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Construction of hybrid solar cells exploiting the interaction of TiO2/Photosystem I complexes

Rahul K Desai[1], Alex S Khristy[2], Piyush J Bhatt[1], Laxmi J Tomar[1], Preet D Vyas[3], C Ratna Prabha[2]*, Kireetkumar D Patel[3] & Biswajit S Chakrabarty[1]*

[1]Department of Applied Physics, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara-390 002, Gujarat, India

[2]Department of Biochemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara-390 002, Gujarat, India

[3]Physics Department, S.P. University, Vallabh Vidhya Nagar-388 120, Gujarat, India

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Proteins produce chemical energy by absorbing light in the process of photosynthesis. The use of biological photonic system has recently gained interest, especially in the field of solar energy conservation. The applications of photosynthetic components in photovoltaic material and solar cells are very promising due to their environmental compatibility and efficiency of energy conservation in photosynthesis. The recent advancement in the solar cell design includes the use of photosystem, thylakoid membrane immobilised on polymeric electrode. Previous reports have confirmed the use of PSI as photoelectric material in solar cells. The present work studies the integration of TiO_2/PSI complexes with polymer electrodes. Light harvesting complexes (LHC) were isolated from spinach by homogenising cell in lysis buffer. The isolated proteins were then loaded onto DEAE-cellulose a type of ion-exchange chromatography for further purification. TiO_2 layer was then spin coated onto Indium Tin Oxide coated (ITO) plates followed by dipping in a solution containing LHCs for 30 min. Upon drying, using spin coating, a thin layer of Polypyrrole electrode was casted onto it. Optical parameters and structural parameters were determined using UV-Vis analysis and XRD respectively. Efficiencies of the resulting devices were calculated under Air mass 1.5 (AM 1.5) conditions. The results establish the successful preparation of a solar cell.

Keywords: Efficiency, Light-harvesting complexes (LHCs), Photosynthesis, Photosystem, Polypyrrole, Proteins, Solar cells, TiO2/PSI complexes

Photosynthesis is an essential biological process that transforms solar energy into chemical energy, supporting life on Earth by producing oxygen, food, and regulating atmospheric carbon dioxide levels. Within this process, photosystem I (PSI) plays a crucial role in generating energy for the conversion of $NADP^+$ to NADPH, while photosystem II (PSII) catalyzes the water-splitting and oxygen-releasing reaction. Alongside these, the light-harvesting complexes (LHCs) work in conjunction to optimize light absorption and energy transfer[1]. The PSI complex is comprised of polypeptides and cofactors essential for the absorption and utilization of photons. Within chloroplasts, PSI consists of 19 distinct polypeptides that exhibit significant variations in molecular weights, hydrophobicities, and locations relative to the lipid bilayer. Alongside proteins, the PSI complex includes approximately 175 Chlorophyll molecules, multiple β-carotenes, two phylloquinone molecules, and three [4Fe-4S] clusters[2]. The PSI cofactors specifically associate with the PsaA, PsaB, and PsaC proteins, while the remaining subunits do not bind any redox centers. PhotosystemI (PSI), a substantial membrane protein complex, possesses the capability to facilitate electron transfer from the soluble copper-containing protein plastocyanin found within the thylakoids to ferredoxin located on the stromal side of the thylakoid membrane. The photosynthetic membrane gets charged by this process, and an electrochemical gradient is developed, which drives the synthesis of ATP[3]. Photosystem-I achieve the most negative redox potential known in nature and boasts remarkable efficacy in harnessing light for efficient electron transport.

TiO_2 has been extensively used in Dye Sensitized solar cells (DSSC) for its unique properties of being mesoporous, good dye absorbent, proper photocatalytic activities and its stability at higher

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*Correspondence:
E-mail: Bschakrabarty-apphy@msubaroda.ac.in (BSC); cratna.prabha-biochem@msubaroda.ac.in (CRP)

temperatures. In the present work we have attempted to replace the dye with LHCs to study the efficiency of the device.

Materials and Methods

All the chemicals were purchased from Loba chemicals and used as received except when mentioned.

Synthesis of TiO_2 nanoparticles

TiO_2 was synthesized according to method reported in previous work[4]. In summary two solutions A and B were made. Solution A consists of 20 mL of titanium isopropoxide diluted in 5 mL of 30% isopropanol. Solution B was made by diluting 0.5 mL HNO_3 in 0.5 mL H_2O. Solution B was added to A drop wise under constant stirring. Alcogel obtained after 30 min. was added to stainless steel autoclave and was kept for 24 h in an oven maintained at 240°C. TiO_2 nanoparticles obtained were washed several times with water and dried in an oven.

Synthesis of Polypyrrole (ppy) nano particles:

Polypyrrole was synthesized using previous reports and certain modification in procedure was made[5,6]. Pyrrole was purchased from sigma Aldrich and distilled twice before use. Ppy nanoparticles were fabricated using chemical oxidative polymerization using methyl orange (MO) solution as solvent. Typically, 2.592 g $FeCl_3.6H_2O$ was added to 320 mL 5 mM methyl orange and stirred for 30 min. 0.56 mL of pyrrole was added drop-wise into the mixture. Reaction was carried out at 12°C for 4 h. The sample obtained was washed with water several times to assure removal of unbound and excess MO particles. Ppy particles were dried and powdered well. These particles were then doped with 2N HCl for 12 h.

Isolation of light harvesting complexes

Isolation of photosystem-I from spinach leaves

Preparation of buffers

Buffer A containing 0.3M sucrose, 15 mM NaCl, 30 mM tricine, was prepared and its pH was adjusted to 7.8 with 1N NaOH solution. Buffer B solution was prepared with 5 mM EDTA and 5 mM tricine and its pH was adjusted to 7.8 with 1N NaOH solution. Buffer C solution consisting of 0.3 M sucrose and 30 mM tricine was prepareand its pH was adjusted to 7.8 with 1N NaOH solution.

Fresh spinach (*Spinacia oleracea* L.) leaves were purchased and stored at 4°C overnight after washing. Next day, leaves were then homogenized in homogenizing buffer A. Paste obtained was then filtered through 4 layered cheese-cloth and centrifuged at 2000 g for 2 min. Pellet containing chloroplasts was washed twice with the hypotonic buffer B and centrifuged at 2000 g for 2 min. Unstacked membrane were obtained by centrifugation at 25000 g and then suspended in suspension buffer *C. Spinach* thylakoids were then solubilized in triton-X 100 (4.8% *w/v*). After stirring the solution for 15 min., sample was centrifuged at 15000 g for 15 min. The complex was then further purified, using DEAE-cellulose column chromatography.

DEAE-cellulose column preparation

DEAE-cellulose dry resin was suspended in 5 volumes of distilled water and allowed it to settle for 45 min. The settled volume of the resin was then measured. This is the column volume (CV) to be used for measuring the solution. The suspension was filtered using Whatman filter paper. The resin was suspended in two column volumes (CV) of buffer-A (0.1 M NaOH, 0.5 M NaCl) for 10min and then the resultant slurry was filtered. Washing of the slurry was continued with 2 CV of buffer A. Washing step was repeated using buffer-B (0.5M NaCl), and subsequently with buffer-C (0.1 M HCl, 0.5M NaCl). Finally, the resin was washed with 5-10 CV distilled water, until the pH of effluent was greater than 5. The slurry was suspended in 2 CV of 1M NaCl and the pH adjusted to 7.8 using NaOH and stored at 0-5°C. To use resin, it was filtered and washed with 5 CV of distilled water. Subsequently, the resin was resuspended with 2 CV of 1 X starting buffer for 15 min. The readiness of resin for further use was confirmed by filtering small amount of the suspension, and finding that the pH is within 0.15 units of the buffer. The resin was packed in the column under gravitational flow.

Column chromatography

Column prepared was washed with 100 mL of starting buffer (10 mM Tris-HCl, 0.2% Triton X-100, 20% sucrose and pH 7.8 NaOH), keeping the flow rate constant at 1 mL/min throughout procedure. The supernatant containing PSI was loaded onto the column using peristaltic pump. After which the column was washed with 1000 mL of starting buffer, supplemented with 10 mM NaCl and then with the 300 mL of starting buffer supplemented with 50 mM NaCl, and finally with 400 mL of linear gradient of 50-200 mM NaCl. Fractions of 5 mL volume were collected and were subjected to further analysis.

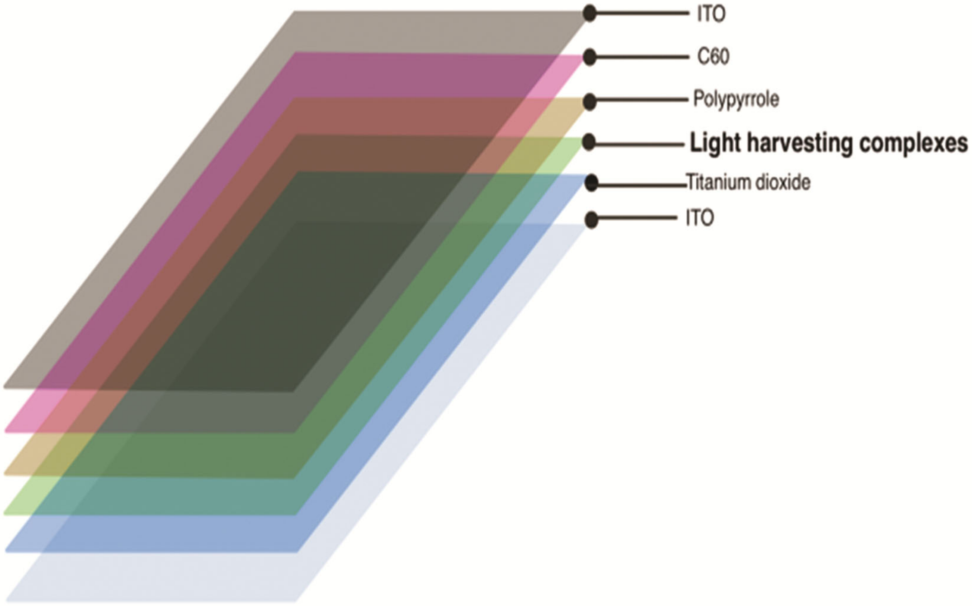

Fig. 1 — Bio-organic solar cell stack

Fabrication of device

Solar cell was fabricated according to the structure (Fig. 1). Transparent cellulose sheet was initially taken and washed with distilled water and ethanol respectively. Indium Tin Oxide (ITO) was coated using magnetron sputtering. TiO_2 was coated using doctor blade technique. TiO_2 coated film was dipped in the solution of LHC's for two h. to allow complete absorption. Polypyrrole nano powder was homogenised in ethanol and spin coated over the existing layers. A layer of graphene was also spin coated serving as a supporting electrode. Finally, another ITO coated cellulose sheet was placed over it and the device was sealed using dual side tapes after placing a drop of iodine electrolyte.

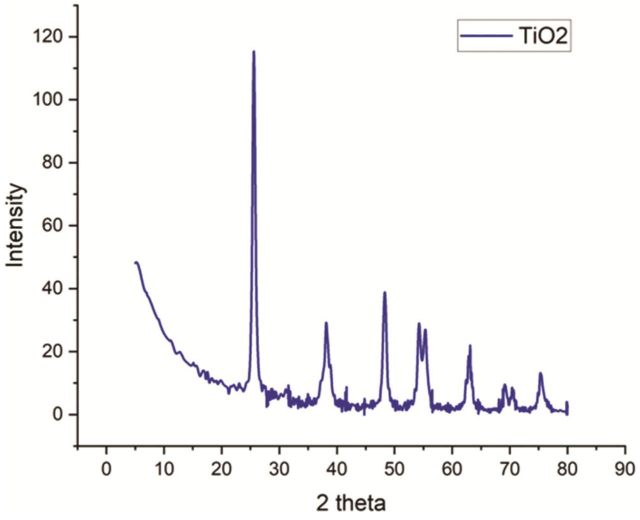

Fig. 2 — XRD analysis of TiO_2

Results

XRD analysis

XRD pattern was taken on Bruker D8 Advance X-ray diffract meter (Fig. 2). XRD analysis revealed a clear crystalline structure of TiO_2. Anatase phase of TiO_2 was confirmed using JCPDS data 21-1276. Crystallite size was calculated using Scherrer's formula:

$$D = \frac{k\lambda}{\beta cos\theta}$$

where D: crystallite size, λ: 1.54 Å, β: FWHM of diffraction peak which would be different for every peak found in XRD graph, θ: Bragg's angles, k= 0.9 is the correction factor. Average crystallite size was found to be around 15.01 nm. Also lattice strain was calculated using the equation:

$$\eta = \frac{\left[\frac{\lambda}{tcos\theta} - \frac{\beta\pi}{180}\right]}{tan\theta}$$

whereas, grain size and all the other parameters hold the same meaning as mentioned above. Lattice strain was found to be around 0.15 which is reasonably lower compared to the previous reports.

XRD analysis of polypyrrole revealed its amorphous structure. Though looking at the XRD graph and using previous reports, it can be concluded that almost pure form of polypyrrole has been formed. But particle size analysis of polymer estimates size range from 8 nm to 20 nm.

UV-Visible spectral analysis

UV-visible absorption spectra were recorded on Thermo Scientific (Evolution 600 UV-Vis) in wavelength range of 200 nm to 900 nm. A clear absorbance peak was observed at 310 nm that corresponds to characteristic absorbance of TiO_2 (Fig. 3). Band gap was determined using Tauc's relation was found to be around 1.9 eV[7-9].

UV-Vis analysis of polypyrrole showed major absorbance at around 430 nm. Another small absorbance has been observed at 250 nm (Fig. 4). These peaks are also the characteristic peaks of polypyrrole. Tauc's relation was used to estimate the band gap of polypyrrole and is found to be around 2.8 eV (Fig. 5). Use of polypyrrole has also been reported for the application in chemical sensors owing to its bandgap in the range observed in our work and also because of its stability and good conductivity[10].

Isolation of Light harvesting complexes was confirmed using UV-Vis Analysis. The major peak at around 430 nm and 680 nm are the characteristic peaks of Chlorophyll a and b, respectively, (Fig. 6). During purification of the complexes, multiple phases of solutions in the batch size of 5 mL were collected where phase 1 was found to have the highest concentration of LHCs. Hence it was coated on to the cell.

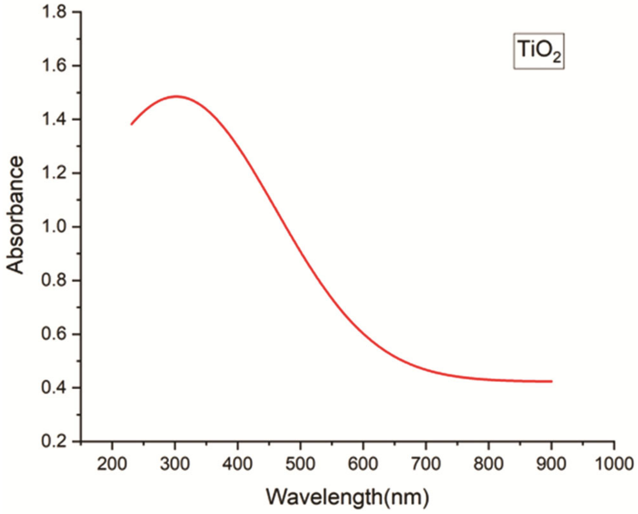

Fig. 3 — UV-Vis Analysis of TiO_2

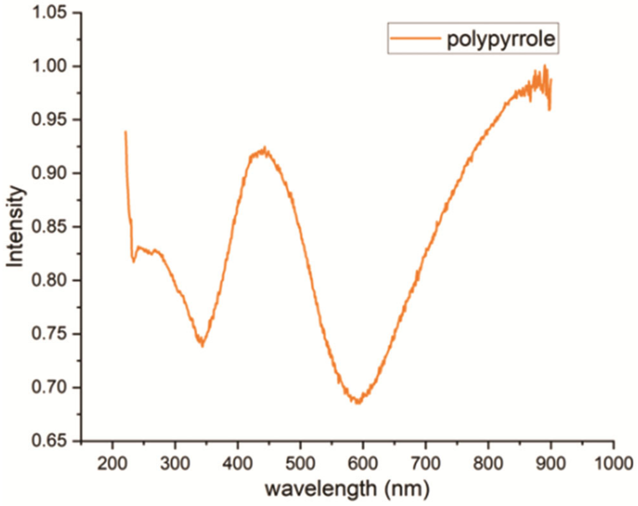

Fig. 4 — UV-Vis Analysis of Polypyrrole

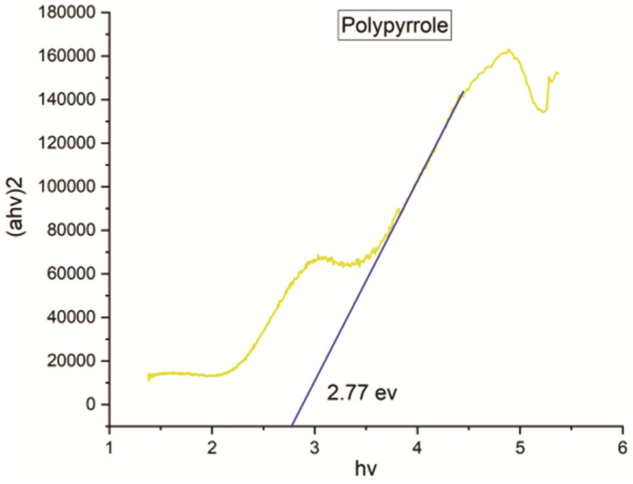

Fig. 5 — Tauc's plot of polypyrrole

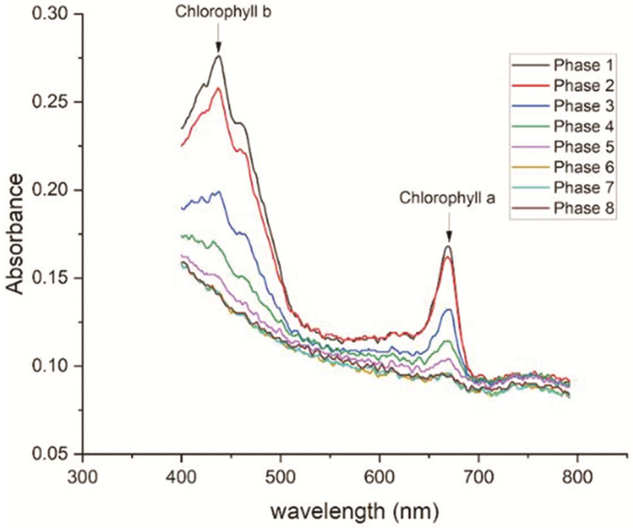

Fig. 6 — UV-Vis Analysis of PS-I

Table 1 — Device parameters

Devise	Jsc (mA/cm^2)	V_{OC} (V)	Fill Factor	Efficiency
With LHC	13.01	0.71	0.63	5.81

Working of the device

The extracted light harvesting complex contains five major protein molecules besides p700 chlorophyll molecule. These are A_0, A_1, F_x, F_a and F_b. The P700 molecule absorbs photon and donates electron, whereas the later mentioned subunits accept the electron and are responsible for oxidizing P700 molecule. For a pure light harvesting complex without its interaction with TiO_2 the excited photoelectron from P700 is accepted by $A_0 \rightarrow A_1 \rightarrow F_x \rightarrow F_a$ and F_b. This transition is expected to result in high efficiency but quenching and heating effects are considered to be notable reasons for the decrease in efficiency. The interaction of TiO_2 with LHCs has provided stability to the protein units to a great extent. The reported efficiency without the use of oxide was 0.5%. Interestingly, use of TiO_2 could raise the efficiency to 5.81% (Table 1).

Discussion

The efficiencies obtained here indicate a scope for improving the values by increasing the interaction between TiO_2 and proteins. Here, sintering was not done to prepare TiO_2 films, which resulted in less mesoporous structure. Lack of microporosity could be a cause for less absorbance of light harvesting complexes, which resulted in poor interaction between the materials. Further, fabrication of similar device on flexible substrates for indoor application can be thought of as suggested earlier in literature, counter electrodes of polypyrrole could be replaced by carbon-based electrodes to increase the stability of the cell[6].

Conflict of interest

All authors declare no conflict of interest.

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