response of the devices was recorded in 10 nm
increments using a power meter (Newport 2936–C). The measured currents were
referenced to a calibrated Silicon detector (Newport 71675).

**Results and discussion**

We mixed the new composite material SiW₁₁Ni/TiO₂ with P25 in different mass ratio
and applied them as photoanode in DSSC and bare P25 based DSSC was also fabricated for comparison. Photovoltaic parameters of a series of DSSCs based on SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25 are listed in Table 1. As the wt % of SiW\textsubscript{11}Ni increased, $\eta$ rises first and then descends. When the blending ratio is 2:8, the cell gives the best performance. This may attribute to the higher SiW\textsubscript{11}Ni/TiO\textsubscript{2} contents brought about more grain boundaries for more recombination within DSSCs and result in the poor performance. Fig. 1 shows the optimized current density-voltage ($J$-$V$) curves of the P25- and SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25-based DSSCs. The DSSC based on SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25 photoanode gives a short circuit current density ($J_{sc}$) of 17.38 mA cm\textsuperscript{2}, an open circuit voltage ($V_{oc}$) of 0.73 V and a fill factor of (FF) 0.61, resulting in a power conversion efficiency ($\eta$) of 7.82%. Comparing with that of the DSSC using bare P25 as the photoanode, a 31% and 22% increase in $J_{sc}$ and $\eta$ was obtained. The performance of P25 is analogous to the references\textsuperscript{26-29}

Table 1 Photovoltaic parameters of a series of DSSCs based on SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25, measured under 100 mW cm\textsuperscript{-2} (AM1.5G) illuminations. The active areas were 0.16 cm\textsuperscript{2} for all of the cells (with the mask area 0.25 cm\textsuperscript{2}).

<table>
<thead>
<tr>
<th>SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25</th>
<th>$J_{sc}$/mA cm\textsuperscript{-2}</th>
<th>$V_{oc}$/mV</th>
<th>FF</th>
<th>$\eta$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>13.28</td>
<td>0.76</td>
<td>0.64</td>
<td>6.42</td>
</tr>
<tr>
<td>1:9</td>
<td>15.49</td>
<td>0.75</td>
<td>0.59</td>
<td>6.93</td>
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<tr>
<td>2:8</td>
<td>17.38</td>
<td>0.73</td>
<td>0.61</td>
<td>7.82</td>
</tr>
<tr>
<td>3:7</td>
<td>14.22</td>
<td>0.70</td>
<td>0.57</td>
<td>5.66</td>
</tr>
<tr>
<td>4:6</td>
<td>13.54</td>
<td>0.69</td>
<td>0.55</td>
<td>5.11</td>
</tr>
<tr>
<td>5:5</td>
<td>12.61</td>
<td>0.65</td>
<td>0.57</td>
<td>4.67</td>
</tr>
<tr>
<td>6:4</td>
<td>12.28</td>
<td>0.65</td>
<td>0.57</td>
<td>4.51</td>
</tr>
<tr>
<td>7:3</td>
<td>11.98</td>
<td>0.64</td>
<td>0.56</td>
<td>4.29</td>
</tr>
<tr>
<td>8:2</td>
<td>11.21</td>
<td>0.64</td>
<td>0.56</td>
<td>4.02</td>
</tr>
<tr>
<td>9:1</td>
<td>10.34</td>
<td>0.64</td>
<td>0.55</td>
<td>3.64</td>
</tr>
<tr>
<td>10:0</td>
<td>10.01</td>
<td>0.63</td>
<td>0.55</td>
<td>3.47</td>
</tr>
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</table>
Fig. 1 The current density versus voltage curves of dye-sensitized solar cells based on the P25 and SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25 photoanodes under 100 mW cm\textsuperscript{-2} (AM1.5G) illuminations.

\[ J_{sc} = 17.38 \text{ mA/cm}^2, V_{oc} = 0.73 \text{ V} \]
\[ \text{FF} = 0.61, \eta = 7.82\% \]

\[ J_{sc} = 13.28 \text{ mA/cm}^2, V_{oc} = 0.755 \text{ V} \]
\[ \text{FF} = 0.64, \eta = 6.42\% \]

Fig. 2 IPCE spectra of the DSSCs based on P25 and SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25 photoanodes.

The corresponding IPCE spectra of the DSSCs were also measured and shown in Fig. 2, the photoanode DSSC based on SiW\textsubscript{11}Ni/TiO\textsubscript{2}-P25 exhibits a significant effect on absorbed photon-to-collected electron efficiency. The improvement of the charge collection yield in the IPCE spectra were in good agreement with the measured photocurrent density. To explore the reason of the enhancement, we studied on the working mechanism of SiW\textsubscript{11}Ni modified TiO\textsubscript{2} in detail.

Fig. 3 shows the UV-visible absorption spectra and the band gap (the inset graph) of TiO\textsubscript{2} and SiW\textsubscript{11}Ni/TiO\textsubscript{2}. For both pristine SiW\textsubscript{11}Ni and SiW\textsubscript{11}Ni/TiO\textsubscript{2}, an absorption in the visible region is observed. It is well known that TiO\textsubscript{2} only absorb
UV light ($\lambda < 387$ nm) without any absorption in visible and infrared regions. After the modification with SiW$_{11}$Ni, the absorption of TiO$_2$ in the visible region changed obviously from 365 nm to 525 nm, which effectively compensates the weak absorption of titania in the visible region. More importantly, N719 has weak absorption in the range of 400 nm~450 nm and this compensation effect is conducive to improve the utilization efficiency of light as shown in Fig. S4 (ESI). The band gap of the SiW$_{11}$Ni/TiO$_2$ is found to be 2.92 eV which is lower than the band gap of the TiO$_2$ (3.14 eV). According to the Tauc plot equation, the direct band gap energies of samples are calculated using the point of intersection of the tangents to the plots of $(\alpha h\nu)^2$ vs $(h\nu)$. In addition, the reduction of the band gap energy of SiW$_{11}$Ni/TiO$_2$ compared to the pristine TiO$_2$ indicates that an obvious red shift on the absorbance toward the visible region and increasing energy difference from the LUMO of N719 to the CB of TiO$_2$, and then increase the driving force of the electrons injection.

**Fig. 3** UV-visible absorption spectra of TiO$_2$, SiW$_{11}$Ni and SiW$_{11}$Ni/TiO$_2$ and Tauc plot representing band gap energy of TiO$_2$ and SiW$_{11}$Ni/TiO$_2$ (inset graph).

To make clear the contribution of SiW$_{11}$Ni/TiO$_2$ in the electrons injection and transport, spectro-electrochemistry spectroscopy and dark current were studied. The chemical capacitance of the TiO$_2$ and SiW$_{11}$Ni/TiO$_2$ photoanode films as a function of applied potential was measured and shown in Fig. 5a. The chemical capacitance of
SiW₁₁Ni/TiO₂ film leftward shifts compared with that of the pristine TiO₂ film, which is because of the band edge of SiW₁₁Ni/TiO₂ decrease downward the I₃⁻/I⁻ potential. From Fig. 5a, we can deduce the flat band potential ($V_{fb}$) which is a very important parameter in spectro-electrochemistry and it can directly reflect the location of the energetic position of the valence band and conduction band edge of a given semiconductor material. Michael Grätzel proposed that the main contribution to the optical absorption at 780 nm comes from interband transitions or from free carrier absorption, therefore the absorbance is proportional to the density of electrons in the conduction band. The $V_{fb}$ of TiO₂ and SiW₁₁Ni/TiO₂ was shown in Fig. 5b. We can see that the absorbance of TiO₂ and SiW₁₁Ni/TiO₂ transparent films at 780 nm with the applied potential. By introducing SiW₁₁Ni into the photoanode, the $V_{fb}$ of TiO₂ (around -0.6 V) positively shifts to -0.4 V, which indicates the Fermi level of SiW₁₁Ni/TiO₂ is lower than pristine TiO₂. The shift of conduction band edge will be accompanied by an equal displacement of quasi-Fermi level relative to the I₃⁻/I⁻ Fermi level. If the band edge shifts positively, the electrons quasi-Fermi level also shifts toward the positive direction. The lower Fermi level increases the energy gap between the LUMO of the dye and the conduction band of TiO₂, which results in an enhanced injection driving force of electrons and then improves the photogenerated electrons injection efficiency from the LUMO of dye to the conduction band of TiO₂. This result will benefit for charge transfer. At the same time, the recombination between injected electrons, dye cations and iodide ions is reduced. In addition, the decrease of the Fermi level of SiW₁₁Ni/TiO₂ results in the decrease of $V_{oc}$. It is because $V_{oc}$ is related to the difference between the Fermi level of the photoanode and the redox potential of the electrolyte. The schematic energy level diagram for the electrode interface is presented in Scheme S1 (ESI).
Fig. 5 (a) Chemical capacitance of the TiO$_2$ and SiW$_{11}$Ni/TiO$_2$ photoanode film while the films were immersed into 0.1 M LiClO$_4$ as a function of applied potential; (b) Optical absorbance at 780 nm of the TiO$_2$ and SiW$_{11}$Ni/TiO$_2$ photoanode film.

The electrons transfer of SiW$_{11}$Ni/TiO$_2$ was studied by the dark current vs voltage. As shown in Fig. 6a, the onset of the dark current of the bare DSSC occurred at 0.3V, whereas for the SiW$_{11}$Ni/TiO$_2$ based DSSC, the onset of the dark current was suppressed. The reduction of the dark current demonstrates that the SiW$_{11}$Ni based photoanode successfully reduced the recombination reaction of the electrons. Therefore, the dark current density in the DSSCs with SiW$_{11}$Ni was obviously suppressed, which enhanced the $\eta$ values of the DSSCs. The result is also supported by the outcome of IMPS-IMVS shown in the following.

Fig. 6 (a) The dark current density versus voltage curves and (b) Nyquist plots of electrochemical impedance spectra of devices P25 and SiW$_{11}$Ni/TiO$_2$-P25 in dark.

Electrochemical impedance spectroscopy was used to study the electron transport behavior and the internal resistances of the DSSCs. Fig. 6b is the EIS measurements that we carried out in the dark to further determine the effect of SiW$_{11}$Ni modified
TiO$_2$ about electron recombination progress. In the dark, there were no electrons injected from dye sensitizer into TiO$_2$ network, electrons were just transported through the TiO$_2$ nanoparticles and reacted with the redox electrolyte ($\text{I}_3^-$). Fig. S5 (ESI) is the equivalent circuit obtained by using transmission line model: $R_s(C_1(R_1O))(R_2Q_2)$. The series resistance ($R_s$) can account for the resistance of the FTO glass substrate, the contact resistance of the cell and the resistance of the external circuits. The semicircle in high frequency corresponds to $R_2$, which represents the charge transfer resistance at the counter electrode/electrolyte interface; the second semicircle ($R_1$) in the intermediate frequency region reflects the electron transport resistance in the photoanode/dye/electrolyte interface related to the charge transport/recombination. The corresponding parameters obtained by the equivalent circuit were listed in Table 2. The two values of $R_2$ are similar because of the identical Pt counter, and the $R_1$ values of P25 and SiW$_{11}$Ni/TiO$_2$-P25 are 11.08 and 28.77 ohm respectively, which indicates the SiW$_{11}$Ni/TiO$_2$ photoanode based DSSC is better at retarding the recombination progress than the pristine TiO$_2$ between the injected electron and the redox electrolyte. The EIS result is in good agreement with the dark current discussed above.

<table>
<thead>
<tr>
<th>DSSC</th>
<th>$R_s/$Ω cm$^2$</th>
<th>$R_1/$Ω cm$^2$</th>
<th>$R_2/$Ω cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>18.92</td>
<td>11.08</td>
<td>13.97</td>
</tr>
<tr>
<td>SiW$_{11}$Ni/TiO$_2$-P25</td>
<td>19.36</td>
<td>28.77</td>
<td>13.82</td>
</tr>
</tbody>
</table>

In DSSCs, the electrons recombination time ($\tau_n$) and the electrons transport time ($\tau_d$) are very important factors for the performance of DSSCs. They are the consequence of the competition between the recombination and transport of electrons across the photoanode. $\tau_n$ and $\tau_d$ are calculated by IMVS and IMPS measurements through eq (1) and (2) respectively: $^{42,43}$

$$\tau_n = \frac{1}{2\pi f_n}$$  \hspace{1cm} (1)

$$\tau_d = \frac{1}{2\pi f_d}$$  \hspace{1cm} (2)
where $f_n$ and $f_d$ are the characteristic frequency minima of the IMVS and IMPS imaginary components, respectively. The $\tau_n$ and $\tau_d$ of P25 and SiW$_{11}$Ni/TiO$_2$-P25 as a function of the incident light intensity are shown in Fig. 7. Fig. 7a and 7b show the $\tau_n$ and $\tau_d$ of the DSSCs based on two different photoanodes noted above. $\tau_n$ of SiW$_{11}$Ni/TiO$_2$-P25 is higher than that of P25 while $\tau_d$ of SiW$_{11}$Ni/TiO$_2$-P25 is lower than that of P25. It is because the excellent electrons injection and good electrons transport of the SiW$_{11}$Ni/TiO$_2$-P25 photoanode, which suppresses the excited electrons to react with iodine in the interfacial region between the electrolyte and the photoanode. The above results strongly demonstrate that the prepared SiW$_{11}$Ni/TiO$_2$-P25 is a promising photoanode candidate for the DSSCs.

![IMVS response and IMPS response](image)

**Fig. 7** The IMVS response (a) and IMPS response (b).

The electrons recombining with the electrolytes can be further revealed by the open-circuit voltage decay (OCVD) technique which monitors the decay of $V_{oc}$ after turning off the illumination in a setting time.\textsuperscript{44,45} Fig. 8a shows the OCVD curves of the DSSCs with the pristine P25 and SiW$_{11}$Ni/TiO$_2$-P25 photoanodes. It can be seen that the electrons lifetime in the DSSCs with SiW$_{11}$Ni/TiO$_2$-P25 photoanode was longer than that of pristine P25, which indicates that its rate of decay is much slower. The recombination rate between electrons and the oxide electrolyte has been restrained effectively, finally resulting in the much longer electrons lifetime. Fig. 8b shows the electrons lifetime derived from equation (3) as a function of $V_{oc}$.

$$\tau_n = -\frac{T k_B}{e} \left(\frac{dV_{oc}}{dt}\right)^{-1}$$

(3)
The electrons lifetime of pristine TiO$_2$ photoanode was shorter than that of the modified one. The results were consistent with the ones we concluded from IMVS and IMPS.

![Graph](image)

**Fig. 8** (a) The OCVD curves of the DSSCs with P25 and SiW$_{11}$Ni/TiO$_2$-P25 photoanodes and (b) the electrons lifetime derived from equation (3) as a function of $V_{oc}$.

Based on the above analyzation, the considerable improvement in $J_{sc}$ and $\eta$ can be attributed to the following reasons: (1) for the modified TiO$_2$, the flat band ($V_{fb}$) (about -0.6 V) shifts positively to -0.4 V. This result increases the driving force for electrons injection, improving the electrons injection efficiency from the LUMO of N719 to the conduction band of TiO$_2$. The modified SiW$_{11}$Ni on TiO$_2$ also improves the electrons transport. The improved electrons injection and transport for the new photoanode restrains the electrons recombining between the oxide electrolyte and dye cations effectively and prolongs the lifetime of electrons; (2) the band gap of SiW$_{11}$Ni/TiO$_2$ turns narrow and the response in the visible region is expanded. The good electrons transport makes it possible to increase the utilization percentage of visible light.

Finally, a possible working mechanism of SiW$_{11}$Ni/TiO$_2$-P25 photoanode for efficient DSSCs is proposed and shown in Scheme 1. Upon being excited by the illumination, the sensitizer dye molecules (N719) absorb the visible light and reach their excited state (Dye*), by which electrons are excited from the HOMO to the LUMO of the dye and photoelectrons will be injected from the LUMO of the dye to the conduction band (CB) of TiO$_2$. At the same time, SiW$_{11}$Ni particles absorb the visible light into HPB (heteropolyblue) and remove holes from photoanode and then...
inject them into the electrolyte. Unfortunately, a certain amount of injected electrons return back from the CB of TiO$_2$ to HOMO of the dye before flowing into the external circuit and some occur at the SiW$_{11}$Ni/TiO$_2$-P25/dye/electrolyte interface (dotted lines in Scheme 1).$^{46}$ Particularly at the interfacial region, electrons recombination may be overcome by introducing a powerful electrons acceptor. HPA leads to a decrease in the recombination of electrons-hole because it accepts electrons from the TiO$_2$ conduction band so that electrons and holes can be separated as effective charge carriers. Thus, HPA can serve as an electrons mediator, which shuttles electrons from the electrolyte to the electrode effectively and helps to enhance the efficiencies. Under illumination, the most injected electrons are recaptured by I$_3^-$ before being extracted to the external circuit. SiW$_{11}$Ni captured the returning electrons to reduce itself to form HPB. In this process, HPB also plays an important role in the DSSCs, absorbing visible light into HPB$^+$, and HPB$^+$ can inject electrons into the CB of TiO$_2$. $^{47,48}$ The intermediate HPB was excited and reduced to the excited SiW$_{11}$Ni, which subsequently returned to the ground state of SiW$_{11}$Ni. $^{49}$ Thus, it avoided the photoreduction of iodine on the surface of the photoanode. Such an effective electrons transfer in SiW$_{11}$Ni can remove the fast electrons–hole recombination on TiO$_2$ and is ascertained from the lifetime of the transient species available in the literature. $^{49}$ Meanwhile, the oxidized dye and SiW$_{11}$Ni are regenerated by I$^-$. As a result, the absorbed photon energy is converted to heat through the two coupled redox cycles involving sensitized electrons injection, dye regeneration and electrons recapture by I$_3^-$. In general, the introduction of SiW$_{11}$Ni can inhibit most of the backward reactions that take place in standard dye sensitized solar cell system and then increase the photocurrent generation by enhancing the absorption and retarding the regeneration of electrode. All the above merits improved the performance and stability of DSSCs.
Scheme 1 Mechanism of photoinduced electrons flow through HPA/TiO$_2$ film electrode.

Conclusions

In summary, we have successfully synthesized a novel composite material of SiW$_{11}$Ni/TiO$_2$ that can effectively modify photoanode. The DSSC based on SiW$_{11}$Ni/TiO$_2$-P25 (2:8) photoanode exhibits high performance in both $J_{sc}$ and $\eta$, increasing from 13.28 mA cm$^{-2}$ and 6.42% (P25 as photoanode) to 17.38 mA cm$^{-2}$ and 7.82% (SiW$_{11}$Ni/TiO$_2$-P25 as photoanode). The overall improvement in the photocurrent and efficiency is 31% and 22% respectively. The considerable improvement in the $J_{sc}$ and $\eta$ can be attributed to the following reasons by the introduction of SiW$_{11}$Ni: (1) excellent electrons injection and good electrons transport; (2) retarding the electrons recombination between the oxide electrolyte and dye cations; (3) the narrowed band gap of SiW$_{11}$Ni/TiO$_2$ and the expanded response to the visible region. All these merits are beneficial to the improvement of the performance of the device.

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Notes and references
