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REVIEW AIRTICLE

Electrolyte-dependent photovoltaic responses in dye-sensitized solar cells

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Abstract Promoted by the growing concerns about the worldwide energy demand and global warming, dye-sensitized solar cells (DSSCs) are currently attracting worldwide scientific and technological interest because of their high energy conversion efficiency and simple fabrication process. Considering long-terms stability and practice applications, growing attentions have been paid to non-volatile, 3-methoxyproprionitrile (MPN)-based electrolyte, ionic liquids (ILs) electrolyte, as well as quasi-solid state electrolyte. In this present review, recent progress in electrolyte for DSSCs made by our group are summarized, including component-optimization of the non-volatile electrolyte, the fluidity-dependent charge transport mechanism in the binary IL electrolytes as well as the structure dominance of the employed ILs. Furthermore, progress on the quasi-solid state electrolyte based on inorganic nanomaterials as gelators in our group has also been outlined.

Keywords electrolyte, non-volatile, ionic liquid (IL), quasi-solid state, dye-sensitized solar cell (DSSC)

1 Introduction

Dye-sensitized solar cells (DSSCs) are currently attracting worldwide scientific and technological interest because of their high light-to-energy conversion efficiency [1–3] and simple fabrication process. They have been widely regarded as a promising alternative to conventional silicon-based photovoltaic devices for sustainable energy supply at low cost and high environmental friendliness. By using a highly volatile electrolyte, a current record of about 11% has been achieved among all types of organic photovoltaic cells [4–8]. While growing attentions have been paid to the development of efficient sensitizers and mesoporous semiconducting films, the crucial effect of electrolytes for further device performance and stability enhancement of DSSCs should also be emphasized.

It was generally believed that the effective charge transport in the electrolyte plays an important role in the regeneration of the oxidized dye to achieve high efficiency for DSSCs. For practical application of DSSCs, recently, a large amount of researches and development efforts on electrolyte composition have been undertaken to improve the efficiency and long-term stability. To date, a non-volatile, 3-methoxyproprionitrile (MPN)-based electrolyte was widely used [9–13]. Compared to acetonitrile-based ones, these non-volatile electrolytes showed somewhat lower but more stable conversion efficiency under prolonged thermal stress at elevated temperatures [9,10].

On the other hand, ionic liquids (ILs) are used as promising alternatives for volatile organic solvents due to their unique properties, such as negligible vapor pressure, excellent electrochemical and thermal stability, and high ionic conductivity [14–18]. But disappointingly, the high viscosity of the ionic liquids is a serious problem for the development of such devices using these promising solvents. The viscosity of typical ionic liquids is about 100 times larger than that of acetonitrile, a usually used solvent for electrolyte, and also 30 times larger than that of water at room temperature [19,20]. Photocurrents in such systems are commonly affected by the series resistances of the electrolytes, which are usually in proportion to the viscosity.

To mitigate the diffusion limitations, electrolytes based on binary ionic liquids with a high mole fraction of PMII (1-methyl-3-propylimidazolium iodide) together with another low-viscous ionic liquids [17,21–24] were reported as attractive solutions of the dilemma between viscosity and photocurrent. High concentration of the redox couple is usually needed to achieve a domination of the exchange reaction-based fast charge transport process

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between iodide and triiodide in viscous electrolytes [14,25]. On the other hand, the absorption of visible light by triiodide competes with the absorption of the dye, thus lowering the photocurrent. Furthermore, high concentration of triiodide promotes the back electron transfer from conduction band of photoanodes to triiodide anions [25].

In spite of great advantages with the use of ionic liquid electrolytes, it may still be desirable to replace a liquid electrolyte by a solid or gel-like electrolyte. The main motives for such a replacement arise from concerns regarding manufacturing procedures and long-term stability when a liquid electrolyte is used. Encapsulation of volatile solvents is a critical issue for device stability. The costly hermetic sealing of volatile electrolytes will counteract the merit of DSSCs as photovoltaic technologies with a high performance/price ratio. Up to date, a large number of publications during the last decade were devoted to the development of new solid or quasi-solid materials which may be used as electrolytes for DSSCs. Three general approaches were introduced: the use of oganic gelators, the use of inorganic materials for solidification of liquid electrolytes, and polymerization in ionic liquid media. Different inorganic nanomaterials, such as fumed silica nanoparticles, TiO_2 nanoparticles, carbon nanotubes and also some two dimensional nanomaterials, i.e. exfoliated montmorillonite, synthetic nanoclay and layered titanates have been used as gelators to solidify the ionic liquid electrolyte [26–34].

In the present review, we will address some of our recent advances regarding the electrolyte-dependent photovoltaic responses in DSSCs. Considerations on the component-optimization of the non-volatile electrolyte, the fluidity-dependent charge transport mechanism in the binary IL electrolytes as well as the structure dominance of the employed ILs will be outlined. Moreover, progress on the quasi-solid state electrolyte based on inorganic nanomaterials as gelators in our group will be highlighted. Some important contributions from other groups will also be included.

2 Component-optimization of non-volatile electrolyte

A recent study has focused on the influence of iodide concentration on the photovoltaic performance and stability of the DSSC with the non-volatile electrolyte [35]. It was concluded that 1-propyl-3-methylimidazolium iodide (PMII) concentrations lower than 1 M were responsible for incomplete dye regeneration, however further increase in iodide concentration became kinetically redundant for charge recombination between oxidized dye sensitizer and electron in the conduction band of TiO_2. Devices containing 1.0 M PMII electrolyte show excellent stability during long-time thermal aging at 80°C and under light soaking at 60°C. But to the best of our knowledge, there is no detailed study about the iodine dependence of the photoelectrochemical performance of DSSCs containing non-volatile electrolyte.

Motivated by the above concerns, the effect of iodine concentration in the electrolyte with non-volatile solvent of DSSCs on photovoltaic performance was systematically studied [36]. The electron transport and interfacial recombination kinetics were also systematically investigated by electron impedance spectroscopy (EIS). As shown in Fig. 1, with the iodine concentration increased from 0.025 to 0.1 M, open-circuit voltage (V_{oc}) and photocurrent density (J_{sc}) decreased while fill factor (FF) increased significantly. The decline of the V_{oc} and J_{sc} was mainly ascribed to increased electron recombination with tri-iodide ions (I_3^-). The increased fill factor was primarily brought by a decrease in the total resistance. With optimum iodine concentration, device showed a photocurrent density of 16.19 $mA \cdot cm^{-2}$, an open-circuit voltage of 0.765 V, a fill factor of 0.66, and an overall photo-energy conversion efficiency of 8.15% at standard AM 1.5 simulated sunlight (100 $mW \cdot cm^{-2}$).

Further insight into the electron transfer and recombination of the devices was investigated by the electrochemical impedanc spectroscopy technique (EIS) as shown in Fig. 2. It can be concluded that increasing the iodine concentration in electrolytes could significantly decrease the charge transfer resistance (R_{ct}) and the chemical capacitance (C_m), accompanying a slightly increased electron transport resistance (R_t) in the TiO_2 electrode. Subsequently, the electron lifetime (τ) and the effective diffusion coefficient (D_n) of electrons in the TiO_2 semiconductor were decreased along with increment of the iodine content. It should be indicated that recombination between the injected electrons in TiO_2 and I_3^- in the electrolyte must be suppressed for the high performance of DSSC.

3 Fluidity-dependent charge transport in binary IL electrolytes

It was generally proposed that the triiodide transport in ionic liquid electrolyte was created by a combination of an ordinary physical diffusion process and a Grotthuss-type charge-exchange mechanism [14,37–39]. Diffusion-controlled currents reflect the contribution from physical diffusion of triiodide and iodide and electron exchange between them, as described for the coupling of physical diffusion mass transport and electron-exchange by the Dahms-Ruff equation [14,40–42].

$$D_{app} = D_{phys} + D_{ex} = D_{phys} + k_{ex}\delta^2 c/6, \qquad (1)$$

where D_{app}, D_{phys}, and D_{ex} are the apparent diffusion coefficient, physical diffusion coefficient, and electron exchange diffusion coefficient, respectively; k_{ex} is the rate constant of electron exchange; c and δ are the concentration

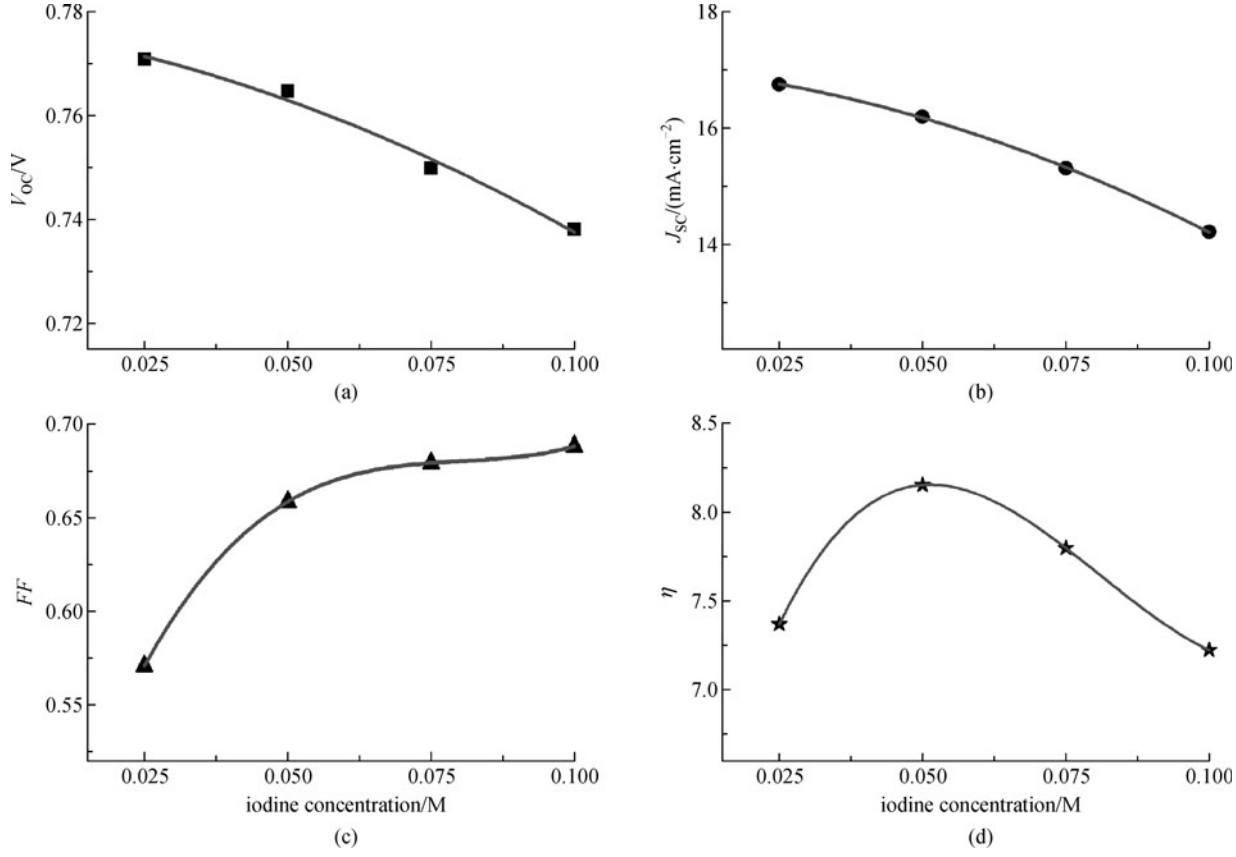

Fig. 1 Dependency of V_{oc} (a), J_{sc} (b), FF (c), and η (d) on concentration of iodine in non-volatile electrolyte

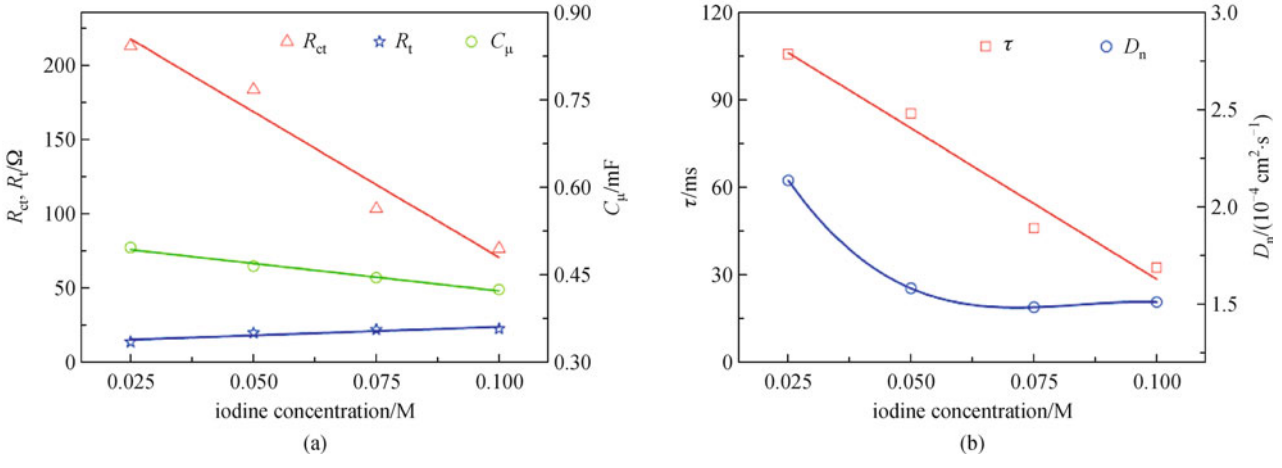

Fig. 2 Characteristic parameters of impedance spectra of DSSCs with various iodine concentrations in dark at applied forward bias of − 0.75 V. (a) shows R_{ct}, R_t, and C_μ; (b) depicts τ and D_n

and average center-to-center distances between redox species, respectively.

However, the low-viscous imidazolium based ionic liquid with anions, such as thiocyanate, dicyanoamide, tricyanomethide, tetracyanoborate, triflate, etc. are nonelectroactive. Note that mixing iodide melts with such nonelectroactive ionic liquids to lower the electrolyte viscosity may not only increase the physical diffusion coefficient (D_{phys}) but also decrease the electron exchange diffusion coefficient (D_{ex}). Actually, a high diffusion flux of iodide is desirable for the

fast dye regeneration, which can avoid the charge recombination between oxidized sensitizers and injected electrons in TiO_2 films.

To distinguish the above-mentioned triiodide transport mechanism, the viscosities, conductivities, triiodide diffusion coefficients, and photovoltaic performance of a potential DSSC electrolyte systems based on binary IL mixtures, namely, 1-ethyl-3-methylimidazolium dicyanamide [EMIDCA]/1-methyl-3-propylimidazolium iodide [PMII] with a fixed iodine concentration at varying EMIDCA volume fraction were investigated in details [43]. As depicted in Fig. 3, within the range of EMIDCA volume fraction increased from 0 to 40%, I_{lim} increases from 3.75 to 11.29 $mA \cdot cm^{-2}$, D_{app} increases from 1.21×10^{-7} to 3.66×10^{-7} $cm^2 \cdot s^{-1}$ meanwhile. The observed linear increase of D_{app} is primary due to a decrease in the viscosity of the binary IL electrolyte and enhanced conductivity. This indicates that the viscosity-dependent physical diffusion dominates over the exchange reactions when the EMIDCA volume fraction is less than 40%. However, when further increased the EMIDCA fraction to 80%, I_{lim} decreases to 7.99 $mA \cdot cm^{-2}$, D_{app} decreases to 2.59×10^{-7} $cm^2 \cdot s^{-1}$ at the same time. This change suggests that when the EMIDCA volume fraction is higher than 40%, the exchange reactions become the determinant factor over the physical diffusion. Therefore, it can be concluded from the observed change of the apparent diffusion coefficient that the binary ILs electrolyte with 40 volume percents of EMIDCA can get a balance between the viscosity-dependent physical diffusion and the exchange reactions.

Both the impedance spectroscopy (figure not shown) and photovoltaic results (as shown in Fig. 4) support the existence of an optimized binary ILs electrolyte composition. Hence, for optimizing an IL-based electrolyte in regards to triiodide transport, a low viscosity is not the exclusive crucial factor since exchange reactions transport effects also play an important role to resolve the diffusion limitation of DSSC efficiency.

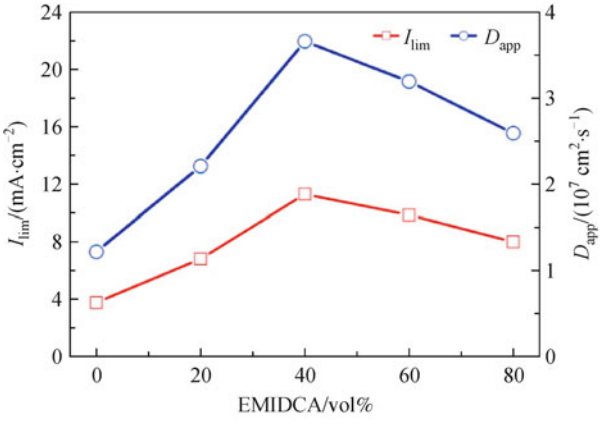

Fig. 3 Dependence of limiting current density and apparent diffusion coefficient on EMIDCA volume fraction in binary IL electrolyte

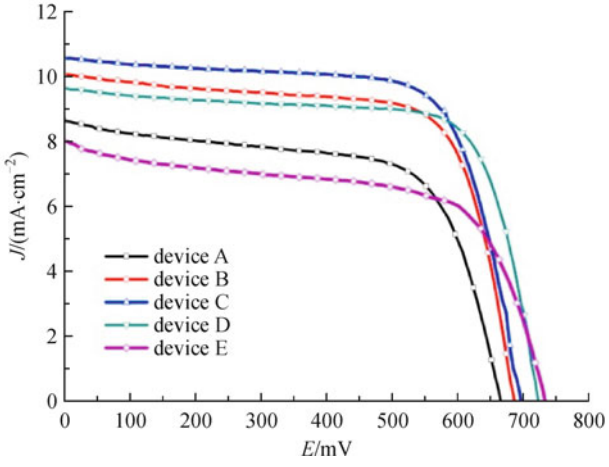

Fig. 4 *J-V* characteristics of devices A-E with various EMIDCA/PMII binary IL electrolytes measured under AM 1.5 illumination (100 $mW \cdot cm^{-2}$)

4 Structure-dominated charge transport in binary IL electrolytes

One fascinating feature of room temperature ionic liquids (RTILs) is that their physicochemical properties can be easily tuned by controlling the structure of the component ions [44]. However, the structural effects of RTILs on the photoelectrochemical performance of DSSCs are rarely reported [45]. Since a comprehensive understanding of the effect of the ionic structures on the physicochemical characteristics of a wide variety of ionic liquids is needed for further judicious selection of the ionic liquid candidates for application in DSSCs. Initiated by this propose, PMII containing I^-/I_3^- redox couple system with a fixed cation structure coupling with various anions based RTILs (shown in Fig. 5), i.e., 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIPF_6$), 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMITFSI), 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) and 1-ethyl-3-methylimidazolium trifluoroacetic acid (EMIATF), were used as electrolytes of DSSCs [46]. The physical properties were investigated in details, which include apparent diffusion coefficient of triiodide species, viscosity, and ionic conductivity over a wide temperature range, with focusing on the fluidity dependence of the RTILs on the diffusion property of the electrolyte, as well as the corresponding photoelectrochemical responses of DSSC devices.

It is found that both the diffusibility of the electrolyte and the photovoltaic performance of device show strong dependence on the fluidity of the ionic liquids, which is

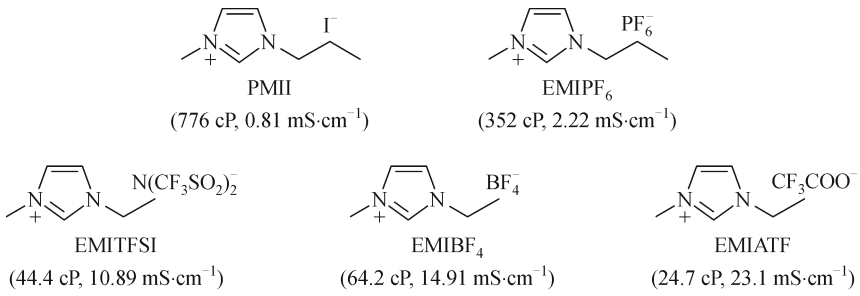

Fig. 5 Structure, viscosity and ionic conductivity (measured at 298 K) of various RTILs employed

primarily altered by the anion structure. Further insights into the structure-dependent physical property of the employed RTILs are discussed in terms of the reported Van Der Waals radius, the atomic charge distribution over the anion backbones, the interaction energy of the anion and cation coupling with the existence of ion-pairs and ion aggregates. It is revealed that the anionic donor ability of a certain RTIL, intrinsically, the negative charge distribution over the anion backbones is suggested to be a dominant factor for the fluidity property. Furthermore, it is noticed that increasing the fluidity of the ionic liquid electrolytes could significantly decrease diffusion resistance of I_3^- in electrolyte, and increase the charge recombination resistance between the injected electrons with triiodide in the high-viscous electrolyte (as indicated in Fig. 6), thus improving the effective electron diffusion coefficient and the electron diffusion length in the device, as well as the photovoltaic response. The observed results imply that the performance of DSSCs can be dominated by the anion structure of the ionic liquids in the electrolyte and support the view that judicious structural modification of the anionic moieties in the electrolyte can lead to enhanced device performance.

5 Quasi-solid state electrolyte based on novel inorganic nanomaterials

In our group, quasi-solid electrolytes based on 1-propyl-3-methylimidazolium dihydrogenphosphate (MPIDP) ionic liquids, iodide-triiodide redox couples along with layered α-zirconium phosphate (α-ZrP) have been prepared. In combination with the ruthenium-based sensitizer N719, the photo-to-energy conversion efficiency of the DSSC containing 6% α-ZrP increased by a factor of >2 to 2.61%, as compared to the DSSC without α-ZrP. Such a difference was explained by interaction between the additive *tert*-butylpyridine (TBP) and α-ZrP leading to an enhancement of the diffusion coefficient of I_3^- (as shown in Fig. 7) and, as a consequence, photocurrent. The highest diffusion coefficient of I_3^- (2.89×10^{-7} cm$^2\cdot$s^{-1}) and exchange photocurrent density (1.02 mA·cm^{-2}) are reached at an optimal concentration of α-ZrP (6%). It was proved

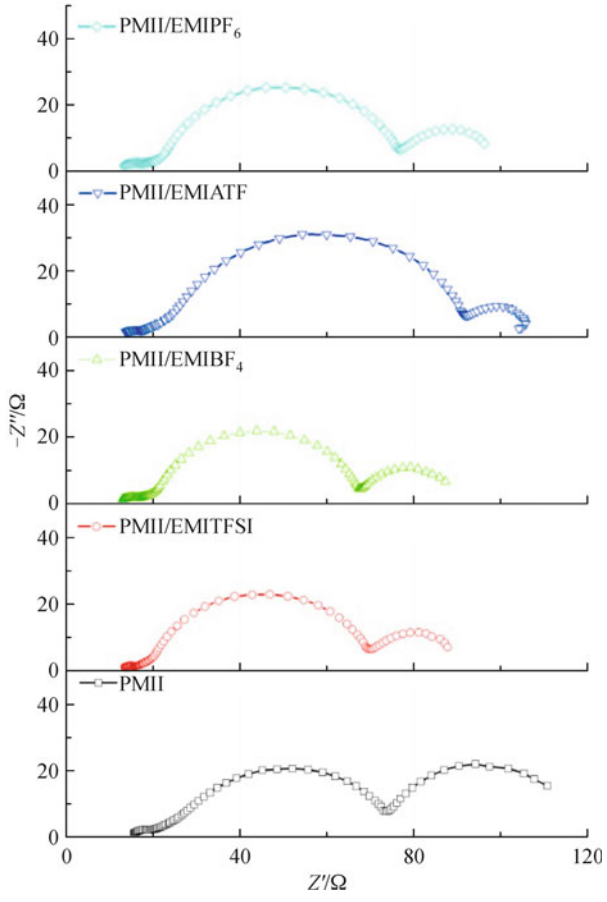

Fig. 6 Nyquist plots of devices with various RTIL electrlytes measured in dark at applied forward bias of – 0.65 V

that the intercalation behavior of TBP into layered α-ZrP contributed to their enhancement. The enhancement of exchange current density value, with the addition of α-ZrP, can be ascribed to the increase of the active area of electrolyte/α-ZrP interlamellar interface after the intercalation of TBP into α-ZrP. The confinement effect by the nanochannels in the interlayer of α-ZrP may be the reason for the enhancement of diffusion coefficient of I_3^- [34].

Inorganic NiO nanosheets were also added into iodide/triiodide liquid electrolyte containing TBP for DSSCs in our group [47]. The hydrothermally prepared NiO

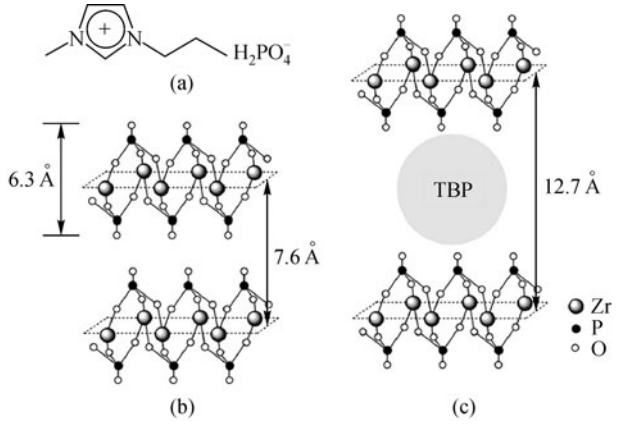

Fig. 7 (a) Molecular structure of MPIDP; (b) molecular structure of layered α-ZrP; (c) intercalation schematic of TBP into layered α-ZrP

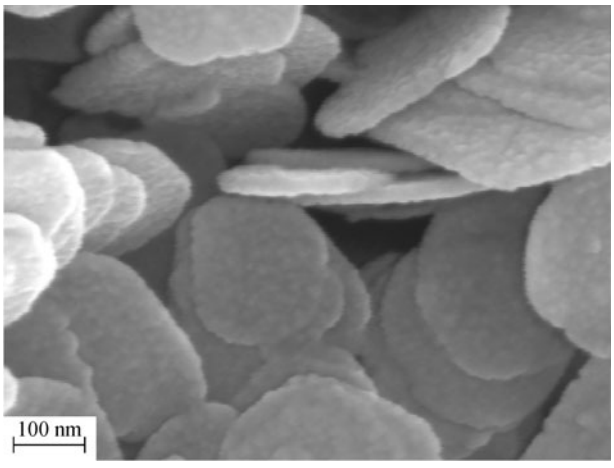

Fig. 8 FESEM images of as-obtained NiO nanosheets

nanosheets showed a high aspect ratio, confirmed by SEM (Fig. 8). Introduction of the NiO nanosheets significantly increased the viscosity of the composite electrolyte, which would facilitate the device assembly and improve the long-term stability of the devices. DSSCs assembled with such nanosheet-based composite electrolytes showed more than 15% increased photocurrent while maintained a similar open-circuit voltage, giving rise to significantly promoted light-to-energy conversion efficiency relative to reference one. The enhancement of the photocurrent is primarily due to the light-scattering effect which is brought by the incorporating of inorganic nanosheets. Also, EIS was employed to investigate the charge-transfer kinetics at the interface between the counter electrode and the composite electrolyte of DSSCs. The symmetric cells (TCO/Pt/electrolyte/Pt/TCO) assembled with such nanosheet-based composite electrolyte showed a decreased charge-transfer resistance (R_{ct}). The optimum DSSC including NiO nanosheets showed a short-circuit current of 15.35 $mA \cdot cm^{-2}$, an open-circuit voltage of 0.75 V, a fill factor of 0.53, and an overall conversion efficiency of 6.07% at 100 $mW \cdot cm^{-2}$.

6 Conclusions

Up to date, 3-methoxyproprionitrile (MPN)-based non-volatile electrolyte has been widely employed, although somewhat lower conversion efficiency is obtained when compared to the acetonitrile-based ones. However, the obtained efficiency is proved to be more stable, especially under prolonged thermal stress at elevated temperatures. Judicious component engineering has raised the efficiency over 9% and exhibited a remarkable stability under long-term thermal and light-soaking dual stresses [48]. It should be indicated that recombination between the injected electrons in TiO_2 and I_3^- in the electrolyte must be suppressed to make a further forward step.

Ionic liquids have received great interest over the past decade because of their unique properties as solvent-free electrolytes. Although we are only at the beginning of exploiting these unique electrolyte systems, progress has been staggering as conversion efficiencies of IL-based DSSCs have been rising from initially 1% to over 8% today. These trends will continue as we develop a deeper understanding of the fundamental factors that rule the complex behavior of ILs. The next goal is to develop ILs that match the photovoltaic performance of volatile electrolytes. To avoid the transport limitations in the electrolyte, it will be important to find a low viscosity IL as an iodide source. New and creative work is to be expected on this aspect.

For the DSSCs incorporating quasi-solid state electrolyte, improving on the present systems will rely on enhancing the electron transport in the mesoporous titanium oxide and further increasing the electron lifetime. Improving the pore infiltration of the mesoscopic films with the quasi-solid state electrolyte is also still an open issue that needs addressing. Alternatively, high-extinction-coefficient dyes may enable thin ($< 2\,\mu m$ of TiO_2 photoanode film) DSSCs to operate efficiently, obviating the need to achieve effective penetration of the highly-viscous electrolyte through thicker films.

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