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Growth of Zr/N-codoped TiO₂ nanorod arrays for enhanced photovoltaic performance of perovskite solar cells

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In this paper, Zr and N co-doped TiO₂ (Zr/N–TiO₂) nanorod arrays were synthesized using a hydrothermal method and perovskite solar cells were fabricated using them as an electron transfer layer. The solar cells based on Zr/N–TiO₂ presented an enhanced performance compared with those based on un-doped TiO₂. The solar cell performance was optimized by changing the Zr doping content. The efficiency of solar cells based on Zr/N–TiO₂ with a Zr doping content of 1% (Zr/Ti, atomic ratio) has been achieved at 12.6%, which was 31.6% higher than that of solar cells based on un-doped TiO₂. To get an insight into the enhancement, some investigations were carried out. The results indicate that the larger open voltage (V_{oc}) could be due to the larger conduction band offset resulting from the smaller energy band gap for Zr/N–TiO₂, and the enlarged short current (I_{sc}) could be attributed to the faster electron transfer and reduced recombination rate for Zr/N–TiO₂ NRs. These induce the enhancement of solar cell efficiency.

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1. Introduction

Recently, perovskite solar cells (PSCs) have attracted more attention due to their high efficiency, low cost, and long charge diffusion length.^{1–4} The power conversion efficiency (PCE) of perovskite solar cells has increased to over 22% (ref. 5) within a very short period of time. Typically, mesoporous PSCs are composed of three layers, the electron transfer material (ETM) layer, the perovskite material layer, and the hole transfer material (HTM) layer. TiO₂ has been widely utilized as an ETM in PSCs due to its chemical inertness, photostability, non-toxicity and low cost production.^{6,7} However, the wide band gap (3.2 eV) and rapid recombination rate of photogenerated carriers limit the applications of TiO₂.

One of the strategies to reduce the recombination rate of photogenerated carriers is element doping of TiO₂. It has been reported that metal element doping, such as Mg–TiO₂,⁸ Cd–TiO₂,⁹ Zr–TiO₂,¹⁰ W–TiO₂,¹¹ etc., and nonmetal doping, such as F–TiO₂,¹² can effectively improve the performance of electron transfer layer in PSCs. Recently, theoretical calculations and experimental data have demonstrated that the recombination rate of photogenerated carriers in TiO₂ can be further reduced by metal and nonmetal co-doping, such as Zr/N co-doping.^{13–16} The Zr/N co-doping TiO₂ could enhance the energy conversion efficiency of dye-sensitized solar cells (DSSCs), narrow the band

gap, and improve the absorption in visible light range.¹⁶ However, there are no reports on the applications of Zr/N co-doping TiO₂ in perovskite solar cells until now.

In our previous paper,¹⁷ we investigated the effect of doping N content on the performance of perovskite solar cells, in which the solar cells with the doping N content of 1% (N/Ti, nominal atomic ratio) presented the best performance. Based on the previous work, in the present study, we synthesized Zr and N co-doped TiO₂ (Zr/N–TiO₂) nanorod arrays and fabricated the perovskite solar cells using them as electron transfer layer. The solar cell performance was optimized by changing the Zr doping contents. The PCE of solar cells based on Zr/N–TiO₂ with the Zr doping content of 1% (Zr/Ti, nominal atomic ratio) has been achieved 12.6%, which was 31.6% higher than that of solar cells based on un-doped TiO₂. The possible mechanisms of the enhancement were investigated.

2. Experimental

2.1 Growth of TiO₂ nanorod arrays

FTO-coated glass substrate was patterned by etching with Zn metal powder and 2 M HCl diluted in deionized water, and cleaned by sonication for 20 min in detergent, acetone, 2-propanol, and ethanol, respectively. Oxygen plasma was subsequently used to treat the substrate for 20 min. A compact layer of TiO₂ was formed on FTO by treating the substrate in a 0.2 M aqueous solution of TiCl₄ at 70 °C for 30 min. TiO₂ nanorods (NRs) were grown on the compact layer by a hydrothermal method.¹⁸ In brief, 20 mL of 37% hydrochloric acid and 20 mL of deionized water were mixed. Subsequently 0.7 mL of

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titanium(IV) *n*-butoxide (99%, Aladdin reagent) was added and stirred for 30 min. In the next step, nothing was added to the solution for the growth of un-doped TiO₂, a certain amount of CO(NH₂)₂ (N/Ti, nominal atomic ratio, 1%) was added for the growth of N doped TiO₂ (N-TiO₂), and pre-calculated amount of CO(NH₂)₂ (N/Ti, nominal atomic ratio, 1%) and Zr(NO₃)₄·5H₂O (Zr/Ti, nominal atomic ratio, 0.5%, 1%, 3%, and 5%) were added for the growth of Zr/N codoped TiO₂ (Zr/N-TiO₂). The mixed solution and a compact layer coated FTO substrate was sealed in a stainless steel autoclave. The sealed autoclave was placed inside the oven preheated to 170 °C for several hours. After cooling down to room temperature, the TiO₂ nanorods film was rinsed with ethanol and deionized water, and annealed at 500 °C for 60 min.

2.2 Materials preparation

Methylammonium iodide (CH₃NH₃I) was synthesized using a previously reported method.¹⁹ Typically, aqueous solution of hydroiodic acid (HI) (5 mL, 57 wt% in water, Aladdin Reagent) was reacted with methylamine (CH₃NH₂) (12 mL, 33 wt% in absolute ethanol, Aladdin reagent) at 0 °C for 2 h with constant stirring under nitrogen atmosphere. Methylammonium iodide was crystallized by removing the solvent with a rotary evaporator. The generated white powder was washed with diethyl ether for three times and dried in vacuum for overnight at 60 °C. The perovskite precursor solution was prepared by dissolving CH₃NH₃I and lead(II) chloride (PbCl₂) in anhydrous *N,N*-dimethylformamide (DMF) at a 3 : 1 molar ratio at 60 °C.

2.3 Solar cell fabrication

The perovskite precursor solution was spin-coated on the annealed TiO₂ film at 2000 rpm for 60 s in an argon-filled glove box. The sample was dried on a hotplate at 110 °C for 60 min. The hole-transporter layer was deposited by spincoating a solution of 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)9,9'-spirobifluorene (spiro-MeOTAD) at 2000 rpm for 60 s. The spiro-MeOTAD solution was prepared by dissolving 72.3 mg of spiro-MeOTAD in 1 mL of chlorobenzene, to which 28.8 μL of 4-*tert*-butylpyridine and 17.5 μL of lithium bis(trifluoromethanesulfonyl) imide (Li-TFSI) solution (520 mg Li-TFSI in 1 mL acetonitrile,

Aladdin reagent) were added. Finally, a gold layer with a thickness of 80 nm was thermally evaporated on top of the device.

2.4 Characterization

X-ray diffraction (XRD) patterns were recorded on a DX-2700 diffractometer with Cu Kα radiation with $\lambda = 0.1542$ nm. Photocurrent–voltage (*I*–*V*) measurements were performed using a Keithley 2440 Sourcemeter under AM 1.5 G illumination from a Newport Oriel Solar Simulator with an intensity of 100 mW cm^{−2}. The active area was 0.1 cm² determined by a shadow mask. Morphologies and microstructures were observed with a scanning electron microscope (SEM, JEM-7001F, JEOL) equipped with an energy dispersive spectrometer (EDS). UV-vis absorption spectra were collected on a UV-vis spectrophotometer (Varian Cary 5000). Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements were acquired with a FLS 980 E fluorometer (Edinburgh Photonics), with an excitation source of 515 nm diode laser. The electrochemical impedance spectroscopy (EIS) was performed under a forward bias of 0.6 V under 1 sun illumination conditions with an electrochemical workstation (CHI660e, Shanghai CHI Co., Ltd.) with the frequency range from 1 Hz to 300 kHz. The magnitude of the alternative signal was 10 mV.

3. Results and discussion

We synthesized un-doped, N doped, and Zr/N co-doped TiO₂ nanorod arrays, and fabricated perovskite solar cells using them as an electron transfer material. *I*–*V* measurements were performed by reverse scan (RS) and forward scan (FS). The photovoltaic parameters were obtained by the average of RS and FS for each device. The short current (*I*_{sc}), open voltage (*V*_{oc}), fill factor (FF), and power conversion efficiency (PCE) of the solar cells were obtained by an average of the data from 20 pieces of devices. Fig. 1A shows the dependence of PCE on Zr doping contents. It displays that the PCE of solar cells is the maximum at the Zr doping content of 1% (Zr/Ti, nominal atomic ratio). There is an optimal doping content for Zr incorporation. When the content of Zr was lower than its optimal level, the Zr impurity energy level would be a separation center, which could improve the separation of photoinduced carriers. In contrast,

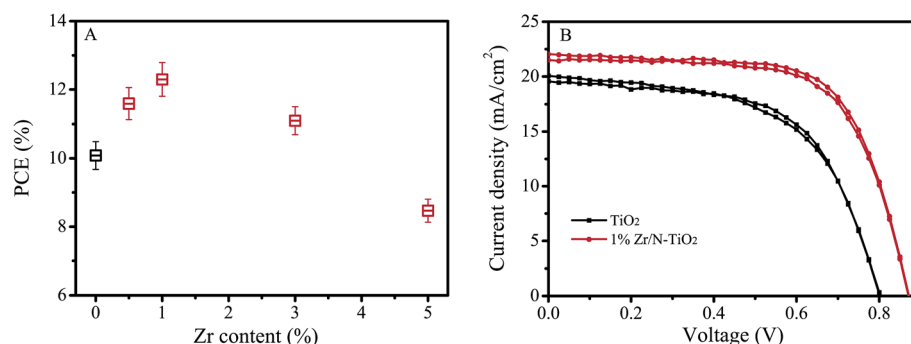
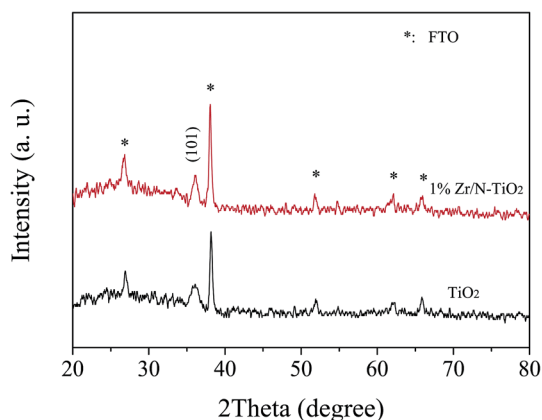


Fig. 1 (A) Dependence of solar cells PCE on Zr doping contents. (B) *I*–*V* curves of best performance solar cells based on un-doped TiO₂ and 1% Zr/N-TiO₂ NRs.



Table 1 Photovoltaic parameters of the solar cells based on un-doped TiO₂, 1% N-TiO₂, and 1% Zr/N-TiO₂ NRs

Sample	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
TiO ₂	0.80 ± 0.02	19.2 ± 0.6	0.62 ± 0.03	9.5 ± 0.3
1% N-TiO ₂	0.82 ± 0.01	20.5 ± 0.7	0.65 ± 0.02	10.9 ± 0.2
1% Zr/N-TiO ₂	0.88 ± 0.03	21.6 ± 0.7	0.66 ± 0.02	12.5 ± 0.1

**Fig. 2** XRD patterns of un-doped TiO₂ and 1% Zr/N-TiO₂ NRs.

when the content of Zr was higher than its optimal level, Zr impurity energy level would be a recombination center, which could increase the recombination of photoinduced carriers.^{14,20}

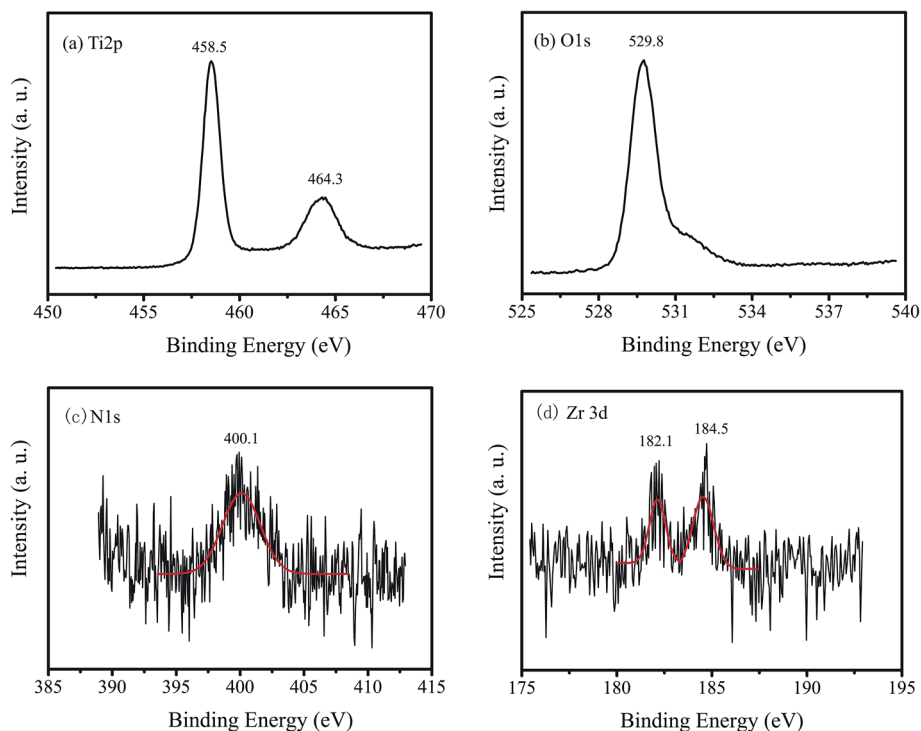
Table 1 shows the photovoltaic parameters of the solar cells based on un-doped TiO₂, 1% N-TiO₂, and 1% Zr/N-TiO₂ NRs.

The photovoltaic parameters of solar cells on 1% Zr/N-TiO₂ NRs are enhanced compared with those of solar cells on un-doped TiO₂ and 1% N-TiO₂ NRs. The high PCE of 12.6% has been obtained for the solar cells on 1% Zr/N-TiO₂ NRs, which is 31.6% higher than that of solar cells on un-doped TiO₂ NRs. Fig. 1B shows the *I*-*V* curves of best performance solar cells based on un-doped TiO₂ and 1% Zr/N-TiO₂ NRs.

To explain the enhancement phenomenon, we carried out some investigations. Fig. 2 shows the XRD patterns of un-doped TiO₂ and 1% Zr/N-TiO₂ NRs. The peaks labelled with stars were assigned to SnO₂ (JCPDS card, 41-1445) on FTO substrate. The diffraction peak at 36.1° is assigned to the (101) planes of rutile TiO₂ (JCPDS card, 21-1276).²¹ Only one peak appears in the XRD patterns, which suggests that almost all the crystallites grew preferentially along the (101) plane parallel to the substrate surface.²² For the XRD patterns of Zr/N-TiO₂ NRs, Zr peaks did not observed, which might be due to the homogeneous distribution of Zr with Ti in the samples²³ and small amount of Zr doping contents.

Fig. 3 shows the XPS spectra of 1% Zr/N-TiO₂ NRs. The peaks located at 458.5 and 464.3 eV in Fig. 3a are corresponding to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively.^{24,25} The binding energy at 529.8 eV in Fig. 3b is attributed to the O 1s.^{24,25} The peak at 400.1 eV in Fig. 3c is ascribed to the N 1s.^{24,25} The peaks at 182.1 and 184.5 eV in Fig. 3d are assigned to the Zr 3d_{5/2} and Zr 3d_{3/2}, respectively.²⁴ The XPS spectra demonstrated that both Zr and N atoms are doped into the TiO₂ samples.

Fig. 4A and B show the plane-view SEM images of un-doped TiO₂ and 1% Zr/N-TiO₂ NRs, respectively. Fig. 4C and D show the cross sectional SEM images of un-doped TiO₂ and 1% Zr/N-

**Fig. 3** XPS spectra of 1% Zr/N-TiO₂ NRs. (a) Ti 2p, (b) O 1s, (c) N 1s, and (d) Zr 3d.

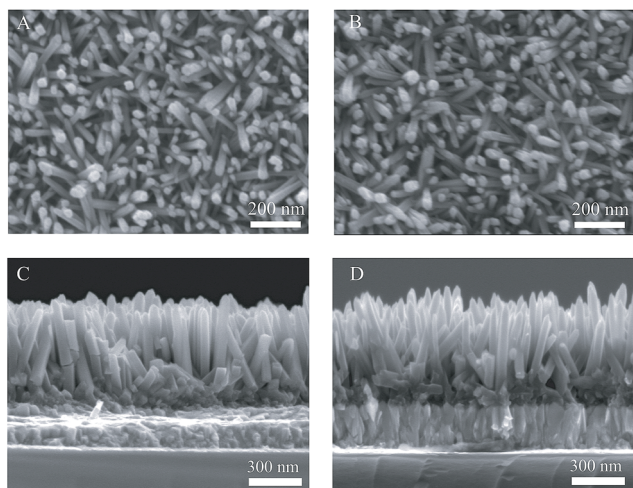


Fig. 4 SEM images of un-doped TiO₂ (A and C), and 1% Zr/N-TiO₂ (B and D).

TiO₂ NRs, respectively. The diameter and length of the un-doped TiO₂ NRs were determined to be 50 ± 5 nm and 480 ± 15 nm, respectively. The diameter and length of the 1% Zr/N-TiO₂ NRs were determined to be 40 ± 8 nm and 460 ± 35 nm, respectively. The diameter of N-TiO₂ NRs is slightly decreased compared with that of un-doped TiO₂ NRs. The length distribution of 1% Zr/N-TiO₂ NRs is more ununiform than that of un-doped TiO₂ NRs. This could be attributed to the effect of Zr/N doping.

Fig. 5A shows the UV-vis absorption spectra of un-doped TiO₂ and 1% Zr/N-TiO₂ NRs. The Zr/N-TiO₂ NRs presented a stronger absorption intensity than un-doped TiO₂. The energy band gap (E_g) can be determined using the Tauc plot which is shown below,²⁶

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (1)$$

where α , ν , A , and E_g are the optical absorption coefficient, frequency, proportionally constant, and energy band gap, respectively. The Tauc curve is shown in Fig. 5B, from which energy band gap (E_g) can be determined to be 3.03 and 2.63 eV for un-doped TiO₂ and 1% Zr/N-TiO₂ NRs, respectively. With the doping of Zr atom, the energy band gap of TiO₂ NRs becomes smaller. This is in accordance with the previous

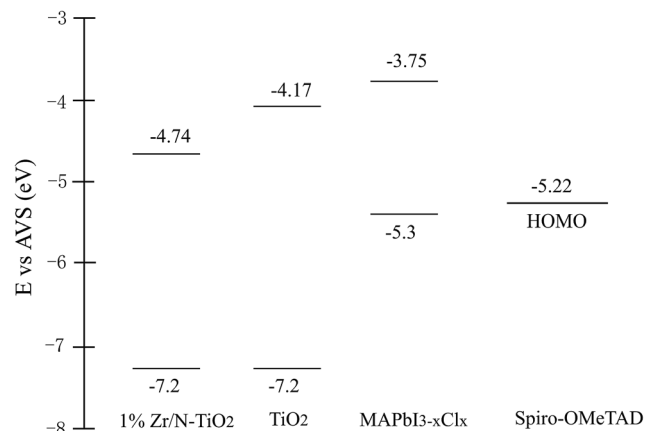


Fig. 6 Energy band diagrams of TiO₂, MAPbI_{3-x}Cl_x, and spiro-OMeTAD.

report,¹³ which demonstrated that N/Zr-co-doped TiO₂ narrowed the band gap, brought the N 2p gap states closer to the valence band, and enhanced lifetimes of photoexcited carriers with density functional theory (DFT) calculations. According to the energy band gaps calculated from Fig. 5 and the previous report,²⁷ the energy band diagrams of TiO₂, MAPbI_{3-x}Cl_x, and spiro-OMeTAD are schematically shown in Fig. 6. The conduction band offset between 1% Zr/N-TiO₂ and MAPbI_{3-x}Cl_x is the larger than that between un-doped TiO₂ and MAPbI_{3-x}Cl_x due to its narrow energy band gap, which might be one of the reasons to present a higher voltage for Zr/N-TiO₂ based solar cells.²⁸

Photoluminescence (PL) can provide an evidence of electron extraction and transfer efficiency.^{29,30} Therefore we measured the PL spectra of un-doped TiO₂/MAPbI_{3-x}Cl_x and 1% Zr/N-TiO₂/MAPbI_{3-x}Cl_x and shown in Fig. 7A. The peak at 780 nm is attributed to the emission from MAPbI_{3-x}Cl_x.¹ The PL intensity of Zr/N-TiO₂/MAPbI_{3-x}Cl_x is weaker than that of un-doped TiO₂/MAPbI_{3-x}Cl_x, which demonstrated that the efficiency of electron extraction and transport of Zr/N-TiO₂/MAPbI_{3-x}Cl_x is more than that of un-doped TiO₂/MAPbI_{3-x}Cl_x.

Fig. 7B displays the time-resolved photoluminescence (TRPL) kinetic decay curves of un-doped TiO₂/MAPbI_{3-x}Cl_x and 1% Zr/N-TiO₂/MAPbI_{3-x}Cl_x. The TRPL curve was fitted to a biexponential function,

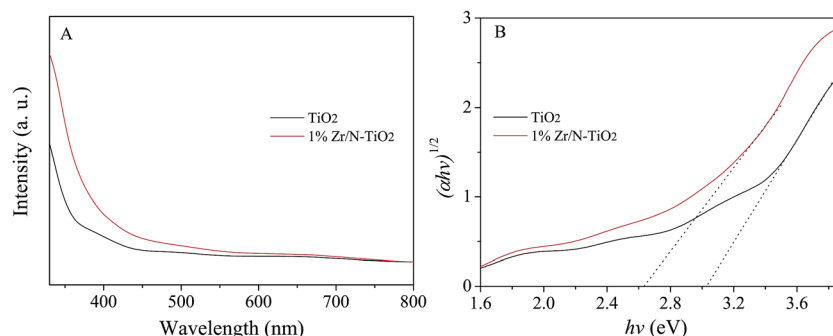


Fig. 5 (A) UV-vis absorption spectra of un-doped TiO₂ and 1% Zr/N-TiO₂ NRs. (B) Tauc curves.



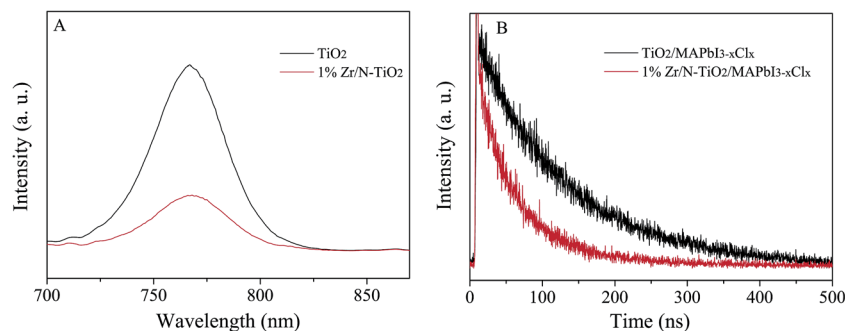


Fig. 7 (A) PL, and (B) TRPL spectra of un-doped $\text{TiO}_2/\text{MAPbI}_{3-x}\text{Cl}_x$ and 1% $\text{Zr/N-TiO}_2/\text{MAPbI}_{3-x}\text{Cl}_x$.

Table 2 Parameters of the TRPL spectra

Sample	τ_1/ns	% of τ_1	τ_2/ns	% of τ_2
$\text{TiO}_2/\text{MAPbI}_{3-x}\text{Cl}_x$	55.1	31.3	121.4	67.7
1% $\text{Zr/N-TiO}_2/\text{MAPbI}_{3-x}\text{Cl}_x$	28.5	43.3	95.2	56.7

Table 3 Fitting parameters of EIS data

Sample	R_s/Ω	R_{co}/Ω	R_{rec}/Ω	CPE-T/F
TiO_2	34.8	59.3	12.7	6.3×10^{-6}
1% Zr/N-TiO_2	17.4	22.2	83.1	4.8×10^{-5}

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (2)$$

The detailed parameters are summarized in Table 2. The fast decay (τ_1) might be originated from the transportation of free carriers from perovskite layer to the respective hole or electron contact. The slow decay (τ_2) could be attributed to the radiative

recombination of free charge carriers before the charge collection.^{31,32} From Table 2, we can see that the fast decay time (28.5 ns) and slow decay time (95.2 ns) of $\text{Zr/N-TiO}_2/\text{MAPbI}_{3-x}\text{Cl}_x$ are less than those of un-doped $\text{TiO}_2/\text{MAPbI}_{3-x}\text{Cl}_x$ (55.1 ns and 121.4 ns), while the fraction of fast decay process (31.3% and 43.3%) was increased. This proves the improved electron extraction and transport efficiency, and reduced charge recombination of Zr/N-TiO_2 contrast to un-doped TiO_2 .

Electrochemical impedance spectroscopy (EIS) is a powerful technique to reveal the underlying carrier transport behavior in perovskite solar cells.^{33,34} The Nyquist plots of solar cells based on un-doped TiO_2 and 1% Zr/N-TiO_2 NRs are shown in Fig. 8A, in which two RC arcs were observed. The data were fitted to an equivalent circuit shown in Fig. 8B. The high-frequency RC element is attributed to contact resistance (R_{co}) at the interfaces, while the low-frequency element is ascribed to the recombination resistance (R_{rec}) and chemical capacitance (C_μ) of the system, and the R_s is an additional contribution from series resistance.^{18,35} The fitting parameters are listed in Table 3. The total series resistance ($R_s + R_{co}$) for the cells based on Zr/N-TiO_2 is smaller than that on un-doped TiO_2 , while the recombination resistance of the former is larger than that of the latter, which indicates that an enhanced charge transport ability and induced carrier recombination rate for the cells based on Zr/N-TiO_2 . This agrees well with the I - V measurements.

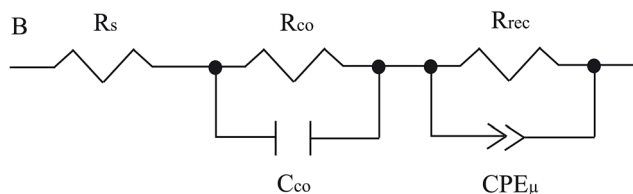
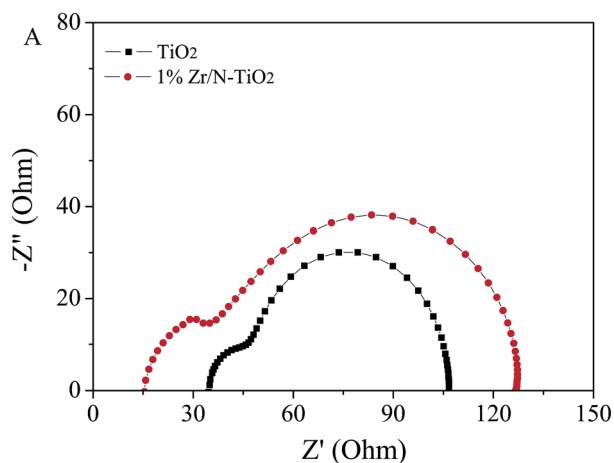


Fig. 8 (A) EIS spectra of solar cells that based on un-doped TiO_2 and 1% Zr/N-TiO_2 NRs based solar cells. (B) Equivalent circuit for fitting the EIS data.

4. Conclusion

In this study, Zr/N -codoped TiO_2 NRs were synthesized and perovskite solar cells based on them were fabricated. The solar cells based on Zr/N-TiO_2 NRs presented an enhanced performance compared with those on un-doped TiO_2 NRs. The solar cell performance was optimized by changing the Zr doping contents. The PCE of solar cells based on Zr/N-TiO_2 with the Zr doping content of 1% (Zr/Ti , atomic ratio) has been achieved 12.6%, which was 31.6% higher than that of solar cells based on



un-doped TiO₂. To explain the enhancement, some investigations were performed. EDS and Tauc plot spectra indicated the incorporation of Zr in TiO₂ nanorods. Absorption spectra showed higher absorption of visible light for Zr/N-TiO₂ than un-doped TiO₂. The Zr doping reduced the energy band gap from 3.03 to 2.64 eV. The PL and TRPL spectra displayed the faster electron transfer from perovskite layer to Zr/N-TiO₂ than to un-doped TiO₂. EIS showed the smaller resistance of device based on Zr/N-TiO₂ than that on un-doped TiO₂.

Acknowledgements

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