Enhanced Energy Conversion Efficiency of the Sr²⁺-Modified Nanoporous TiO₂ Electrode Sensitized with a Ruthenium Complex

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The absorption of a nanoporous TiO₂ thin film was enhanced throughout the visible wavelengths with surface modification of Sr^{2+}, especially in the range of shorter wavelengths. Charge separation efficiency from laser experiment was measured. Data show that the incident photon to current efficiency of a solar cell based on the dye Ru[LL′(NCS)₂] (L = 2,2′-bipyridine-4,4′-dicarboxylic acid, L′ = bis(tetrabutylammonium) 2,2′-bipyridine-4,4′-dicarboxylate) sensitized Sr^{2+}-modified TiO₂ electrode increased from 9.2% to about 11.8% under the irradiation of a laser pulse energy of 23 μJ at 532 nm. The photoelectrical conversion efficiency is increased from 7.3% to 9.3% under the illumination of a white light of 93.1 mW/cm².

1. Introduction

The dye sensitization of nanoporous semiconductors has been intensively investigated since Gratzel and co-workers reported a highly efficient solar cell based on dye-sensitized nanoporous TiO₂ thin film electrode, and power conversion efficiency as high as 10% was obtained under AM 1.5 simulated solar light.[1,2]

The high light to energy conversion efficiency achieved with dye-sensitized solar cells may be attributed to the nanoporous TiO₂ electrode.[3] The nanoporous TiO₂ film possesses large surface to volume ratio. As a result, the light harvesting ability of the dye, adsorbed on nanoporous film, is tremendously increased, leading to improved efficiency of solar cells. An unusual feature of these nanoporous film based solar cells, however, is the lack of the depletion layer at the electrode and electrolyte interface.[4−6] As a result, the back electron transfer, i.e., the charge recombination between the electrons injected in the conduction band of the semiconductor and the oxidized species in the electrolyte, still remains one of the major limiting factors to the efficiency of the solar cells. Some suppression of charge recombination, as demonstrated by high open-circuit photovoltage V_{oc}, has been achieved by passivating

recombination centers at the interface of nanoporous TiO₂ thin film with 4-*tert*-butylpyridine.[2] Kamat et al. also found that charge carriers could be more efficiently separated in coupled semiconductor systems,[7,8] and the back electron transfer was largely suppressed. The work reminds us that the surface modification of nanoporous TiO₂ film is probably a potential way to the improvement of light to power efficiency.

It has been observed in our previous work that the light to current conversion efficiency of nanoporous TiO₂ electrodes was enhanced when the electrodes were capped with ZnO and different sulfides on surface.[9−11] We report here on the fabrication of nanoporous SrO-modified TiO₂ electrodes (abbreviated as TiO₂−SrO electrode) and the investigation of their photoelectrochemical properties. The results show that the charge carriers are more efficiently separated in the TiO₂−SrO electrode compared with TiO₂ electrodes.

2. Experimental Section

2.1. Materials and Solutions. Optically transparent electrodes (OTE) were made from an F-doped SnO₂-coated glass plate (2 mm thick, 80% transmittance in the visible, 20 Ω/□). Water (R ∼ 18 MΩ) from an easy pure RF system is used in the preparation of all solutions. Ti(OCH(CH₃)₂)₄, propylene carbonate, and *tert*-butylpyridine were purchased from Acros. The dye Ru[LL′(NCS)₂] (L = 2,2′-bipyridine-4,4′-dicarboxylic acid, L′ = bis(tetrabutylammonium) 2,2′-bipyridine-4,4′- dicarboxylate) was purchased from Solaronix SA. 70% aqueous

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HNO$_3$ solution, acetic acid, and Sr(NO$_3$)$_2$·3H$_2$O, purchased from the Beijing Reagent Co., were reagent grade and used as received.

2.2. Preparation of the Dye-Sensitized Nanoporous TiO$_2$ Electrodes. The TiO$_2$ nanoporous film is prepared from colloids with particles of about 20 nm diameter. The preparation of the colloids and film fabrication was similar to that reported.[1,2] In this work, the suspension of colloidal TiO$_2$ with a concentration of 120 g dm^{-3} is dispersed ultrasonically before use. Four drops, ca. 0.2 mL, of the suspension are applied onto a piece of transparent conducting glass and spread evenly. The sample was dried in air, then calcinated at 450 °C for 30 min, and finally cooled to room temperature. Repeating this process until the optimal thickness reached. In this system this thickness is about 13 μm, measured with a Tencor Alpha-Step profiler. The TiO$_2$ thin film was dipped in 0.2 mol dm^{-3} TiCl$_4$ aqueous solution for over 24 h and again sintered at 450 °C for 30 min. The surface modified TiO$_2$−SrO electrode was fabricated by dipping TiO$_2$ thin film in saturated Sr(NO$_3$)$_2$ aqueous solution for 30 min, washed thoroughly with water, dried, and sintered in air at 450 °C for 30 min.

For coloration with the dye, the TiO$_2$−SrO or TiO$_2$ film was immersed in absolute ethanol containing 5×10^{-4} mol L^{-1} Ru-[LL′(NCS)$_2$] for 24 h at room temperature. To minimize adsorption of impurities from moisture in the ambient air, the electrodes were dipped in the dye solution while they were still warm (∼80 °C). The dye-covered electrodes were then rinsed with ethanol thoroughly and dried.

2.3. Instrumentation. The absorption spectra were recorded on an UV-3100 spectrophotometer (Shimadzu, Japan). The electrochemical experiments were conducted in a three-electrode cell with the dye-sensitized TiO$_2$ or TiO$_2$−SrO film as the working electrode, a Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Electrochemical experiments were performed on a CH100 electrochemical analyzer (model 600, CH Instrument). A sandwich-type solar cell was employed in the photoelectrochemical measurements. The dye-sensitized TiO$_2$ or TiO$_2$−SrO film was used as the working electrode, and a conduction glass with a layer of 200 nm thick platinum was used as the counter electrode. The electrolyte was 0.5 mol/dm^3 LiI, 0.05 mol/dm^3 I$_2$, and 0.1 mol/dm^3 *tert*-butylpyridine in 1:1 acetonitrile−propylene carbonate. A 500 W xenon lamp was used as the source of excitation. To get a given band-pass of light, the light beam is passed through a group of filters (Schott Co.). An KG4 filter (Schott) is set in the light beam to protect the electrodes from heating, and both WG360 and GG420 cutoff filters (Schott) are usd to prevent the TiO$_2$ film from being excited by light with wavelength less than 420 nm. The light intensity is calibrated with a light gauge radiometer/photometer (Coherent). The effective illumination area of a flat window is 0.2 cm^2.

A GCR-4 Nd:YAG laser (Spectra Physics) is employed for transient photocurrent measurement. The laser pulse width is 6 ns. Transient photocurrent generation is recorded by a TDS3032 oscilloscope (Tektronix).

3. Results and Discussion

3.1. Absorption Properties. Absorption spectra of the bared and dye-sensitized nanoporous TiO$_2$ films could be used as standards to monitor the changes of the absorbance under different conditions. Figure 1 presents the absorption spectra of the TiO$_2$ and TiO$_2$−SrO films in both bared and dye-sensitized states. It is evident that the absorption of the TiO$_2$−SrO film in the range of shorter wavelengths is much higher than that of the unmodified TiO$_2$ film. When adsorbed with dye, the absorbance of the TiO$_2$−SrO film is enhanced compared with that of the TiO$_2$ film in the visible range. It was found that the adsorption of the dye molecules on Sr^{2+}-modified electrodes would become very poor if
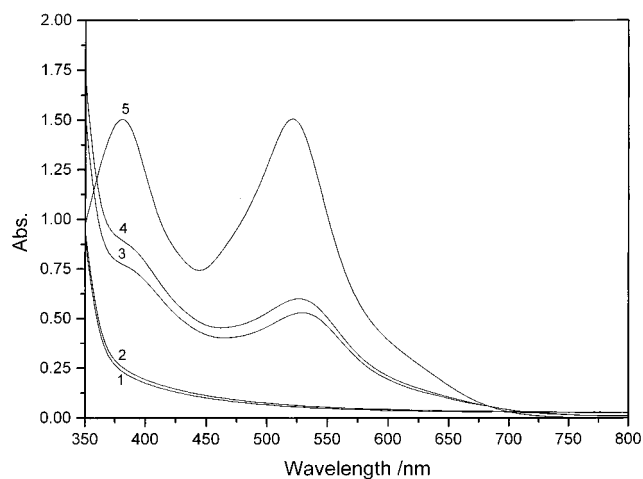

Figure 1. Absorption spectra of the TiO$_2$ film (1), the TiO$_2$−SrO film (2), the dye-sensitized TiO$_2$ film (3), the dye-sensitized TiO$_2$−SrO film (4), and the dye−alcohol solution (5).
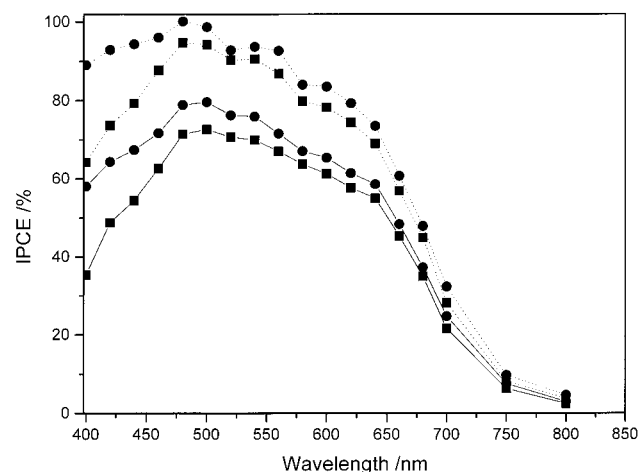

Figure 2. IPCE curves of two solar cells based on the dye-sensitized TiO$_2$ electrode (■) and the dye-sensitized TiO$_2$−SrO electrode (●). The dotted lines represent the IPCE values corrected for the absorption and reflection of conductive glass. The electrolyte is 0.5 mol dm^{-3} LiI, 0.05 mol dm^{-3} I$_2$, and 0.1 mol dm^{-3} 4-*tert*-butylpyridine in 1:1 acetonitrile−propylene carbonate.

TiO$_2$ films were treated in concentrated Sr^{2+} solutions, resulting in poor photoelectrochemical properties. So too many Sr^{2+} ions must be washed away after the TiO$_2$ films were dipped in concentrated Sr^{2+} solution. On the basis of the previous work, relative amount of Sr^{2+} ions which were chemically adsorbed onto the TiO$_2$ could still remain on the surface after this washing.[10,12] What is important is that more dye molecules would be adsorbed on the modified electrode compared with the unmodified one.

3.2. Incident Photon to Current Efficiency (IPCE). The IPCE values of the dye-sensitized TiO$_2$ and TiO$_2$−SrO electrodes are plotted vs wavelengths in Figure 2. The TiO$_2$−SrO electrode shows higher photoelectrical response, and the IPCE at 400 nm reaches about 60%, nearly 2 times as much as that of TiO$_2$ electrode. On the other hand, the difference between the IPCE values of these two electrodes in longer wavelength range is small. If corrected for the absorption and
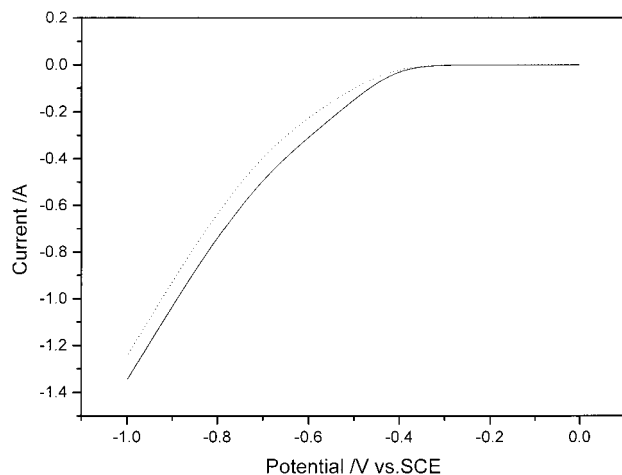
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Figure 3. Current−voltage characteristics of the dye-sensitized TiO$_2$ electrode (−) and the dye-sensitized TiO$_2$−SrO electrode (· · ·) in dark. Scan rate is 10 mV/s, and the electrolyte is 0.5 mol dm^{-3} LiI, 0.05 mol dm^{-3} I$_2$, and 0.1 mol dm^{-3} 4-*tert*-butylpyridine in 1:1 acetonitrile−propylene carbonate.

Figure 4. Photocurrent transients of the dye-sensitized TiO$_2$ electrode (−) and the dye-sensitized TiO$_2$−SrO electrode (· · ·). A single 10 ns laser pulse of 23 μJ at 532 nm is employed as the irradiation source. The electrolyte is 0.5 mol dm^{-3} LiI, 0.05 mol dm^{-3} I$_2$, and 0.1 mol dm^{-3} 4-*tert*-butylpyridine in 1:1 acetonitrile−propylene carbonate.

reflection of conductive glass, the IPCE values are more than 90% in the range of shorter wavelengths for the TiO$_2$−SrO electrode, coincident with the relatively strong absorption of glass in this range. As mentioned in the former section, the improvement of the IPCE values are wavelength dependent. It was reported that the wavelength dependence of the improvement factor could be directly related to the electron collection.[13] The mean distance which a light injected electron must diffuse in order to reach the substrate collector increases as the absorption coefficient of the dye decreases. This phenomenon means that charge recombination is expected to increase as the absorption coefficient of the dye decreases.[13] In other words, a change in the rate of the back electron transfer is expected to have a significant effect at the low dye absorption coefficient regions, which is just the case in the Sr^{2+}-modified electrode. The IPCE values are exceptionally increased in the wavelengths between 700 and 800 nm, while the absorbance is nearly unchanged. On the other hand, the absorption coefficients are rather low in this region, which means that the charge recombination is rather higher. An energy barrier is most possibly formed at the electrode−electrolyte interface with the SrO modification. This energy barrier could suppress the back electron-transfer process and bring about a higher photon to current efficiency. The energy barrier is further demonstrated by the measurement of the dark current of the TiO$_2$ and TiO$_2$−SrO electrodes. Figure 3 shows the dark current curves of both electrodes in a three-electrode cell as a function of the applied potentials. The results show that the dark current of the TiO$_2$−SrO electrode is lower than that of the TiO$_2$ electrode throughout the measured potential range. This phenomenon can be understandable by the existence of an energy barrier at the electrode−electrolyte interface, which can retard the transport of charges through it.

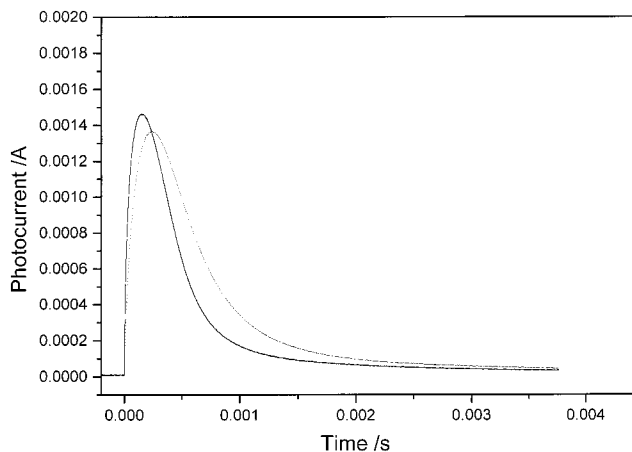**3.3. Transient Photocurrent Measurement.** Transient photocurrent measurement was also performed to

further evaluate the advantages of the TiO$_2$−SrO electrode. The results are presented in Figure 4. It is seen that, at the moment the dye was excited, a higher photocurrent appeared in the TiO$_2$ electrode, but it experienced faster decay. On the other hand, the photocurrent of the TiO$_2$−SrO electrode was lower at the beginning of excitation, but it decayed more slowly. Although more electrons are injected into the conduction band of TiO$_2$ at the beginning in the TiO$_2$ electrode, many of the electrons recombined with the oxidized dyes and I$_3$- in the electrolyte. In contrast, because of an energy barrier existing at the interface in the TiO$_2$−SrO electrode, the photoinjected electrons would be less at beginning, but the energy barrier could suppress the back electron transfer and more electrons could be collected in the substrate. Integration of the photocurrent transients of Figure 4 yields an electrical charges of $Q = 1.16$ and 0.91 μC for the TiO$_2$−SrO and TiO$_2$ electrodes both sensitized with the dye, respectively. With a laser pulse energy of 23 μJ at 532 nm, these correspond to an incident photon to current efficiency (IPCE) of 11.8 and 9.2%, respectively. Under continuous illumination the IPCE values of ca. 76% and 69% were measured at 540 nm. The lower IPCE values under pulsed illumination can in part be attributed to the much higher recombination rate at the very high cation radicals and trapped electron concentration created by the intense laser flash.[14]

3.4. Dependence of IPCE on Applied Bias Potentials. To further investigate the photosensitization of both electrodes with the dye, IPCE were recorded as a function of applied bias potentials, and the results are summarized in Figure 5. It is seen that the IPCE values increase with the increase of bias potentials applied on ITO in the range of −1.0 to −0.4 V vs SCE quickly and then level off at −0.3 V vs SCE for both electrodes. This may result from the smaller applied negative potential which benefit electron injection and decrease the probability of charge recombination on the way before they reach the back contact. With application of a negative

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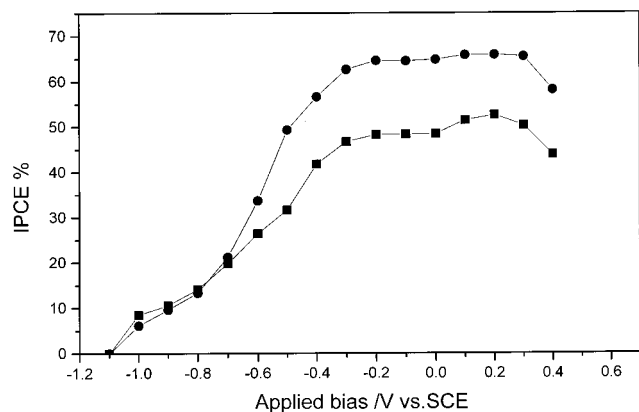
Figure 5. Dependence of IPCE under the illumination of 540 nm light on applied bias potentials: (■) the dye-sensitized TiO₂ electrode; (●) the dye-sensitized TiO₂−SrO electrode. The electrolyte is 0.5 mol dm⁻³ LiI, 0.05 mol dm⁻³ I₂, and 0.1 mol dm⁻³ 4-*tert*-butylpyridine in 1:1 acetonitrile−propylene carbonate.

bias, the Fermi level of TiO₂ is shifted to negative energies, and at a potential of ∼−1.0 V vs SCE it becomes higher in energy than the oxidization potential of the excited dyes, which is at ∼−1 V vs SCE,[2] thus resulting in an inefficient electron transfer from the dye to TiO₂ and leading to zero IPCE. With positive bias, the Fermi level is shifted to lower energies, which increases the driving force to an efficient electron transfer, resulting in higher IPCE values. However, the increase in IPCE values with positive bias may also due to the increase in charge collection efficiency as the photoinjected electrons will be more efficiently withdrawn and transported to the back contact. It should be mentioned that the IPCE values will again decrease at more positive bias. A similar dependence of IPCE on applied bias has also been observed by others.[15,16] For both electrodes the charge recombination may not be an important factor in IPCE at negative bias below −0.8 V because the amount of the photoinjected electrons is small. As discussed in the former section, more electrons will be injected into TiO₂ at the beginning of illumination in the TiO₂ electrode, so its IPCE values are higher at bias bellow −0.8 V vs SCE. When the bias reached −0.7 V or higher, the concentration of the injected electrons will increase, and the charge recombination will become a more and more important factor in IPCE. The IPCE values of the TiO₂−SrO electrode will increase more rapidly due to its less charge recombination.

3.5. Dependence of Short-Circuit Photocurrent (I_{sc}) and Open-Circuit Photovoltage (V_{oc}) on Incident Intensity. The I_{sc} and V_{oc} values of both cells were measured at various incident light intensity (I_{inc}) and are shown in Figures 6 and 7, respectively. The photocurrent characteristics with incident light intensity follow the relation $I_{sc} = \alpha I_{inc}^{\gamma}$, where γ is the light exponent.[17,18] The inset in Figure 6 is the logarithmic plot of I_{sc} vs I_{inc}. Both lines have the same slope with a light exponent γ of 0.92, which is close to unity,

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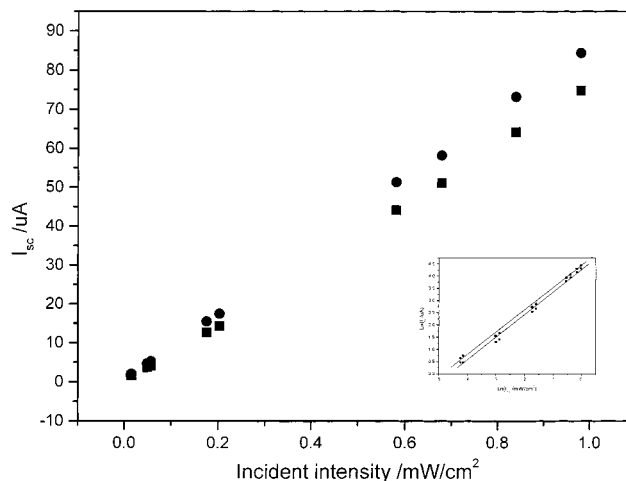

Figure 6. Variation of short-circuit photocurrent (I_{sc}): (■) the dye-sensitized TiO₂ electrode and (●) the dye-sensitized TiO₂−SrO electrode, measured at 540 nm illumination as a function of incident light intensity (I_{inc}). The inset shows that the logarithmic plot of I_{sc} vs I_{inc}. The electrolyte is 0.5 mol dm⁻³ LiI, 0.05 mol dm⁻³ I₂, and 0.1 mol dm⁻³ 4-*tert*-butylpyridine in 1:1 acetonitrile−propylene carbonate.
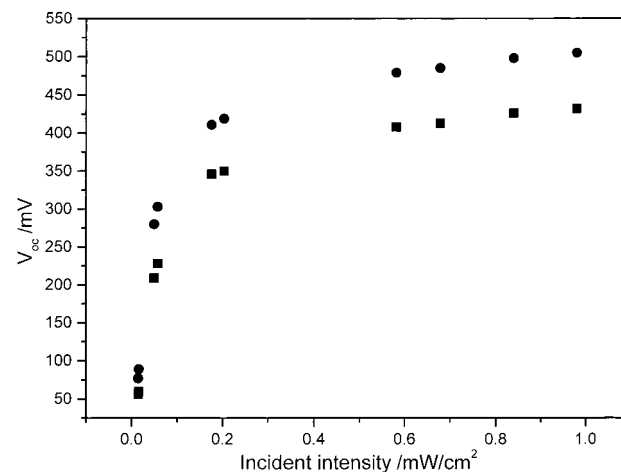

Figure 7. Variation of open-circuit photovoltage (V_{oc}): (■) the dye-sensitized TiO₂ electrode and (●) the dye-sensitized TiO₂−SrO electrode, measured at 540 nm illumination as a function of incident light intensity (I_{inc}). The electrolyte is 0.5 mol dm⁻³ LiI, 0.05 mol dm⁻³ I₂, and 0.1 mol dm⁻³ 4-*tert*-butylpyridine in 1:1 acetonitrile−propylene carbonate.

indicating that the photogeneration of charge carriers is a monophotonic process.

The variation of V_{oc} with I_{inc} is initially large when I_{inc} is below 0.2 mW/cm². Once the incident intensity was larger than 0.2 mW/cm², the photovoltages gradually reached saturation.

3.6. Power Conversion Efficiency. For overall light to electricity conversion efficiency measurements, a thin sandwich type solar cell was fabricated. The dye-sensitized TiO₂−SrO or TiO₂ electrode was used as the photoanode, while an ITO glass plate on which 200 nm thick of Pt was deposited by sputtering was used as the photocathode. The two electrodes were clamped tightly, followed by introducing one drop of the electrolyte solution into interelectrode space. Figure 8 shows the photocurrent−voltage characteristics of both solar cells under illumination of a white light from a Xe lamp (93.1 mW/cm²). The short-circuit photocurrent (I_{sc}) and open-
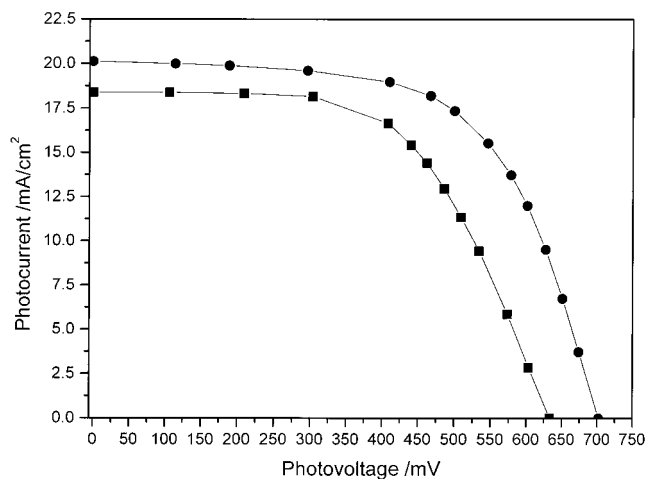
Figure 8. Photocurrent−voltage characteristics of two sandwich-type solar cells based on (■) the dye-sensitized TiO$_2$ electrode and (●) the dye-sensitized TiO$_2$−SrO electrode. The irradiation source is a white light of 93.1 mW/cm^2 from a 500 W Xe lamp.

circuit photovoltage (V_{oc}) were found to be 20.12 mA/cm^2 and 702 mV for the cell based on the TiO$_2$−SrO electrode, while the I_{sc} and V_{oc} values of the cell based on the TiO$_2$ electrode are 18.38 mA/cm^2 and 633 mV, respectively. The fill factor (FF) of both cells are calculated to be 0.58 and 0.62 for the TiO$_2$ and TiO$_2$−SrO electrodes. The overall light to electricity conversion efficiency (η) was obtained by the relation

$$\eta = \frac{I_{sc} V_{oc} FF}{I_{inc}}$$

where I_{inc} is the incident light intensity. Other terms have already been defined. According to Figure 8, the power conversion efficiency of the solar cell based on the TiO$_2$−SrO electrode is calculated to be 9.3% and that of the solar cell based on the TiO$_2$ electrode is 7.3%. So the power conversion efficiency of TiO$_2$ based solar cells is increased about 27% with the modification of SrO.

In conclusion, two of the most important processes in dye-sensitized solar cells are the electron injection and recombination which are all closely related to the surface states of nanoporous semiconductor films. In the present work the back electron transfer was effectively suppressed with the surface modification of a nanoporous TiO$_2$ film with SrO. As a result, the photoelectrical conversion efficiency of the TiO$_2$−SrO electrode was improved. More research work is underway in our group to investigate the advantage role of the surface modification of nanoporous semiconductor films in wider regions.