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ORIGINAL PAPER

Dependence of photovoltaic parameters on the size of cations adsorbed by TiO_2 photoanode in dye-sensitized solar cells

J.M.K.W. Kumari[1,2] · **G.K.R. Senadeera**[1,3] · **M.A.K.L. Dissanayake**[1,2] · **C.A. Thotawatthage**[1,2]

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Abstract The effects of "pre-adsorbed cations" in photoanodes on the performances of dye-sensitized solar cells (DSSCs) were studied using two different size cations (K^+ and guanidine cation (G^+)). While the DSSCs with optimized K^+ ions pre-adsorbed photoanodes showed a maximum efficiency of 7.04%, the DSSCs with G^+ ions pre-adsorbed photoanodes showed an efficiency of 6.73%. DSSCs fabricated with conventional photanodes (without pre-cation adsorption) showed an efficiency of 6.21%. Differences in efficiencies are very likely due to the cation pre-adsorption effects and could be due to a higher number of K^+ cation adsorption per unit area of TiO_2 surface of the photoanode compared to a smaller number of G^+ cation adsorption in TiO_2, due to their difference in sizes. This pre-cation adsorption technique can be used to improve the overall efficiency of a DSSC by about 14% fold over the conventional photoanodes use in DSSCs, specially using smaller cations.

Keywords Dye-sensitized solar cells · Cation adsorption · Layered TiO_2

Introduction

During the past two decades, various investigations have been carried out on dye-sensitized solar cells (DSSCs) based on oxide semiconductors [1]. DSSCs have emerged as low-cost alternatives to silicon-based photovoltaic solar cells. The main components of a DSSC are a nanocrystalline oxide semiconducting photoanode, sensitizing dye, redox electrolyte, and a counter electrode. Various investigations have been carried out on modified oxide semiconductor photoanode with doping metal nanoparticles [2–5], non-metal materials [6–8], cation or anion adsorption [9, 10], etc., aiming to enhance the overall light to electricity conversion efficiency of these devices.

Moreover, the influence of cations in the redox electrolyte on the performances of DSSCs has been discussed widely in the literature. O' Regan and Grätzel reported in 1991 an increase in photocurrent with an electrolyte containing LiI compared to an electrolyte containing tetrapropylammonium iodide [1]. These findings have shown that the effect of the cation in the electrolyte is important for the performance of DSSCs. According to the review by Watson and Meyer, cations have been found to affect many parameters that influence the solar cell performances such as sensitizer surface attachment, energy band shifting of the semiconductor and sensitizer and charge transport rate, etc. [11]. Hara et al. studied the influence of electrolytes on the photovoltaic performance of mercurochrome-sensitized nanocrystalline TiO_2 solar cells using LiI, LiBr, and tetraalkyl ammonium iodides as the electrolyte. They reported that the short circuit photocurrent density (J_{sc}) and the open circuit photovoltage (V_{oc}) depend strongly on the salts used in the redox electrolyte [12]. Liu et al. have also investigated the influence of redox species on the interfacial energetics of DSSCs. They reported the effect of I_3^- concentration and cation species such as Li^+, Na^+, K^+,

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✉ G.K.R. Senadeera
rsena@ifs.ac.lk

[1] National Institute of Fundamental Studies, Hanthana Road, Kandy, Sri Lanka

[2] Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka

[3] Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda, Sri Lanka

Rb$^+$, and Cs$^+$ inthe electrolyte on J_{sc} and V_{oc} of DSSCs [13]. Our group has already observed in several systems of DSSCs, the beneficial effect of using iodide electrolytes containing two cations of different sizes, one containing a quaternary ammonium ion and the other containing an alkali or magnesium ion [14, 15]. However, according to our knowledge, there is no study on the effect of pre-cation adsorption in photoanode before assembling the DSSC with the redox electrolyte.

Therefore, in this study, we have investigated the size effect of the pre-adsorped cations in the photoanode on the performances of the DSSCs with liquid redox electrolyte. The effect was studied by dipping the photoanodes with dye layer either in potassium thiocyanate (KSCN) or guanidine thiocyanate (GSCN) dissolved in propylene carbonate (PC). Significant efficiency enhancements were observed with the DSSCs comprising with pre-cation adsorbed photoanodes than the DSSCs with conventional cation free photanodes.

Experimental

Photoelectrode preparation

Photoanodes with two different types of TiO_2 layers were fabricated on F-doped SnO_2 conducting glass substrates (FTO). Firstly, layer of TiO_2 was prepared with a TiO_2 slurry containing well grounded, 0.25 g of P90 TiO_2 powder with 1 ml of 0.1 M HNO_3 in an agate mortar about 20 min. Then, this paste was coated on the well-cleaned F-doped SnO_2 glass substrate (FTO) with a spin coater at 3000 rpm for 60 s. These spin-coated FTO glass electrodes were sintered at 450 °C for 30 min. After cooling the FTO with first layer, the second layer of TiO_2 was coated on the first layer by using a paste of P25 TiO_2 powder prepared as follows. 0.25 g of TiO_2 powder and 0.1 M HNO_3 1.0 ml solution were ground using mortar and pestle. 0.02 g of Triton X-100 and 0.05 g of PEG 1000 were used as the binder and mixture was ground until it becomes a creamy paste. The paste was “doctor bladed” on the first TiO_2 layer by making solar cells with 0.25 cm^2 cell area. The bi-layered electrodes were then sintered at 450 °C for 45 min to obtain a porous TiO_2 electrode and after cool down to room temperature, electrodes were dipped in ethenolic solution of Ru N719 dye for 15 h.

Preparation of cation adsorbed photoanodes

Two cations with different ionic radii were chosen for determination of the cation size effect on the performances of DSSCs with cation pre-adsorbed photoanodes. Potassium thiocyanate (KSCN) with ionic radius of 0.138 nm and guanidine thiocyanate (GSCN) with ionic radius 0.210 nm were selected as the cation sources. K$^+$ and guanidine (G$^+$) ions were adsorbed to above dye loaded bi-layered TiO_2 photoelectrodes by simple dipping method using either 0.2 M KSCN or 0.2 M GSCN in propylene carbonate (PC). Dipping time was varied and cell performances of DSSCs fabricated with the electrolyte mention below were measured.

Preparation of liquid electrolyte

The electrolyte solution for the DSSCs was prepared by adding 0.738 g of tetrapropyl ammonium iodide (Pr_4NI) and 0.060 g of I_2 to a pre-cleaned 10 ml volumetric flask containing 3.6 ml of molten (MP 40 °C) ethylene carbonate (EC) and 1.0 ml of acetonitrile. The solution mixture was stirred overnight.

DSSC fabrication and I–V characterization

DSSCs were fabricated by sandwiching the liquid electrolyte between TiO_2 photoanode and a platinum (Pt)-coated glass plate in the configuration FTO/cations pre-adsorbed TiO_2 photoanode coated with dye/electrolyte/Pt/FTO. Pt-coated FTO glasses were used as counter electrodes of above DSSCs. Aforementioned liquid electrolyte was used to fabricate the devices. The photocurrent–voltage (I–V) characteristics of the cells were measured under the illumination of 100 mW cm^{-2} (AM 1.5) calibrated, simulated sunlight using a homemade computer-controlled setup coupled to a Keithley 2000 multi-meter and a potentiostat/galvanostat HA-301. A Xenon 500 W lamp was used with AM 1.5 filter to obtain the simulated sunlight with above intensity. In order to compare the performances of DSSCs with and without cation pre-adsorbed photoanodes, DSSCs were also fabricated and tested comprising with no cation pre-adsorbed photoanodes.

Flat band potential measurements

Mott-Schottky measurements were taken by immersing TiO_2 electrodes without dye either in 0.2 M KSCN and 0.2 M GSCN solutions in PC as the electrolyte. Measurements were taken by changing dipping time. In each solution, the TiO_2 electrode was immersed for different period of time and the stabilized voltage was measured with respect to a standard calomel electrode (SCE) using Metrohm Autolab PGSTAT128N potentiostat. The scanned frequencies were 1.5 and 2.0 kHz.

EIS measurements

In order to see the effects of cation adsorbed TiO_2 on the interfacial charge transfer resistances, electrochemical impedance spectroscopy (EIS) measurements were performed on the efficiency optimized DSSCs using a Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128 N with a FRA 32 M Frequency Response Analyzer (FRA) covering the 1 MHz–

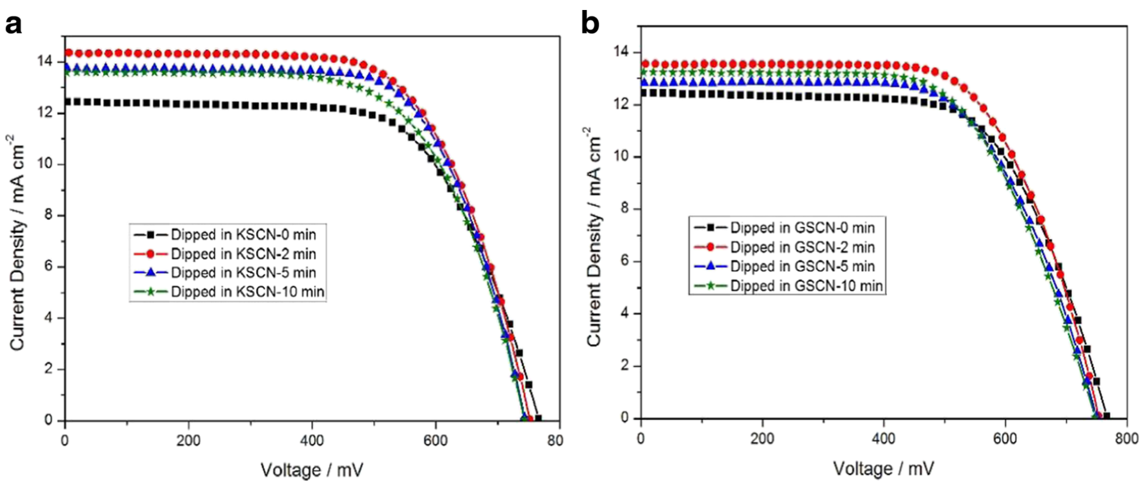


Fig. 1 The photocurrent density–voltage (J–V) characteristics of DSSCs with **a** potassium ions (K+) and **b** guanidine ions (G+) adsorbed photoanodes

0.01 Hz frequency range. These measurements were carried out under the illumination of 100 mW cm^{-2} using the same solar simulator that was used for I–V measurements.

Results and discussion

Photovoltaic performance of DSSCs

DSSCs were fabricated using different photoanodes consisting either with K^+ or G^+ adsorbed TiO_2 structures. Cation pre-adsorption was carried out by dipping the dye attached TiO_2 electrodes in cation containing solutions for different dipping times such as 2, 5, and 10 min. For comparison, DSSCs were also fabricated with the same structures having the same thickness but without pre-adsorption of cations. The photo current density–voltage (*J–V)* curves of DSSCs made either with K^+ or G^+ cations adsorbed photoanodes are shown in Fig 1a, b, respectively. The short circuit photocurrent density J_{sc}, open-circuit photovoltage V_{oc}, the fill factor *FF*, and the efficiency η, derived from photo current–voltage measurements of different types of DSSCs are summarized in Table 1.

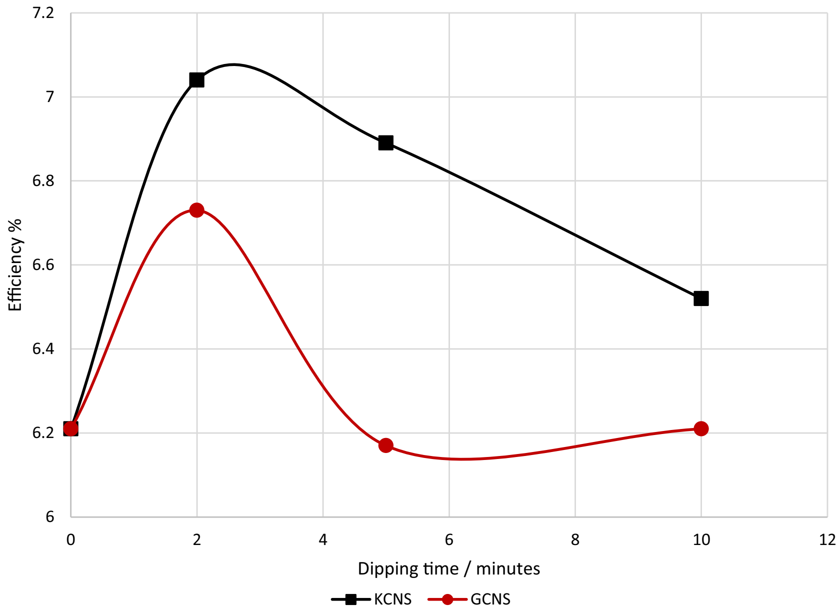
It is interesting to see that both K^+ and G^+ attached DSSCs follow a similar trend of efficiency variation with the J_{sc} value. With the increased dipping time, efficiency of DSSCs also increase up to some extent and at longer dipping times, efficiency tends to decrease (Fig. 2). Since there is no very big decrement in the efficiencies of DSSCs with photoanodes dipped for 2 and 5 min times, in this study, the optimum dipping time is considered as 2 min.

As seen from Fig. 1a and Table 1, DSSC fabricated with K^+ ion containing photoelectrode with 2 min dipping time shows the highest short circuit photo current density of 14.32 mA cm^{-2} and the highest energy conversion efficiency of 7.04%. The solar cells fabricated using the same photo anodes with dipping times of 5 and 10 min show the efficiencies of 6.89 and 6.52%, respectively. DSSC fabricated with electrodes containing no cations pre-adsorbed (conventional type) shows an efficiency of 6.21%. V_{oc} values of DSSCs with K^+ ion adsorbed TiO_2 electrodes tend to decrease with

Table 1 Solar cell parameters obtained by employing different types of photoanodes

Type of dipped solution	Dipping time (minutes)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF %	Eff %
With no cation pre-adsorbed P90/P25 photoanodes (conventional type)					
No dipping solution	0	12.43	767.1	65.1	6.21
With K^+ pre-adsorbed P90/P25 photoanodes)					
KSCN/PC	2	14.32	753.6	65.3	7.04
KSCN/PC	5	13.75	745.3	67.3	6.89
KSCN/PC	10	13.56	745.1	64.6	6.52
With G^+ pre-adsorbed P90/P25 photoanodes					
GSCN/PC	2	13.55	754.2	65.8	6.73
GSCN/PC	5	12.83	750.5	64.1	6.17
GSCN/PC	10	13.26	748.8	62.5	6.20

Fig. 2 Variation of efficiency vs dipping time for DSSCs with K+ and G+ adsorbed photoanodes



increasing dipping time. However, J_{sc}, which is mostly determined by the relative amount of adsorb cations in the TiO_2 electrode, contributes significantly to the solar cell efficiency. The efficiency variation with the dipping time of the DSSCs with G^+ adsorbed electrodes also show the same variation as in the case of K^+ ions adsorbed TiO_2 electrodes. Here, again the DSSC with photoanode dipped for 2 min shows the highest J_{sc} and the efficiency. Respective values of J_{sc} and the efficiency of the highest DSSC are 13.55 mA cm^{-2} and 6.73%. The solar cells fabricated with G^+ adsorbed photoanodes with 5 and 10 min dipping time showed efficiencies of 6.17 and 6.20%, respectively. As it is evident from Fig. 1b and Table 1, V_{oc} of DSSCs with G^+ adsorbed photoanodes also tends to decrease with increasing dipping time. Therefore, it is evident from these studies that pre-cation adsorption in the photanode tends to increase the overall efficiency of the DSSC. As can be seen from Fig. 1 and also from Table 1, significant enhancement in the efficiency (~14%), over the conventional photoanodes use in DSSCs, can be achieved by using smaller cation in this pre-adsorption method.

One of the reasons for the higher efficiencies of the DSSCs with small cation (K^+) adsorbed photoanodes could be explained as follows. It is generally known that the speed of the electrons with random walk through the nanoporous TiO_2 layer in the photoanode is mainly reduced by the traps in the layer. Small cations like K^+ (ionic radius, 0.138 nm) can possibly intercalate into these traps than bulky G^+ ions (ionic radius, 0.21 nm) [14]. The adsorption of cations on the surface of nano titania grains would cause the positive shift of the Fermi level, thereby decreasing the V_{oc} values. This positive shift in the Fermi level or the flat band potential is leading to

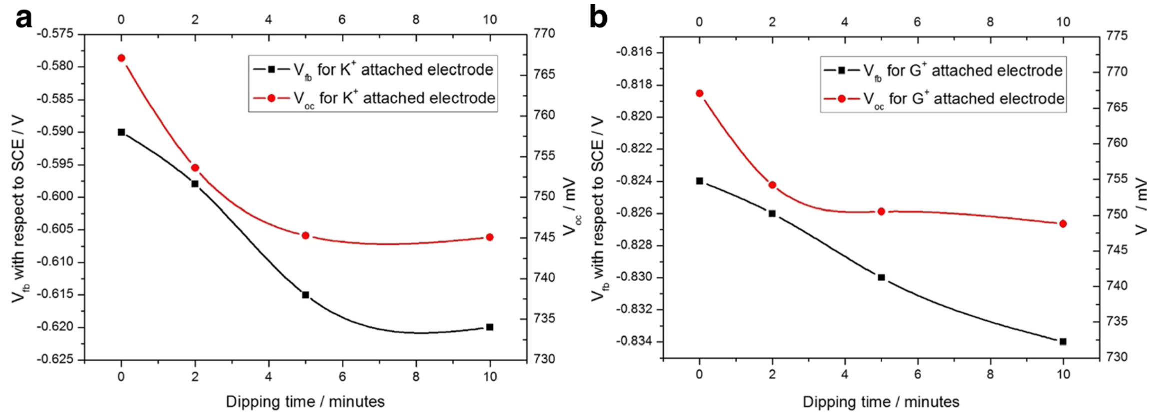


Fig. 3 Variation of the flat band potential (V_{fb}) with open-circuit photovoltage (V_{oc}) of **a** K+ attached **b** G+ attached TiO2 electrodes with dipping time

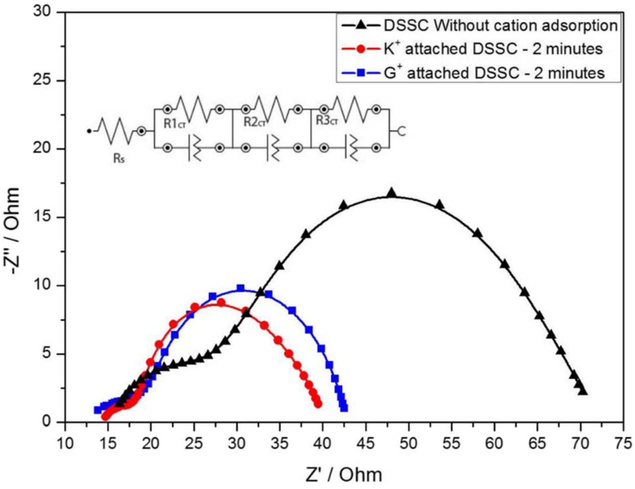


Fig. 4 Impedance plots obtained for the DSSCs either with K+ or G+ cation adsorbed and no cation adsorbed photoanodes

an increase in the J_{sc} by increasing the charge injection rate. This effect is expected to be more favorable for smaller K^+ ions than for larger G^+ ions as the number of adsorbed K^+ cations per unit area of nano titania grain surface would be much greater than the number of G^+ ions adsorbed, due to the difference in their sizes. It should also be noted that DSSCs fabricated with photoanodes, in which cation pre-adsorption were carried out prior to the dye adsorption, showed lower overall efficiencies than the DSSCs fabricated with this proposed method. Possible reason might for this reduction in efficiency could be due to the removal of pre-adsorbed cations during the process of prolong dye adsorption in ethanolic solution.

Electron dynamics at the TiO_2 electrode play a major role in determining the photovoltaic performances. As discussed earlier, the dependence of J_{sc} and V_{oc} on the type and the nature of the cation take place due to interfacial kinetics of the TiO_2 film with dye. Small cations are more readily adsorbed into the TiO_2 electrode than the cations having larger sizes, and in return, the Fermi level of TiO_2 is shifted to the more positive side, which eventually reduces the V_{oc} of the device. The positions of the Fermi level or the flat band potential V_{fb} determined from Mott-Schottky plots ($1/C^2$ vs V) taken from a TiO_2 electrode immersed in an electrolyte containing 0.2 M KSCN and 0.2 M GSCN dissolved in PC are shown in Fig 3a, b, respectively. This experiment was performed by taking measurements at certain dipping times namely 2, 5, and 10 min. As can be seen in Fig. 3a, b, the flat band potential V_{fb} of the TiO_2 electrode in contact with the cation containing solutions decreases with the increasing dipping time and hence the reduction in the V_{oc}. Similar trend in the decrease of the V_{oc} is reported with the different electrolytes contaning different sizes of cations in the electrolyte [2, 16–19].

In order to see the electron transport mechanism and the interfacial resistance of the dye adsorbed TiO2 electrode and the electrolyte interfaces in the pre-cation adsorbed TiO_2 photoanodes, electrochemical impedance spectroscopy (EIS) measurements were carried out under the illumination of 100 mW cm^{-2} and obtained relevant Nyquist plots. Figure 4 shows the Nyquist plots of DSSCs fabricated either with K^+ or G^+ cation adsorbed photoanodes with 2 min dipping time together with no cation pre-adsorbed photoanodes. EIS measurements were done in the frequency range from 1×10^{-2} to 1×10^6 Hz. In an ideal impedance spectrum, three semicircles could be seen which corresponds to the charge transfer resistance of Pt counter electrode/electrolyte interface ($R1_{CT}$), TiO_2 electrode/electrolyte interface ($R2_{CT}$), and ion diffusion of the electrolyte ($R3_{CT}$), respectively [16, 17]. However, in this study, only the first two semicircles appeared in the impedance spectrum. The third semicircle which corresponds to the ion diffusion could not be obtained due to the instrument limitations. The impedance parameters were extracted using the equivalent circuit model as shown in the insert of Fig. 4. The calculated values of the R_S, $R1_{CT}$, R2CT, and $R3_{CT}$ based on the equivalent circuits for the three types of DSSCs are tabulated in Table 2. As it is evident from Table 2, the R_S, $R1_{CT}$, and $R2_{CT}$ values of DSSCs fabricated either with K^+ adsorbed (K^+-DSSCs) or G^+ ion adsorbed (G^+-DSSCs) photo anodes are significantly lower than the corresponding quantities of the DSSCs fabricated with no cation free-adsorbed electrodes. However, the DSSCs with the smaller cation (K+) pre-adsorbed electrodes show the lowest R_{2cT} among these three types. This decrease in the charge transfer resistance ($R2_{CT}$) due to the pre-adsorption of cations in the photoanode confirms the improvement in the charge transfer between the photoanode and the electrolyte. Therefore, this improvement in interface contacts might also be an another reason for this enhancement of the overall efficiency of the solar cells as

Table 2 Series resistance (R_S) and charge transfer resistances of without cation adsorbed and K^+ and G^+ adsorbed DSSCs

Cell configuration	R_S (Ω)	$R1_{CT}$ (Ω)	$R2_{CT}$ (Ω)	$R3_{CT}$ (Ω)
DSSC without cation adsorption	15.2	14.6	30.8	11.4
K^+ attached DSSC—2 min	12.7	2.8	7.0	26.9
G^+ attached DSSC—2 min	13.2	11.7	21.0	7.68

reflected by the higher photo currents observed in them. On the other hand, as observed in our previous systems, the decrease in the $R1_{CT}$ value of the cation pre-adsorbed photolectrodes is an indication of the increase in the oxidation rate of the mediator (I_3^-) at the counter electrode surface [2, 16–19]. Therefore, it can be concluded that the pre-adsorbed smaller cation in the photoanode essentially increases the overall performances of the DSSCs by improving the electron transfer processes inside the devise.

Conclusions

The influences of the cation adsorption in the photoanode on the photovoltaic characteristics of DSSCs have been investigated. The overall efficiency can be enhanced by pre-adsorption of cations in the photoanode. Smaller cation, K^+ adsorbed photo anode showed superior devise performances than the pristine, conventional photoanode. The degree of adsorption of cation or the dipping time in cation solution and the size of the cation play major roles towards the performances of solar devices. Compared with the normal DSSC with pristine, conventional TiO_2 photoanode, ~14% enhancement in the overall efficiency can be achieved by using this cation pre-adsorped method. As it is observed, the low charge transfer resistance of the photoanode/electrolyte interface and the positively (downward) shift of the Fermi level of TiO_2 cause the faster electron transfer dynamics at the TiO_2 (dye) and the electrolyte interface eventually resulting the higher efficiencies.

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