

Role of titania photoanode phase on the performance of the Dye Sensitized Solar Cell

Pujita Ningthoukhongjam
Department of Physics
National Institute of Technology Silchar
Silchar, India
pujita.ningthoukhongjam@gmail.com

Ranjith G. Nair
Department of Physics
National Institute of Technology Silchar
Silchar, India
rgnair@phy.nits.ac.in

Abstract— The photoanode is one of the crucial components of a Dye Sensitized Solar Cell (DSSC) and understanding the effects of photoanode properties on DSSC performance is imperative. Titania (TiO_2) one of the popular photoanode materials, exist in different phases. The current study reports the low temperature, environment induced synthesis of its two primary phases: anatase and rutile. The anatase and rutile samples were found to have similar crystallite sizes whilst forming into different morphologies. The anatase was found to have a particulate nature while the rutile formed into larger microspheres, which ultimately led to a lower dye absorption capability of the rutile photoanode. The anatase photoanode was also found to have a lower charge transfer resistance and lower charge recombination rate as compared to rutile. All of these factors contributed to the DSSC with anatase having superior performance with a photoconversion efficiency that is more than twice that of the rutile DSSC. Thus, the multifaceted effects of the photoanode properties need to be accounted to improve the performance of the DSSC.

Keywords— Dye Sensitized Solar Cell, Anatase, Rutile, Photoanode, Charge Transport.

I. INTRODUCTION

Dye Sensitized Solar Cell (DSSC) is one of the emerging alternatives to traditional silicon based solar cells. The low cost, low toxicity and ease of manufacturing has made DSSCs an attractive option for sustainable harvesting of solar energy. In addition of these factors, the high transparency and ability to perform well even in diffuse light conditions has made it a desirable option as compared to conventional Si based solar cells [1]–[3]. The DSSC has four major components namely, metal-oxide photoanode, dye sensitizer, electrolyte and counter electrode. Among them, the dye sensitized photoanode is responsible for the transport for the photo-generated electrons from the dye to the external circuit [4]–[6]. Wide band-gap semiconductor metal oxides like TiO_2 , ZnO etc. have generally been used as the materials for photoanodes. The physicochemical and charge transport properties of the photoanode material play a crucial role in the overall performance of the DSSC [7]. As such it is imperative

that the effects of the different properties of the photoanode material on DSSC performance is explored and understood.

One of the most popular materials used as photoanode is TiO_2 , which has also been widely used for other applications such as sensors and photocatalysis. TiO_2 is a polymorph that exists in three different phases viz. anatase, rutile and brookite. The different physicochemical properties of the phases lead to varying effectiveness in the various applications [3]. The rutile phase is the most stable phase, as the anatase phase transitions to rutile at higher temperatures, with complete transition being reported in the 600°C to 800°C range, some even reported as high as 1000°C [8]–[10]. In fact, rutile is the preferred phase for a number of applications especially those involving bulk phases like plastics, paints, cosmetics etc [11]. However, at the nanoscale applications like photocatalysis, DSSCs, photosensors etc., the anatase phase is found to outperform the rutile phase [4], [12]. In fact, anatase phase is the most studied out of the reported three phases as it is more effective than the other phases especially in the applications like photocatalysis. This has generally been attributed to the higher charge recombination rate in the rutile phase [13]. As such, it is vital to understand the properties of anatase and rutile nanoparticles that affect the performance of the DSSC photoanode. In regards to performance of DSSC, the charge transport properties are of particular interest. The current study aims to study the role different properties of anatase and rutile titania on the performance of DSSCs.

As mentioned earlier, high temperature induced phase transition from anatase is the most common way to obtain rutile titania. However, this method leads to large variations of the nanoscale properties like crystallite sizes in the rutile phase. Other methods like pH regulation have been reported that allows temperature independent formation of rutile [14]–[16]. In this study, a low-temperature facile method for the synthesis of anatase and rutile phases through variation in the acid content of the reaction environment has been reported. The effect of structural, morphological, optical and charge transport properties have been studied and their effects on the DSSC performance have been elucidated.

II. EXPERIMENTAL

A. Material Synthesis

The titania samples were synthesized using a facile hydrothermal process. 4mL of titanium isopropoxide (Sigma-Aldrich, >97%) was dispersed in 25 mL of ethanol (Sigma-Aldrich, EMSURE) and stirred for 30 mins. 25 mL of Deionized (DI) water was added and stirred further for 30 mins. The mixture was then transferred to a 100 mL Teflon lined Autoclave which was kept at 150°C for 12 hours. The resulting white precipitate was then recovered via decantation and dried at 100°C for 12 hours. The dried sample was then calcined at 500°C for 1 hour in a muffle furnace and this sample was named as T-A. A second sample was prepared with the same process except with aqueous hydrochloric acid (Sigma-Aldrich, 35%) solution used in place of the DI water. This sample was named T-R.

B. Characterization

X-Ray Diffraction (XRD) studies were conducted using PANalytical Xpert3 Powder XRD with Cu K α 1 source. Field Emission Scanning Electron Microscopy (FESEM) images were obtained using Carl Zeiss Gemini300. UV-Visible absorbance spectra of the samples were analysed using UV-Vis-NIR Spectrophotometer (Agilent Cary 5000).

Electrochemical impedance spectroscopy (EIS) analyses were carried out using the PGSTAT 302 Metrohm Autolab workstation. The EIS study was conducted using an aqueous solution of 0.1 M KCl containing 0.01 M K₃[Fe(CN)₆] solution as the electrolyte and was recorded for frequency range of 100kHz to 0.01 kHz at an amplitude of 10mV. Doctor blade deposited titania films of dimensions 1 cm x 1 cm, were used as working electrodes whereas Ag/AgCl and platinum foil were taken to be the reference and counter electrodes respectively.

C. DSSC Fabrication and Testing

All the prepared samples were used as photoanodes to fabricate DSSCs. Uniform pastes of the samples were made prepared with polyethylene glycol (Merck) as binder. The paste was coated onto a Fluorine Doped Tin Oxide (FTO) (Solaronix, $\sim 7\Omega$) using doctor blade method in order to fabricate the photoanode. The coated films were then dried at 400°C in a muffle furnace. Platinum paste, Platisol (Solaronix) was similarly coated onto FTO substrate and dried to fabricate the counter electrode. The as-fabricated photoanodes were dipped in an ethanolic 0.6 mM solution of N719 dye (Solaronix) for 8 hours to sensitize the photoanodes. The sensitized photoanode and as-fabricated counter electrode were assembled together and the iodide electrolyte (Iodolyte, Solaronix) was injected to produce the complete DSSC. In this manner, DSSC of both the samples were fabricated, both with an effective area of 1cm². The DSSCs were illuminated at 1 Sun at 1.4 AM by a solar simulator (Sciencetech, SciSun-300) and a Keithley Sourcemeter was used to measure the JV characteristics of the solar cells.

III. RESULTS AND DISCUSSION

The XRD pattern of the prepared samples are shown in Fig. 1 and it confirms the formation of titania in both the samples. The diffraction peaks of T-A, indexed using JCPDS: 89-4921 confirms that the sample is solely composed of tetragonal anatase phase of titania. On the other hand, the increase in the HCl content in the T-R sample was found to have led to a phase transition to form rutile phase (JCPDS: 89-4920).

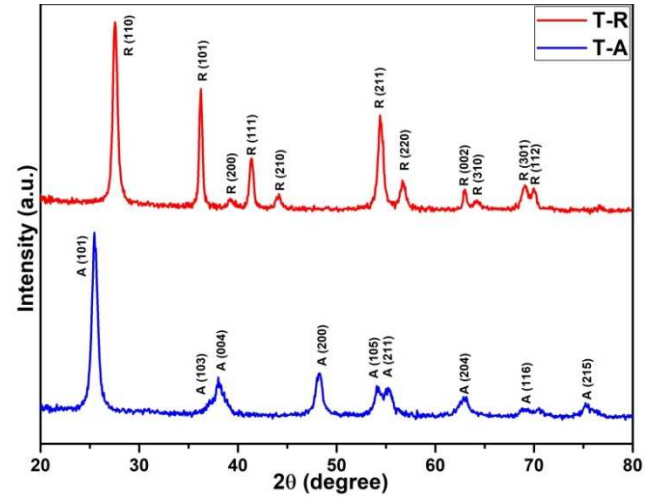


Fig. 1 XRD pattern of the samples

In both the samples, no impurity peaks were detected, indicating the high purity and single phase nature of the samples. The crystallite sizes of the samples were calculated using Debye Scherrer method [17] and listed in Table 1. The crystallite sizes of the samples were found to be similar despite of the difference in the phases present.

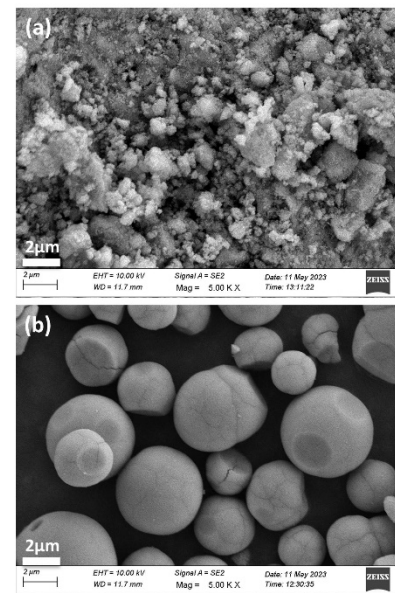


Fig. 2 FESEM images of the (a) T-A and (b) T-R samples

The morphological characteristics of the samples have been studied from the Field Electron Scanning Electron Micrographs as shown in Fig 2. FESEM image of the T-A sample shows that the anatase has aggregated to form particulates of varying sizes. Whereas, in the case of the T-R, rutile has been formed into microspheres.

Table 1: Structural and optical properties of samples

Sample	Crystallite Size (nm)	Band Gap (eV)
T-A	12.40	3.12
T-R	15.92	3.01

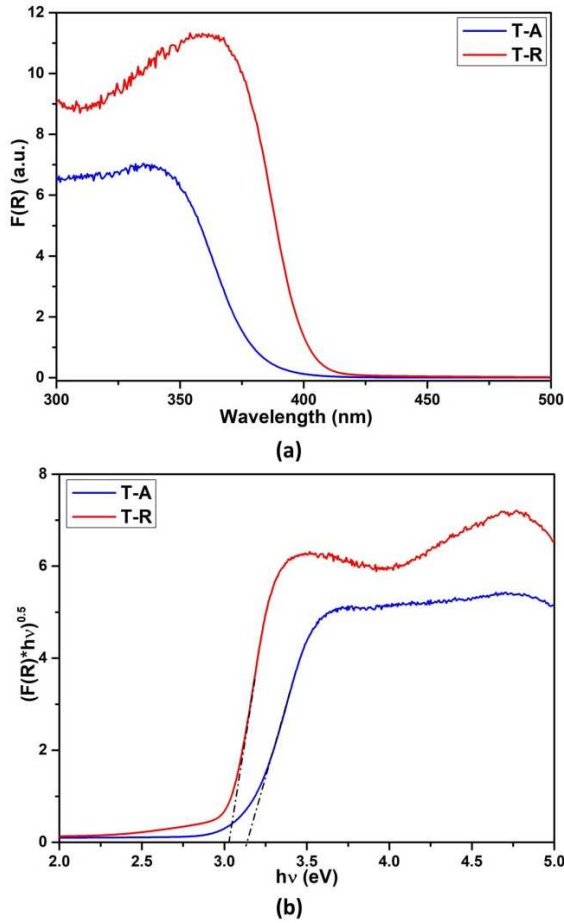


Fig. 3 (a) UV-Vis absorbance spectra (b) Tauc's plot of the samples

The optical properties of the samples were analysed using UV-Vis-DRS studies (Fig. 3). Both the samples were found to have a high absorption in the UV spectral range which is in agreement with previous reports. The optical band gaps of both the samples were calculated using Tauc's plot [18] and listed in Table 1. The rutile sample was found to have a slightly lower band gap than the anatase phase.

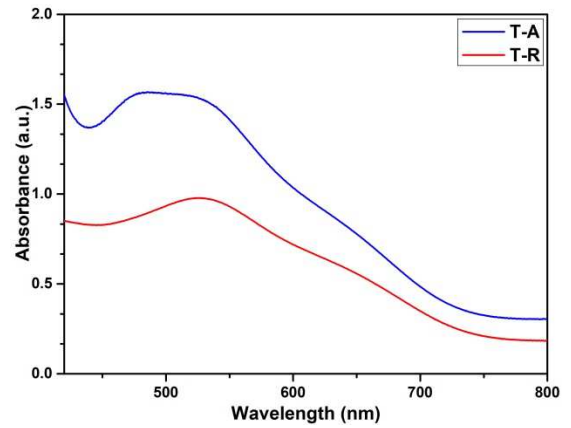


Fig. 4 UV-Vis absorbance of the dye sensitized photoanodes

In addition, the UV-vis absorbance spectra of the sensitized photoanodes are shown in Fig 4. It can be seen that the anatase

T-A sample shows a higher absorbance at ~520 nm as compared to the rutile T-R sample. This indicates that there is higher dye loading on the anatase photoanodes than the rutile photoanodes. The lower dye absorption on the rutile photoanodes may be attributed to the low surface area resulting from the micro-spherical nature of the rutile sample as was seen in the FESEM images.

Electrochemical Impedance Spectroscopy (EIS) studies have been used to evaluate the charge transfer characteristics of the samples. The charge transfer resistances (R_{ct}) of the samples have been calculated from the Nyquist plots of the samples shown in Fig. 5. R_{ct} represents the interfacial charge transfer resistance and is given by the diameter of the arc at the lower frequency end [19]. The anatase photoanodes are found to have a lower R_{ct} value than the rutile photoanodes. This indicates a more effective transport of electrons across the anatase photoanode/electrolyte interface than that of the rutile one which may affect the overall performances of their respective DSSCs. Additionally, the electron lifetimes (τ) in the photoanodes have been calculated from the Bode plots (Fig. 6) which gives an estimate of the charge separation efficiencies of the samples [20]. The electron lifetime values are listed in Table 2. It is observed that the anatase photoanodes exhibit a better lifetime of the photo-induced electrons. This indicates a suppressed charge carrier recombination and a more effective charge separation in the anatase photoanode as compared to the rutile photoanode.

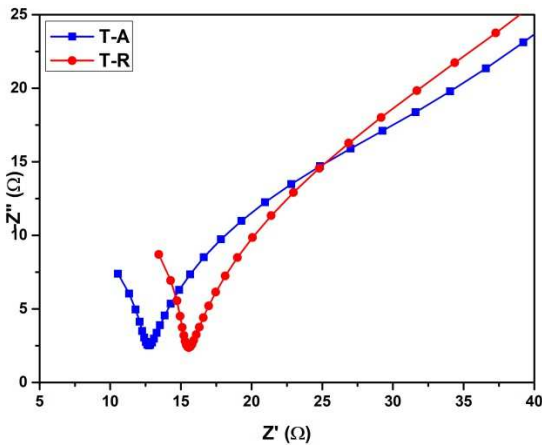


Fig. 5 Nyquist Plot of the samples

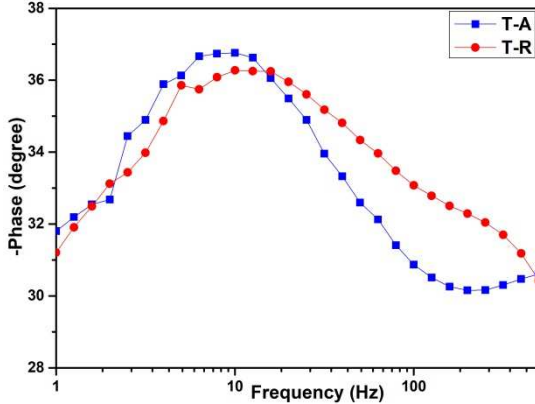


Fig. 6 Bode Plot of the Samples

Table 2: Photoelectrochemical properties of samples

Sample	R_{ct} (Ω)	τ (ms)
T-A	45.98	17.49
T-R	60.74	12.53

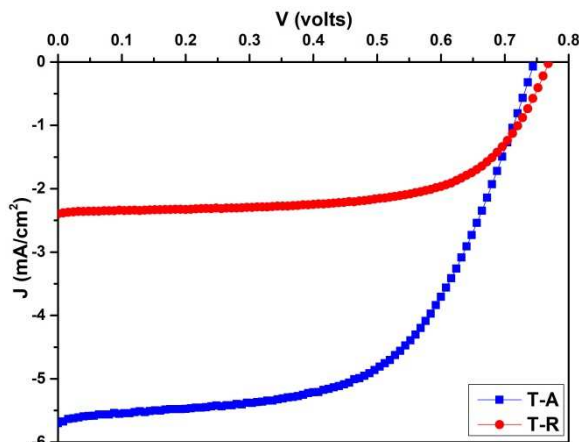


Fig. 7 J-V characteristics of the DSSCs

The JV characteristics of the DSSCs fabricated with anatase and rutile photoanodes are shown in Fig. 7 and the characteristic cell parameters namely V_{oc} , J_{sc} , fill factor and

the photoconversion efficiency (PCE) has been calculated and are listed in Table 3.

Table 3: DSSC performance of the samples

Sample	V_{oc} (V)	J_{sc} ($mA\ cm^{-2}$)	P_{max} (mW)	Fill Factor	PCE (%)
T-A	0.74	5.69	2.45	0.58	2.45
T-R	0.77	2.40	1.18	0.64	1.18

The open circuit voltage of the rutile photoanode based DSSC was found to be slightly higher than that of the DSSC using anatase one. The rutile photoanode based DSSC also displayed a better fill factor. On the other hand, the short circuit current of the anatase photoanode based DSSC was much higher than that of the rutile based one. On the whole, the anatase photoanode based DSSC had a PCE of 2.45% which was more than 2 times higher than that of the rutile photoanode based DSSC. The superior PCE performance of the anatase photoanode based DSSC can be attributed to the lower R_{ct} and higher τ values of the photoanode. The lower charge transfer resistance and the greater electron lifetime has led to a more effective transfer of photogenerated electrons across the anatase photoanodes leading to a high J_{sc} value and subsequently a higher PCE of the DSSC. It is to be noted that the difference in performance of the DSSCs also corresponds to the difference in the dye loading on the sensitized photoanodes. The greater dye loading in the anatase photoanode alludes to a greater charge carrier generation which may also have positively contributed to the higher PCE of the DSSC. As mentioned before, the micro-spherical morphology of the rutile samples may have led to a lower dye absorption which in combination with the higher R_{ct} and charge recombination of the photoanode has hindered the performance of the rutile based DSSC. Thus, the overall performance of the DSSC is dependent on the cohesion of a number of factors ranging from morphology to the charge transport characteristics of the photoanode. As such effective tuning of the photoanode is essential to improve the DSSC performance.

IV. CONCLUSION

Low temperature phase transition from anatase to rutile through hydrothermal method has been carried out through simple variation of acid content in the reaction environment. This method of phase variation led to formation crystallites of similar sizes as calculated through XRD analyses. However, the rutile sample was found to form into microspheres while anatase remained as particulates of varying sizes as seen from the FESEM micrographs. This difference in morphology led to variance in the dye absorption capability of the photoanodes, with the rutile photoanode showing a lower dye loading. The photoelectrochemical analyses showed the superior charge transport properties of

the anatase photoanodes, showing lower charge transfer resistance and higher electron lifetime than the rutile photoanode. The conjunction of all these factors has led to the DSSC with anatase photoanode outperforming the rutile photoanode based DSSC by a factor of 2. Thus, the effect of photoanode properties on DSSC performance is multifaceted and careful tuning of the photoanode properties is essential to ensure improved performance of the DSSC.

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