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Enhancing photocurrent of perovskite solar cells via modification of TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction interface with amino acid

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In this communication, glycine, an amino acid, was applied to modify the TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction interface for reducing the inevitable defects formed during crystallization of perovskite. The power conversion efficiency of resulting perovskite solar cell was increased from 8.35 to 12.02%, attributed to the enhancement of short-circuit current density.

Since the pioneering work at 2009, organolead halide perovskites (CH$_3$NH$_3$PbX$_3$, X=Cl, Br, I) have evolved as a promising light sensitizer for the next generation of dye-sensitized solar cells$^1$, due to their superb light-harvesting characteristics and ambipolar transport property$^{2-4}$. Within a short period of time, the configuration of devices from liquid type$^{1,5}$ to all solid type$^6$ was achieved by substituting the liquid electrolyte with hole transporting material such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD). Nowadays, perovskite solar cells can be divided into two categories: one is heterojunction (with mesoporous metal oxide) and the other is planar structure cells with a p-i-n junction, both exhibited the high power conversion efficiency (PCE) of 18.4%$^7$ and 19.3%$^8$, respectively.

Although planar perovskite solar cells showed the higher PCE and simpler manufacturing process, mesoporous metal oxide such as TiO$_2$ could prevent short circuiting between working and counter electrodes$^9$. In addition, the porous TiO$_2$ (p-TiO$_2$) layer may plays as a scaffold to elongate the optical light path and retard the charge recombination$^{10}$. However, the incomplete pore-filling of TiO$_2$ with perovskite to decline the performance of devices was the major concern with this process$^{11}$. Hence two-step deposition by spin-coating PbI$_2$ on top of the p-TiO$_2$ layer and then crystallizing with CH$_3$NH$_3$I to fabricate the perovskite light harvester was developed to reduce the morphological variation of perovskite$^{12}$. Notably, although the photovoltaic performance and reproducibility of the solar cells were improved, the deposition of perovskite crystals on the TiO$_2$ scaffold still inevitably caused defects at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction. Recently, several research groups reported that the photovoltaic performance of perovskite solar cells could be improved through amphipathic molecule treatment on TiO$_2$ surface$^{13-15}$. Therefore, in this work, we modified the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface by introducing glycine, a kind of amino acid, as a coupling agent. Through this modification, the best PCE of perovskite solar cell was increased from 8.35 to 12.02%, mainly due to the enhancement of short-circuit current density ($J_{sc}$) from 14.42 to 19.54 mA cm$^{-2}$.

Photovoltaic characterization of solar cells was carried out at full sunlight (100 mW cm$^{-2}$) with a 1000 W ozone-free Xenon lamp equipped with a water-based IR filter and AM 1.5 filter (Newport Corporation). Measured condition was set as forward scan (from forward bias to short-circuit) with a scan rate of 0.1 V s$^{-1}$. Fig. 1 shows the best $J$–$V$ curves of perovskite solar cells based on the TiO$_2$ treated with and without glycine.

![Fig. 1 $J$–$V$ curves of the best perovskite solar cells with bare TiO$_2$ (dark gray curve) and glycine-treated TiO$_2$ (red curve).](image-url)
Fig. 2 Histograms of photovoltaic PCEs. Data were collected from 10 perovskite solar cells based on TiO$_2$ with (red) or without (dark gray) glycine treatment.

Table 1 Photovoltaic performance data of the perovskite solar cells with and without modification of glycine.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare TiO$_2$</td>
<td>12.56±1.70</td>
<td>0.95±0.02</td>
<td>0.58±0.04</td>
<td>6.99±1.11</td>
</tr>
<tr>
<td>Glycine-TiO$_2$</td>
<td>16.20±2.31</td>
<td>0.98±0.02</td>
<td>0.60±0.05</td>
<td>9.48±1.40</td>
</tr>
</tbody>
</table>

Obviously the glycine modified sample exhibited much higher photocurrent than the non-modified one. Fig. 2 shows the statistical PCE values on a larger batch of ten photovoltaic devices. All the average parameters with glycine-treated TiO$_2$ were superior to those with bare TiO$_2$ as can be seen in Table 1. The average PCE of perovskite solar cells was increased from 6.99 to 9.48%, mainly due to the improvement of $J_{sc}$ since the open-circuit voltage ($V_{oc}$) and fill factor (FF) were barely enhanced. X-ray diffraction (XRD, PANalytical X’Pert PRO) was conducted to analyze the crystallography of perovskite with a scan step size of 0.013° and 3.57 s for each step (Fig. S1). The appearance of diffraction peaks were agreed with the published literatures$^{12,16}$. However, unfortunately, it is hard to compare the results of the perovskite deposited on mesoporous TiO$_2$ with and without treatment of glycine. It might be due to the fact that the tiny amount of perovskite crystals formed in the interface of TiO$_2$/CH$_3$NH$_3$PbI$_3$ was barely detected by X-ray diffraction.

Therefore, to realize how the amino acid affected the crystallization of PbI$_2$, we investigated the crystal structure of PbI$_2$ on top of the compact TiO$_2$ (c-TiO$_2$) with and without glycine treatment in a planar configuration first. Fig. 3(a) shows their XRD patterns. The crystal of PbI$_2$ is a layered structure with the basic building block that Pb atoms are sandwiched in between two layers of I atoms$^{17}$. In Fig. 3(a), the diffraction peaks of PbI$_2$ can be indexed as a hexagonal system (JCPDS, PDF number 07-0235), the (001) lattice plane is clearly observed for both samples. However, the sample treated with glycine exhibited stronger signals at (002), (003), and (004) lattice planes, implying the PbI$_2$ tended to grow in an orientation along the c axis. As can be seen in scanning electron microscope (SEM, JEOL JSM-6300) images, the morphology of PbI$_2$ deposing on glycine-treated c-TiO$_2$ (Fig. 4(a)) differ from the bare c-TiO$_2$ (Fig. 4(b)). Without glycine, PbI$_2$ crystallized into a broader size range of 200-600 nm with more voids. In contrast, the PbI$_2$ grown on the glycine-treated c-TiO$_2$ displays less and smaller voids with narrow crystal size range of 200-300 nm. Obviously, glycine has induced PbI$_2$ crystals to grow along the c axis with the direction perpendicular to the TiO$_2$ surface, beneficial to the following perovskite crystallization.

Fig. 3(b) shows the XRD patterns of CH$_3$NH$_3$PbI$_3$ perovskite prepared by using the previous PbI$_2$ to crystallize with CH$_3$NH$_3$I (see ESI† for experimental details). Compared to the bare c-TiO$_2$, the treatment of glycine rendered the perovskite to appear stronger diffractions at (111) and (404) lattice planes. However, we did not observe any apparent difference between these two perovskites in the SEM investigation (see Fig. S2). It may be due to the fact that the usual information depth of XRD measurement ranging from a few micrometers to a few hundred...
Fig. 4 SEM images of PbI₂ deposited on (a) bare c-TiO₂ and (b) glycine-treated c-TiO₂.

micrometers is deeper than the thickness of perovskite (~300 nm) and the subtle change of lattice plane induced by glycine was beneath the surface investigated by SEM. To further explore the crystal growth immediately on the surface of TiO₂, we diluted the original 1.0 M PbI₂ solution to ~0.1 M and investigate the surface morphology of resulting perovskite with SEM. Notably, the crystalline structure of PbI₂ immediately grew on the glycine-treated c-TiO₂ also shows less and smaller voids (see Fig. S3). As it was crystallized with CH₃NH₃I, the resulting CH₃NH₃PbI₃ perovskite crystals covering on the surface of TiO₂ was significantly more completed than that on non-modified TiO₂ (see Fig. 5), possibly owing to the denser PbI₂ crystals on the surface performing as the foundation for growth of the perovskite crystals.

Moreover, the growth of CH₃NH₃PbI₃ perovskite crystals on glycine-treated c-TiO₂ preferred their [111] direction which is consistent with the XRD Patterns (see Fig. 3b) and the size was also larger. Presumably, the carboxylic acid group of glycine was prone to anchor on the TiO₂, whereas its outward amine group acted as the nucleation center for PbI₂ deposition and crystal growth and herewith directly participated in the crystallization process of perovskite. The well-covered crystals on the TiO₂ surface observed in Fig. 5(b) support this proposed mechanism. By comparing the SEM images between Fig. S3(a) and Fig. 5(a), the CH₃NH₃PbI₃ perovskite crystals did not fully hold onto the top of bare c-TiO₂ during crystallization. In contrast, the glycine-treated surface was apt to keep the perovskite on the TiO₂ surface and promoted the crystal to grow evenly. This advanced the higher coverage of crystallized perovskite at the interface of TiO₂/CH₃NH₃PbI₃.

To further investigate the contribution of TiO₂/CH₃NH₃PbI₃ interface to the photovoltaic performance, electrochemical impedance spectroscopy (EIS) was employed to characterize the charge transfer dynamics of perovskite solar cells with a real configuration (containing p-TiO₂) by analysing the variation in impedance related to the different interfaces of the device. As shown in Fig. 6, Nyquist plots of the perovskite solar cells based on bare TiO₂ and glycine-treated TiO₂ analysed under illumination were fitted well with Z-view software by setting the equivalent circuit shown in the inset figure. Three R-C circuits in series were employed. (Note: We did not observe the feature contributed by the interface of spiro-MeOTAD/gold counter electrode at high frequency mentioned in ref. 15, probably due to the limited frequency range of our instrument.) In our case, the difference between two specimens was only the presence of glycine. The first arc in Fig. 6 shows the huge difference between the perovskite solar cells with and without modification of glycine. This result points out the strong influence of the TiO₂/CH₃NH₃PbI₃ interface upon the feature of the first arc. Similar result has also been reported in the literature. Accordingly, in our system, the first arc combines the complex interfaces of TiO₂/CH₃NH₃PbI₃/spiro-MeOTAD. The reduced resistance at the first arc of glycine-modified device (from 213.6 Ω to 101.8 Ω) would be due to the better contact and coverage of perovskite on the TiO₂ surface. Besides, we also observed the transmission line following the first arc at intermediate frequency. The appearance of transmission line has been suggested to be due to the transport resistance of charges lower than the recombination resistance at the interface. Therefore, the much lower resistance (reduced from 230.4 Ω to 44.8 Ω) at this region means the modification of glycine leaded to the more efficient charge transfer from perovskite to TiO₂. However, the feature of the second arc in Fig. 6 did not have much difference after modification of glycine (139.3 Ω for bare TiO₂ and 109.2 Ω for glycine-TiO₂). After all, the reduced
resistance by the modification of TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction with glycine was considered to be the major contribution to the better photovoltaic performance for perovskite solar cells.

Conclusions

We have successfully demonstrated the crucial role of amino acid as a coupling agent to modify the TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction interface for enhancing photovoltaic performance of two-step solution-processed perovskite solar cells. With this promising glycine modification, higher coverage of the CH$_3$NH$_3$PbI$_3$ crystals on TiO$_2$ surface was obtained, resulting in more efficient charge transfer and higher photocurrent. Based on our results, we believe that this modification has created a new breakthrough for the research of perovskite solar cells.

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Novel modification of TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface using glycine as a coupling agent induced higher coverage of perovskite through two-step solution process.