Efficiency Enhancement for DSSCs using Metal Ion–doped TiO_2 Electrodes Analyzed by EIS and ESCA

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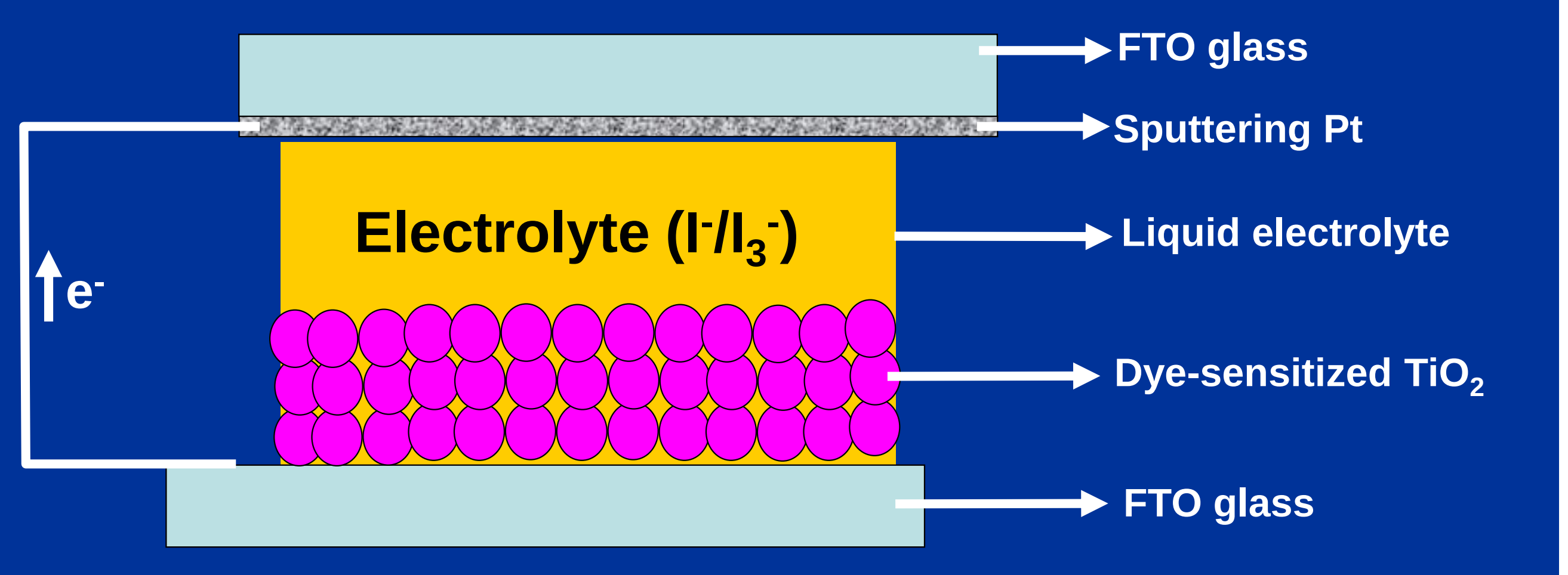
Introduction

The dye sensitization of nanoporous semiconductors has been intensively investigated since Gratzel and coworkers reported a highly efficient solar cell based on dye-sensitized nanoporous TiO_2 thin film electrode, and power conversion efficiency as high as 10% was obtained under AM 1.5 simulated solar light [1]. The nanoporous TiO_2 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. However, 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. Hence, some proper ways have been employed to suppress the charge recombination, such as, passivating recombination centers at the interface of nanoporous TiO_2 thin film with 4-*tert*-butylpyridine [1] and modifying the surface of TiO_2 photocatalyst by the doping of metal ions in TiO_2 particles [2]. We report here on the fabrication of nanoporous metal ion (Zn^{2+}, Sr^{2+} or Y^{3+})-doped TiO_2 electrodes and the investigation of their photoelectrochemical properties by AC impedance and ESCA techniques. The results show that metal ions surface modification of nanoporous TiO_2 film is probably a potential way to the improvement of light to power efficiency.

Experimental

DSSC structure

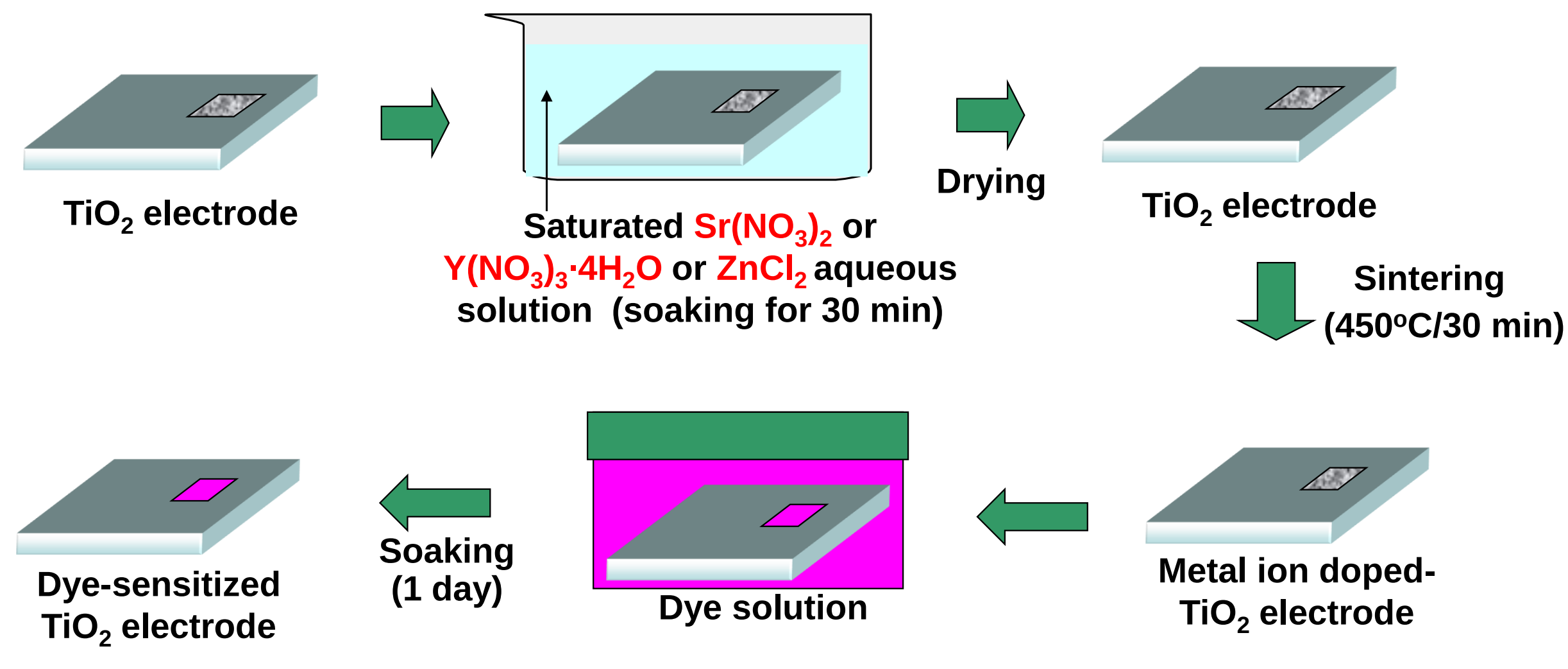


Materials

- Substrate - glass sheet with the conductive layer of F-doped SnO_2 (sheet resistance: 15 Ω/square)
- TiO_2 suspension (Ti nanoxide-T: colloidal anatase, particle size of ~20 nm) – applied onto a conductive glass, sintered for 30 min at 500⁰C in order to obtain nanocrystalline layer
- Sensitizers (dyes) - Ru (II) complexes: N3 (Solaronix)
- Electrolyte - 0.5 M of LiI, 0.05 M of iodine and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile

Main Steps of TiO_2 electrode Preparation

- The pre-prepared TiO_2 thin films were dipped directly into the saturated metal ion solution for several hours and washed thoroughly with water, dried, and sintered in air at 500ºC for 30 min. The preparation procedure of the metal-ion doped TiO_2 electrode is following.



Results and Discussions

AC impedance analysis

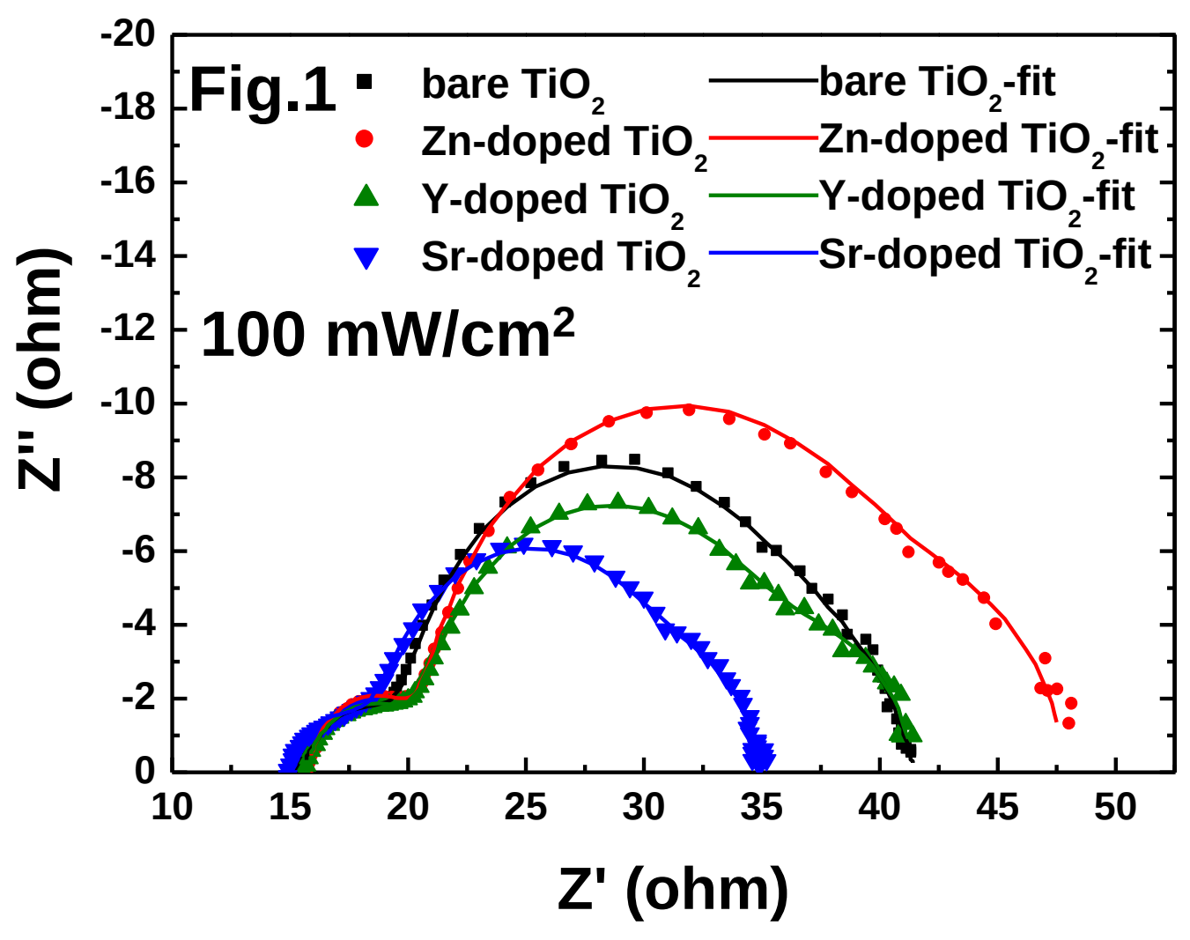


Fig. 1. AC impedance spectra of the metal ion-doped TiO_2 based DSSCs under illumination of 100 mW/cm². Frequency: 0.01~65kHz; Amplitude: 10mV.

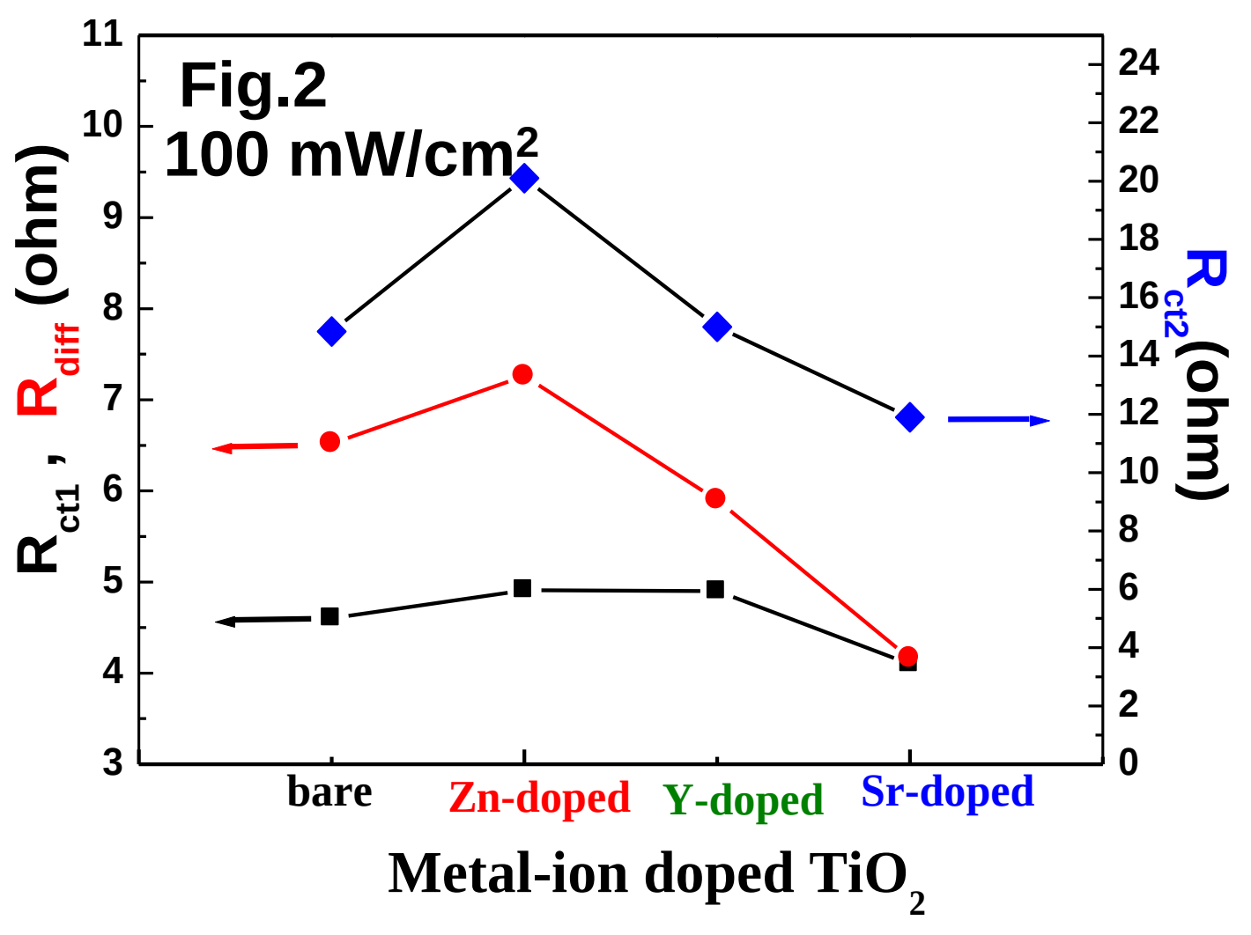


Fig.2. Three AC impedance parameters of the metal ion-doped TiO_2 based DSSCs under illumination of 100 mW/cm². Frequency: 0.01~65kHz; Amplitude: 10mV.

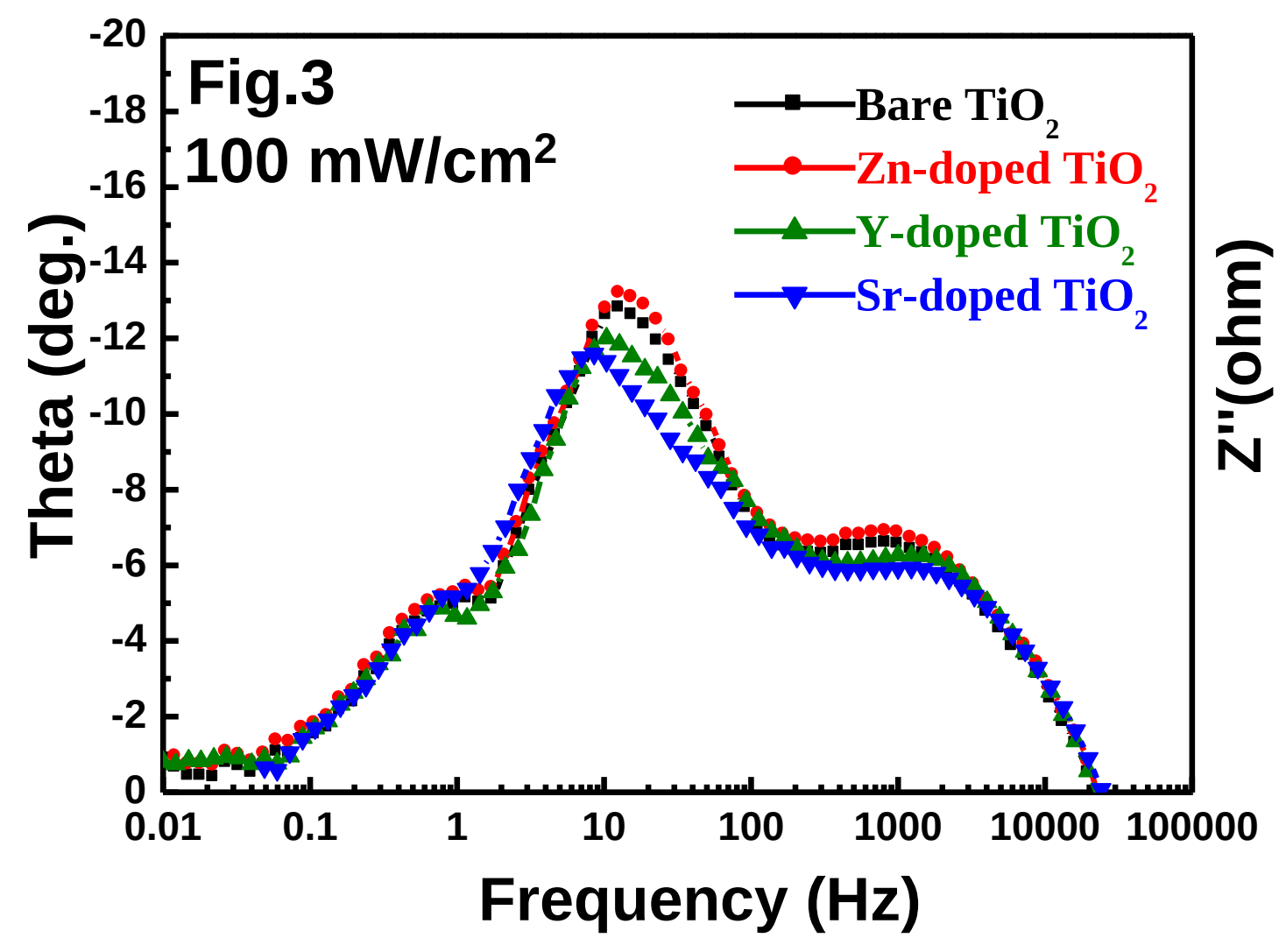


Fig.3. Bode plots of the metal ion-doped TiO_2 based DSSCs under illumination of 100 mW/cm². Frequency: 0.01~65kHz; Amplitude: 10mV.

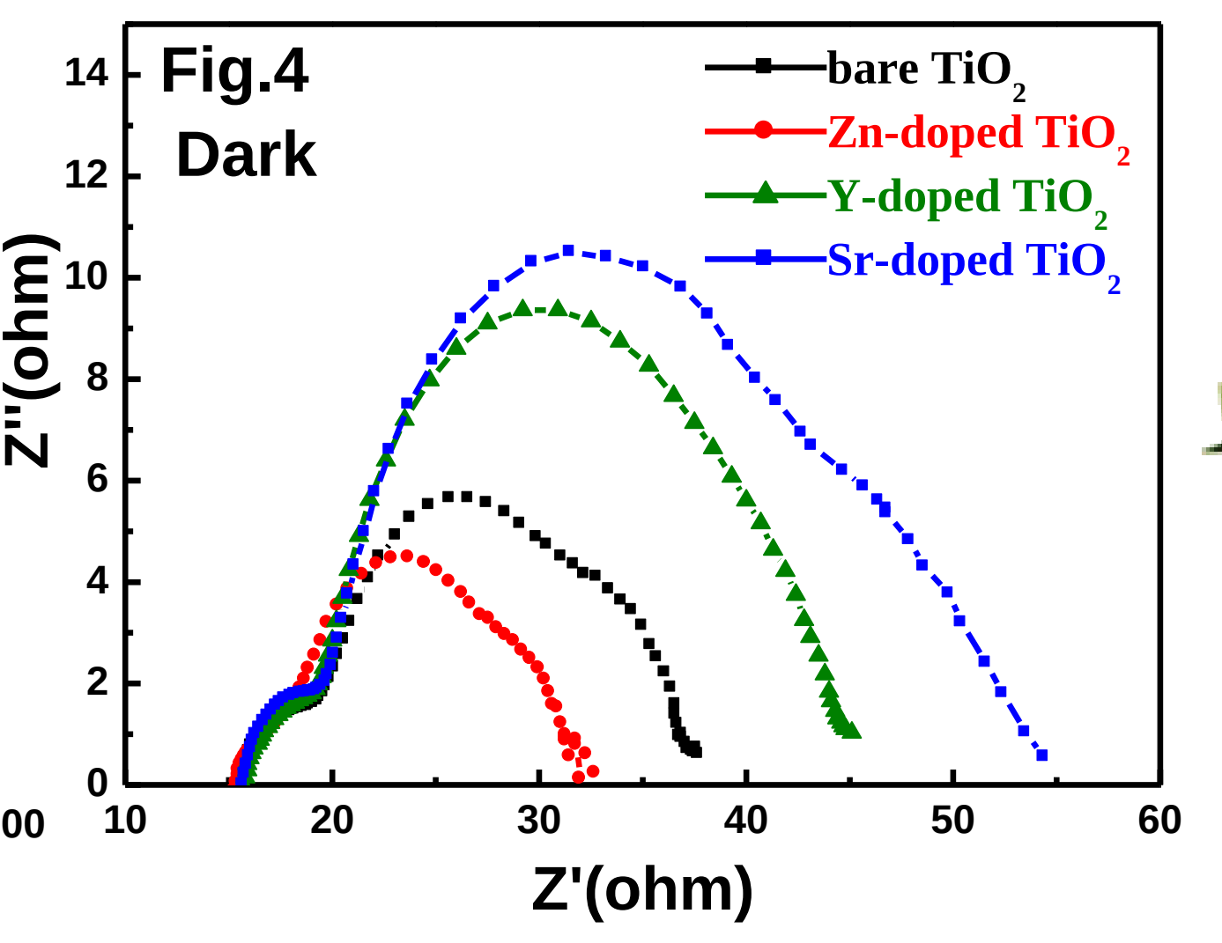


Fig. 4. AC impedance spectra of the metal ion-doped TiO_2 based DSSCs in dark. Frequency: 0.01~65kHz; Amplitude: 10mV.

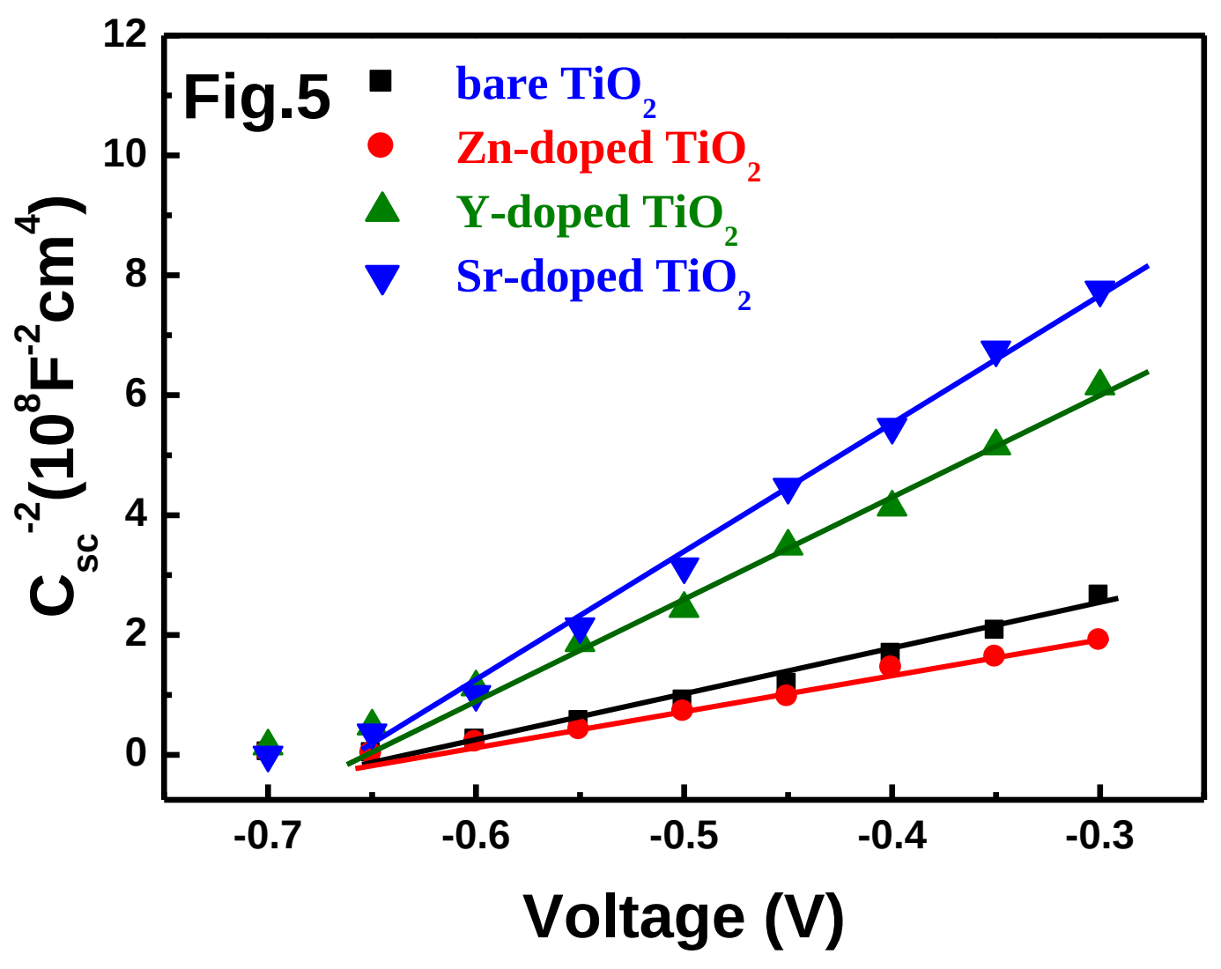


Fig. 5. Mott-Schottky plots of the metal ion-doped TiO_2 based on DSSCs.

Table 1. The experimental Mott-Schottky plots for metal ion-doped TiO_2

Electrode	slope×10^8	V_{fb}(V)	N_D×10^{21}(cm^{-3})
Bare TiO_2	5.11	-0.65	5.51
Zn-doped TiO_2	6.69	-0.64	4.22
Y-doped TiO_2	2.05	-0.64	13.80
Sr-doped TiO_2	1.52	-0.64	18.61

Donor density, N_D, and flatband potential, V_{fb}, determined from Eq. as follows.

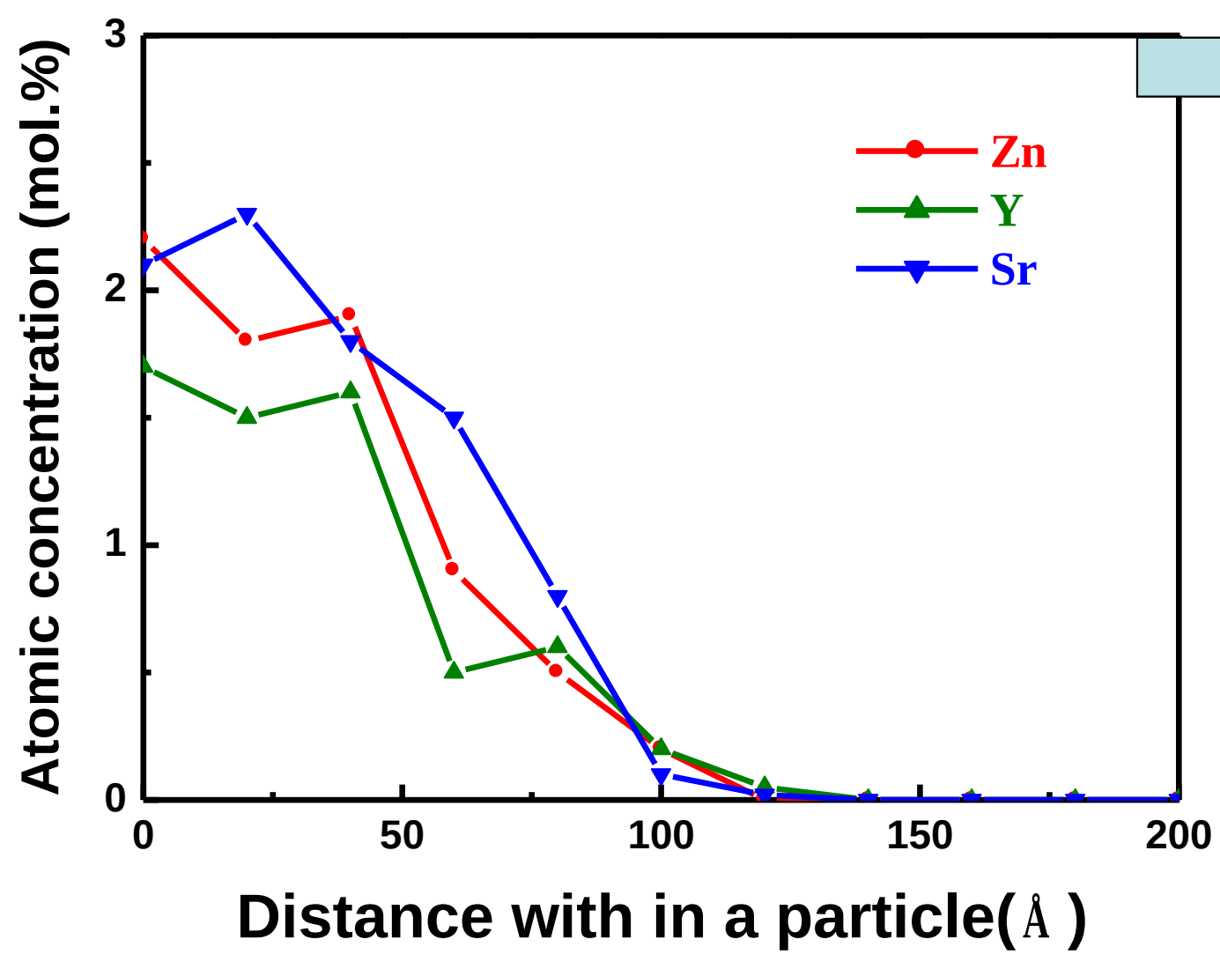
$$\frac{1}{C_{sc}^2}=\frac{2}{e\varepsilon_0\varepsilon N_d}(-\Delta\phi-\frac{kT}{e})$$

C_{sc}: capacitance of space charge
ε_0 : vacuum permittivity
ε : dielectric constant
κ : Boltzmann constant
$\Delta\phi$: $E-E_{fb}$

Fig. 1 and 2 show the EIS spectra and three parameters of the DSSC fabricated with three metal-ion (Zn, Y, Sr)-doped TiO_2 electrodes under identical experimental conditions, respectively. From this result, it is interesting to note that smallest R_{ct1}, R_{ct2} and R_{diff} values of the DSSC made with Sr-doped TiO_2 electrode is achieved. By comparing the intermediate-frequency regime from the Fig. 3, DSSCs made with Sr-doped TiO_2 electrode could facilitate the charge transfer because of the rich-electron contributing property under illumination of 100 mW/cm². To be obvious, the charge resistance can be suppressed by employed the doping of Sr ion in a TiO_2 particle. Besides, the charge recombination can be decreased by the use of the Sr or Y ion surface modified TiO_2 electrode, showed in Fig. 4.

Fig. 5 shows the Mott-Schottky plots of the DSSC fabricated with three metal-ion (Zn, Y, Sr)-doped TiO_2 electrodes and Table 1 summarizes the results obtained from Mott-Schottky analyses for different sample compositions. The flat band potential V_{fb} for the metal ion-doped TiO_2 electrode is -0.64 V, shifted of 0.01V towards positive potentials for bare TiO_2 electrode was observed. The donor density (N_D) was also calculated from the slope of the Mott-Schottky plot. The value of the donor density was found to be between 5.51×10^{21} and 18.61×10^{21} cm^{-3} at a frequency of 10 kHz. Consequently, the Sr-doped TiO_2 electrode possesses the highest the donor density.

ESCA analysis



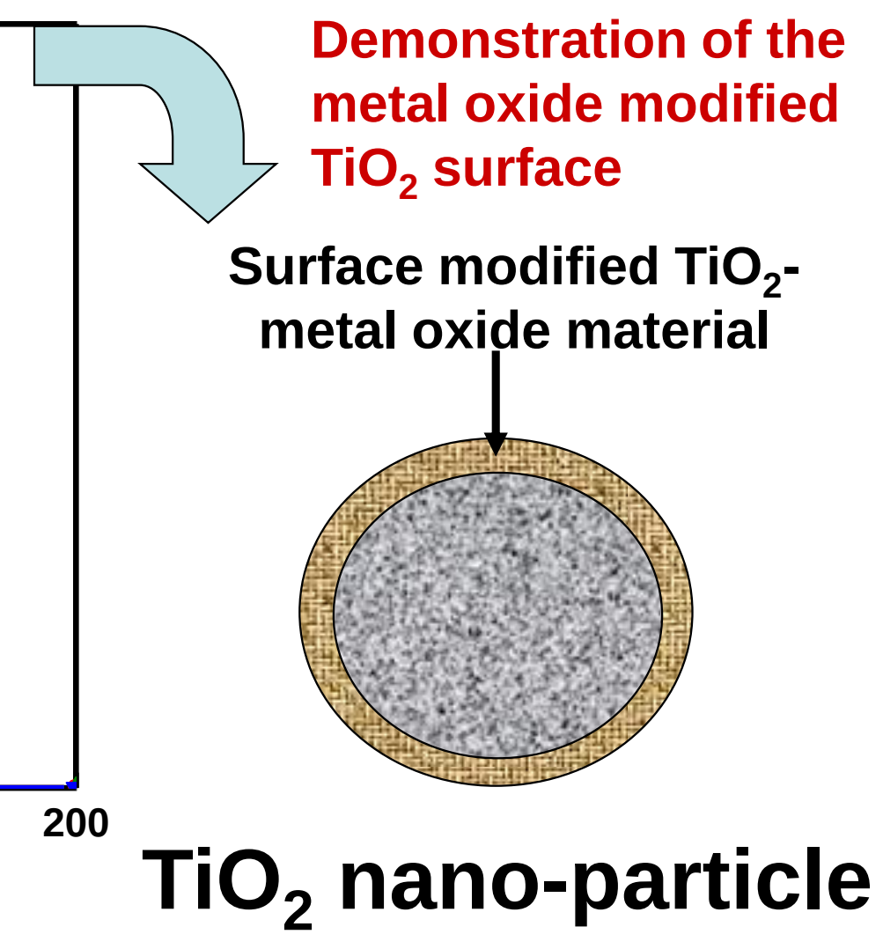


Fig. 6. ESCA depth profiles of Zn, Y, Sr in a TiO_2 particle.

In Fig.6, the concentration of Ti in a TiO_2 particle maintains about 33 mol.%. It is demonstrated, three metal ion (Zn^{2+}, Sr^{2+}, Y^{3+}) can permeate inside the TiO_2 particle, then form the metal oxide till the distance of 10 nm from the surface of a TiO_2 particle.

Improvement of performance

Table 2. the cell performance of DSSCs made with metal-ion doped TiO_2 electrode

Working electrode	I_{sc} (mA/cm²)	V_{oc} (V)	FF	Efficiency (η)
Bare TiO_2	19.52	0.69	0.57	7.70
Zn-doped TiO_2	16.26	0.69	0.58	6.51
Y-doped TiO_2	19.08	0.70	0.59	7.92
Sr-doped TiO_2	21.52	0.68	0.58	8.41

When comparing the performance of DSSCs incorporating both metal ion-doped TiO_2 photoelectrodes, the superior efficiency was found with electrodes using Sr^{2+}-doped TiO_2 films, in contrast to other metal ions under 100 mW/cm² illumination. In Table 2, the conversion efficiencies of Sr^{2+} (8.41%) and Y^{3+} (7.92%) doped TiO_2 films are also superior to nondoped-TiO_2, and Zn^{2+} (6.51%) doped TiO_2 film is the worst among all.

Conclusions

It is demonstrated, small amounts of Sr and Y ions doped inside the TiO_2 particles can facilitate the charge transfer in the TiO_2 network due to the higher donor density. In addition, from the results of EIS analysis, the doping of Sr and Y ions can restrain the charge recombination between the TiO_2 working electrode and I^-/I_3^- redox couple, apparently. However, the doping of Zn ion in TiO_2 particles can't enhance the efficiency of DSSCs in this work.

Acknowledgments

This work was financially supported by the Academia Sinica, Taipei, Taiwan. The work was also partially supported by the National Research Council of Taiwan.

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A Study of Photoelectrochemical Kinetics at the TiO_2 Electrode/Electrolyte Interface by SECM

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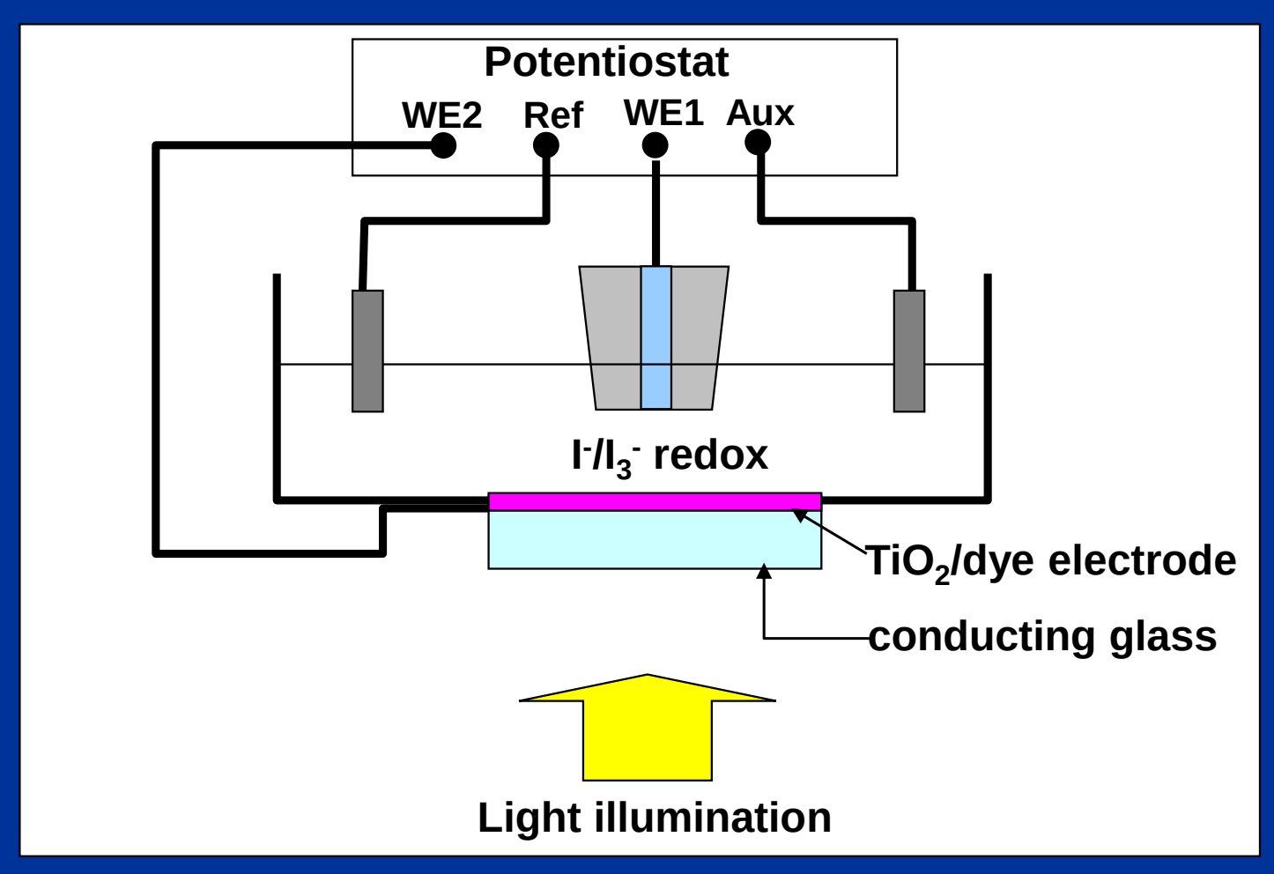
Introduction

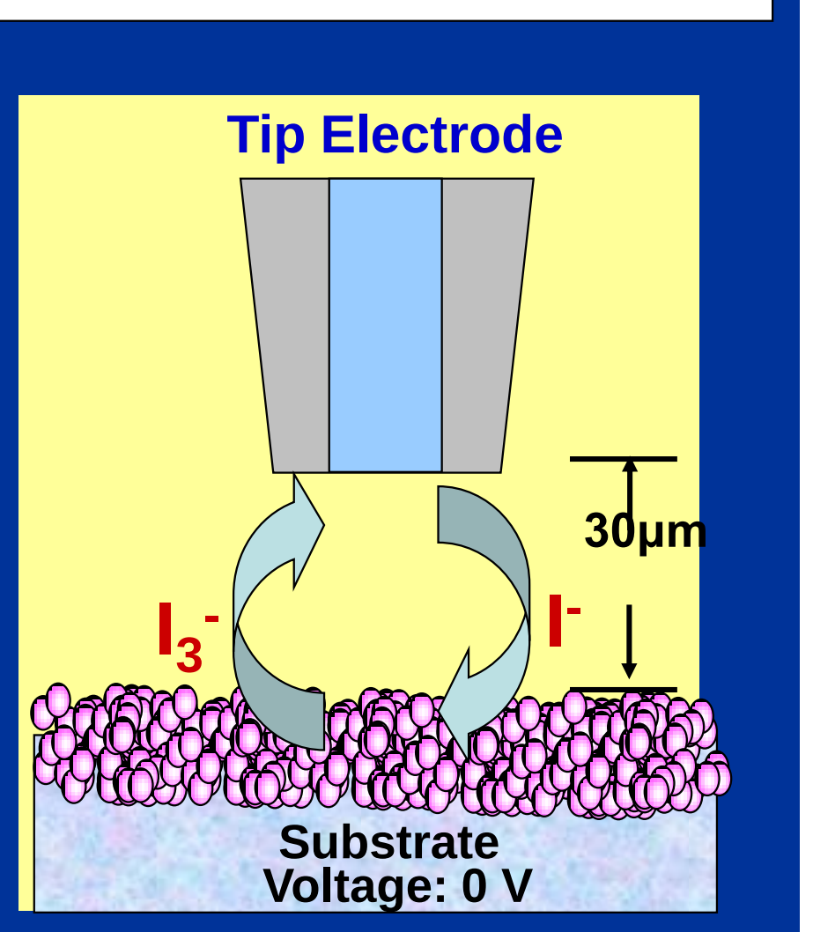
Because of high photon-to-electron power conversion efficiency and low production cost, dye-sensitized solar cells (DSSCs) have been established as the promising alternative to silicon solar cells. Nevertheless, the photoelectrochemical reaction of the TiO_2/dye/electrolyte interface is so complicated and some pending debates can't be solved due to lack of valuable tool to analyze. Scanning electrochemical microscopy (SECM) has been demonstrated to be a powerful tool for understanding kinetic processes at various electrode/electrolyte interfaces [1]. Although the photoelectrochemical processes at the semiconductor electrode/electrolyte interface have drawn much attention in recent years, only few studies on the photoelectrochemical kinetics at the nanostructured electrode/electrolyte interface by using SECM have been reported [2, 3]. In this study, we report an application of the SECM to study dye-sensitized nano-crystalline surfaces and estimate the apparent reaction rate constant, k_{eff}, under different illuminations.

Experimental

SECM set up for DSSCs

$TiO_2|S^+ + 3/2\ I^- \rightarrow TiO_2|S + 1/2\ I_3^-$





Materials

- Substrate - glass sheet with the conductive layer of F-doped SnO_2 (sheet resistance: 12 Ω/square)
- TiO_2 suspension (Ti nanoxide-T: colloidal anatase, particle size of ~20 nm) – applied onto a conductive glass, sintered for 30 min at 500⁰C to obtain a nanocrystalline layer
- Sensitizers (dyes) - Ru (II) complexes: N3 (Solaronix)
- Electrolyte - 0.5 M of LiI in 3-methoxypropionitrile (MPN)

Experimental details

- The electrochemical and photoelectrochemical experiments have been performed in a 3-electrode setup with a Pt counterelectrode and a Pt reference electrode. A Pt microelectrode (r = 10 μm) was used as working electrode and was placed with a positioner (CH Instruments 900B) close to an illuminated dye-sensitized nanocrystalline TiO_2 film (3 μm thickness) on a glass substrate.

- The TiO_2 nano-crystalline films have been made by "doctor blading" a paste of TiO_2 onto a microscope slide followed by drying and heating the film at 500 ºC for 30 minutes. The surfaces produced in this way were then immersed into a 3 mM solution of the dye-sensitizer N3 (cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium) in t-butanol and acetonitrile .

- The sample was irradiated from the bottom with a 500 W projector lamp (Oriel solar simulator (#6266)). The Pt microelectrodes were polished with alumina, sonicated and electrochemically cleaned in sulfuric acid prior use.

Results and Discussions

CV and SECM topographies

Fig. 1 shows the cyclic voltammogram of at a Pt microdisk electrode in the bulk phase of the solution. It shows a well-defined oxidation wave for the reaction $3I^- \rightarrow I_3^- + e^-$ due to presence of only LiI, and measures accurately the concentration of I_3^- produced from N3-dye sensitized TiO_2 surface. Therefore, we assume, as a simplification, that the bulk solution contains only I^- but no I_2 or I_3^-. SECM topographies, as shown in Fig. 2 (a)-(c), were carried out at a UME potential V = -0.5 V where a diffusion-controlled reduction of I_3^- took place and I^- was produced. The approach curves to TiO_2 electrode surface and the excellent agreement with the theory for hindered diffusion indicate that this redox system can be treated with reasonable accuracy by using the theory developed for a simple redox couple.

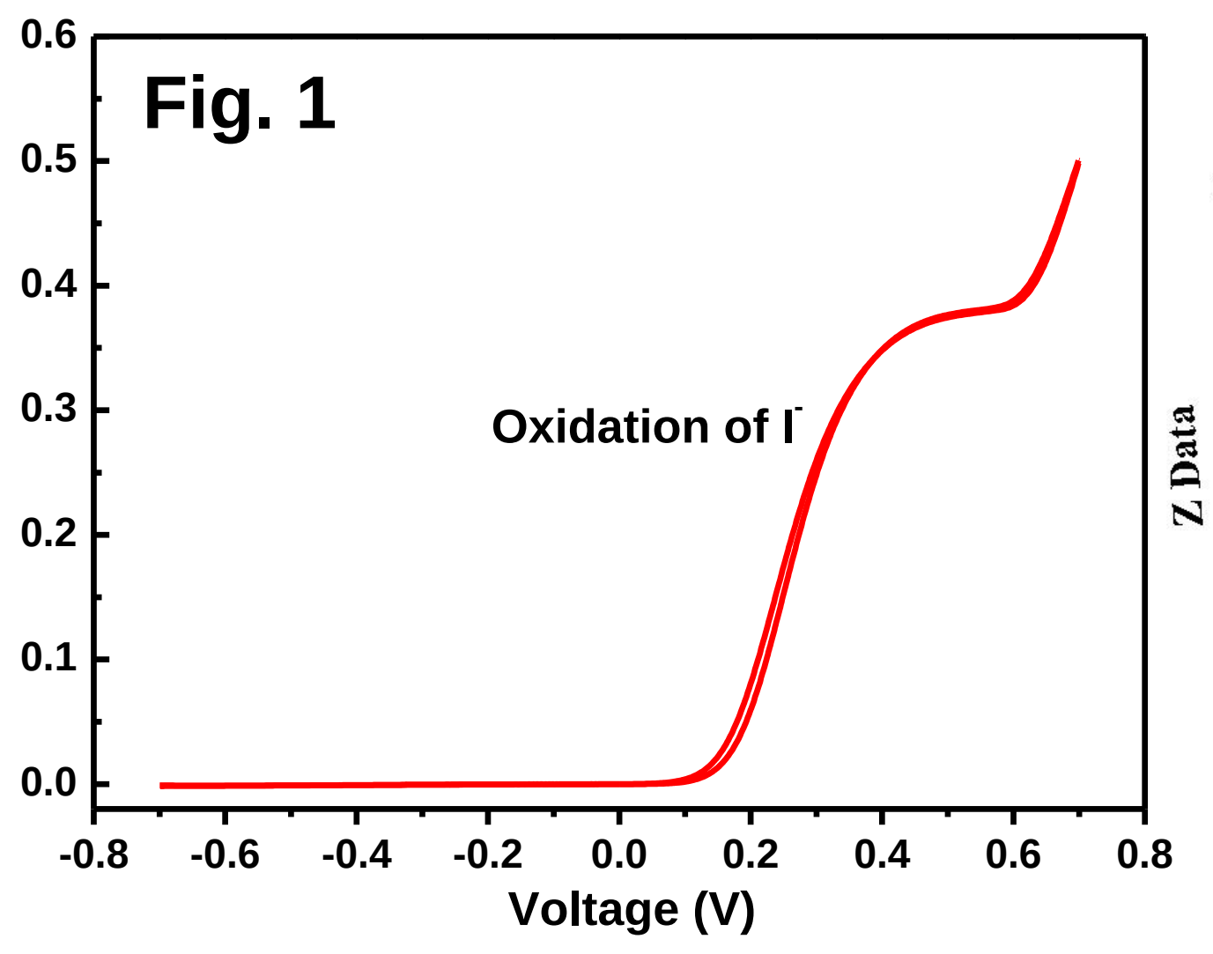
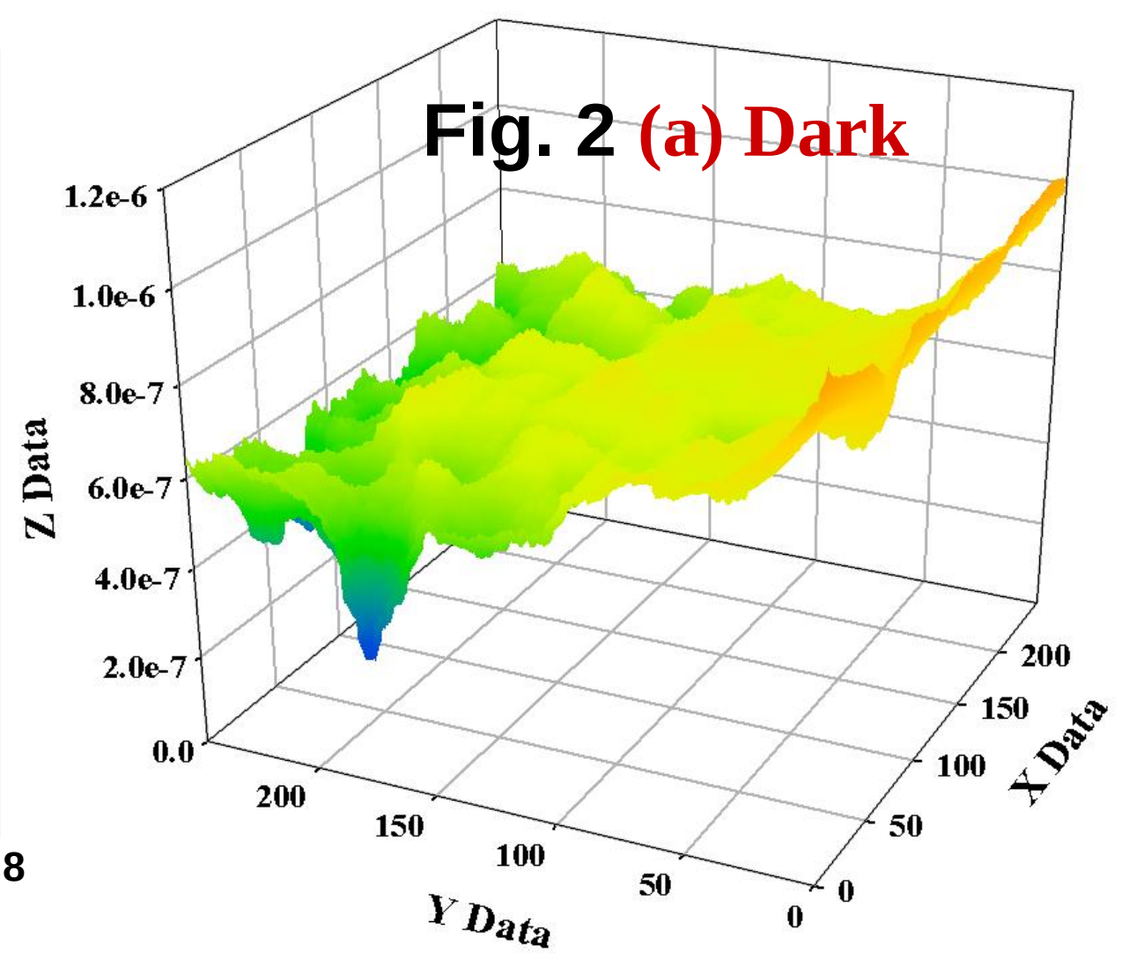


Fig. 1. Cyclic voltammogram of 0.5M LiI in MPN at a Pt UME, scan rate 0.05 V/s



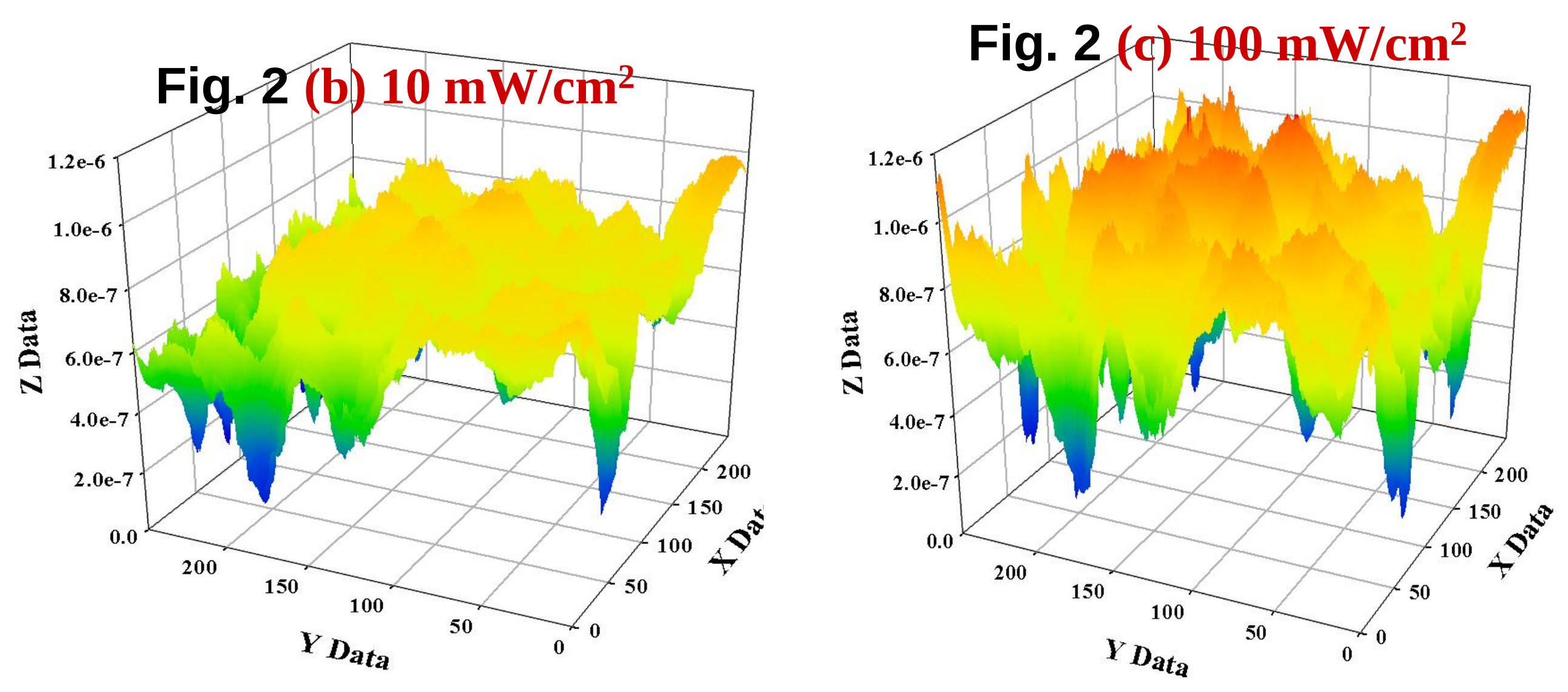


Fig. 2. SECM topographies of N3 dye sensitized TiO_2 under different illumination intensity (in dark(a); 10 mW/cm² (b); 100 mW/cm². Scan rate 1 μm/s

In Fig. 2 the SECM topographies of the experiments are plotted: with a potential of -0.5 V, a strong reduction current increase can be observed at the UME at a distance of 30 μm while illuminating (10 mW/cm², 100 mW/cm²), supporting the working principle of the experiment. Furthermore, the higher illumination intensity induces more I_3^- from the dye-sensitized TiO_2 surface is acquired.

Approaching studies

In Fig. 3, the increase of the current after the start of illumination can be a slow process on a time scale of many seconds. Obviously, the higher photocurrent induced more of N3 dye-sensitized TiO_2 electrode than that of the blank TiO_2. To verify the production of I_3^- at the surface of dye-sensitized TiO_2 under illumination, approach curves were recorded in the dark and under illumination (10, 50, 100 mW/cm²) in Fig. 4. The curves are presented in normalized coordinates $i_T(L)$ versus L, where the normalized current at the UME $i_T = i_T/i_{T,\infty}$, where i_T = the current at the UME and $i_{T,\infty}$ = the current in the bulk solution. The normalized distance L is the distance d in units of the UME radius r_T. The curves agree with the theoretical negative feedback approach curve to an insulating sample expected for a UME of this geometry. The exact curve $i_T(L)$ can be described by Eqn (1) for a first-order reaction at the sample and infinitely fast reaction at the UME. This equation considers the contribution $i_{T,ins}(L)$ of hindered diffusion of I^- from the bulk solution to the UME and a substrate current $i_S(L)$ that originates from the conversion of the mediator at the sample. $i_{T,cond}(L)$ is the current that results if the reaction at the sample is diffusion controlled. Analytical approximations for the individual contributions to Eqn (1) which were used to form an analytical function to which the individual experimental curves can be fitted are taken from Eqn (2) to Eq. (4). $\kappa = k_{eff}r_T/D$ is a normalized, first-order rate constant which can be obtained by fitting each curve to the analytical approximations, showed in Table 1. As a result, the apparent first-order rate constant k_{eff} decreases with increasing the intensity of illumination.

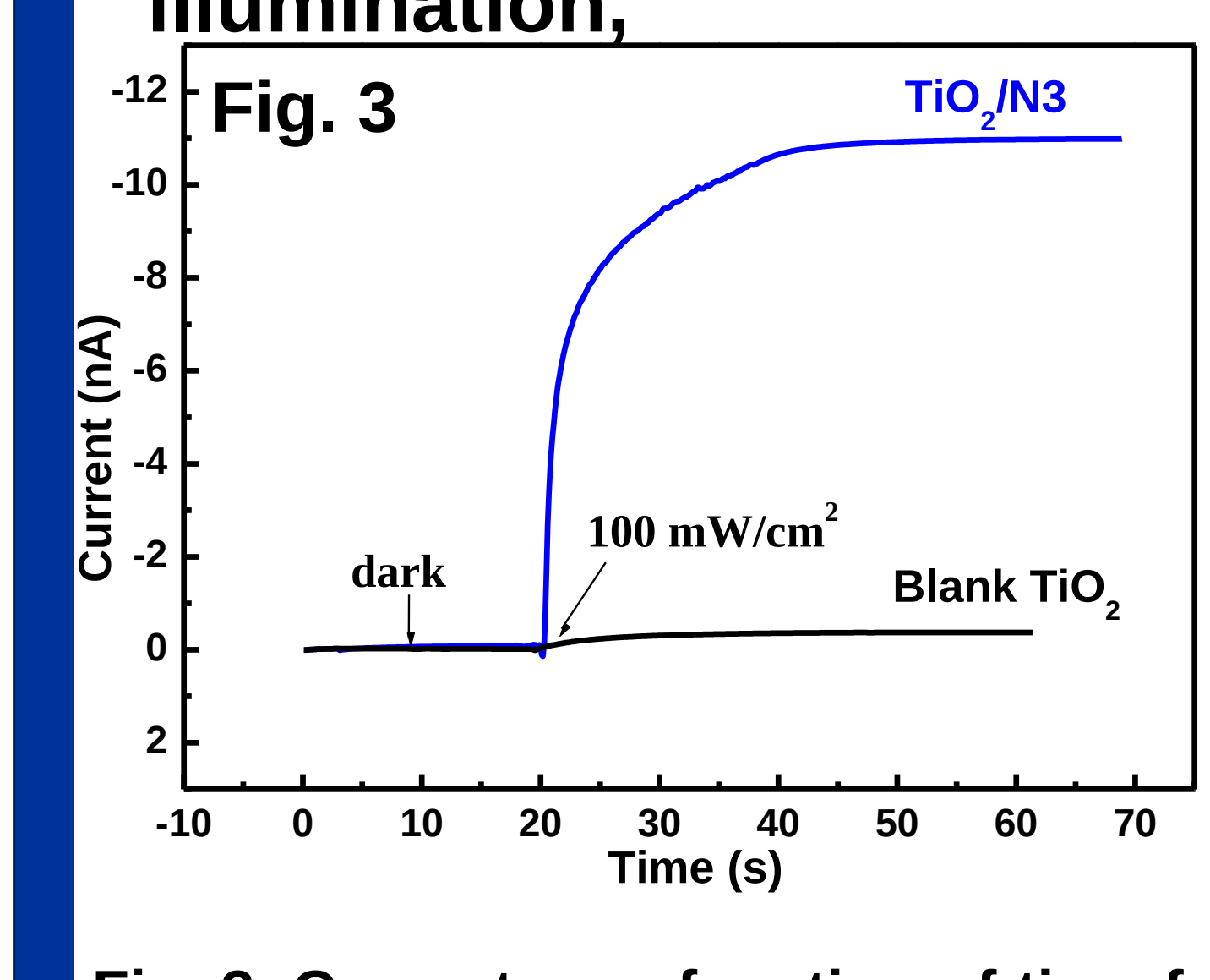


Fig. 3. Current as a function of time for N3-dye-sensitized and blank TiO_2 electrodes. The surfaces were illuminated for 20 seconds.

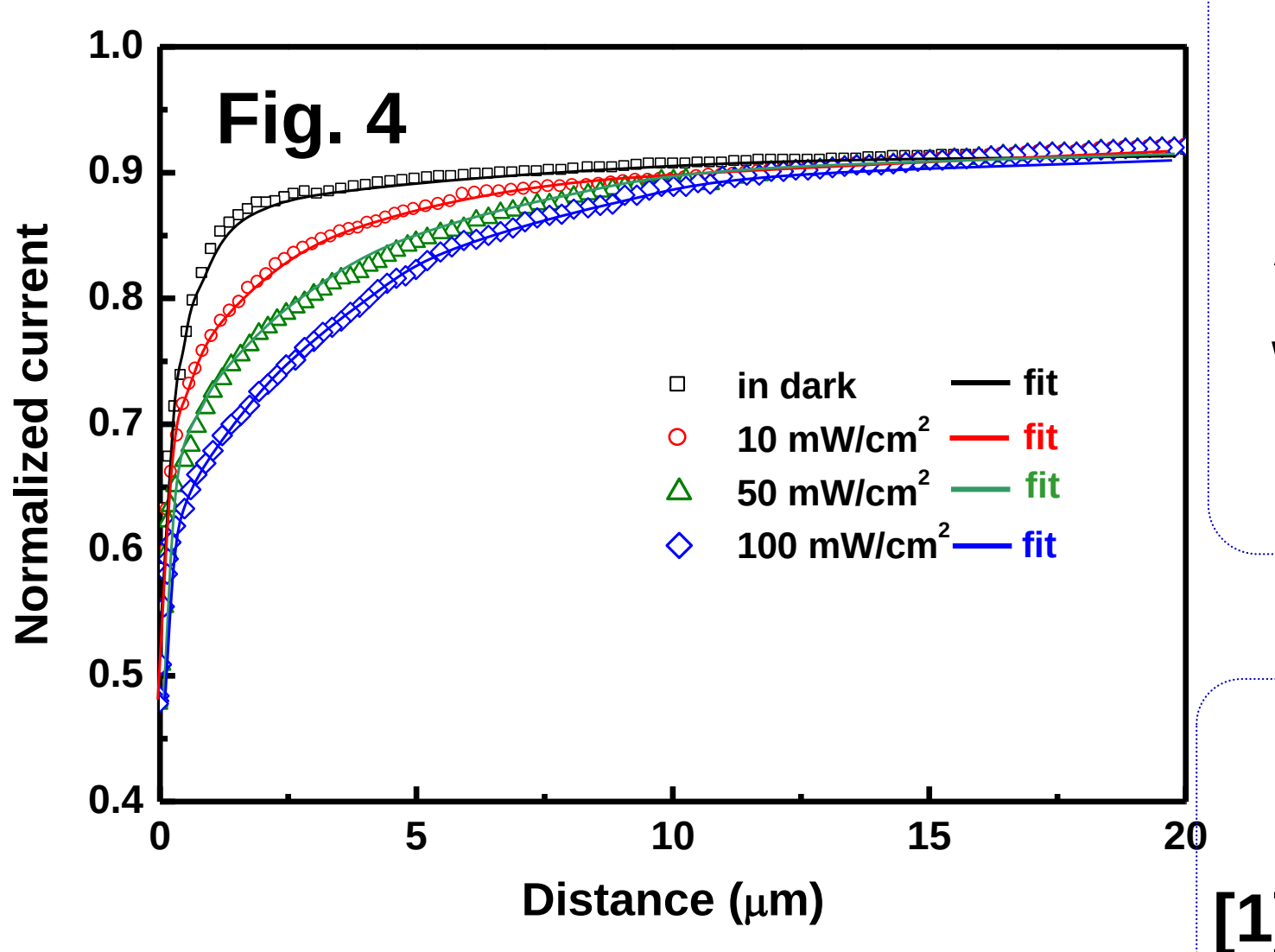


Fig. 4. Normalized SECM feedback approach curves for the approach of a Pt disk electrode, (r_T=5 μm)

$$I_T(L) = I_{T,ins}(L) + \left(1 - \frac{I_{T,ins}(L)}{I_{T,cond}(L)}\right) I_s(L) \qquad (1)$$

$$I_{T,ins}(L) = \frac{1}{0.292 + \frac{1.5151}{L} + 0.6553\exp(\frac{-2.4035}{L})} \qquad (2)$$

$$I_{T,cond}(L) = 0.68 + \frac{0.78377}{L} + 0.3315\exp(\frac{-1.0672}{L}) \qquad (3)$$

$$I_s(L) = \frac{0.78377}{1 + \frac{1}{\kappa L}} + \frac{0.68 + 0.3315\ \exp(\frac{-1.0672}{L})}{1 + \frac{\frac{11}{\kappa L} + 7.3}{110 - 40L}} \qquad (4)$$

Table 1. Normalized apparent heterogeneous first-order rate κ and apparent heterogeneous first-order rate *k*

	D (10^{-6} cm²/s)	κ	k_{eff} (10^{-3}cms^{-1})
In dark		0.175	2.98
10 mW/cm²	8.5	0.138	2.34
50 mW/cm²		0.113	1.92
100 mW/cm²		0.07	1.21

Conclusions

The application of SECM for the investigation of dye-sensitized nano-crystalline TiO_2 films was carried out. It is demonstrated that the theoretical modeling of SECM can provide the apparent first-order rate constant. In the future we will apply the method to discriminate the redox function of different dyes used in DSSCs.

Acknowledgments

This work was financially supported by the Academia Sinica, Taipei, Taiwan. The work was also partially supported by the National Research Council of Taiwan.

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