Sol-gel approach for the growth of vertically aligned 3D–TiO\textsubscript{2} nanorod arrays as an efficient photoanode for high-performance dye-sensitized solar cells
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Abstract
In this study, a facile, low cost, and scalable sol-gel method has been proposed for the coating of ultra-thin layer of TiO\textsubscript{2} on FTO substrate as a seed layer for the growth of 3D-TiO\textsubscript{2} nanorod (3D-TiO\textsubscript{2}-NR) arrays on FTO. Then, two-step hydrothermal process including nanorod growth and the chemical etching treatment was proceed for the fabrication of FTO/3D-TiO\textsubscript{2}-NR photoanodes. The thickness of the deposited TiO\textsubscript{2} in FTO/TiO\textsubscript{2}-sg samples was measured with small angle X-ray scattering (SAXS) technique and it was obtained to be 21.3 nm. FE-SEM and TEM techniques were used for the morphological characterization of 3D-TiO\textsubscript{2}-NR and it was obtained that the tightly adhered film of vertically aligned 3D-TiO\textsubscript{2}-NR with two-layer nanostructuring is formed with a cubic base and a nanorods head. Finally, DSSCs with iodine-based and cobalt (II/III) tris (2,2'-bipyridine) complex-based electrolytes with two different photoanodes including 3D-TiO\textsubscript{2}-NR and TiO\textsubscript{2}-NP were assembled and their photovoltaic characteristics were investigated. For [Co(bpy)\textsubscript{3}]^{2+/3+} shuttle-based DSSC, the obtained power conversion efficiency (\(\eta\)) was about 3.5% with J\textsub{sc} of 9.36 mA cm\textsuperscript{-2} in 3D-TiO\textsubscript{2}-NR-based DSSC, while \(\eta\) of TiO\textsubscript{2}-NP-based DSSC was about 1.4%. The results showed that employing 3D-TiO\textsubscript{2}-NR-based photoanode in DSSCs with bulky electron shuttles remarkably improves the photovoltaic characteristics of DSSCs. Electrochemical impedance spectroscopic (EIS) studies also showed the lower charge transfer resistances for DSSCs with nanorod-based photoanode building blocks.

Keywords: DSSC, TiO\textsubscript{2} nanorod arrays, electron shuttle, adhesion, sol-gel, cobalt (II/III) tris (2,2'-bipyridine) complexes
Introduction

With the strong demand in green and renewable energies, solar energy is attracting global attention [1-3]. Dye-sensitized solar cells (DSSCs) have rapidly emerged as a promising alternative to conventional silicon photovoltaics due to their combined benefits of low cost, simple fabrication, environmentally friendly operation and scalable components [6-9]. A high-performance photoanode is expected to possess a large specific surface area for sufficient dye loading, a direct pathway for fast transport of photo-generated electrons, a pronounced light-scattering effect and a low charge recombination in the trapping-detrapping site [10-12]. Although the randomly dispersed TiO$_2$ nanoparticles provide a large specific surface area for sufficient dye loading, but create numerous grain boundaries which hinder the facile electron transport through the thin film and increase the charge recombination. To overcome this problem, a well-aligned TiO$_2$ nanostructure arrays such as 1D TiO$_2$ nanorod arrays [13-15] and TiO$_2$ nanotube arrays (TNAs) [16-19] have been proposed which can provide a direct pathway for electron transport. However, these ideal nanostructures are subject to a vital shortcoming, i.e. a low surface area when compared with a TiO$_2$ nanoparticle photoanode of similar thickness, which can lead to insufficient dye absorption and result in lower cell performance. To increase the surface area, usually the post-etching treatments result in TiO$_2$ paper-like films detached from the conductive glass substrate [11,13]. So, to fabricate the photoanode, the detached TiO$_2$ film should be carefully transferred to a new FTO glass substrate coated with ultra-thin adhesive TiO$_2$ paste. The partial etching of the nanorod arrays in TiO$_2$/substrate interface and the existence of nanoparticle-based TiO$_2$ paste between nanorods and FTO substrate will act as the charge recombination sites in the interfaces and increase the charge transfer resistance.

In this study, we proposed a facile, low cost, and scalable sol-gel method to coat an ultra-thin layer of TiO$_2$ on FTO substrate as a seed layer for the growth and post-treatment of TiO$_2$ nanorod arrays. In fact, before the two-step hydrothermal growth and the chemical post-etching treatment of TiO$_2$ nanorods as well as TiCl$_4$ post-treatment, the sol-gel method was used for the deposition of about 21 nm of TiO$_2$ thin film on FTO glass substrate to prepare FTO/TiO$_2$–sg. This is the first report on the growth of tightly adhered TiO$_2$ nanorod
arrays on FTO by the aid of sol-gel method. The results showed that the sol-gel derived seed layer on FTO/TiO$_2$-sg has a pivotal role for the tightly adhesion of TiO$_2$ nanorod arrays on FTO. So, the resulted 3D–TiO$_2$ nanorod arrays with high surface area is expected to provide a direct pathway for the electron transport with minimized charge recombination sites in nanorod/FTO interface and decrease in the charge transfer resistance. Finally, DSSCs with iodine- and cobalt complex-based electrolytes were assembled and their characteristics were investigated as well. Based on the results, it was established that a replacement of the photoanode building-blocks from commercial TiO$_2$ nanoparticle to tightly adhered vertically aligned 3D–TiO$_2$ nanorod arrays enabled a remarkable improvement in the ionic diffusion of cobalt(II/III) tris(2,2'-bipyridine) complexes toward the photoelectrode.

2. Experimental

Fabrication of FTO/3D–TiO$_2$-NR photoanode

Sol-gel derived TiO$_2$ thin films on FTO (FTO/TiO$_2$–sg) were prepared via a facile sol-gel method. At first, TiO$_2$ sol was prepared by mixing titanium $n$-butoxide (1.15 mL) with absolute ethanol (11.50 mL). After 0.5 h stirring, 4 drops of the concentrated nitric acid were added to the sol as catalyst. The mixed final sol was stirred for 2 h and then agitated for 24 h [20]. The deposition process was performed by using a dip-coating method by dipping the pre-cleaned FTO (1.5×1.5 cm$^2$) into the prepared TiO$_2$ sol for 60 s and pulling it up slowly. The deposited film was dried at 120 °C for 1 h and then annealed in air atmosphere by using the thermal programming with the up ramp rate of dT/dt = 4 °C/min from $T_{\text{Initial}}$ = 25 °C to $T_{\text{Final}}$ = 500 °C, 120 min dwell and then, down ramp rate of 4 °C/min to room temperature. The fabricated TiO$_2$ coated FTO glass substrate is designated as FTO/TiO$_2$–sg sample.

For the fabrication of 3D–TiO$_2$ nanorod electrode (FTO/3D–TiO$_2$-NR), two-step hydrothermal method was used as growth and chemical etching treatment steps. In the hydrothermal nanorod growth step [21], at first, a solution of HCl:H$_2$O (1:1, v/v) was
prepared by mixing 15.0 ml of concentrated hydrochloric acid (HCl 35%) with 15.0 ml of ultra-pure deionized water (DI water, Millipore, 18 MΩ) under the magnetic stirring. Then, 0.9 ml of titanium \( n \)-butoxide was added to the mixture and stirred until a clear solution was obtained. The solution was then transferred to a pre-cleaned 100-mL Teflon-lined stainless steel autoclave, and a FTO/TiO\(_2\)-sg film was immersed horizontally into the solution with the coated side facing up and heated to 150 °C for 10 h. After cooling to room temperature, the film was rinsed with DI water and ethanol, and dried in air atmosphere. In the hydrothermal chemical etching step [13], a solution of HCl:H\(_2\)O was prepared by mixing 11.0 ml of concentrated HCl with 5.0 ml of DI water. The solution was transferred to a 50-mL Teflon-lined stainless steel autoclave, and a prepared TiO\(_2\) nanorod film was immersed vertically into the solution and heated to 150 °C for 12 h. After cooling to room temperature, the obtained 3D–TiO\(_2\) nanorod film was rinsed with DI water and ethanol, and dried in air atmosphere. Finally, the electrode was annealed in air atmosphere by using the thermal programming with the up ramp rate of \( \frac{dT}{dt} = 4 \, ^\circ\text{C}/\text{min} \) from \( T_{\text{initial}} = 25 \, ^\circ\text{C} \) to \( T_{\text{final}} = 500 \, ^\circ\text{C} \), 120 min dwell and then, down ramp rate of 4 °C/min to room temperature.

**Composition of the electrolytes**

In this study, two types of electrolytes were used in DSSC fabrication: iodine-based and cobalt complex-based electrolytes. The iodine-based electrolyte contained lithium iodide (LiI, 0.10 M), iodine (I\(_2\), 0.010 M), 4-\( \text{tert} \)-butylpyridine (TBP, 0.50 M), butyl methyl imidazolium iodide (BMIMI, 0.60 M), and guanidinium thiocyanate (GuSCN, 0.10 M) in a mixture of acetonitrile (CH\(_3\)CN):valeronitrile (n-C\(_4\)H\(_9\)CN) (85:15 v/v) solvent.

For the preparation of cobalt complex-based electrolyte, at first, cobalt(II) tris(2,2'-bipyridine) and cobalt(III) tris(2,2'-bipyridine) complexes were synthesized [8]. Briefly, for the synthesis of [Co(bpy)\(_3\)](PF\(_6\))\(_2\) complex, a solution containing 2,2'-bipyridine (0.5154 g of 2,2'-bipyridine (bpy) in a minimum amount of methanol) was added dropwise to an stirred solution of Co\(^{2+}\) (0.2379 g of CoCl\(_2\).6H\(_2\)O dissolved in 10.0 mL of DI water) and the reaction was allowed to proceed with constant stirring under the reflux conditions for 2 h. An excess amount of ammonium hexafluorophosphate (NH\(_4\)PF\(_6\)) was added to the
solution to precipitate [Co(bpy)₃](PF₆)₂ complex. The obtained solid was filtered, washed with methanol and ethanol, and dried in vacuum oven for 6 h. For the synthesis of [Co(bpy)₃](PF₆)₃ complex, a solution containing 2,2'-bipyridine (0.550 g of 2,2'-bipyridine (bpy) in a minimum amount of methanol) was added dropwise to an stirred solution of Co²⁺ (0.250 g of CoCl₂.6H₂O dissolved in 10.0 mL of DI water) and the mixture was stirred for 5 min. Then, 4.0 mL of H₂O₂ (30%) and 4.0 mL of HCl (30%) were added to the mixture and the reaction was allowed to proceed with constant stirring under the reflux conditions for 3 h. Finally, an excess amount of NH₄PF₆ was added to the solution to precipitate [Co(bpy)₃](PF₆)₃ complex. The obtained solid was filtered, washed with methanol and ethanol, and dried in vacuum oven for 6 h. The cobalt complex-based electrolyte consisted of 0.20 M [Co(bpy)₃](PF₆)₂ complex, 0.02 M [Co(bpy)₃](PF₆)₃ complex, 0.50 M TBP, and 0.10 M LiClO₄ in acetonitrile.

3. Results and discussion

**Morphology, surface analysis, and characterizations**

To fabricate the 3D–TiO₂ nanorod photoanodes (3D–TiO₂-NR), at first, an ultra-thin layer of TiO₂ film was coated on FTO glass substrate as a seed layer via sol-gel method to prepare FTO/TiO₂–sg sample. The SEM image of the prepared FTO/TiO₂–sg sample (Fig. 1) shows that the TiO₂ thin film has been uniformly coated on FTO. Atomic force microscopy (AFM) was also used for the analysis of surface topography of FTO/TiO₂–sg sample. According to the results, the measured average surface roughness of thin film was 6.2 nm and the mean height of the deposited material on FTO was between 19 nm to 28 nm. As it is clear from the SEM and AFM images, by using sol-gel method, a very uniform thin film of TiO₂ has been coated on FTO as a seed layer and has a pivotal role for the tightly adhesion of TiO₂ nanorod arrays on FTO. The average crystal seed of TiO₂ was estimated by AFM to be about 160 nm.
To investigate the thickness, roughness, and the crystal phase of the coated film, the small angle X-ray scattering (SAXS) technique was used. As shown in Fig. 2a, the characteristic diffraction peaks of anatase TiO$_2$ is feasible in pattern, and according to the SAXS results (Fig. 2b), the thickness and roughness of the deposited TiO$_2$ thin film are 21.3 nm and 2.7 nm, respectively, which confirms the AFM results.

The surface morphology of the samples was characterized by FE-SEM and TEM (Fig. 3). The size of the TiO$_2$ foursquare side is about 400 nm with about 3-4 μm long. In the chemical etching step (second hydrothermal process), according to the hydrolysis of TiO$_2$ in acidic media (TiO$_2$ +4H$^+$ →Ti$^{4+}$ + 2H$_2$O), the core of each square-shaped nanorod is hydrolyzed, and in the top of nanorod, several nanorods with a diameter of about 30 nm is formed. These results have been reported in several works [11, 13]. However, by using the FTO/TiO$_2$–sg as a substrate, after the chemical etching step, a tightly adhered film of vertically aligned 3D–TiO$_2$ nanorod was obtained (Fig. 3f). It means that the sol-gel derived ultra-thin film has a crucial role for the tight adhesion of nanorods on FTO substrate during the two-step hydrothermal processes. Based on this finding, it is expected that the synthesized structure brings a remarkable improvement in the electron transfer rate, lack of contact between the redox mediator in the electrolyte and FTO substrate, and decrease in the charge recombination sites in the FTO/TiO$_2$ interfaces. EDX elemental mapping and diffuse reflectance spectra (DRS) of photoanode and sensitized photoanode were investigated. In the EDX elemental mapping of sensitized photoanode (Fig. 4), the Ru, C, N and S elements come from dye N719.
The diffuse reflectance spectra (DRS) of photoanode and sensitized photoanode were also investigated (Fig. 5). The UV-Vis absorption spectra of dye N719 shows two main absorption peaks at $\lambda_{\text{max}}$ of 388 nm and 535 nm. According to DRS spectra of pristine photoanode, the absorption edge of TiO$_2$ is about 380 nm, in good agreement with its energy band gap ($E_g = \sim 3.4$ eV). However, DRS spectra of dye-sensitized FTO/3D–TiO$_2$-NR photoanode shows the absorption peak of N719, confirming that the dye was loaded on photoanode.

**Fig. 5**

**Photovoltaic measurements of DSSCs**

At the first stage, a common iodine-based electrolyte was injected to DSSC devices. Then, the photovoltaic performances of these fabricated DSSCs were investigated by measuring the current density ($J$, mA cm$^{-2}$) versus voltage ($V$) under the simulated sunlight irradiation (AM 1.5G, 100 mW cm$^{-2}$). **Fig. 6** presents the J-V curves of two DSSCs fabricated by different photoanodes and the injected iodine-based electrolyte. The detailed photovoltaic (PV) parameters including short-circuit photocurrent density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and efficiency ($\eta$) values of DSSCs are summarized in **Table 1**.

**Fig. 6**

These results can be mainly attributed to two factors including (i) the efficient photo-harvesting due to the high reflection of 3D-TiO$_2$-NR compared to the TiO$_2$ nanoparticles which increases the photon trapping time in the photoanode [8], and (ii) direct pathway of the electrons provided by vertically aligned TiO$_2$ nanorods [11] which are tightly adhered to FTO substrate. On the other hand, TiO$_2$ nanoparticles have higher surface area compared to 3D-TiO$_2$ nanorods which increases dye loading on photoanode and consequently, causes
higher photo-harvesting. So, based on the PV parameters in Table 1, the two factors mentioned above make nanorods to overcome the drawbacks of its lower surface area.

**Table 1**

As reported, when the bulky mediators such as cobalt \((\text{bpy})_3\) complexes are used in the electrolyte, due to their lower diffusion coefficients in the electrolyte, the lower efficiencies for the constructed DSSC are unavoidable [8, 22-24]. To examine the feasibility of the proposed FTO/3D–\(\text{TiO}_2\)-NR as photoanode building blocks in DSSCs containing bulky redox mediators, \([\text{Co(bpy)}_3]^{2+/3+}\) complexes-based electrolyte was injected to the assembled DSSC devices. Finally, the photovoltaic performances of the fabricated DSSCs were investigated (**Fig. 7, Table 2**).

**Fig. 7, Table 2**

According to the results, all of the PV parameters of DSSC-4 which is fabricated by FTO/3D–\(\text{TiO}_2\)-NR photoanode have been improved significantly compared to DSSC with common \(\text{TiO}_2\) nanoparticles as photoanode building blocks (DSSC-3). Interestingly, \(\eta\) and \(J_{sc}\) of DSSCs-4 are improved 2.5 and 2.43 times respectively. The enhanced efficiency in DSSC-4 is mainly due to the restricted recombination reaction in photoanodes with 3D–\(\text{TiO}_2\)-NR building blocks [16, 27].

From the above-mentioned results, it can be concluded that 3D–\(\text{TiO}_2\)-NR as photoanode building blocks could provide an adequate inter-space region in microscale as ionic diffusion freeways allowing a rapid diffusion and storage of the bulky cobalt redox complexes [8, 24]. In fact, the 3D–\(\text{TiO}_2\)-NR well compensates the slow diffusion of \([\text{Co(bpy)}_3]^{2+/3+}\) complexes in the limited space of the foursquare building-blocks with the nanorod end. This demonstrates that 3D–\(\text{TiO}_2\)-NR is an ideal alternative photoanode candidate for the fabrication of DSSCs with bulky mediators for practical applications.
**Electrochemical impedance spectroscopy**

In order to get more insight into the charge transfer resistance of the fabricated DSSCs, EIS was used. Figures 8 and 9 show the Nyquist plots, their corresponding equivalent circuits, Bode plots and phase plots of the fabricated DSSCs obtained in open circuit voltage in the frequency range of 0.1 Hz to 100 kHz under the light illumination conditions. Generally, the first gap ($R_s$) is attributed to the sheet resistance of the FTO substrate and the contact resistance between FTO and TiO$_2$. Also, two semicircles can be expected in EIS, the first semicircle observed in the high-frequency region (left side of the diagram) indicates the charge transfer resistance at the platinum electrode/electrolyte interface ($R_{pt}$) and the second semicircle observed in the low-frequency region (right side of the graph) is attributed to the charge transfer resistance ($R_{ct}$) at the TiO$_2$/dye/electrolyte interface [13]. Based on the impedance spectra and fitting the data, the value of $R_s$, $R_{ct}$ and $R_{pt}$ for the fabricated DSSCs are presented in Table 3.

Fig. 8a shows the Nyquist plots for DSSCs fabricated with iodide/triiodide mediator in solution. As it is clear, the charge transfer resistances of $R_s$, $R_{ct}$ and $R_{pt}$ for DSSC-2 with FTO/3D–TiO$_2$-NR photodanode building blocks are lower than that of DSSC-1 indicating the increase in the electron transfer rate as well as the easier diffusion of redox couple in the electrolyte/electrodes interfaces. For DSSCs fabricated with [Co(bpy)$_3$]$^{2+/3+}$ complex shuttles, as Fig. 9a shows, the lower charge transfer resistances for DSSC-4 indicates the suitable structural matching of photoanode building block and the lower diffusion coefficient of bulky [Co(bpy)$_3$]$^{2+/3+}$ complexes. In fact, the nanorod structure of 3D-TiO$_2$-NR provides an adequate inter-space region in microscale as ionic diffusion freeways to easier diffusion of the redox shuttles. Therefore, it can be concluded that employing the nanorode structure instead of the nanoparticle as photoanode building block would greatly overcome the diffusion problem of the bulky redox shuttles.

**Fig. 8, Fig. 9, Table 3**
The overall charge transfer scheme for the DSSCs is shown in Fig. 10.

4. Conclusions
In this study, a facile, low cost, and scalable sol-gel method was proposed to coat an ultrathin layer of TiO$_2$ on FTO substrate as a seed layer for the growth of 3D-TiO$_2$ nanorod arrays. The sol-gel derived seed layer on FTO/TiO$_2$-sg had a pivotal role for the tightly adhesion of TiO$_2$ nanorod arrays grown on FTO and the resulted 3D–TiO$_2$–NR provided a direct pathway for the electron transfer in nanorod/FTO interface. The 3D–TiO$_2$–NR nanostructure was used as photoanode building block in the fabrication of DSSCs based on iodide/triiodide as well as [Co(bpy)$_3$]$^{2+/3+}$ redox shuttle and the photovoltaic parameters of fabricated DSSCs were compared with DSSCs with TiO$_2$–NP photoanode. Due to the rapid diffusion of redox couple especially [Co(bpy)$_3$]$^{2+/3+}$ shuttles in 3D–TiO$_2$–NR structure, the photovoltaic parameters were improved significantly in DSSC-4. The rapid diffusion of cobalt redox couple in 3D–TiO$_2$–NR structure leads to the remarkable reduction in the charge transfer resistance in DSSC-4.

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Figure Captions

Fig. 1. SEM image (a) and AFM image analysis (b-d) of FTO/TiO$_2$–sg sample
**Fig. 2.** (a) X-ray diffraction pattern (grazing incidence: 0.3°ω) of FTO/TiO₂–sg sample. The theoretical reflection positions of TiO₂ (anatase) and SnO₂ (rutile) are indicated by vertical lines. (b) Reflectometry measurement (SAXS) of FTO/TiO₂–sg sample.

**Fig. 3.** FE-SEM images of (a) TiO₂ nanorod after the first hydrothermal process (nanorod growth), (b,c) 3D–TiO₂ nanorod after the second hydrothermal process (chemical etching), (d) 3D–TiO₂ nanorod after TiCl₄ post treatment, (e) TEM image of a needle-like TiO₂ nanorod, (f) photograph of the resulted FTO/3D–TiO₂-NR photoanode (left) 3D–TiO₂ film (right).

**Fig. 4.** EDX elemental mapping of N719 sensitized FTO/3D–TiO₂-NR photoanode

**Fig. 5.** UV-Vis spectra of N719 and DRS spectra of 3D-TiO₂-NR and dye sensitized 3D-TiO₂-NR photoanodes

**Fig. 6.** J-V curves of the fabricated DSSCs with different photoanodes: DSSC-1 with FTO/TiO₂-NP and DSSC-2 with FTO/3D–TiO₂-NR photoanodes. The injected electrolyte was common iodine-based electrolyte and the experiments were performed under AM 1.5G simulated solar irradiation with 100 mW cm⁻².

**Fig. 7.** J-V curve of the fabricated DSSCs with different photoanode: (DSSC-3) FTO/TiO₂-NP, (DSSC-4) FTO/3D–TiO₂-NR. The injected electrolyte was cobalt complex-based electrolyte and the experiments were performed under AM 1.5G simulated solar irradiation with 100 mW cm⁻².

**Fig. 8.** The Nyquist plot (a), Bode plot (b) and the phase plot (c) of DSSCs fabricated with different photoanods including DSSC-1 (TiO₂-NP) and DSSC-2 (TiO₂-3D-NR). The injected electrolyte in the cells contained iodide/triiodide redox mediator.

**Fig. 9.** The Nyquist plot (a), Bode plot (b) and the phase plot (c) of DSSCs fabricated with different photoanods including DSSC-3 (TiO₂-NP) and DSSC-4 (TiO₂-3D-NR). The injected electrolyte in the cells contained redox shuttle (Co(bpy)₃)²⁺/³⁺ complexes.

**Fig. 10.** Overall charge transfer scheme. Charge transfer scheme for the DSSCs fabricated with [Co(bpy)₃]²⁺/³⁺ - based electrolyte.
Fig. 4

Fig. 5

Absorbance (a.u.)

Wavelength (nm)
**Fig. 6**

![Graph showing current density versus voltage for DSSC-1 and DSSC-2](image)

**Fig. 7**

![Graph showing current density versus voltage for DSSC-3 and DSSC-4](image)
Fig. 9

a: Complex plane plot showing the impedance (Z') and Z'' for DSSC-3 and DSSC-4.

b: Log-log plot of the electrochemical impedance spectroscopy (EIS) showing Log Z at different frequencies for DSSC-3 and DSSC-4.

c: Phase angle (º) vs. Log frequency (Hz) plot for DSSC-3 and DSSC-4.

Fig. 10

Diagram showing the electrochemical system with labels for different components including FTO, GO, NT19, [Co(bpy)3]³⁺, and Co(bpy)³⁺ with electrode connections.
Table 1. Photovoltaic parameters of DSSCs based on different photoanodes with iodine-based electrolytes.

| DSSC   | Photoanode   | Mediator | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | Fill factor (FF) | Efficiency ($\eta$, %) |
|--------|--------------|----------|--------------|--------------------------|------------------|------------------------|
| DSSC-1 | FTO/TiO$_2$-NP | $I^-/I_3^-$ | 0.69         | 10.7                     | 0.63             | 4.63                   |
| DSSC-2 | FTO/3D–TiO$_2$-NR | $I^-/I_3^-$ | 0.75         | 9.6                      | 0.58             | 4.16                   |

Table 2. Photovoltaic parameters of DSSCs based on different photoanodes with cobalt complex-based electrolytes.

| DSSC   | Photoanode   | Mediator           | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | Fill factor (FF) | Efficiency ($\eta$, %) |
|--------|--------------|--------------------|--------------|--------------------------|------------------|------------------------|
| DSSC-3 | FTO/TiO$_2$-NP | [Co(bpy)$_3$]$^{2+/3+}$ | 0.62         | 3.84                     | 0.59             | 1.4                    |
| DSSC-4 | FTO/3D–TiO$_2$-NR | [Co(bpy)$_3$]$^{2+/3+}$ | 0.64         | 9.36                     | 0.58             | 3.5                    |

Table 3. Details of the resistance values of the fabricated DSSCs

| DSSC   | Photoanode   | Mediator           | $R_s$ (Ω) | $R_{pt}$ (Ω) | $R_{ct}$ (Ω) |
|--------|--------------|--------------------|-----------|--------------|--------------|
| DSSC-1 | FTO/TiO$_2$-NP | $I^-/I_3^-$        | 7.0       | 151          | 421          |
| DSSC-2 | FTO/3D–TiO$_2$-NR | $I^-/I_3^-$       | 2.5       | 47           | 71           |
| DSSC-3 | FTO/TiO$_2$-NP | [Co(bpy)$_3$]$^{2+/3+}$ | 0.5       | 289          | -            |
| DSSC-4 | FTO/3D–TiO$_2$-NR | [Co(bpy)$_3$]$^{2+/3+}$ | 0.7       | 79           | 1616         |