Surface modification of photoanodes by HCl treatment to improve the efficiency of DSSC

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By

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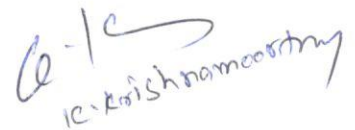Department of polymer science and engineering

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Certificate

This is to certify that this dissertation entitled 'Surface modification of photoanodes by HCl treatment to improve the efficiency of DSSC' towards the partial fulfilment of the BS-MS dual degree program at the Indian Institute of Science Education and Research, Pune represents work carried out by Mohidh K M at CSIR- National Chemical Laboratory under the supervision of Dr. K Krishanamoorthy, Principal Scientist, Department of polymer science and engineering, during the academic year 2018-2019.

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Signature of the student

Signature of the supervisor

Date: 20-3-2019
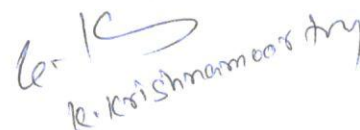Place: Pune

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Declaration

I hereby declare that the matter embodied in the report entitled 'Surface modification of photoanodes by HCl treatment to improve the efficiency of DSSC' are the results of the work carried out by me at the Department of polymer science and engineering, CSIR-National Chemical Laboratory, Pune, under the supervision of Dr. K Krishnamoorthy and the same has not been submitted elsewhere for any other degree.

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Abstract

Dye-sensitized solar cells are having an essential role in future photovoltaic devices. To improve the efficiency of DSSC is become very relevant and we are trying it by doing a simple solution method HCl treatment on photoanodes before dye anchoring. So we have used two different dyes for this purpose in this project. Ruthenium based N719 dye, which has been reported for high photon to current conversion efficiency in DSSC. And a squarine based organic SQ1 dye, as it is more environmental friendly and having great importance. And by using the solution method treatment of HCl, we were successfully increased the efficiency of N719 dye and SQ1 dye. This is mainly because of the surface protonation taking place at the photoanodes by the HCl treatment, and we have confirmed it by different characterization techniques. As both the dyes are having a carboxylic anchoring group, surface protonation having an essential role in dye anchoring. Dye desorption studies carried out to understand how dye anchoring effect is effected by HCl treatment. With the help of electrochemical impedance spectroscopy, we were able to detect the increment in the recombination resistance, chemical capacitance and lifetime of the electrons of the HCl treated devices. The method we have used is easier, efficient and low cost to improve DSSC efficiency.

1. INTRODUCTION

We are in need of finding new renewable energy sources to fulfil the requirement of the energy demand as it becomes higher with increasing global population and industrialization. Fossil fuels are a widely used energy source. However, these sources are nonrenewable (Finite resource), prone to diminish and leads to pollution. Photovoltaic devices are considered to be the next renewable energy source as the other natural sources are not that dependable. Notably, solar energy is endless and abundantly received by the earth's surface. Conversion of 0.1% of sunlight received by earth surface by photovoltaic technology with 10% conversion would fulfil the world's current energy demand

By the photovoltaic effect, the devices convert light into electrical energy using semiconducting materials. The discovery of the photovoltaic effect leads to the creation of the first solar cell in 1883 by Charles Fritts which was giving 1-2% efficiency by using a thin layer of gold coated with Selenium[1]. During 1950s Silicon-based solar cells are being produced as the Silicon is more efficient than that of Selenium. The increment in oil prices also helped the solar industry to grow as the demand for solar power was increased. 90% of solar cells present in the market are made up of silicon-based. There are three generations of the solar cells present. The first generation of solar cells are very costly and giving high efficiency. The material used for the fabrication of these solar cells is incredibly pure silicon. Even though silicon is very abundant, nontoxic and gives high cell efficiency, the purification process is highly expensive. Thus the production of such solar cells is declining nowadays. But these solar cells are capable of giving theoretical maximum efficiency of 33%. The second generations are low cost and low efficiency solar cells. These solar cells are using thin layers for the excitation of the electron. And these can be used in large areas as well as flexible areas. Cadmium Telluride/Cadmium Sulfide (CdTe/CdS) solar cells, Copper Indium Gallium Selenide (CIGS) solar cells and amorphous Si (a-Si) based thin films solar cells are examples of second generation solar cells. These solar cells are not only cheaper but also less efficient than that of conventional silicon-based solar cells. Third generation solar cells include dye-sensitized solar cell (DSSC), polymer solar cell, nanocrystal-based solar

cells, perovskite solar cells and concentration solar cells. The efficiency of these third generation solar cells has increased from 3.8% to 22 % recently. So these solar cells can reach higher efficiencies in future[2-5].

In 1991, Gratzel and coworkers developed the first DSSC[6]. Recently, Dye-sensitized solar cells (DSSC) have been getting lots of attention from researchers as it is an efficient method to convert solar energy into electrical energy. DSSCs are considered a good alternative for costly silicon-based photovoltaic devices since it is low cost, simple and environmentally friendly. DSSC consist of photoanode with an organic or metal organic dye attached to it, electrolyte usually of iodide/triiodide complex and platinum cathode. When the dye is sensitized by the light, the electrons get excited from the dye, and it injects it into the TiO_2 layer. This nanocrystalline layer conducts the electrons to the transparent conducting oxide current collector and the external circuit. The electrolyte completes the circuit by helping the electrons to come back to dye. The electricity produced can be stored and used. The working principle of the DSSC shown in **Figure 1**.
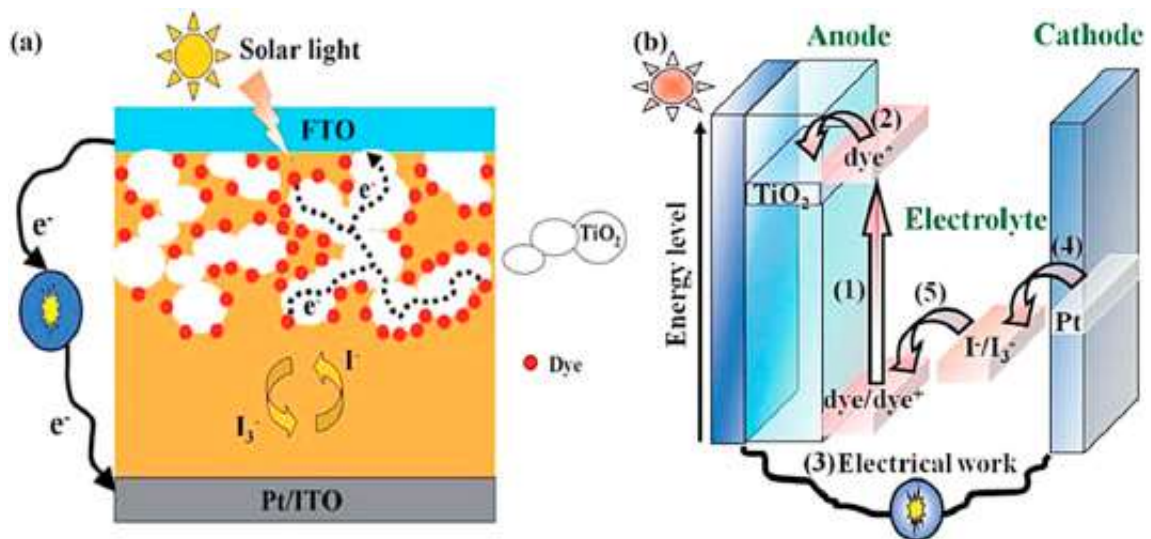

Figure 1 Schematic representation of working of DSSC[7]

Recombination is a vital issue in DSSC[8-10]. Anatase TiO_2 has been widely used as a semiconducting material for photo anode fabrication as it has high electron injection rates[11-12]. TiO_2 is one of the core materials of the solar cell, and it acts as the electron

transport layer (ETL) in dye-sensitized solar cell (DSSCs). Unfortunately, TiO_2 has deep trap states (Oxygen vacancy) that induce electron-hole recombination[13]. This process called back electron transfer (BET). BET is the vital issue, which predominantly reduces the photoconversion efficiency (PCE) and stability of the solar cell. Mainly there are two ways the electrons can recombine back, firstly by recombine with dye molecule itself and secondly by recombining with electrolyte DSSC could not reach the theoretical maximum photoelectrical conversion efficiency of 33% because of the electron recombination and back electron transfer happening at the interface of dye and TiO_2, even though were able to get above 13% efficiency. To replace the silicon-based traditional solar cell, DSSC needed to overcome challenges like suppressing the recombination process.

In order to enhance the photon to current conversion efficiency researchers have been working in all parts of DSSC as it is very cheap and easy to fabricate compared to silicon-based solar cells. To replace the silicon-based traditional solar cell, DSSC needed to overcome several challenges.TiO_2 is found to be the most promising semiconducting material for DSSC. Mesoporous TiO_2 layer is used as it helps to increase the surface area several times. Still, DSSC cannot overcome the electron recombination, and it leads to a reduction in the photoelectron conversion efficiencies.

Along with TiO_2 other metal oxides like ZnO, SnO_2 are used as photoanode material[14-15]. Still, TiO_2 is the ideal material so far because of its high energy level matching and chemical stability. Many studies have been carried out to enhance the solar energy conversion by modifying the TiO_2 mesoporous film by surface treatment, doping, complex structure formation etc[16-21].

In this project, we have used solution method to modify the TiO_2 surface to enhance the performance of DSSC. This method is very effective and easy to do. It does not require sophisticated mechanisms. And by using this method we can easily control and modify the surface of the TiO_2 and thereby the dye anchoring can be monitored. Here, we are treating the surface of photo anodes with diluted HCl by solution method. And using two different dyes for anchoring and checking how does the treatment of HCl effect on the

performance of DSSC. This is done by measuring the efficiencies of the devices, treated with HCl for different time intervals, anchored by different dyes. We have used a metal centered dye, N719, and an organic dye, SQ1. N719 dye is a Ruthenium centred dye and commercially available (**Figure 2(a)**). When light falls on the N719 dye, the electron is excited from the ground state Ru^{2+}. Ruthenium based dyes are most extensively studied and are capable of giving efficiency more than 11%[22-23]. But, metal centred dyes are not very environmental friendly and cost-effective. So researchers are interested in organic dyes.

N719   SQ1
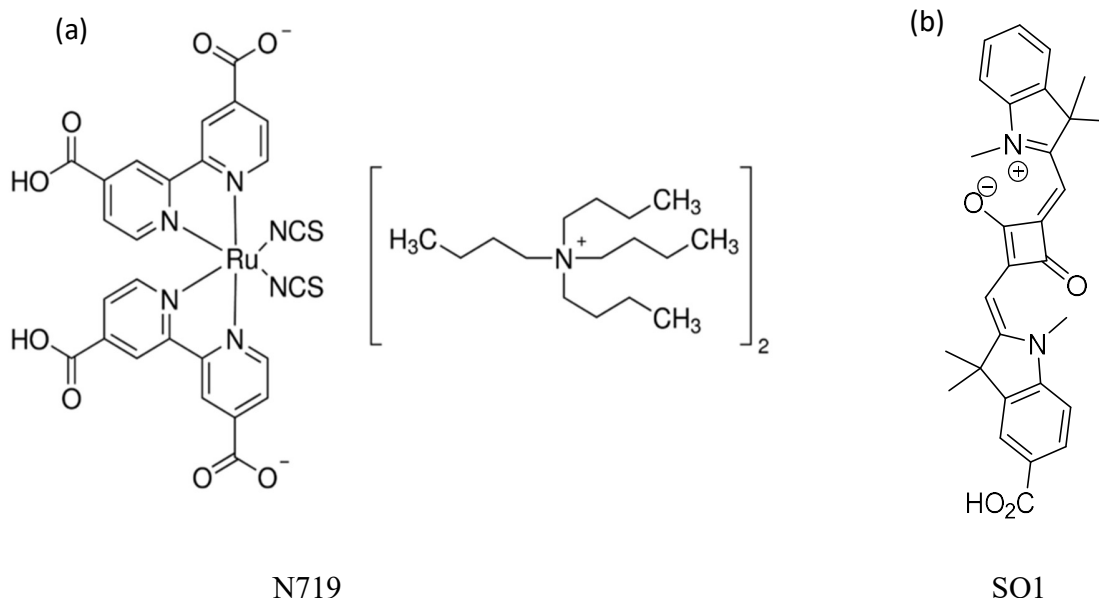
Figure 2: Structure of the **(a**) N719 dye and **(b)** SQ1 dye

SQ1 is squarine based dye and is shown in **Figure 2(b).** This dye is showing higher absorption and emission near the NIR region. It is an organic dye with donor acceptor donor SQ framework[24]. This dye also has a carboxylic anchoring group like N719 dye. Squarine based dyes are capable of giving moderate efficiencies and having lower molar absorption coefficient than that of N719 dye. But modified squarine dyes are capable of providing higher efficiencies. This SQ1 dye has a problem of dye aggregation which leads to more dye to aggregates on the photoanodes and reducing the electron transfer between dye and TiO_2. We have chosen this dye because this dye has a linear structure and different alkyl groups can be attached to it and will result in

very much difference in the efficiency of the devices. This will help to reduce the dye aggregation. Usually, people use CDCA (chenodeoxycholic acid) to prevent the dye aggregation[25-26]. But here we are not using any additives and just treating the photoanodes by HCl. The role HCl treatment on the photoanodes and its overall effect on the metal-centred and organic dye's efficiency is studied in this project. As solar energy is the most prominent and cheapest energy source available, even a small increment in the efficiency can be very much beneficial, and we are aiming for that through this project.

2   EXPERIMENTAL SECTION

2.1   Materials

N719 dye (solaronix), FTO (fluorine doped SnO_2 glass; 10-12Ω /sq; Solaronix) plates, Sq1 dye, HCl (Sigma Aldrich), 20 nm size TiO_2 (solaronix), 400 nm size TiO_2 (solaronix), $TiCl_4$ (Sigma Aldrich), NaOH (Rankem), DI water, I^-/I_3^- (AN-50, Solaronix), ethanol (Sigma Aldrich), acetonitrile (Sigma Aldrich), Platinum electrode (Global nanotech).

2.2   Fabrication of DSSCs

FTO (fluorine doped SnO_2 glass; 10-12Ω /sq; Solaronix) plates are washed using acetone and sonicated in isopropanol for 30 minutes to remove the impurities present on the surface of the plates and dried. FTO plates are pretreated with 40mM $TiCl_4$ at 70°C. After that, plates are washed with distilled water and ethanol followed by sintering at 500°C for 30 minutes. 20 nm size TiO_2 (solaronix) active layer were deposited on the FTO plates using simple doctor blade technique and thickness of the TiO_2 layer is of 9-10 μm. The samples are sintered at 325°C for 10 minutes, 375°C for 10 minutes, 450°C for 10 minutes and 500°C for 15 minutes. Once samples attain the room temperature, 400 nm size TiO_2 (solaronix) were coated over 20 nm size TiO_2 particle and thickness of

the scattering layer is 3-4 μm. This layer helps to scatter the light back to the active layer of TiO_2 to increase the efficiency of the cell. Then again sintered at 500°C with ramping temperature increase. After this, post $TiCl_4$ treatment carried out by followed by photoanodes were sintered at 500°C. The schematics for the preparation of the photoanodes are shown in **Figure 3**

FTO plate

Active layer TiO_2 coated on FTO plate

Scattering layer TiO_2 coated over active layer TiO_2

Photo anodes are treated by HCl using solution method

Dye anchored on photo anodes

Devices are measured after adding electrolyte using Pt electrode.
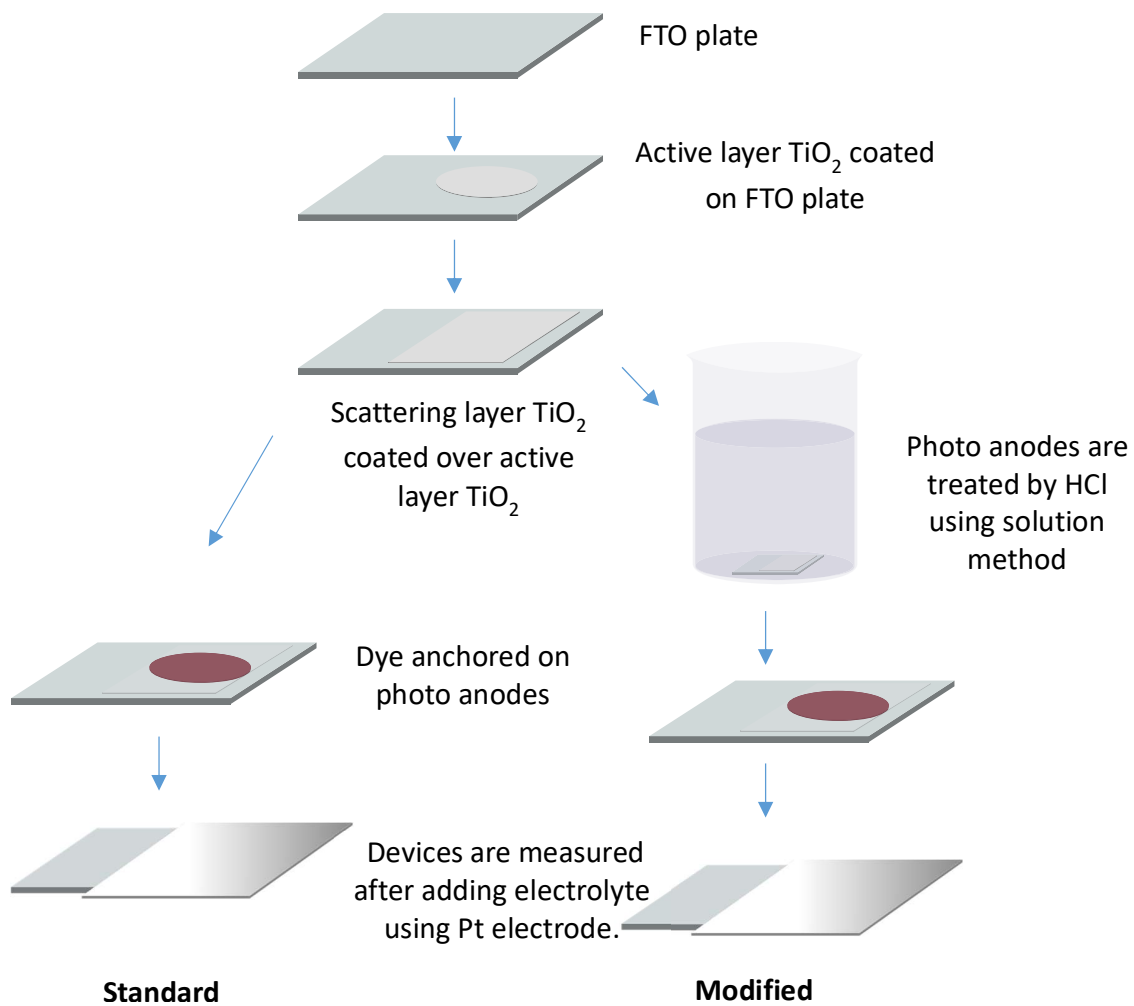
Standard

Modified

Figure 3: Schematic representation of the preparation of DSSC

For the modified device, prepared standard photoanodes are immersed in 0.1M HCl solution for different time intervals and after taking out heated at 80°C for 5 minutes.

Once the photoanodes attain room temperature, they were immersed in dye. Firstly we have used N719 dye for it. The 0.5mM N719 dye (solaronix) dye solution prepared by mixing the dye with acetonitrile and tert-butanol solution of 1:1 ratio. And the devices were immersed in the dye for 24 hours. After dye loading, photoanodes were washed with acetonitrile to remove the unanchored dye molecules from the surface of the photoanodes and subsequently dried using air drier. These photoanodes are properly masked for the measurement. A platinum electrode is used as a counter electrode. The electrolyte used in between the photoanode and Pt electrode is I_3^-/I^- (AN-50, Solaronix).

Secondly, we have used the SQ1 dye. We have made 0.1mM dye solution by mixing the SQ1 dye with acetonitrile. And we are immersed the photoanodes in the dye for 8 hours. And washed it using acetonitrile. After that same steps are carried out for these devices as well. The dye immersing time and concentration of the dye taken are optimized to give better performance.

2.3   Characterization Techniques

2.3.1 IV measurement

It is a fundamental technique to characterize the electrical devices. The photovoltaic parameters of the devices measured using AM 1.5 G sun illuminations (power 100 mW cm^{-2}). The fill factor and power conversion efficiencies of the devices were calculated using the following equations.

$$FF = \frac{P_{max}}{J_{SC} \times V_{OC}}$$

$$\eta(\%) = \frac{P_{max}}{P_{in}} \times 100 = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \times 100\%$$

Where P_{max} is the maximum output power, J_{SC} is the short circuit current density, V_{OC} is the open circuit voltage, and P_{in} is the incident light power. From this, we are calculating

the efficiency of the devices and the V_{OC} and I_{SC}. The HCI treated devices are measured using solar simulator with the different dyes to find out whether they are helping to improve the efficiency or not.

2.3.2 IPCE measurement

To study the electrical sensitivity of the device to light, we have carried out IPCE, which will provide the current produced when a light wave of particular wavelength falls on the device[27]. And it scans through a range of wavelength and the integrated value of the curve produced by IPCE will be the total current produced when the light fall on the device. The external quantum efficiency of our devices have been measured and can be calculated using the equations below.

$$EQE = \frac{electrons/seconds}{photons/seconds} = \frac{current/charge\ of\ one\ electrons}{total\ power\ of\ the\ photons/energy\ of\ one\ photon}$$

We have prepared photoanodes as explained earlier and used to measure the external quantum yield of the HCI treated devices and untreated devices which are anchored by N719 dye.

2.3.3 Electrochemical impedance spectroscopy

It is a steady state method to measure the response of the current to voltage over different frequencies. It can be used to study the effect of small perturbations in the voltage over the circuit. To study electron transfer kinetics and the processes involves in controlling charge dynamics in the DSSC, we are performing electrochemical impedance spectroscopy. This technique gives more insight towards the interfacial charge recombination between TiO_2 and electrons from the conduction band. The Nyquist plot of DSSC contains three semicircles due to the different interfaces present in DSSC. As shown in **Figure 4(a)**, the first semicircle corresponds to the counter electrode/electrolyte interface, the second one is the dye/TiO_2/electrolyte interface, and the third one is because of the Nernst diffusion in the electrolyte[28-30]. The equivalent circuit of the DSSC, which is making this three semicircled plot also shown in **Figure 4(b).** From EIS we can calculate recombination resistance, chemical capacitance and

lifetime of the electrons in the conduction band of TiO_2. Recombination resistance is the resistance exerted by the electrons to recombine with the dye molecule. And higher the recombination resistance it is good for the device. Chemical capacitance is due to the accumulation of the electrons in the conduction band of TiO_2. As the chemical capacitance increases, it will lead to higher efficiency of the devices.

For the experiment, measurements were carried out in the range of 300mv to 600mv scan rate in steps of 50 mv for the devices anchored by N719 dye and SQ1 dye. This is to analyze the kinetics of the performance of these different dyes to the HCl treated photoanode. And also to find out how they affect the lifetime of the electrons present. We have used the device Biologic for the measurements.

(a)

(b)

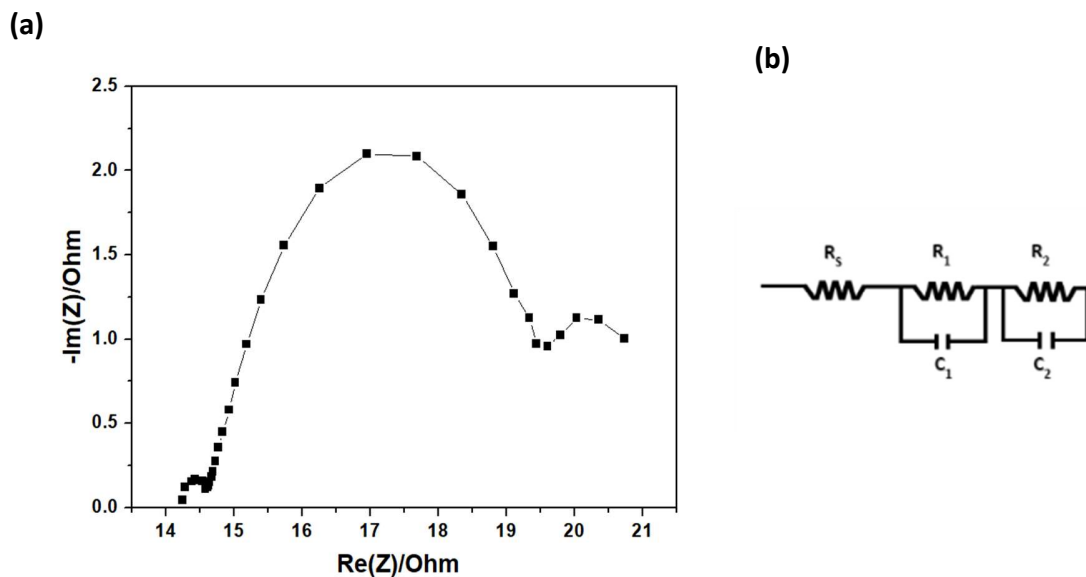**Figure 4: (a)** Nyquist plot for a dye sensitized solar cell. **(b)** The equivalent circuit of a DSSC

2.3.4 UV - Vis spectroscopy

We have carried out the UV-Vis spectroscopy to find out the effect of HCl treatment on the bandgap of the TiO_2 on the photoanode[31]. We have coated the active layer TiO_2 paste on a glass plate and sintered it at 500°C. After that, some of the glass plates are

immersed in 0.1M HCl for different time intervals. These glass plates are used for the measurement. So we have used the instrument Analytical Gena to carry out the experiments. TiO_2 coated glass plates are kept in the instruments and measurements are taken. The Bandgap of the TiO_2 can be calculated using the equation

$$E = \frac{hc}{\lambda}/e \ \text{eV}$$

Where

E - Energy in electron volt

λ - Wavelength of the light wave (m)

c- Speed of the light (3×10^8 m/s)

e- Charge of the electron (1.602×10^{-19} C)

2.3.5 Dye desorption studies

Dye desorption studies is an indirect way to estimate the dye anchored on the surface of the photoanode and to understand how the HCl treatment is affecting it[32-33]. We have made a 0.1M NaOH solution in which water and ethanol took in a 1:1 ratio. We dipped the dye anchored devices in 3 ml of NaOH solution for a fixed time interval. Both N719 dye, as well as SQ1 dye, are used to anchor on the photoanodes. The anchored dye will be desorbed very fast in a few seconds. The desorbed dye's concentration is measured using UV-vis absorption. We have used Analytical Gena for the measurements. By using Beer Lambert's law, the concentration of the dye in the solution is measured and compared. So the equation used is

$$A = c\varepsilon l$$

Where

A - Absorption

c- Concentration of the solution

ε- Molar extinction coefficient

l- Optical path length

Absorption is monitored from 300-800 nm range. And the concentration is calculated form the first peak value.

2.3.6 Powder X-ray diffraction

To understand the molecular and atomic arrangement of the compounds this technique is used[34]. When x-ray pass through the crystals the ray's get diffracted. And from the intensity and the angles, the beam got diffracted, the structure and atomic positions of the crystals can be determined. And this technique will help to understand the 3D arrangements of the atoms as well. Bragg's equation is used to understand the crystal structure and is given by

$$2dsin\theta = n\lambda$$

Where

d – Spacing between diffracting planes

θ – Incident angle

n – Order of diffraction (n=1,2,3, …..)

λ – Wavelength of the beam

PXRD of standard TiO_2 and HCl treated TiO_2 are carried out to find out the effect of HCl treatment on the crystal structure of the TiO_2. Here the instrument scan through different 2θ values and collecting all the diffracted waves from all the angles. The TiO_2 powder prepared by sintering the TiO_2 paste ate 500°C and grinding it after it cools down. 0.1 M HCl is added into the powder and kept for different time intervals. The treated powder kept in 80°C for 30 minutes and ground to make powder. And it is used for the measurement.

2.3.7 Field emission scanning electron microscopy

This is a microscopic technique which is used to make images of the sample to give information about the topography and composition. It scans over the surface using an electron beam. This interaction of the atoms and electrons produces signals about topography and composition of the sample. It is different from normal scanning electron microscopy. For normal SEM the thermionic emitters are used. They use electrons to heat the filament and electrons are escaping when the heat is enough to overcome the work function. But which in turn results in reduced brightness, evaporation of the cathode material etc. But in FESEM these problems are overcome by the use of field emission gun. This method is not heating the filament but in turn, they eject the electrons by placing the filament in a big electrical potential gradient. FESEM gives better resolution, less electrostatically distorted and clearer images. We took images of HCl treated and untreated photoanode to analyze the effect of HCl treatment on the surface of photoanodes. Necessary steps are followed for the preparation of photoanodes and modification.

2.3.8 X-ray photoelectron spectroscopy

This technique is used to analyze the surface of a material. This technique helps us to understand elemental composition, chemical state and elemental state of the material[35]. And it can also give information about which all elements are bonded to each other. This is done by passing an X-ray beam onto the surface of the material and collecting the electrons escaping from the top of the surface (1-10 nm) and the energy of it. X-ray beam ejects the electron from the inner orbitals which makes a vacant space there. So electron from the outer orbitals jumps into the unoccupied position in inner orbitals by releasing energy in the form of EM waves. Which is collected by the instrument. The electrons coming from outer orbitals to inner orbitals are called Augur electrons. From this experiment, we will get an idea about the surface modification happening on the TiO_2 by HCl treatment.

3 Results and Discussion

3.1 Measurement of DSSC

To enhance the photon conversion efficiency of the DSSC, we have carried out HCl treatment on the surface of the photoanode by solution method. The devices are treated for different time intervals to check the effect of treatment in their efficiency. So different dyes are used to know the effect of HCl treatment on photoanode. We have optimized the dye anchoring time for different dyes. N719 and SQ1 are used for the measurements.

No	Sample	HCl treatment (h)	V_{OC} (V)	Current density (mA/cm^2)	FF (%)	Efficiency (%)
1	Standard	0 hour	0.7588	15.84	77.9	8.70
2	modified	4 hour	0.7650	19.22	76.1	10.27
3	modified	8 hour	0.7561	18.58	79	10.21

Table 1: DSSC device metrics of HCl treated and untreated devices of N719 dye
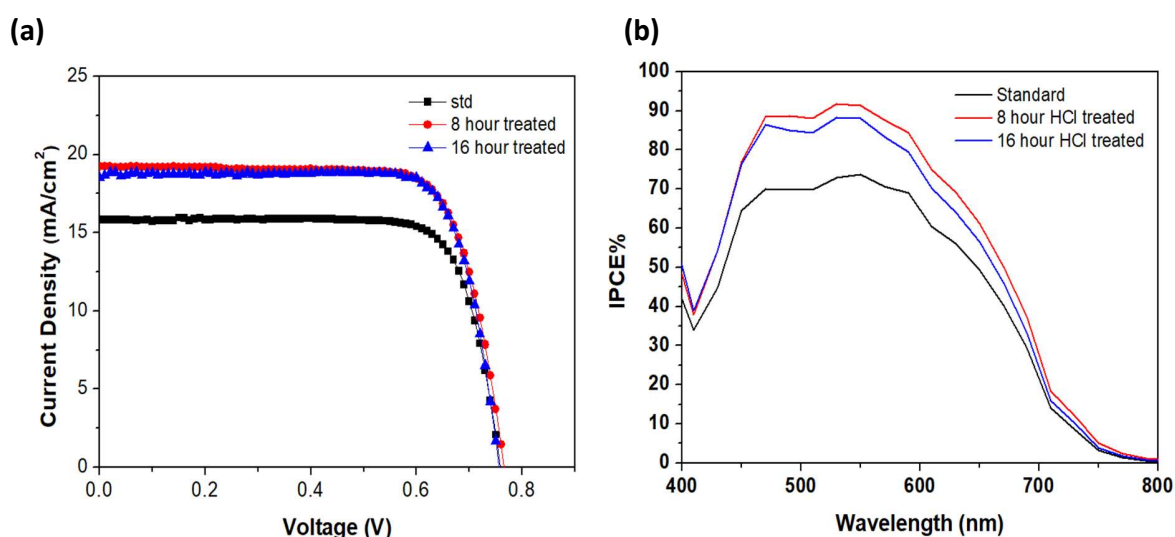
Figure 5: **(a)** J-V curves of modified and standard devices with N719 dye anchored. **(b)** IPCE spectra of modified and standard devices with N719 dye anchored

It is evident from the data provided in **Table 1** that the 8 hour treated devices are giving higher efficiency. And HCl treatment is increasing the efficiency of the DSSC. We are getting about 18% improvement in the efficiency just by HCl treatment on the TiO_2.

No	Sample	HCl treatment (h)	V_{OC} (V)	Current density (mA/cm^2)	FF (%)	Efficiency (%)
1	Standard	0	0.5348	2.28	60.4	0.67
2	Modified	4 hour	0.5506	2.82	70.7	1.00
3	Modified	8 hour	0.5362	2.4	67.1	0.76
4	Modified	16 hour	0.5387	2.57	67.7	0.99
5	Modified	20 hour	0.5283	2.28	66.0	0.79

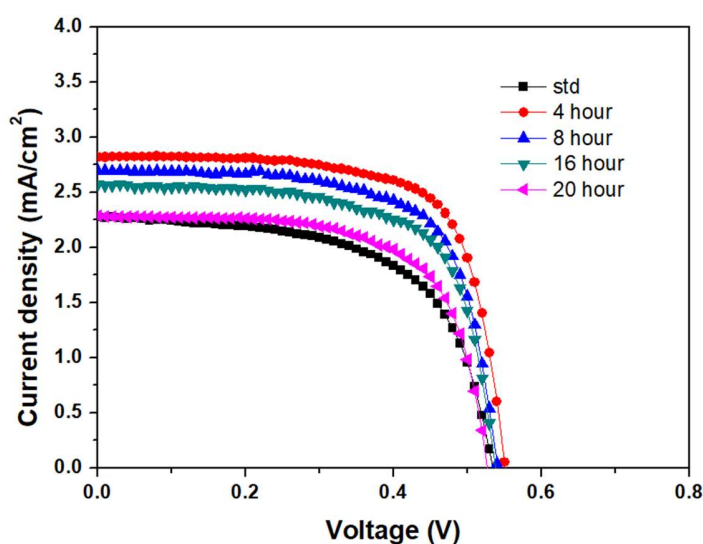**Table 2:** DSSC device metrics of HCl treated and untreated devices of SQ1 dye

Figure 6: J-V curves of modified and standard devices with SQ1 dye anchored

We have measured the SQ1 dye in HCl treated devices with different time intervals to know whether organic dyes are also showing this difference in their efficiency. And from the IV measurements, we got to know SQ1 also showing an increase in efficiency. 4 hour HCl treated devices were giving higher efficiency. And it is 33% higher than that of standard devices. As this SQ1 dye is giving very poor efficiency, it is difficult to talk about the difference in efficiency by percentage. 4, 8 and 16 hour treated devices showing improvement in the efficiency compared to that of standard devices. But we were able to confirm that there is an increase in the efficiency in DSSC with SQ1 dye by HCl treatment. This implies that simple HCl treatment by solution method is helping us to improve the efficiency of DSSC.

3.2   Incident photon to current efficiency (IPCE)

So we have carried out IPCE measurements of devices HCl treated devices of N719 dye to confirm there is a difference in efficiency. IPCE help us to find the current produced when light falls on the device. And it is shown in **Figure 5(b)**

In IPCE spectra 8 hours diluted HCl dipped devices are showing the maximum efficiency of 92% whereas the standard devices are only giving 75% only. And 16 hours dipped devices showing 88% quantum efficiency for N719 dye. We got a higher current density for 8 hours dipped devices in IV measurements, and it agrees with the data we got here. We have calculated the current density of the devices by integrating over the graph with wavelength and given in **Table 3**. 8 hours diluted HCl treated devices giving highest current density than that of 16 hours diluted HCl treated and standard devices. 8 hour treated devices are giving a current density of 14.61 mA/cm^2 whereas our standard devices were only giving 11.71 mA/cm^2 current density. It is giving almost 2.9 difference in current density. 16 hour treated devices are giving current density more than that of standard devices but lower than that of 8 hour treated devices. The results show that the HCl treatment is enhancing the recombination resistance and thereby the J_{SC} of the DSSC devices. Higher chemical capacitance and lifetime of the electrons helps the electrons flow through the TiO_2 layer and increases the J_{SC} and giving the improved performance of DSSC devices by HCl treatment.

Sample	Current density (mA/cm^2)
Standard	11.71
8 hour	14.61
16 hour	13.86

Table 3: Integrated Current density (J_{SC}) calculated from IPCE

3.3   Electrochemical impedance spectroscopy

We have plotted Nyquist graph for 8 and 16 hours HCl treated DSSC and unmodified DSSC for N719 dye which is given **Figure 7(a)** to get an idea about the kinetics taking place in the devices.
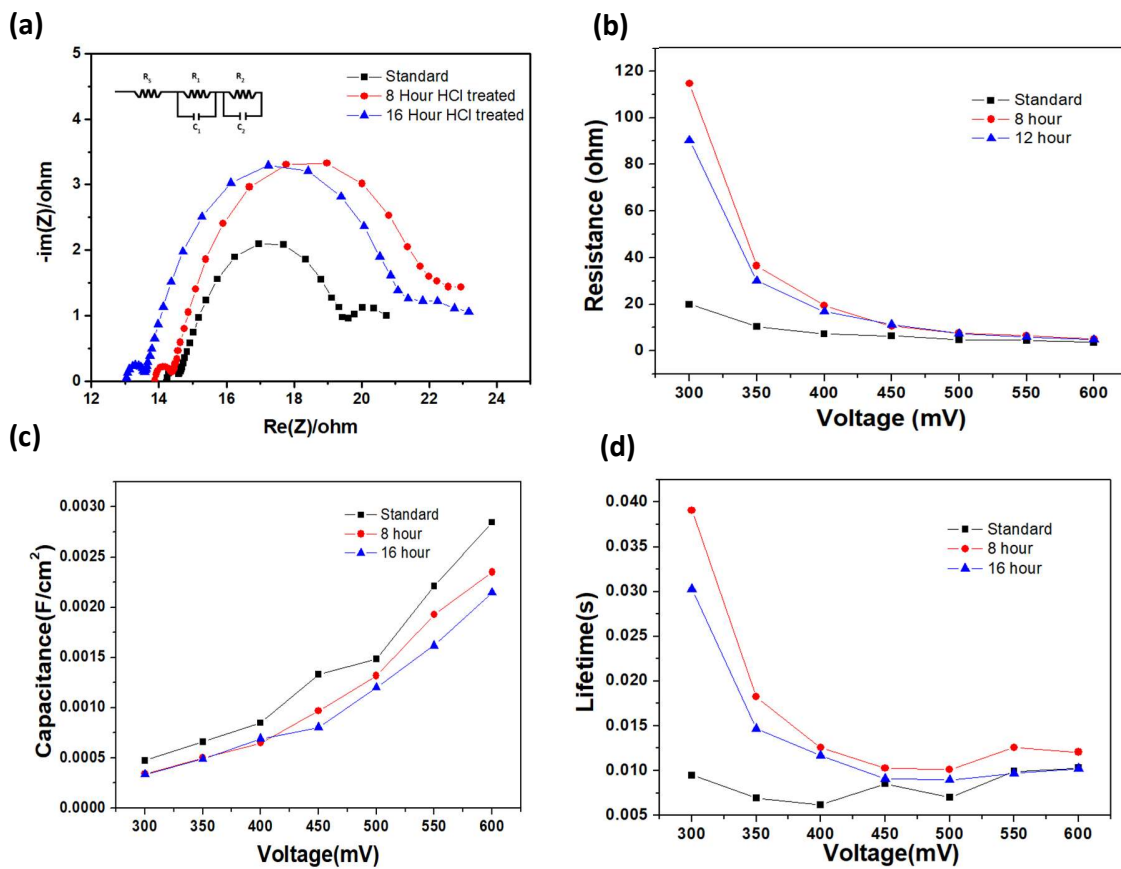
Figure 7: **(a)** Nyquist plot of the HCl treated and untreated devices anchored by N719 dye. Plot showing **(b)** variation of resistance, **(c)** variation of capacitance, **(d)** variation of lifetime

From the **Figure 7**(**a**), we have found out the chemical capacitance, which is due to charge accumulation on the LUMO of TiO_2, and recombination resistance (R_{rec}), which is preventing electrons from recombining back with the dye, of different scan rate. Electron lifetime of photoanode also found out which is the multiplicative product of this chemical capacitance and recombination resistance. These parameters are plotted and given in **Figure 7**.

We can see that, 8 hours HCl treated devices showing higher recombination resistance than that of 16 hours HCl treated and untreated devices. Higher R_{rec} helps the electrons to stay in the conduction band more time without recombination, which increases the lifetime of the electrons in the conductions band and thereby increasing charge transfer. And because of this increased recombination resistance and lifetime of the electrons in the conduction band of TiO_2, the devices showed a higher current density values. The increase in Rrec results in increased chemical capacitance and the number of electrons staying in the LUMO which results in an increased lifetime. The HCl untreated device is showing the lowest R_{rec} than HCl treated devices. 16 hour HCl treated devices showing a reduction in R_{rec} and thereby reduction in the chemical capacitance and lifetime of electrons than that of 8 hour treated devices. From impedance spectroscopy, it is evident that the HCl treatment improves the DSSC performance by increasing the current density of the devices by increased recombination resistance and chemical capacitance.

We also plotted the Nyquist plot and the other graphs for SQ1 dye as well. And it is shown in **Figure 8(a).** From the Nyquist plot for different scan rates, we have calculated the recombination resistance, chemical capacitance and lifetime of the devices. And they are plotted to the scan rate and given in the **Figure 8**.
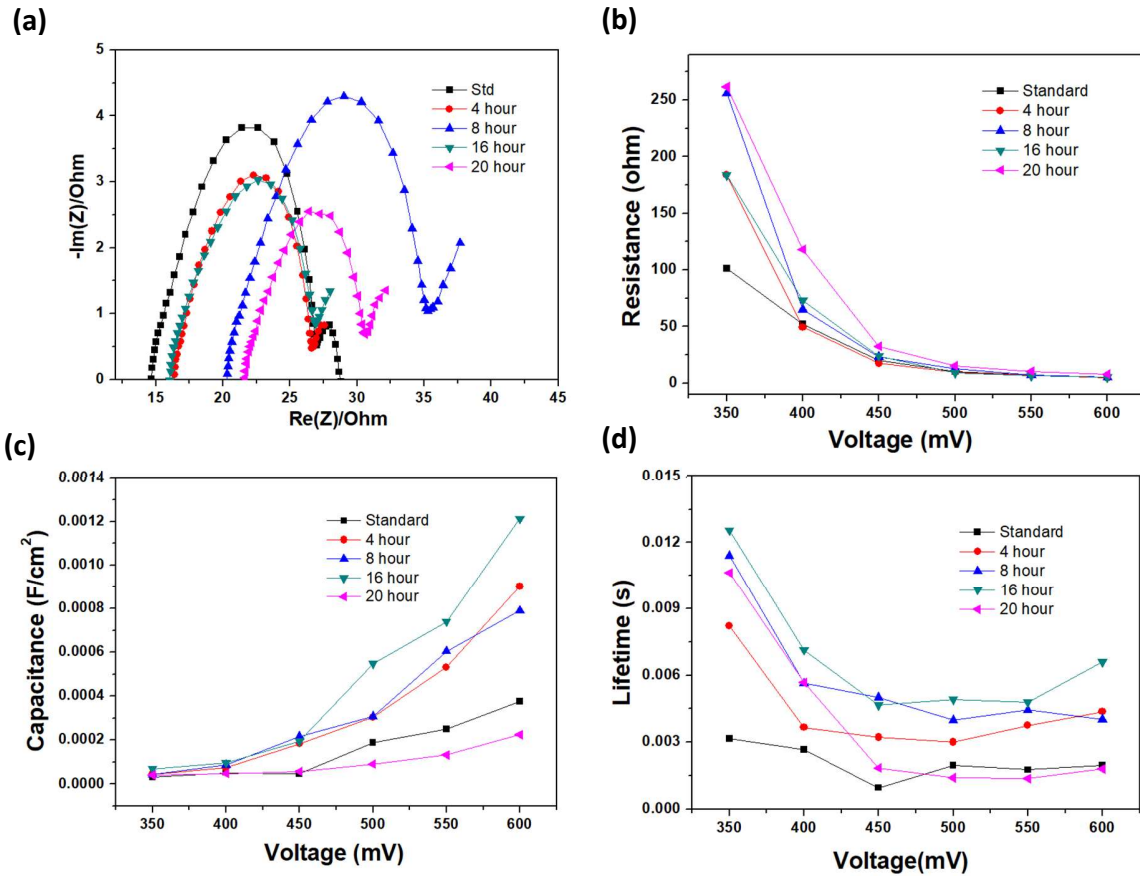
Figure 8: (a) Nyquist plot of the HCl treated and untreated devices anchored by SQ1 dye. Plot showing **(b)** variation of resistance, **(c)** variation of capacitance, **(d)** variation of lifetime

From **Figure 8(b)** we can see that HCl treated devices are showing higher recombination resistance than that of standard devices. 20 hour HCl treated are showing the highest recombination resistance. Followed by 8, 16 and 4 hour treated devices showing higher R_{rec} than that of untreated standard devices. In case of chemical capacitance 16 hour treated devices showing the highest values. Followed by 4, 8, standard and 20 hour treated devices. It is showing that as the time of HCl increases the chemical capacitance first increases and then decreases after 16 hour. Thereby the lifetime of an electron in the conduction band of TiO_2 also decreases after 16 hour HCl treatment. 16 hour treated devices are showing the highest lifetime. And above 16 hour treated devices have a lower lifetime. Standard devices are also showing lower lifetime like 20 hour HCl treated devices. From this impedance spectroscopy

studies, it is evident that HCl treatment helps to increase the efficiency of the DSSC by increasing the parameters recombination resistance, chemical capacitance and lifetime for SQ1 dye as well. We conclude from the EIS that, this HCl treatment is efficient in improving the performance of both N719 and SQ1 dye.

3.4 UV measurements

In order to understand the effect of HCl treatment on the band gap of TiO_2 active layer, we have carried out UV measurements. To find the band gap, we have plotted the tangent of the curves and find the intersecting point. And it is shown in **Figure 9.** But we got that both treated devices and untreated devices are giving bandgap almost same. The data we collected are given in **Figure 9** and **Table 4**.
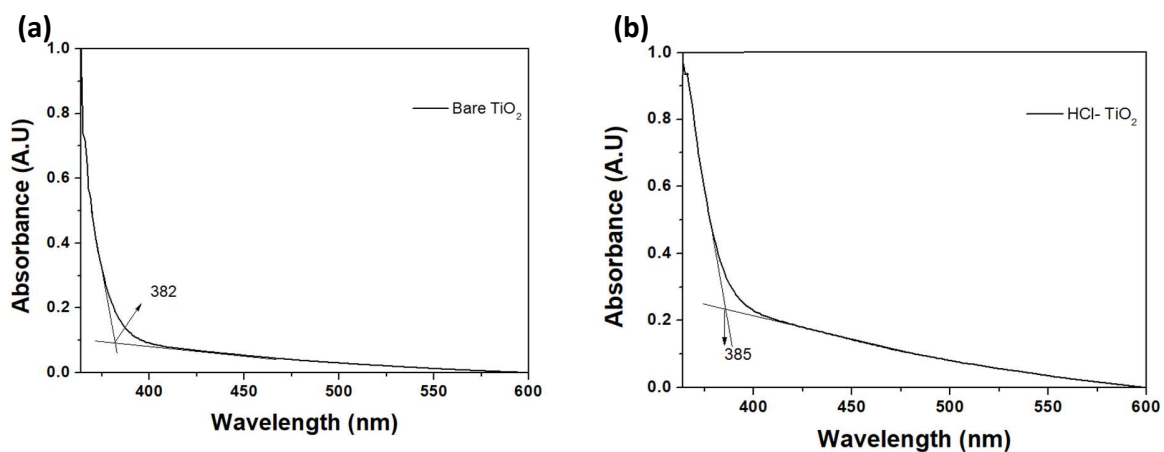
Figure 9: UV absorption spectra of **(a)** untreated TiO_2 and **(b)** HCl treated TiO_2

Sample	Bandgap
Bare TiO2	3.29 eV
HCl treated	3.25 eV

Table 4: Bandgap calculation by optical method

We can see that the bandgap of HCl treated and unmodified TiO_2 are very close. And also we haven't got a big difference in V_{OC} from J-V measurements also. This implies that HCl treatment is not affecting the band gap of the TiO_2.

3.5   Dye desorption studies

We have carried out dye desorption studies to understand how diluted HCl is affecting the adsorption of dye molecule to the surface of TiO_2. We have made a 0.1M NaOH solution in which water and ethanol took like a 1:1 ratio. We dipped the dye anchored devices in 3 ml of NaOH solution for a fixed time interval. The dye anchored on the photoanodes desorbed. Desorption was very fast and was visible that all most all anchored dye was coming off to the NaOH solution. We got molar extinction coefficient of N719 dye from previous studies and is 32349 L $mol^{-1}cm^{-1}$. By using the Beer-Lamberts law, we have calculated the absorbance of NaOH solutions which contain desorbed dye from unmodified, and HCl treated photoanodes. We have carried out this experiment to find out, how the surface treatment of diluted HCl is affecting the surface morphology and thereby the anchoring of dye molecules.

Figure 10: Absorbance spectra of the NaOH solution contain desorbed dye N719 of **(a)** standard, **(b)** 8 hour HCl treated, **(c)** 16 hour HCl treated.

Sample	Average Concentration (mol/cm^2)
Standard	5.03*10^{-6}
8 hour	5.89* 10^{-6}
16 hour	6.04* 10^{-6}

Table 5: Concentration of the dye desorbed in untreated and treated devices anchored by the N719 dye.

And from **Table 5**, we can see that, standard untreated devices showing the lowest concentration of N719 dye compared to treated devices. This clearly shows that HCl treated devices can anchor more N719 dye on its surface than that of untreated devices. So this HCl treatment is altering the surface of the photoanode in a way in which more dye can anchor on the surface. NaOH solution from 16 hour dipped devices showing highest absorbance, and from IPCE and IV measurement we have observed that for 16 hours HCl dipping the efficiency has been reduced which might be due to dye aggregation. So it is evident from this experiment that HCl treatment increases the dye anchoring by making more binding sites on the surface by protonating the surface[36-39].

We have carried out the dye desorption studies of SQ1 dye, and it is shown in **Figure 11**. In the case of SQ1 dye, dye aggregation also taking place. It is explained in the previous studies. The dye anchoring after HCl treatment is checked. And it is clearly showing there is a reduction in the dye anchoring of SQ1 dye after HCl treatment.
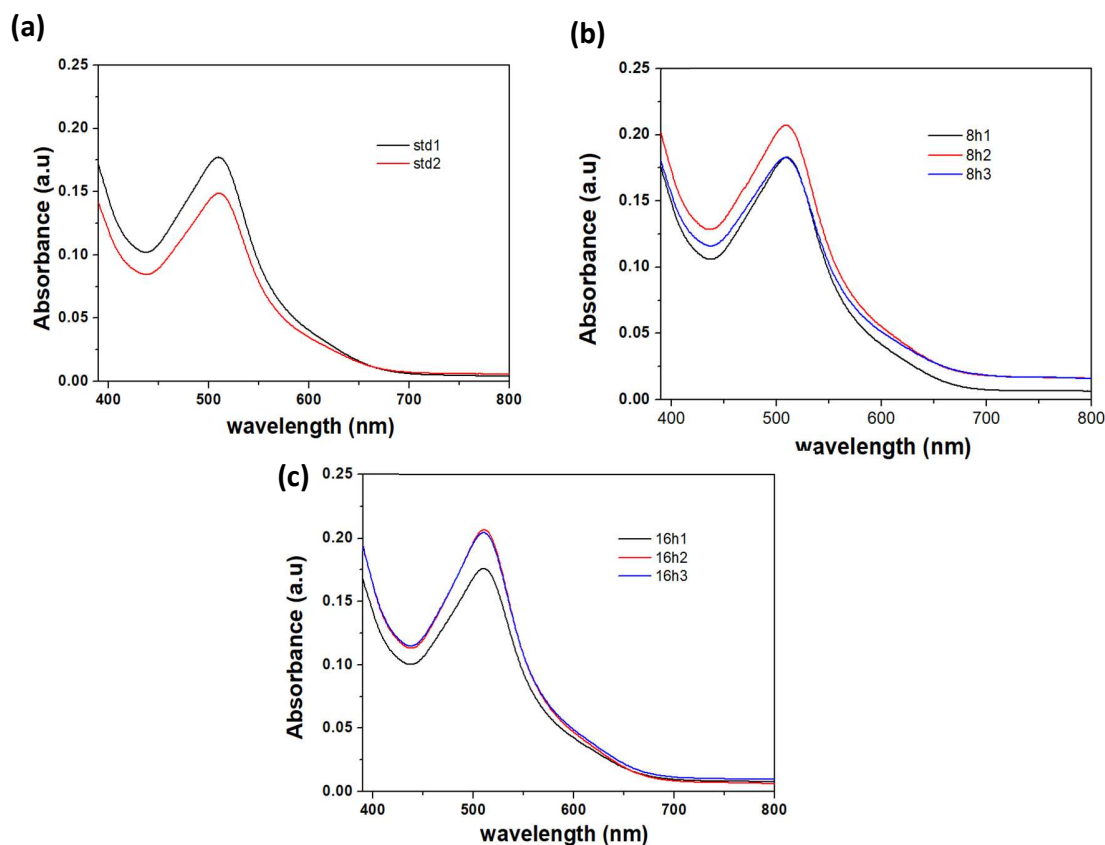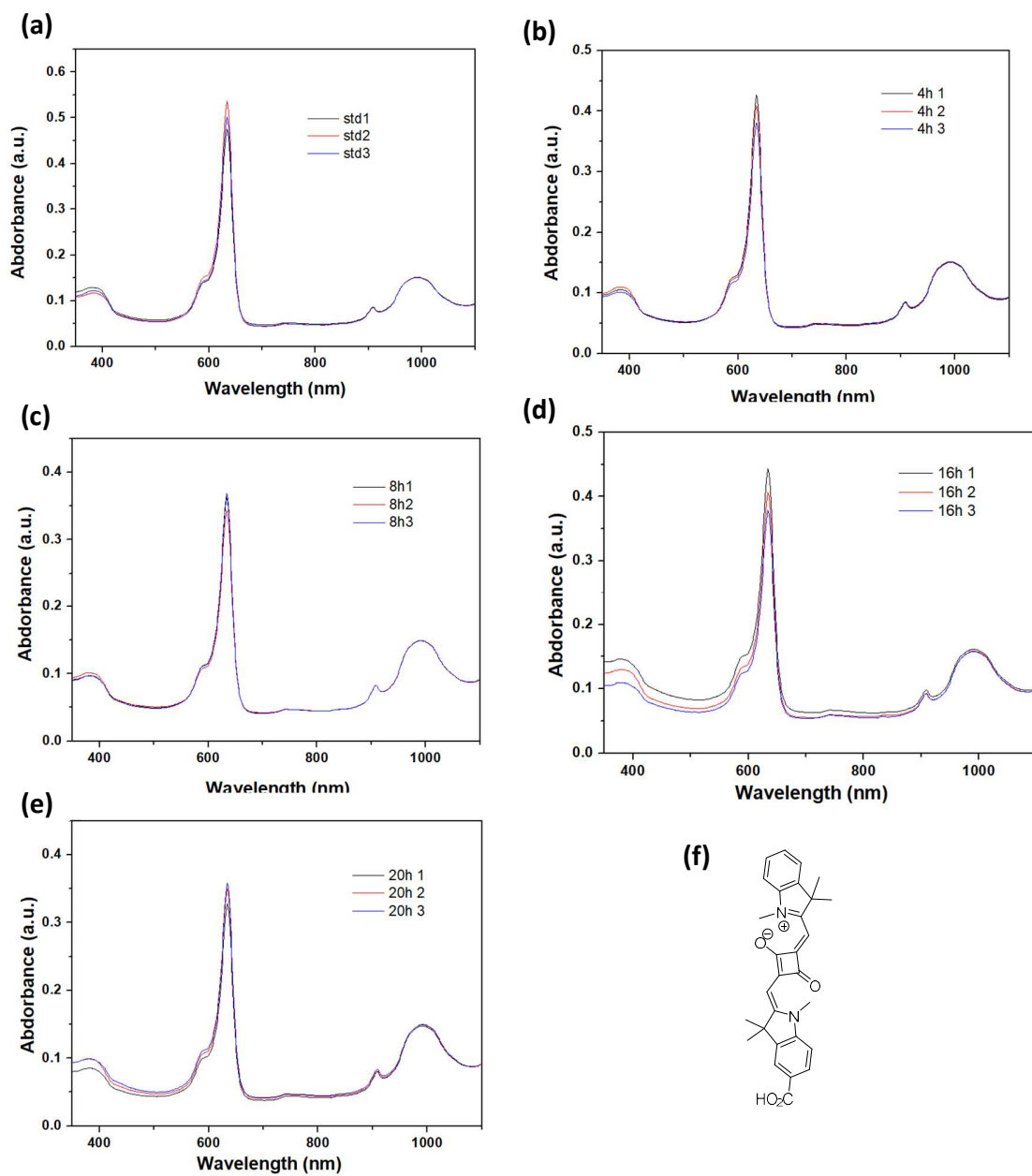
Figure 11: Absorbance spectra of the NaOH solution contain desorbed dye SQ1 of **(a)** standard, **(b)** 4 hour HCl treated, **(c)** 8 hour HCl treated, **(d)** 16 hour treated and **(e)** 20 hour treated. **(f)** Structure of SQ1 dye.

From **Figure 11,** we can see that SQ1 dye gives an absorption peak at 634 nm. And the molar extinction coefficient of the SQ1 is 1.4×10^5 $M^{-1}cm^{-1,}$ and we got it from previous studies. Using it, we have calculated the concentration of the dye desorbed after it immersed in the 0.1 M NaOH solution as described for N719 dye. Averaged concentration for each sample is given in **Table 6**. It is evident from the table that standard devices are having most dye anchored. After the HCl treated photoanodes are showing lower dye concentration than that of standard devices. It indicates the dye aggregation on the surface of the photoanode of standard devices. And HCl treatment helps to reduce the aggregation on the devices and helps to increase the efficiency of the DSSC. This is done by protonating surface of TiO_2 by HCl treatment, which helps the dye to anchor in the way in which arrange properly on the surface instead of binding randomly. This helps to increase the efficiency of the DSSC.

Sample	Average Concentration (mol/cm^2)
Standard	3.6×10^{-6}
4 Hour	2.9×10^{-6}
8 Hour	2.59×10^{-6}
16 Hour	2.92×10^{-6}
20 Hour	2.47×10^{-6}

Table 6: Concentration of the dye desorbed in untreated and treated devices anchored by the N719 dye.

3.6   Powder X-ray diffraction

In order to understand the effect of HCl treatment on the crystalline structure of the TiO_2, we have carried out X-ray diffraction studies on the TiO_2 powder. We have added the HCl into the ground powder and kept it for the different time interval and heated at

90°C for 30 minutes. Then the TiO_2 powder collected, ground and submitted for powder X-ray diffraction.
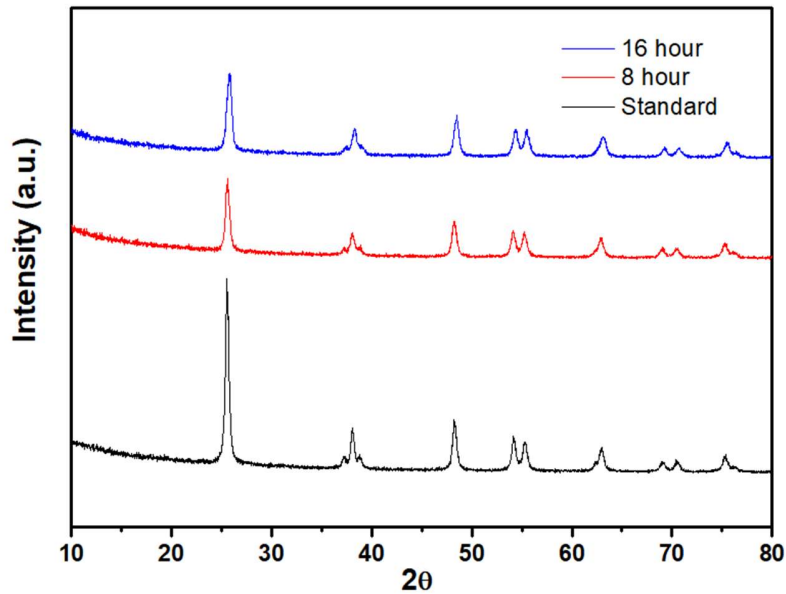
Figure 12: PXRD data of standard, 8 hour and 16 hour HCl treated TiO_2 powder.

From the plot, it is evident that there are no changes in the peak position. But after the HCl treatment, the peak intensity has been reduced for TiO_2 powder. 8 hour and 16 hour treated devices showing lower intensity than that of standard untreated TiO_2 powder. When the electron density increases the peak intensity increases from the structure factor. Here HCl treated TiO_2 showing lower peak intensity which can be due to the surface protonation taking place. This reduces the surface electron density of the TiO_2. This, in turn, helps the dye to anchor more on to the surface of TiO_2. And thus the efficiency also increases.

3.7   FESEM

We have carried out FESEM of the HCl treated photoanodes and untreated photoanodes to understand how the HCl treatment is affecting the surface of

photoanodes. FESEM of the standard devices and HCl treated photoanodes are carried out and are given in **Figure 13**

Standard TiO$_2$　　　　　　　　　　　　　HCl treated TiO$_2$

Figure 13: FESEM images of **(a)** standard TiO$_2$ and **(b)** HCl treated TiO$_2$.

But from the figures, it is evident that there is not much of a change in the surface of photoanodes by the HCl treatment. It implies that the HCl treatment is helping the dye to anchor more on to the surface and it is not due to any visible changes on the surface. And it might be due to the surface protonation take place by the HCl treatment. FESEM gives very clear images of the surface of TiO$_2$. The alteration of the surface by the treatment is very minute. Therefore the surface protonation is not visible by the microscopy techniques.

3.8　X-ray photoelectron spectroscopy

From the XPS data, we were able to get more information about what happening on the surface of TiO$_2$ after the HCl treatment. From **Figure 14**, we can see a strong peak at 533.4 eV for the O1s orbital which is present in both HCl treated and untreated TiO$_2$. It is very evident from **Figure 14** that there is the formation of -OH peak at 530 eV for HCl treated TiO$_2$. This is showing the presence of protonation of the surface of TiO$_2$ by HCl

treatment. In the case of standard TiO_2, there is a small peak around 530 eV. It is due to protonation by water present in the TiO_2. XPS data help us to understand the surface modification happened on TiO_2 by HCl treatment[38].
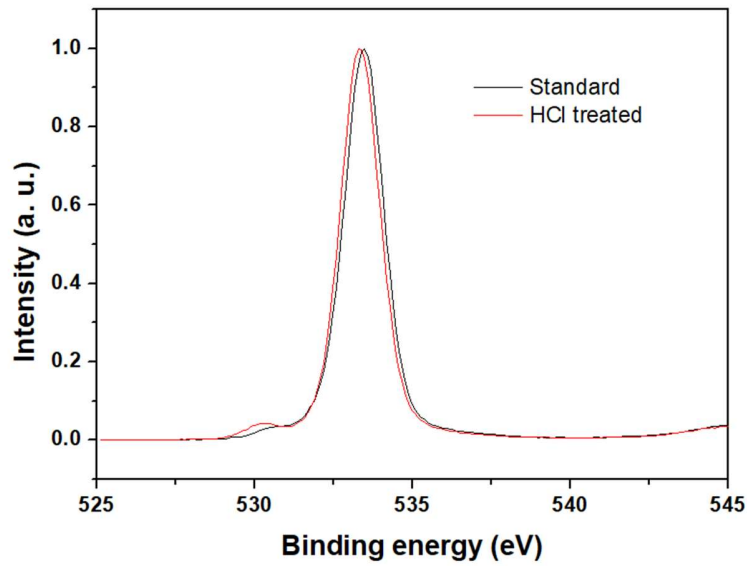

Figure 14: XPS spectra for O1s of treated and standard TiO_2.

4   CONCLUSION

We successfully increased the efficiency of the DSSC by surface treatment of diluted HCl which is 18% higher than that of the unmodified device (8.7%) for N719 dye and 33% for SQ1 dye. This photoconversion efficiency improvement is due to surface protonation, and it helps more positive charges to accumulate on the mesoporous TiO_2, which increase the dye anchoring sites on the TiO_2 for N719 dye. In the case of SQ1 dye, the dye anchoring is reduced and help to reduce the dye aggregation and thereby to increase the efficiency. From impedance spectroscopy, we were able to find out that the recombination resistance is increasing for the HCl treated devices and the chemical capacitance of the devices are also increasing which results in the increased lifetime of electrons in the conduction band. This results in an increase in the current density and efficiency. And from powder X-ray diffraction we were able to understand the peak intensity is decreasing as the HCl is treated. This can be due to surface protonation and which helps to confirm our assumption. And the presence of –OH group is detected from the XPS spectra helps us to conclude surface protonation is taking place at the surface of TiO_2, and it has a significant effect in improving the efficiency of the DSSC.

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