Improved photovoltaic performance of dye-sensitized solar cells using dual post treatment based on TiCl$_4$ and urea solution

1 | INTRODUCTION

Solar power generation owns promising merits of sustainability, pollution-free, reproducible and unlimited resources. Dye sensitized solar cell (DSSC) invented by Michela Grätzel and co-workers at 1991, has attracted intense attentions in photovoltaics field owing to its superiority such as flexibleness, lightweight and low-cost [1–3], expected to be a potential candidate device for alternating traditional inorganic solar cells. As so far, DSSC has made record power conversion efficiencies (PCE) of 14% [4–6] thanks to the unceasing effort of researchers in the field of chemistry, physics and materials science. One way to improve the PCE is to explore varies of novel materials for the main components of DSSC, namely metal-oxide photoanode [7–9], redox shuttle electrolyte couples [10, 11] and catalysing photocathode [12].

Another strategy to optimize the performance of the solar cell is a post-treatment of the photoanode layer, mainly represented by titanium dioxide (TiO$_2$) film. Titanium tetrachloride (TiCl$_4$) has been used as an effective post-treating reagent of TiO$_2$ electrode for high-efficiency DSSC [13–15]. After the TiCl$_4$ treatment, an additional layer of TiO$_2$ is formed on the TiO$_2$ nanoparticles, which will optimize the DSSC performance through several functions of increasing surface area, improving electron transport, light scattering and so on. The hydrolysis reaction occurring during the TiCl$_4$ treatment to constitute a new TiO$_2$ layer influenced mainly by the concentration of the TiCl$_4$ aqueous solution and an optimized value of 10–50 mM is commonly used. In recent years, graphite carbon nitride (g-C$_3$N$_4$) has been also applied to optimize TiO$_2$ electrode due to its high thermal tolerance and chemical stability, easy-preparation and relative negative conduction band morphology, dye-adsorption amount on TiO$_2$ electrode and the photovoltaic performance of the DSSC based on those electrodes were investigated systematically to understand the relationship between device structure and properties. The TiCl$_4$ treatment at the second and forth TiO$_2$ layer were supposed to retain the connectivity of the TiO$_2$ particles in different layers, aiming to improve the electron transfer efficiency and inhibit the charge recombination [19].

2 | EXPERIMENTS

2.1 | Materials and instrumental analysis

Solvents used in this experiments were repurified from appropriate reagents. All reagents were purchased from Shanghai Macklin, Shanghai Aladdin Bio-Chem Technology and Sigma-Aldrich. Perkin–Elmer Lambda 35 UV–visible spectrometer was used to record the light absorption at room temperature. The phase identification was performed using X-ray diffraction (XRD, Cu Ka radiation, Philips PW1830). The 20 scans were taken between 20$^\circ$ and 80$^\circ$ with steps of 0.05$^\circ$, with 2s counting time per angular value. The nanocrystalline morphology was characterized using a field-emission scanning electron microscope (SEM, Hitachi SU-8010), and the microstructure was characterized using a transmission electron microscope (TEM, JEM 210F).

2.2 | General procedure for preparing TiO$_2$ films

Fluorine doped Tin oxide (FTO) glass substrates were cleaned in an order of detergent solution, ultra-pure H$_2$O and ethyl alcohol (EtOH) within an ultrasonic bath, rinsed with H$_2$O and EtOH, and followed by N$_2$ flow for drying. Screen-printing technique was used to prepare nanocrystalline films on the substrate with TiO$_2$ paste purchased from Dalian HeptaChroma Solar Tech Co., Ltd, coded as DHS-TPP3, consisting of 20 nm nanoparticles. The substrates with printed films were slowly sintered from room temperature to 500 °C and retain for 15 min in a muffle furnace. TiCl$_4$ treatment was implemented with a TiCl$_4$ aqueous solution of 40 mM at 70 °C for 30 min and then...
rinsed with H2O and EtOH, serially, followed by sintering again at 450 °C for 30 min. Urea treatment is performed by dipping the photoanode films into the urea solution with a concentration of 1 g/mL at 50 °C for 30 s, followed by calcination in a muffle furnace at 500 °C for 1 h immediately after being pulled out from the urea solution.

2.3 Preparation of TiO2 films with different surface treatment

The post-treatments were prepared as shown in Scheme 1. The film thickness of 6 layers TiO2 film was measured to be 12–14 μm.

Electrode 2T: Sintered two layers of TiO2 films on FTO substrate was processed with TiCl4 treatment and then printed with another four layers of TiO2 films, followed by calcination again.

Electrode 2TU: Sintered two layers of TiO2 films on FTO substrate was processed with TiCl4 treatment and urea treatment in sequence, followed by print of another four layers of TiO2 films, and calcination again.

Electrode 4T: Sintered four layers of TiO2 films on FTO substrate was processed with TiCl4 treatment and then printed with another two layers of TiO2 films, followed by calcination again.

Electrode 4TU: Sintered four layers of TiO2 films on FTO substrate was processed with TiCl4 treatment and urea treatment in sequence, followed by print of another two layers of TiO2 films, and calcination again.

Electrode 6T: Sintered six layers of TiO2 films on FTO substrate was processed with TiCl4 treatment, followed by calcination.

Electrode 6TU: Sintered six layers of TiO2 films on FTO substrate was processed with TiCl4 treatment and urea treatment in sequence, followed by calcination.

2.4 Fabrication of DSSC

Prepared TiO2 electrodes were activated under 80 °C for 30 min before using, and then immersed into a standard N719 dye EtOH solution with concentration 0.3 mM of for 24 h. Pt-counter electrodes were prepared with screen-printing technique on FTO glass substrates using one layer of Pt nanoclusters paste that purchased from Dalian HeptaChroma Solar Tech Co., Ltd., coded as DHS-PtSP. After the screen-print, the counter electrodes were sintered at 400 °C for 30 min. As prepared Pt-counter electrode and dye-sensitized TiO2 electrode were sealed as sandwich structure cells using a hot-melt Surlyn film with thickness of 25 μm as a spacer between the electrodes. A drop of the electrolyte solution [0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI) + 0.1 M LiI + 0.2 M I2 + 0.5 M 4-tert-butylpyridine in acetonitrile] was driven into the cell space through the hole pre-drilled on the counter electrode via vacuum pump. Finally, a thin normal glass slide was used to seal the hole with hot-melt surlyn film.
2.5 | Characterization and measurements of DSSC

The fabricated DSSC were illuminated via an aperture area of 0.03 cm$^2$ using a lightproof black mask to eliminate light diffusions on the apparent surface area of the TiO$_2$ film, which was ca. 0.36 cm$^2$. DSSC photovoltaic performance was characterized by photocurrent–voltage ($I$–$V$) and incident photon-to-current conversion efficiency (IPCE) measurements. $I$–$V$ characteristics were measured by an AAA grade solar simulator (XES-70S1, SAN-EI Electric, Japan) at 100 mW cm$^{-2}$ under a simulated AM 1.5G sunlight. The IPCE measurements were carried out with ZAHNER CIMPS photo-electrochemical workstation in the wavelength range from 380 to 800 nm. In both case, a standard silicon photovoltaic cell (AK-200, Konica Minolta Inc.) was used to calibrate the intensity of the incident light before experiments.

3 | RESULTS AND DISCUSSIONS

3.1 | Morphology and phase analysis

The size and morphology of the TiO$_2$ particles scraped from the electrodes were investigated through TEM and HRTEM as shown in Figure 1. Without urea treatment, the TEM images of the TiO$_2$ particles present an approximately average particle size of 25 nm owing a clear edge (Figure 1(a,b)). After treated with urea solution and sintering, there is a thin layer with thickness of 1–2 nm covering the TiO$_2$ particles as displayed in Figure 1(c,d). These results of g-C$_3$N$_4$ polymeric formation on the surface of TiO$_2$ particles are in accordance with the reference papers [16, 17]. The crystallinity and the morphology of the prepared electrodes were also studied by XRD and SEM methods. Due to the low concentration and weak crystallization, no obvious differences were found between electrodes with and without urea treatment. Figure 2 presents the XRD pattern for the FTO substrate and the TiO$_2$ electrodes 2T, 4T, 6T and 6TU. The diffraction peaks at 26.6°, 37.8°, 54.0° and 55.1° correspond to the anatase TiO$_2$ phase. As shown in Figure 3, the TiO$_2$ particle amounts generated by TiCl$_4$ treatment was too little to modify the thickness of the electrode, the width and appearance of the electrode 2T, 4T and 6T in cross-sectional view remain the same.

3.2 | Dye adsorption

In order to clarify the influence of the different TiO$_2$ surface treatment on the dye adsorption amount, the UV–vis absorption spectra of the dye TiO$_2$-desorption solution (0.1 mol L$^{-1}$ NaOH, THF/H$_2$O = 1:1) were measured and shown in Figure 4. The adsorption capacity $T$ (mol/cm$^2$) can be calculated by the following formula, and the related data was presented in Table 1.

$$A = \varepsilon bc \quad (1)$$

$$n = \sigma v \quad (2)$$

$$T = n/S \quad (3)$$
FIGURE 3 Cross-sectional view of the SEM image of TiO₂ electrode with TiCl₄ treatment in different layers (a) 2T electrode (b) 4T electrode (c) 6T electrode

TABLE 1 Comparison of dye-loading amount of electrodes 2T, 2TU, 4T, 4TU, 6T and 6TU

| Electrodes | A    | C (mol/L) | N (mol) | T (mol/cm²) |
|------------|------|-----------|---------|-------------|
| 2T         | 0.1284 | 9.88 × 10⁻⁶ | 3.95 × 10⁻⁸ | 9.35 × 10⁻⁸ |
| 2TU        | 0.1344 | 1.03 × 10⁻⁵ | 4.12 × 10⁻⁸ | 9.75 × 10⁻⁸ |
| 4T         | 0.1383 | 1.06 × 10⁻⁵ | 4.24 × 10⁻⁸ | 1.00 × 10⁻⁷ |
| 4TU        | 0.1349 | 1.04 × 10⁻⁵ | 4.16 × 10⁻⁸ | 9.85 × 10⁻⁸ |
| 6T         | 0.1521 | 1.17 × 10⁻⁵ | 4.68 × 10⁻⁸ | 1.11 × 10⁻⁷ |
| 6TU        | 0.1157 | 8.90 × 10⁻⁶ | 3.56 × 10⁻⁸ | 8.43 × 10⁻⁸ |

TABLE 1

where $A$ is the absorbance, $\varepsilon$ is the molar absorption coefficient (L/mol·cm), $b$ is the colorimetric plate width (1 cm), $c$ is the concentration of the dye solution (mol/L), $n$ is the amount of substances in the sample solution, and $v$ is the volume of the sample solution (L). $S$ is the TiO₂ electrode area (0.423 cm²). The characteristic absorption peak value of the dye N719 at 500 nm in TiO₂-desorption solution was chosen as the absorbance $A$, which corresponds to the $\varepsilon$ value of the first absorption peak at the long wavelength side in N719 ethanol solution.

The TiCl₄ treatment results in an apparent increase in dye adsorption due to more specific binding sites generated on TiO₂ surface. The dye loading amount augmented by 6.95% from electrode 2T to 4T and further increased by 11% from electrode 4T to 6T, leading to a maximum value of 1.11 × 10⁻⁷ mol/cm². It implies that the binding sites created by TiCl₄ treatment mainly functioned on outer layer of TiO₂ films to adsorb more dye molecules, which will contribute for the better light-harvest and consequently improved photocurrent. While the urea treatment leads to coat a thin layer of g-C₃N₄ outside TiO₂ nanoparticle surface as shown in Figure 1. As comparing the dye adsorption amount before and after urea treatment, it can be drawn that g-C₃N₄ coating largely influence the dye loading at the outer layer of TiO₂ film as well (dye amount changes, 2T to 2TU: +4.28%; 4T to 4TU: −1.50%; 6T to 6TU: −24.10%), whereas the urea treatment at the second and forth layer of TiO₂ film affected the dye adsorption very little.

3.3 Photocurrent–voltage characteristics

$I–V$ characterization of the DSSCs based on those electrodes were measured in accordance with the condition mentioned experiment Section 2.5. Figure 5 illustrates $I–V$ curves plotted for the DSSCs and the data is listed in Table 2. From the results it can be seen obviously that both open circuit voltage $V_{oc}$ and short circuit current $J_{sc}$ were improved gradually according to the TiCl₄ treatment on electrode 2T to 6T ($V_{oc}$: 2T to 4T: +4.4%; 4T to 6T: +2.3%; $J_{sc}$: 2T to 4T: +27.5%; 4T to 6T: +19.7%), leading to the overall photovoltaic conversion efficiency enhancement of 29.9% from 2T to 4T and 24.9% from 4T to 6T. The variation tendency of $J_{sc}$ are in good agreement with the changing tendency of dye adsorption amount.

FIGURE 4 UV–vis absorption spectra of the TiO₂-desorption solutions

FIGURE 5 $I–V$ curves for DSSC based on the electrodes
TABLE 2  Comparison of the photovoltaic performance of DSSC based on electrode 2T, 2TU, 4T, 4TU, 6T and 6TU

| Electrodes | V_{oc} (mV) | J_{sc} (mA/cm^{2}) | FF | η (%) |
|------------|-------------|---------------------|-----|-------|
| 2T         | 545         | 14.67               | 65.9| 5.26  |
| 2TU        | 561         | 16.47               | 68.9| 6.36  |
| 4T         | 569         | 18.70               | 64.2| 6.83  |
| 4TU        | 602         | 22.05               | 64.9| 8.61  |
| 6T         | 582         | 22.39               | 65.5| 8.33  |
| 6TU        | 583         | 24.09               | 63.8| 8.94  |

TABLE 3  Comparison of the electrochemical parameters of DSSC based on electrode 2T, 2TU, 4T, 4TU, 6T and 6TU

| Electrodes | R_s (Ω) | R_{pt} (Ω) | R_{ct} (Ω) | f_{max} (Hz) | τ_e (ms) |
|------------|---------|------------|------------|--------------|----------|
| 2T         | 16.53   | 3.49       | 34.58      | 13.2         | 12.06    |
| 2TU        | 16.89   | 4.67       | 37.01      | 13.0         | 12.25    |
| 4T         | 18.23   | 5.80       | 38.30      | 12.9         | 12.34    |
| 4TU        | 17.83   | 3.92       | 55.10      | 8.82         | 18.05    |
| 6T         | 20.62   | 3.49       | 44.37      | 9.20         | 17.31    |
| 6TU        | 16.58   | 5.09       | 47.82      | 7.56         | 21.06    |

FIGURE 6  IPCE curves for DSSC based on the electrodes

FIGURE 7  Equivalent circuit for the DSC

The increase in V_{oc} probably resulted from small rise of the quasi-Fermi level of nanocrystalline TiO_2 due to the surface-state density [15]. Additional urea treatments on electrode 2T, 4T and 6T, result in further enhanced J_{sc} and V_{oc}, leading to PCE of 6.36%, 8.61% and 8.94%. IPCE spectral response of the cells based on the electrodes are displayed in Figure 6, well correlating with the change of their J_{sc}.

In order to reveal the details of improved J_{sc} and V_{oc}, electrochemical impedance spectroscopy (EIS) was carried out to clarify the interfacial charge transfer and recombination processes for the DSSC. Impedance was performed with AC amplitude of 10 mV at frequency range from 10^{-1} Hz to 10^{5} Hz in the dark. The equivalent circuit was represented in Figure 7, where R_s stand for the series resistance; C_{pt} and R_{pt} represented the interface capacitance and charge transfer resistance at the Pt/electrolyte interface, respectively. Figures 8 and 9 shows the Nyquist and Bode plot of the EIS for the DSSC based on the electrodes and related data were summarized in Table 3. There are two semicircles with different size were observed in the Nyquist plots, identified as charge transfer resistance R_{pt} at the Pt/electrolyte interface and electron transport resistance R_{ct} at the TiO_2/dye/electrolyte interface, respectively. As the same Pt counter electrode and electrolyte components were applied in the cells, the smaller semicircles representing the R_s are quite similar to each other. The radiuses of the R_s semicircles increased after the TiO_2 electrodes were further treated with urea solution, which accord with the V_{oc} values changes of the DSSCs. In the EIS-Bode phase plot, the following equation is

FIGURE 8  Nyquist plots of the DSSC based on the electrodes
used to estimate the electron lifetime ($\tau_e$), where $f$ is the frequency of the mid-frequency peak.

$$\tau = \frac{1}{(2\pi f_{\text{peak}})} \quad (4)$$

Along with the urea treatment on TiO$_2$ electrode, the $f_{\text{peak}}$ in lower frequency range decreased and thus the $\tau_e$ was enhanced accordingly, which were in good accordance with the situation of $V_{\text{oc}}$ increase in $I-V$ curves. These results disclosed that the formation of g-C$_3$N$_4$ on the TiO$_2$ particle surface can effectively suppress the injected electrons recombination and prolong the electron life time, on account of the more negative conduction band of g-C$_3$N$_4$ ($-1.12$ eV) than that of TiO$_2$ ($-0.29$ eV) restraining the electron shift from TiO$_2$ to triiodide in the electrolyte. It resulted in the increase of electron concentration and hence the photocurrent value $J_{\text{sc}}$ as well [17]. Interestingly, the photovoltage and photocurrent of electrode 4TU increased greater extent than those of 2TU and 6TU, probably in respect that not only the modification of interface contact is more effective when the g-C$_3$N$_4$ is constituted in the middle layer of the TiO$_2$ electrode, but also there is less disrupt of the TiO$_2$ particle connection, inducing faster electron transport from TiO$_2$ to FTO substrate [16, 17].

**4.1 CONCLUSIONS**

To enhance the photovoltaic performance of DSSC, a dual post-treatment based on TiCl$_4$ and urea solution was applied on different layers of TiO$_2$ electrode. TiCl$_4$ treatment on the sixth layer of TiO$_2$ film could provide more binding site for dye-adsorption than that on the second and fourth layer, leading to increased dye molecule amount and thus improved $J_{\text{sc}}$ and $V_{\text{oc}}$. On the other hand, g-C$_3$N$_4$ formation from urea treatment on the sixth layer decreased the dye loading, resulting in less extent of $V_{\text{oc}}$ and $J_{\text{sc}}$ increase, but still the DSSC presented the highest PCE of 8.94%. Urea treatment in the fourth TiO$_2$ layer produce more interface contact without interruption of the connection among TiO$_2$ particles that makes for highest rise in $V_{\text{oc}}$ and $J_{\text{sc}}$. These results empirically demonstrated that dual post-treatment of TiCl$_4$ and urea solution could improve the DSSC performance. Further surface modifications and device optimizations for improving energy conversion efficiency and long-time stability are in progress.

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