Effect of Titanium Coating on the Structural and Optical Properties of TiO_2 Thin Films for Improved Performance in Dye-Sensitized Solar Cells

R. Jeba Beula, Suganthi Devadason and V. Mahesh Kumar

Abstract In favor of enhancing the performance of TiO_2 photoanode-based dye sensitized solar cells (DSSCs), a thin layer of titanium was coated on Indium doped tin oxide (ITO) conductive glass substrate prior to the coating of TiO_2 by using sol-gel spin coating technique. Titanium coating was obtained by DC sputtering method using titanium target and its effect on the structure, morphology of TiO_2 and the photovoltaic properties of the subsequent DSSCs were studied. Porous morphology was observed in the TiO_2 film with titanium coating. The photoelectric conversion efficiency of DSSC based on TiO_2 with titanium coating is larger than that without titanium coating. An efficiency of 3 % was obtained for titanium coated TiO_2 electrode. The improvement of the solar cell may be due to the increase in dye adsorption of TiO_2 thin film with titanium coating. In this work, the novelty lies in the role of titanium which is for the first time coated beneath the TiO_2 film resulting in the improved structure and morphology of the photo anode and thereby an enhanced DSSC efficiency.

1 Introduction

The DSSC with thick and porous nanocrystalline electrode is the most affordable photo-electrochemical system for better adsorption of dye molecules owing to their wide surface area. Exclusive studies on the properties and various applications of metal oxide semiconductors namely TiO_2, SnO_2, and ZnO are well documented in the literature. TiO_2, however has been widely explored for solar cell fabrication [1, 2]. TiO_2 with a bandgap of 3.2 eV is found to exhibit enhanced electrical and optical properties for the three well known crystalline structures (rutile, anastase and brookite) [3, 4]. An irradiated DSSC injects electrons and holes from the dye

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molecule into TiO_2 band gap and electrolyte respectively [5, 6]. Increase in electron injection and optical absorption are the key factors for the improved efficiency of the solar cells which however requires more porosity in the TiO_2 film [7–9].

Many techniques have been employed to prepare high-quality TiO_2 films, including pulsed laser deposition (PLD), magnetron sputtering, atomic layer deposition and sol-gel method [10–12]. The sol-gel method seems best choice among others since it does not involve high temperature requirement shunning unwanted crystallite structure creation that is not appropriate for absorbing solar energy [13, 14]. On the other hand, sol-gel processes suffer from a serious problem wherein increase of thickness of the deposited film (>1 μm) creates crack formation due to capillary stress and shrinkage during heat treatment [15]. It is necessary to deposit thick film without any cracks for better efficiency of solar cell. Some groups [16, 17] reported that a compact TiO_2 blocking layer made up of Titanium tetraisopropoxide between ITO substrate and TiO_2 nanoparticles can increase the photovoltaic efficiency. Therefore, In this paper we reported the uncomplicated methodology guiding to the deposition of well-adhered and thick TiO_2 electrodes by sputtering titanium layer between substrate and TiO_2 nanocrystalline particles. The influence of titanium layer on the structural and morphological properties of TiO_2 thin film and photovoltaic properties of resulting DSSC are also discussed.

2 Experimental Methods

2.1 Preparation of TiO_2 Sol

The precursor solution was prepared by mixing titanium (IV) butoxide (2.5 ml), triton x -100 (0.65 ml) and 10 ml of ethanol. In which, triton x-100 was used as a stabilizer to avoid precipitation in solution. After stirring this solution for half an hour, a mixture of 1 ml HNO_3, 10 ml ethanol, 10 ml distilled water and few drops of Poly ethylene glycol(PEG) was added drop by drop and magnetic stirring was sustained for 4 h. In addition to that the sol was aged for 2 h.

2.2 Deposition of TiO_2 Thin Film

Intium tin oxide (ITO) substrates were washed by means of aqua regia, acetone, ethanol and double distilled water successively for 15 min each in ultrasonic bath prior to coating. Titanium was coated on one of the ITO substrate by DC sputtering method (D.C Sputtering vacu Tech, Model-12A4D) using titanium target. The base pressure of the deposition chamber was kept at 6×10^{-5} torr during the process of coating Ti on the substrate. Then, bare ITO and Titanium coated ITO substrates were spin coated (HOLMARC/ HO-TH-05) by the prepared sol with the rotation

speed of 3000 rpm for 30 s followed by drying in air for 1 min. The process was repeated for 3–4 times so as to attain the desired thickness of the TiO_2 film. Then, the film was dried at 100 °C for half an hour and finally annealed at 450 °C for 1 h. TiO_2 films coated on bare ITO substrate is named as S1 and the film coated on Ti-coated ITO substrate as S2. Thickness of the film S1 and S2 are ~ 2 μm.

2.3 Fabrication of Solar Cell Devices

To complete dye adsorption, the TiO_2 photoanodes were dipped in a natural dye prepared by blackberry at room temperature for 24 h. The solar cells were fabricated by assembling the blackberry sensitized TiO_2 films as the working electrode and Ti-coated glass substrate as the counter electrode. Then the prepared polymer electrolyte using Polyethylene Glycol (PEG) in acitonitrile, glacial acetic acid (0.6 ml), 1-methyl-3-propylimidazolium Iodide (0.3 M), KI (0.1 M) and I_2 (0.05 M) was introduced into the gap between the TiO_2 working electrode and titanium counter electrode of the solar cell which was clamped firmly together using binder clips.

2.4 Working Principle of DSSC

Initially, in the mechanism of DSSC, the blackberry sensitizer absorbs the incident photon and gets injected into the conduction band of TiO_2 photoanode resulting in the oxidation of photosensitizer. These injected electrons gets diffused in the direction of back contact of ITO substrate and at last reaching the titanium counter electrode. The oxidized sensitizer accepts electrons from the polymer electrolyte containing redox (I_3^-/I^-) mediator [18].

2.5 Characterization Techniques

The structural and morphological characterization were carried out for prepared TiO_2 thin films by X-ray diffractometer with Cu Kα radiation of wavelength 1.5418 Å (Shimadzu XRD 6000) and Scanning Electron Microscope (Joel JSM6390) respectively . Optical characterization was carried out by UV-Visible spectrometer (JASCO UV Vis NIR, V-670) between 200 to 800 nm . Photovoltaic characteristics of the DSSCs were analyzed by electrochemical analyzer (CHI 6008). The photovoltaic performance parameters of DSSCs were measured using a 100 W Xenon light illumination with the light intensity of 35 mW/cm^2. The chosen area of dye adsorbed TiO_2 working electrodes was 0.25 cm^2. Electrochemical impedance

spectroscopy (EIS) was also performed by the same electrochemical analyzer in the frequency range of 40 Hz to 60 MHz under illumination.

3 Results and Discussion

3.1 Structural Studies

The crystal phase and crystallite size of the TiO_2 films was explored using X-ray diffractometer. Figure 1 illustrates the XRD pattern of S1 which shows amorphous phase of TiO_2 thin film. Again, Fig. 2 shows the diffraction pattern of S2 where the diffraction peaks located at 25.4°, 37.8°, 48.2° and 54° match to the (101), (004), (200) and (105) planes of the anatase phase (JCPDS No. 21-1272), indicating a formation of TiO_2 nanocrystalline nature. There was no peaks corresponds to Ti layer in the spectrum which clearly indicates that the Ti layer is fully oxidized during annealing at 450 °C. Thus Ti layer helps in the formation of nanostructured TiO_2 films of crystalline anatase structure without any impurities. The process of annealing is an important factor for the formation of the crystal phase and an annealing temperature of 450 °C favors the formation of anatase phase [19]. When comparing with the TiO_2 film consisted of rutile and brookite phase, TiO_2 film with anatase phase has the outstanding performance for DSSCs as reported [20]. The average crystallite size calculated by Scherrer formula using the (1 0 1) plane is found to be 10.8 nm for the film S2.

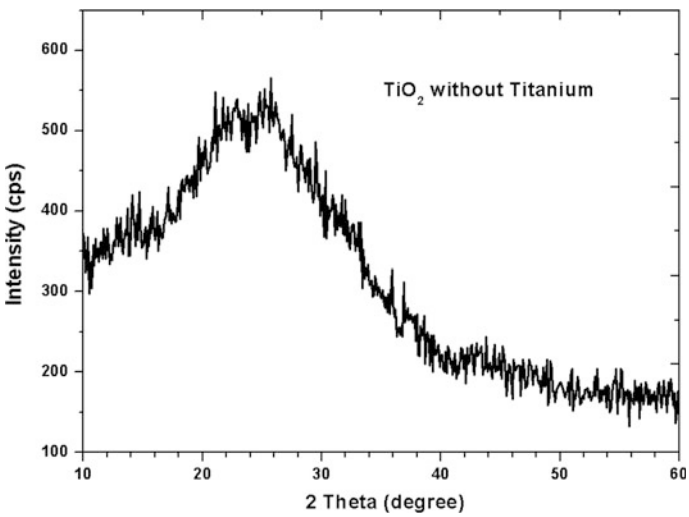

Fig. 1 XRD pattern of TiO_2 thin film without titanium layer

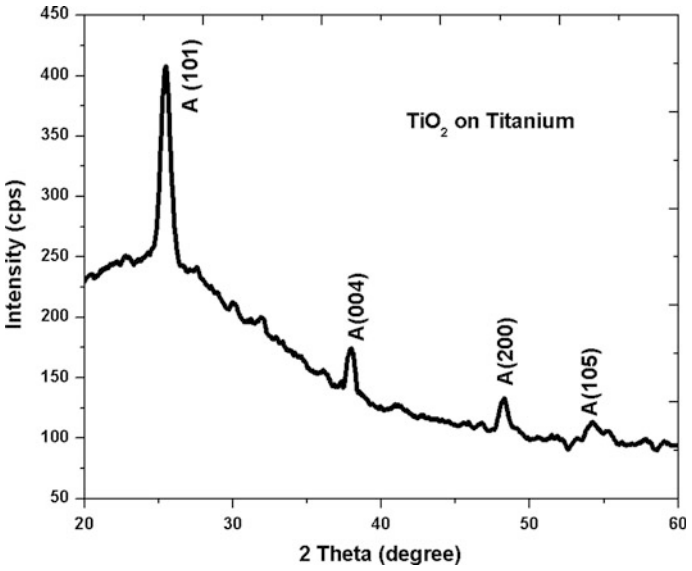

Fig. 2 XRD pattern of TiO_2 thin film with titanium layer

3.2 Morphological Studies

Figure 3a, b shows the surface morphology of the prepared TiO_2 thin films on bare ITO substrate in different magnifications. It can be observed that huge micro cracks appear in the TiO_2 film S1 which may be due to the higher thickness of the film forming cracks on annealing due to lattice mismatch between film and substrate, the same was reported by Ineta et al. [21]. Cracks formation may be due to the poor necking between TiO_2 particles as a result of shrinkage during the heat treatment which will lead to the poor performance of a cell. Therefore, it is necessary to develop the chemical connection between the TiO_2 nanoparticles and also to create the pores on the surface for a better performance of a solar cell.

To improve chemical connectivity between TiO_2 particles and its adherence to substrate, we sputtered Titanium on ITO substrate prior to the spin coating of TiO_2 sol. As thick Ti layer crack often or even peel of from the substrate a thin layer of Ti was coated on ITO substrate. By adding just one Ti layer on ITO substrate before the coating with TiO_2 solution, the morphology had largely changed. As shown in Fig. 3c, d, we successfully fabricated the TiO_2 film with pores on the surface without the formation of crack for the same thickness of the film as S1. The thin TiO_2 layer which was formed from titanium during annealing process binds the TiO_2 nanoparticles making its stronger or connects the TiO_2 nanoparticles with ITO substrate thereby supporting the collected electrons to travel much faster towards the substrate [22].

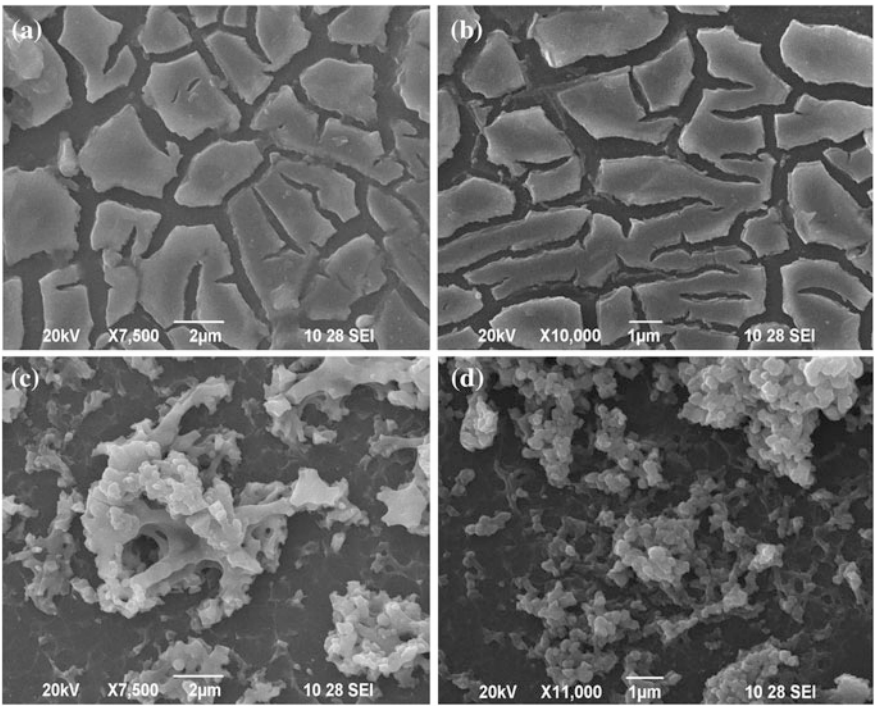

Fig. 3 SEM images of TiO_2 films without titanium layer (**a**) and (**b**) with titanium layer (**c**) and (**d**) in different magnifications

3.3 Optical Studies

Figure 4a, b represents the respective UV-Visible absorption spectra of TiO_2 films before and after sensitization with blackberry dye respectively. Before sensitization the spectral lines for both TiO_2 films show a single absorption band at about 300 nm representing the intrinsic transition between the valence band and conduction band [23]. From Fig. 4b it is obvious that, there was no change in the spectral line of S1 after the loading of dye. But the spectrum of S2 film shows increased absorbance at about 300 nm and a small absorbance at around 450 nm, indicating the increased dye loading amount which can drastically increase effective light absorption [24]. The dye molecule does not completely gets absorbed at the inner surface of porous TiO_2 film when the particle size in TiO_2 film with Ti-layer is comparable with the interparticle distance in the porous TiO_2. However, in our study due to large particle size the dye molecule penetration is much feasible into the porous TiO_2 layer in turn favoring more dye adsorption.

Figure 5a, b shows the graph for determining the direct band gap energy values of prepared samples using $\alpha = A(h\nu - E_g)^2$ equation, where α is the absorption coefficient as a function of frequency, $h\nu$ is the energy of incident photon with

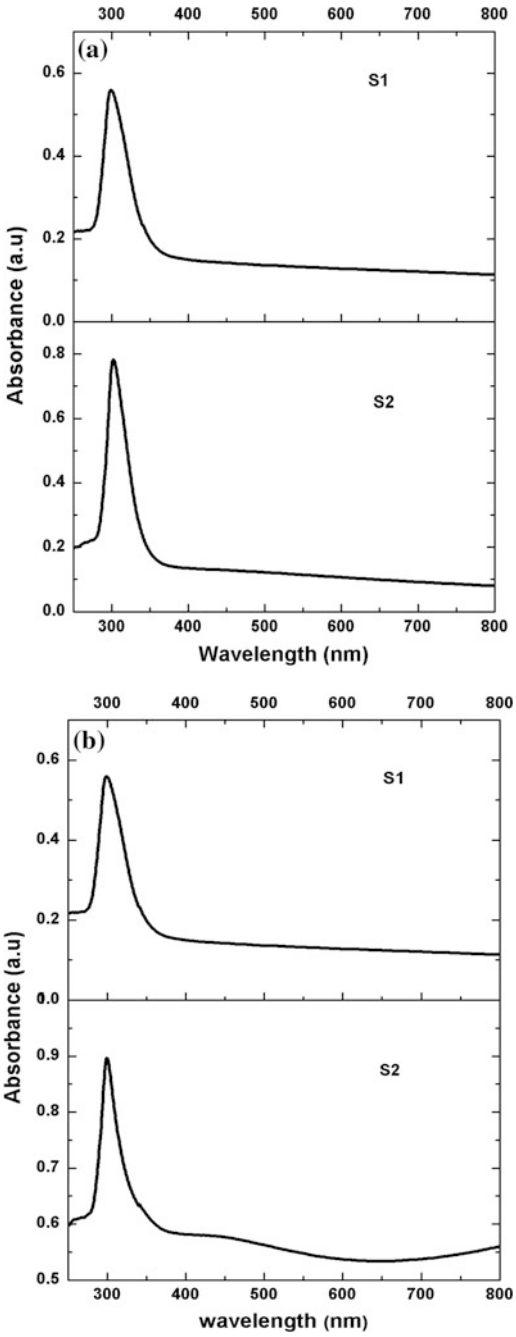

Fig. 4 Absorbance spectra of prepared TiO_2 films S1 (without titanium) and S2 (with titanium coating) (**a**) before and (**b**) after dye immersion

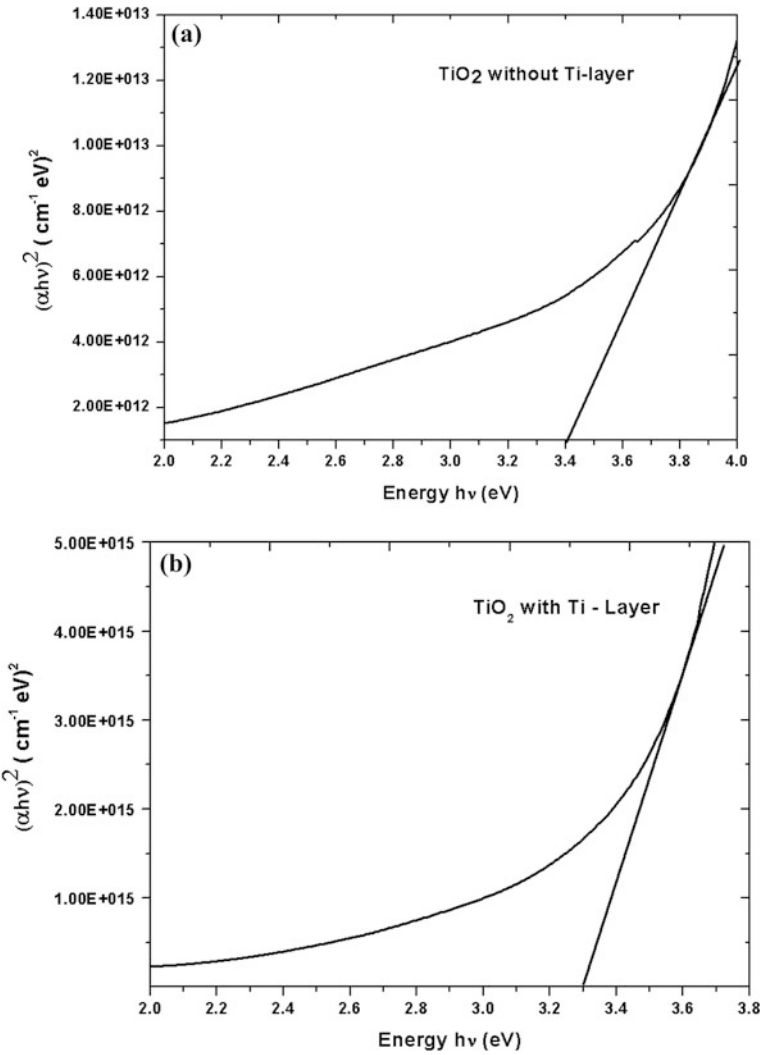

Fig. 5 Determination of direct band gap of prepared TiO_2 thin films

frequency ν, E_g is the optical band gap energy and A is the frequency independent constant for a direct transition. By extrapolating the linear part of the curve to zero, a direct band gap of 3.4 and 3.29 eV were obtained for TiO_2 thin films without (Fig. 5a) and with (Fig. 5b) titanium coating, respectively. Therefore, titanium coating improves the crystalline arrangement of TiO_2 film in the anatase nature and band gap value is red shifted to 3.29 eV which makes it suitable for photovoltaic application.

3.4 Photovoltaic Characteristics

Figure 6 shows the photovoltaic characteristics of fabricated DSSCs. From the J–V curve, the parameters of short circuit current density (J_{sc}) in mA/cm^2, open circuit voltage (V_{oc}) in volts, fill factor (FF) and energy conversion efficiency (η) in % were obtained for DSSC corresponds to S1 electrode are 0.07 mA/cm^2, 0.92 V, 0.15, and 1.2 % respectively. While the photovoltaic parameters of the DSSC that were obtained from S2 electrode are J_{sc} = 0.175 mA/cm^2, V_{oc} = 0.86 V, FF = 0.143 and the overall energy conversion efficiency is 3 %. When using bare ITO substrate the corresponding DSSC had low photovoltaic conversion efficiency due to the lattice mismatch between substrate and TiO_2 nanoparticles. However when using titanium coated ITO substrate due to the enhanced necking between TiO_2 particles and between TiO_2 film and substrate resulted in more adsorption of dye and hence provided a good path for the electrons to transfer more efficiently. From the data that were obtained, the overall efficiency of DSSC is highly associated with the thin coating of TiO_2 (formed from Ti-layer) due to its tendency to occupy the surface of ITO substrate [25]. In addition, the titanium coating also restricts the charges to recombine at the electrolyte and ITO substrate.

From the dark J–V curve (Fig. 7) it is clear that Ti coating also limits the contact between the redox electrolyte and substrate thereby reducing the dark current.

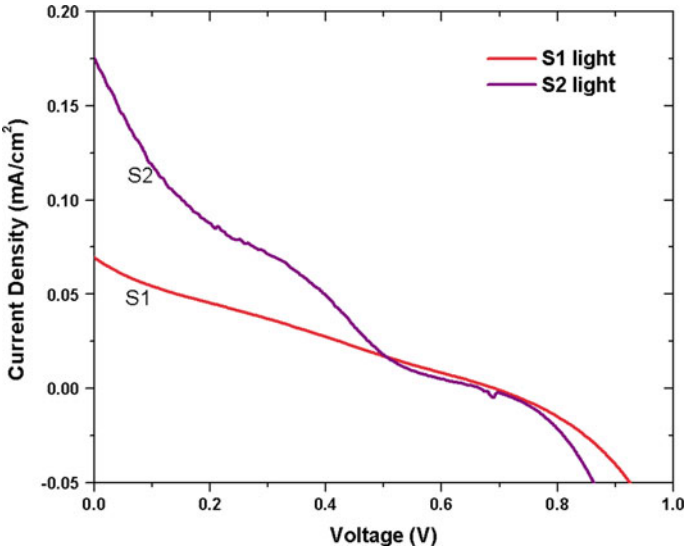

Fig. 6 J–V characteristics of DSSCs assembled with TiO_2 nanoparticles on bare ITO substrate (*S1*) and TiO_2 nanoparticles on titanium coated ITO substrate (*S2*)

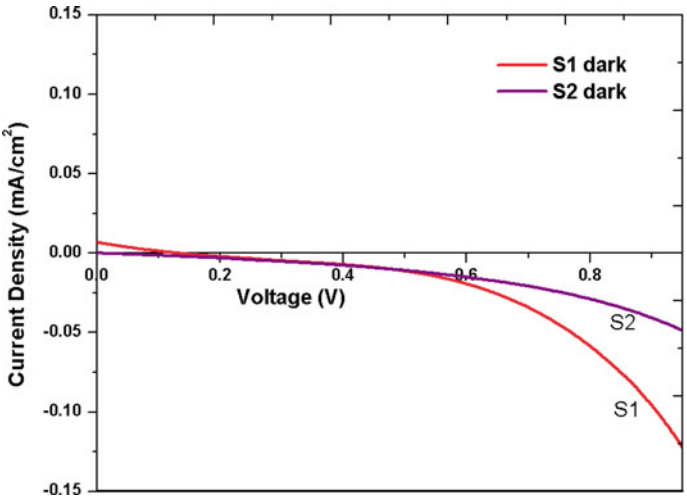

Fig. 7 Dark J–V characteristics of DSSCs assembled with TiO_2 nanoparticles on bare ITO substrate (*S1*) and TiO_2 nanoparticles on titanium coated ITO substrate (*S2*)

Eventhough this study shows the improvement in the cell performance further work is still needed in order to obtain higher efficiency [26].

3.5 Electrochemical Impedance Analysis

Figure 8a, b represents the Nyquist and Bode plots of electrochemical impedance spectra from which one can understand the internal working of solar cell. In Fig. 8a, the half arc obtained at the highest frequency region of Niquist plot describes the electron transport from excited sensitizer dye to the TiO_2 or reverse effect from the injected photo-electrons in TiO_2 to the polymer electrolyte. A slight reduction of bulk resistance was observed in Niquist plot owing to the introduction of Ti layer in the preparation process. The linear behavior in the Niquist plot in the low frequency region narrates the Warburg diffusion of the redox mediator inside the polymer-electrolyte and also reveals the sluggish ionic diffusion in the polymer electrolyte. From this it can be clearly seen that the charge transport in the electrolyte is predominantly from ionic diffusion transmission [27]. A comparable frequency shift from higher region to lower region is noted for DSSC corresponds to S2 electrode than S1 electrode as clearly seen from Fig. 8b. Overall this analysis reveals the reduction of charge recombination between TiO_2 and polymer electrolyte.

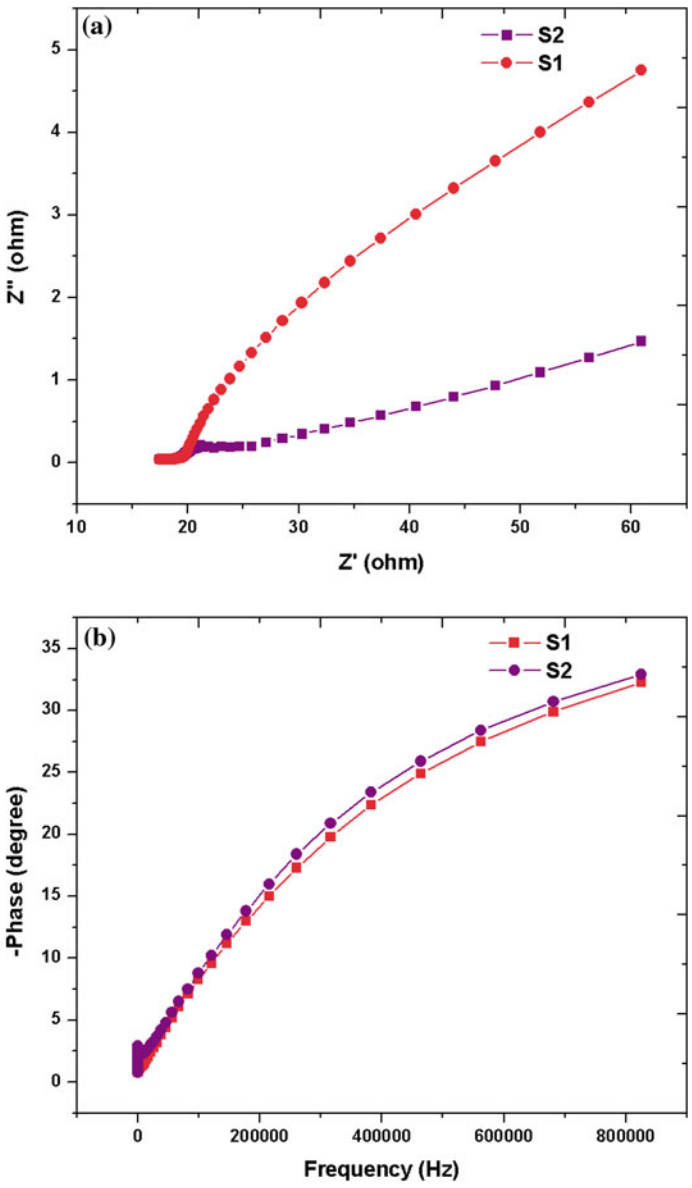

Fig. 8 EIS spectra of fabricated DSSCs **a** Nyquist plot, **b** Bode plot under light

4 Conclusion

This study presents a preparation of TiO_2 nanocrystalline films on pure and Titanium coated ITO glass substrates by sol-gel spin coating method. A profound effect on the structural, morphological, optical characteristics and on the conversion efficiency is obtained for titanium coated TiO_2 films. An efficiency of around 3 % is obtained for DSSC corresponding to TiO_2 film with titanium coating as the working electrode. More dye adsorption and the reduction of carrier recombination at the ITO and polymer electrolyte interface are the main causes for the improved performance of a solar cell. In addition, we verified that titanium coating could stabilize the structure of TiO_2 nanoparticles in anatase phase thereby enhancing the performance of the related DSSC.

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