Volume 5 Issue 1



June 2010

Trade Science Inc.

Physical IEMISTRY

An Indian Journal

TiO₂ nanoparticles;

Solar cells;

Bulk heterojunction solar

cell:

Polymer solar cell;

Quantum dots.

> Review

PCAIJ, 5(1), 2010 [10-19]

Recent developments in dye sensitized titanium dioxide solar cells

S.Ramalakshmi², P.Shakkthivel^{1*}

¹Department of NanoScience and Technology, Alagappa University, Karaikudi - 630 003, Tamilnadu, (INDIA) ²Department of Industrial Chemistry, Alagappa University, Karaikudi - 630 003, Tamilnadu, (INDIA) E-mail : apsakthivel@yahoo.com Beasingd, 22rd February, 2010

Received: 23rd January, 2010; Accepted: 2nd February, 2010

ABSTRACT

Dwindling energy crisis has to be alleviated with the help of latest developed new technologies. The emerging novel concept in harvesting solar radiation may pave the way for enhanced non-polluting, green and sustainable energy sources development. Although conventional solar cells were built from inorganic materials for high efficiency, their usage is limited because of its high cost and complicated processing techniques. Photoelectrochemical cells (dye sensitized solar cells) are the cheap alternatives for conventional solar cell consists of transparent conducting glass electrode coated with porous nanocrystalline TiO₂ (nc-TiO₂), adsorbed dye sensitizer along with redox electrolyte. The blends of organic and inorganic materials in hybrid solar cells offer an unique property in designing hybrid inexpensive and high efficiency photovoltaic (PV) sources. Conjugated polymers can be tailored for band gap uniformity and easy exciton evolutions with reduced exciton decay. The recombination of back electron transfer is diminished by producing barrier layer on the inorganic nanoparticle semiconductor electrodes. By selecting an optimized conducive technology in various steps of fabrication stages, efficient high photon to electricity conversion is achievable. In the present review, latest upto-date perspectives of solar cell technology are organized in various tech-© 2010 Trade Science Inc. - INDIA nological concepts.

INTRODUCTION

Solar cell is a device which converts solar energy into electrical energy by photovoltaic effect. French Scientist A.E.Becquerel was first synthesized the solar cell in 1839^[1]. The conversion of sunlight into electricity is a clean, abundant and renewable energy source. Efficiency of conventional solar cells made from inorganic materials reached up to 24%^[2]. Recent research mainly focused on the conversion efficiency in between 30% and 70% while retaining low cost materials and fast pro-

cessing techniques^[3].

A broad range of solar cell technologies are currently being developed, including dye sensitized nanocrysta-lline photoelectrochemical solar cells, polymer/fullerene bulk heterojunctions, small molecule thin films and organic–inorganic hybrid devices^[4].

KEYWORDS

The dye sensitized solar cells DSSC is attracted the research community because of its high efficiency and long term stability.

Recent reports include the results of an increase in power generation efficiency by conducting surface pro-

cessing through exposing microwaves on the titanium oxide (TiO_2) surface and also an increase in power generation efficiency by doping nitrogen ions on the TiO_2 membrane^[5].

In this review, we have given main focus on the nanostructured TiO_2 DSSC development in the recent years. This review is organized to disseminate the progress of the solid state DSSC and Gratzel cell clearly.

Dye sensitized solar cell

The dye sensitized solar cell is comprised of a transparent conducting glass electrode coated with porous nanocrystalline TiO_2 (nc- TiO_2), dye molecules attached to the surface of the nc- TiO_2 , an electrolyte containing a reduction-oxidation couple such as Γ/I^3 and a catalyst coated counter-electrode^[6]. Schematic representation of the dye sensitized light converting Photovoltaic cell is presented in figure 1.

In DSSC, the incoming photon is absorbed by the dye molecule adsorbed on the surface of the nanocrystalline TiO_2 particle and an electron from a molecular ground state S_0 is excited to a higher lying excited state S*. The excited electron is injected to the conduction band of the TiO₂ particle leaving the dye molecule to an oxidized state S. The injected electron percolates through the porous nanocrystalline structure to the transparent conducting oxide layer of the glass substrate (negative electrode, anode) and finally pass

through an external load to the counter-electrode (positive electrode, cathode). At the counter-electrode, the electron is transferred to triiodide in the electrolyte to yield iodine and the cycle is closed by reduction of the oxidized dye by the iodine in the electrolyte^[7]. Due to the energy level positioning in the system, the cell is capable of producing voltage between its electrodes and across the external load as shown in Figure 2.

Electrical characteristics of a solar cell

The current–voltage characteristics of a solar cell in the dark and under the illumination are shown in Figure 3. In the dark, there is almost no current flowing, until the contacts start to inject heavily at forward bias for voltages larger than the open circuit voltage. Under light illumination, at short-circuit current condition the maximum generated photocurrent flows and at flat band condition the photo-generated current is balanced to zero.

At maximum power point (MPP), the product of current and voltage is larger^[8]. The photovoltaic power conversion efficiency of a solar cell is determined by:

Efficiency =
$$\frac{V_{oc} \times I_{sc} \times FF}{P_{in}}$$

$$FF = \frac{I_{mpp} \times V_{mpp}}{I_{sc} \times V_{oc}}$$

where V_{oc} is the open circuit voltage, I_{sc} is the shortcircuit current, FF is the fill factor and P_{in} is the incident



Physical CHEMISTRY An Indian Journal



Figure 2 : Working principle of dye sensitized solar cell light power density, which is standardized at 1000W/ use, 1000W/m² for solar cell testing with a spectral intensity distribution matching that of the sun on the earth's surface at an incident angle of 48.2, which is called the AM 1.5 spectrum^[9]. I_{mpp} and V_{mpp} are the current and voltage at the maximum power point in the fourth quadrant of the current–voltage characteristic diagram. To improve the current-voltage characteristics, photovoltaic cell is in urge and could be possible to explained by electrode and fabrication techniques.

Role of dyes in photovoltaic system

The dyes having the general structure of $ML_2(X)_2$ where L stands for 2,2'-bipyridyl-4-4'-dicarboxylic acid, M for ruthenium and X for halide, cyanide, thiocyanate, or water^[10,11]. The excitation of Ru complexes via photon absorption is of metal to ligand charge transfer (MLCT) type. This means that the highest occupied molecular orbital (HOMO) of the dye is localized near the metal atom, whereas the lowest unoccupied molecular orbital (LUMO) is localized at the ligand species. In the case of the bipyridyl rings, at the excitation, an electron is lifted from the HOMO level to the LUMO level. Furthermore, the LUMO level, extending even to the COOH anchoring groups, is spatially close to the TiO₂^[12] surface, which means that there is significant overlap between electron wavefunctions of the LUMO level of the dye and the conduction band of TiO₂. The movement of electron in the semiconductor surface is mainly attributed to the size and crystallinity of the semiconductor particles.

Improvements in TiO, semiconductor surface

Physical CHEMISTRY An Indian Journal



Figure 3 : Current-voltage (I-V) curve of an organic solar cell

To enhance the electron conductivity of TiO₂ electrode, rate of electron percolation through the film must be improved. However, the nanoporous TiO₂^[14] is not perfect yet due to the close proximity of electrons and holes throughout the porous film and the absence of a substantial potential barrier at the semiconductor/electrolyte interface. Indicating that the interfacial charge recombination still remains one of the major energy-wasting pathways. The BaTiO₃ coating layer (2.27nm) on TiO₂ surface (12µm thickness) was fabricated on transparent conducting glass using screen printing method and reported an efficiency of 7.52%, V_{∞} of $0.766V^{[15]}$. The BaTiO₃ modification is owing to the formation of an energy barrier against the electron transfer from TiO, to I^3 and the increased electron density in the TiO₂ caused by the increased electron lifetime.

Alternatively a thin TiO, compact layer^[16] with the thickness of 100nm at the FTO/nano-TiO, interface has been developed by spray pyrolysis can increase the performance of V_{oc} of 0.689V, J_{sc} of 17.8mA/cm² and FF of 0.66 from 7.5 to 8.1%. The electrochemical impedance measurements reveal that the effective compact layer of TiO, plays an important role in suppressing charge recombination of DSSCs at the interface between FTO and electrolyte. On the other hand the most efficient DSSC has been reported by covering the transparent films of $(12\mu m)$ the high-purity TiO₂ anatase with a scattering layer(6µm) to improve the redlight harvesting^[17]. The resulting photocurrent and energy-conversion efficiency of the cells are significantly improved to $V_{\rm oc}$ of 0.76V, $J_{\rm sc}$ of 18mA/cm² and conversion efficiency from 8.1 to 9.9%^[18]. Atmosphericpressure nonequilibrium DC pulse discharge plasma jet



technique as a means for the preparation of TiO₂ films on FTO coated glass substrates is used for DSSCs.. The DSSC made by the TiO₂ film with plasma treatment is exhibited an energy conversion efficiency of about 5.7% at 100mW/cm² light intensity, I_{sc} of 16mA/ cm², and V_{oc} of 0.82V^[19]. In plasma treatment the surface impurities are completely removed and N₂ on the surface was progressively promoted.

Oxygen vaccancy in the TiO₂ restricts the absorption of light harvesting dyes on the semiconducting oxides. Barrier for dye sensitization of nano TiO₂ and further electron transfer is reduced by treating the TiO₂ in the atmosphere and O₂ plasma. Exposing of TiO₂ in the O₂ treatment is produce the uniform, clean and stoichiometric structure without any O₂ deficiency. A feasible method to develop DSSC is arrived by using the Ar or O₂ treated TiO₂^[20-25].

 Al_2O_3 coated TiO₂ electrodes by electro deposition gives the efficiency of 5.6%. Better stability is observed by enhancing the TiO₂ electrodes using surface treatment. Al_2O_3 -coated TiO₂ electrode successfully developed by reactive dc magnetron sputtering in DSSC enhancing J_{sc} of 5.97mA/cm², V_{oc} of 0.691V, efficiency from 3.93% to 5.91%^[26]. It is found that the Al_2O_3 coating and the O₂ plasma treatment increase the dye adsorption amount, decrease the trap sites on TiO₂ and suppress the back transfer of photo-generated electrons from Al_2O_3 coated TiO₂ electrode to the electrolyte at the TiO₂/dye/electrolyte interface.

A novel transparent conductive oxide film based on the triple-layered indium tin oxide (ITO)/antimony doped tin oxide (ATO)/titanium oxide (30nm) dye-sensitized solar cells are fabricated by using radio frequency magnetron sputtering technique^[27]. Deposition of ATO layer(100nm) is increased the adhesion and thermal stability of the thin electrode. An impressive change in sheet resistance and optical transmittance are observed by the introduction of insulating thin TiO₂ layer on the top of the ATO layer, whereas photovoltaic performance is enhanced to J_{sc} of 10.27mA/cm², V_{oc} of 0.825V and efficiency from 5.91% to 6.29%.

Instead of using only nanocrystalline TiO_2 particle films, mixture of submicron-sized particle with nanocrystalline TiO_2 one and/or a bilayer structure consisting of light scattering layer and crystalline semitransparent TiO₂ layer can be used to improve photocurrent density. This is due to the fact that the confinement of incident light by light scattering particles can gain more photons in the vicinity of the dye and TiO₂ scattering layer^[28]. When light collides with the large number of TiO₂ particles having sub-micrometer size, the light scatters strongly (Mie scattering), which increases the path length of the incident light in the nanocrystalline TiO₂ films. Eventually, the scattering effect of the large TiO2 particles enhance the photocurrent density and thereby overall conversion efficiency. The scattering effect is dependent on the size^[29], refractive index and position^[30] of the scattering particles. The conversion efficiency of $14\mu m$ thick main-layer is slightly improved to 9.15%, J_{sc} of 16.4mA/cm², V_{oc} of 0.813V upon depositing 0.5µm scattering layer.

A high light-to-electricity conversion of 9.33%, J_{sc} of 19.22mA/cm², V_{oc} of 0.72V is obtained for a cell with titania nano network structure composed of single crystalline anatase nanowires synthesized by a surfactant-assisted "oriented attachment" mechanism at a low temperature of 353 K^[31].

Solid-state dye sensitized solar cell

The use of a liquid electrolyte in the dye sensitized solar cell is problematic for the long-term stability of the cells, because of the volatile solvent of the electrolyte leaks easily out of the cell through possible holes or cracks in the sealant. Replacement of the liquid hole transport medium by a solid-state analogue could solve this problem^[32].

A recent alternative embodiment of the DSSC concept is the replacement of the redox electrolyte with a solid-state hole conductor, which may be either inorganic /organic thereby avoiding the use of a redox electrolyte^[33].

Solid state dye-sensitized solar cell is schematically shown in Figure 4. The meso porous metal oxide electrode (TiO_2) is placed in contact with a solid state hole



Figure 4 : Schematic description of a solid state dye sensitized solar cell



Chemically Modifie

TiO₂ film

OTE/TiOJCdSe

Electrode



Figure 5 : Energy diagram for an efficient charge transfer between solid state dye sensitized solar cell components

conductor. A monolayer of the sensitizing dye is attached to the surface of the nanocrystalline electrode film. After the excitation of the dye, an electron is injected into the conduction band of the semi conductor oxide electrode. The sensitizer dye is regenerated by the electron donation from the hole conductor^[34].

In the solid state cell, the charge transport is electronic whereas when using liquid or polymer electrolyte, ionic transportation takes place^[35]. The hole conductor must be able to transfer holes from the sensitizing dye after the dye has ejected electrons into the TiO₂; that is, the upper edge of the valence band of p type semiconductors must be located above the ground state level of the dye (Figure 5). Furthermore, hole conductors have to be deposited within the porous nanocrystalline layer penetrating into the pores of the nano particle and finally it must be transparent in the visible spectrum, or, if it absorbs light, it must be an efficient in electron injection as the dye. The successful hole transport materials to replace the liquid electrolyte are CuI, CuBr and CuSCN^[36,37].

A better stability was observed by covering the TiO₂ electrode by a thin MgO layer. DSSC fabricated with MgO layer and CuI as a Hole Transport Material have showed the efficiency of $2.9\%^{[38]}$. Although CuI has attracted very much attention as a p-type semiconductor the interface of TiO₂ /CuI degrades due to the release of iodine and the successive formation of a trace amount of Cu₂O and /or CuO^[39].

When 1-methyl-3-ethylimidazoliumthiocyanate (MEISCN) is used as a molten salt in DSSC, a power conversion efficiency of 3.75% was obtained^[40] Compared to inorganic p-type semiconductors, organic p-

Physical CHEMISTRY An Indian Journal



type semiconductors possess the advantage of low cost processability.

Among organic p-type semiconductors, 2,2',7,7'tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'irobifluorene (OMETAD) has gained practical advantage^[41]. A dye-sensitized heterojunction between TiO₂ and OMETAD showed the efficiency of 3.75 %. The performance of the solid state dye sensitized solar cells based on spiro-OMETAD was further improved by blending the hole conductor matrix with a combination of 4-tert-butylpyridine (tBP) and Li[CF₃SO₂] 2N, an efficiency of 2.56% under AM 1.5 illumination was achieved^[42]. The efficiency of a similar device was further improved to $3.2\%^{[43]}$, by improving the dye adsorption in the presence of silver ions in the dye solution.

Polymer electrolyte in dye sensitised solar cell

Recently, Polymer electrolyte based solar cells have attracted a great interest in developing high efficiency, low cost and large area PV devices^[44].

Polymer electrolytes are composed of alkaline salts dissolved in a high molecular mass polyether or polypropylene oxides^[45]. In polymer electrolytes, the polymer matrix should be an efficient solvent for the salt, capable of dissociating it and minimizing the formation of ion pairs^[46]. Poly (3 alkylthiophenes) is used as a polymer electrolyte to replace the liquid electrolyte. Improved performance has been exhibited by DSSC prepared with the I/I_3 redox couple dissolved in solid or gel polymer electrolytes based on poly ethylene oxide, poly acrylonitrile, ethylene carbonate, propylene carbonate, acetonitrile, NaI, and I₂. Poly 3-hexyl thiophene P3HT^[47] has side chains that make it soluble in a variety of common organic solvents. The formation of polymeric semiconductor films by self assembly are offers distinct advantages such as cost effective, uniformity, and scalability over the other solution processing techniques.

In conjugated polymers the delocalized p₂ orbitals constituting the p-bond actually produce two orbitals a lower bonding (p) orbital and a higher antibonding (p*) orbital. The difference between the energies of these diffused states give the energy gap of the semi conducting polymer material. The absorption of light with energy equal to or above the band-gap energy is generates an electron in the p* level and a hole in the p level. In contrast to the inorganic semiconductors, where photo generated electrons and holes are free in the conduction and valence band respectively, the generated electrons and holes in the conductive polymer are loosely bound together by Columbic force. This electron-hole pair is called exciton and it moves within the material as an one entity. The diffusion length of the excitons is typically in the order of 10nm^[48]. When the exciton length is longer than diffusion length, most of the exciton decay occurs which is the main loss factor in the polymer based cells.

DSSC fabricated by employing a copolymer, [poly(epichlorohydrin-co-ethylene oxide)], Epichlomer-16 electrolyte gives 2.6% power conversion efficiencies^[49,50]. A promising result of 5.3% efficiency was obtained when an L/NaI-doped solid state Epichlomer-16 with Al₂O₃ coated TiO₂ electrode^[51]. The most efficient solar cell have been made by using carboxylated P3HT derivative in conjunction with 7µm thick TiO₂ film^[52] showed the I_{sc} of 9.75mA/cm² and V_{oc} of 0.4V. The carboxylated P3HT derivative with 4µm thick TiO₂ films produced V_{oc} of 0.54V^[52]. Karthick shankar and co-workers-demonstrated a higher V_{oc} of 0.76V using carboxylated P3HT derivative in conjunction with 4µm long nano tube arrays^[53].

Gel electrolyte in dye sensitised solar cell

The success of gelled electrolytes is an encouragement outcome to proceed further in the search for alternative contacting charge transport phases to substitute the electrolyte in a sensitized photovoltaic system. A polymeric gel electrolyte is considered as a compromise between liquid electrolytes and hole conductors in quasi solid state dye sensitized solar cells^[54]. A mixture of NaI, ethylene carbonate, propylene carbonate and polyacrylonitrile enhances the solar to electric energy conversion efficiencies upto 5.3% in a quasi-solid-state device^[55].

Gel polymer electrolyte is covered the surface of TiO_2 which could suppress the back electron-transfer in the DSSC, and exhibits the open circuit voltage. The addition of the liquid electrolyte to polymer gel electrolyte based on poly(ethylene-co-methyl acrylate), LiI, and I₂ by casting-injection method has increased the ionic conductivity. Dye sensitized solar cell synthesized using this process has higher conversion efficiency of 5.2%^[56]. The performance of the DSSC has been improved by using Poly (vinylidenefluoride-cohexafluoropropylene) (PVDF-HFP) to solidify 3-ethoxypropionitrile (MPN) showing 6% conversion efficiencies under full sunlight and also high stability under thermal stress^[57].

Bulk hetero junction dye sensitised solar cell

Bulk heterojunction cell is developed based on inorganic/organic solar cells concept. Excitons created upon photoexcitation are separated into free charge carriers at interfaces between two semiconductors in a composite thin film such as a conjugated polymer and fullerene mixtures^[58]. Electrons will then be accepted by the material with the higher electron affinity (electron acceptor, usually fullerene or a derivative), and the hole accepted by the material with the lower ionization potential, which also acts as the electron donor. The solubility of the n-type and p-type components is an important parameter of the construction of hybrid solar cells processed from the solution based method. Bulk heterojunction hybrid solar cells have been demonstrated in various semi-conducting polymer blends containing CdSe, CuInS2, CdS and PbS^[59] nanocrystals.

It is noteworthy that the charge recombination between the injected electrons that are trapped in surface states and the oxidized species in the hole-conducting media remains one of the major limiting factors for the lower efficiency of the DSSCs. To reduce such surface states and to improve the conversion efficiency is done by heterojunction, such as passivating the recombination centers at the interface of a nanoporous TiO_2 film

> Physical CHEMISTRY An Indian Journal

Review

with TiCl_4 . The density of trapping sites is reduced by utilizating the composite or bilayer semiconductor electrodes such as MgO-Al₂O₃, SnO2-ZnO, Al₂O₃-TiO₂, and so forth^[60].

The formation of energy barrier at the surface of the TiO₂ electrode/electrolyte interface can be used for reducing the recombination process of the photo injected electrons. Such barrier can be made by coating the TiO₂ (6µm) with a single layer of Nb₂O₅ (2.7 nm) gives the I_s of 1 1.4mA/cm² and V_{ac} of 0.732V^[61].

Bilayer structure is more advantageous than the single layer structure for several reasons. Exciton splitting is enhanced by the donar-acceptor interface, the active region is extended to both the donor and the acceptor sides of the junction thereby roughly doubling its width to about 20nm, and the transport of electrons and holes is separated into different materials by reducing the recombination losses. In addition to this, by using two different semiconductors, the band gaps can in principle be tuned to match the better solar spectrum. To enhance the exciton splitting process, devices with electron accepting and donating molecules have been developed. In these socalled donor-acceptor bilayer devices as shown in Figure 7, the excitons can be dissociated at the donor-acceptor interface due to a relative energy level difference of the donor and acceptor molecules (Figure 8). The donor and acceptor molecules can be conjugated polymers, organic macromolecules or dyes.

Efficient light scattering is obtained with the bilayer composed of a thin transparent layer containing 20nm particles and a scattering layer containing 275nm TiO_2 spheres. The rough TiO₂ spheres are increased the overall conversion efficiency of DSSCs to $6.56\%^{[62]}$. The use of planar donor-acceptor junction is only doubles the active region of the solar cell with respect to the single layer device, which is still usually not enough for efficient light absorption. To overcome this problem and to increase the optical absorbing thickness the concept of interpenetrating network of electron-accepting and electron-donating molecular species can be done^[63].

A hybrid device by blending MDMO-PPV with titanium(IV)-isopropoxide, exhibited an I_{sc} of 0.6mA/ cm² and V_{oc} of 520mV with a fill factor of 0.42 and an external quantum efficiency of 11%^[64]. Bulk heterojunction solar cells fabricated by blending of

Physical CHEMISTRY An Indian Journal



Figure 7 : Schematic electronic band structure of 3.5nm CdSe with an effective band gap of 2.17eV and nanocrystalline TiO₂/N with a 3.2eV band gap, associated with normal TiO₂ and a N dopant state approximately 1.14eV above the valence band CuInS₂ and a p-type polymer (PEDOT : PSS); poly (3,4-ethylene dioxythiophene) : poly (styrene sulfonic acid) in the same cell configuration showed better photovoltaic response with 20% external quantum efficiencies^[65,66].

Quantum dots as sensitizers

Semiconductor quantum dots are another attractive option for panchromatic sensitizers. These are II-VI and III-V type semiconductor particles, whose size is small enough to produce quantum confinement effects. The absorption spectrum of such quantum dots can be tailored by changing the particle size.

Alternative techniques to increase the photo response besides doping are include the utilization of tunable narrow band gap semiconductor nanoparticles or quantum dot (QDs) sensitizers such as CdS, CdSe, and CdTe to sensitize wide band gap semiconductor such as the metal oxides TiO₂. QDs with their large extinction coefficient are strongly absorb the visible light, eject electrons into the conduction band of metal oxides and thereby, contribute to increased solar energy conversion^[67].

Attachment of CdSe QDs onto nanocrystalline TiO₂ has been shown to be successful with an immersion method using a bimolecular linker. Size quantization is allows us to tune the visible response and to vary the band offsets to modulate the vectorial charge transfer across different sized particles. In addition, these QDs are open up new ways to utilize hot electrons or generate multiple charge carriers with a single photon^[68]. Impact ionization (or inverse Auger scattering) processes

🗅 Review

in PbSe nanocrystals have shown that two or more excitons can be generated with a single photon of energy greater than twice the band gap^[69,70]. To explore the salient features of QDs, Istva'n Robel, have assembled TiO₂ and CdSe nanoparticles using bifunctional surface modifiers such as HS-R-COOH, when employed as a photo anode in a photoelectrochemical cell, exhibits a photon-to-charge carrier generation efficiency of $12\%^{[71]}$.

An exciting discovery made in the recent years is that multiple exciton generation (MEG) obtained from the absorption of a single photon by a quantum dot if the photon energy is at least two times higher than its band. The challenge is now to find the ways to collect the excitons before they recombine in the semiconductor interface. As recombination occurs in an pico second time scale, the use of mesoporous oxides as electron collectors present a promising strategy, because the electron transfer from the quantum dot to the conduction band of the mesoporous oxide electrode is occur within a femto seconds^[72].

The doping of N_2 is alter the surface of the TiO₂ film and alter its surface Interaction between TiO₂ and CdSe QDs becomes stronger. The efficient electron injection into the TiO₂ film could also be facilitated by N doping that in turn, influences nanocrystalline surface. CdSe QDs linked to TiO₂/N nanoparticles were found to be significantly increase the photocurrent and power conversion of the films compared to those of standard TiO₂/N films without QD sensitization or TiO₂/ N without QD sensitization^[73]. A power conversion efficiency (e) of 0.84% was found along with a fill factor (FF%) of 27.7% for 1.1µm thick TiO₂/N-TGA-CdSe thin films^[74]. The results show that the combination of nitrogen doping and QD sensitization of the TiO₂ thin films is an effective way to enhance the photo response, which is promising for photovoltaic and photo electrochemical device applications.

CONCLUSION

Photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilisation will continue as long as the Sun shines! Potential barrier for interfacial charge recombination is formed to receive high electron density with increased electron lifetime. High purity TiO₂ scattering layers have been developed to improve the red light harvesting. Oxygen vacancies in the TiO₂ has been reduced by treating oxygen or argon plasma for uniform and stoichiometric surface layer. Regenerative dye sensitizers can donate electron and hole at the electrode/ electrolyte interface. Until then around 12% of efficiency is achieved with the dye sensitized TiO₂ based solar cells. The conducive polymer can dissolve the alkaline salts to minimize the formation of ion pairs. Epichlomer-16 offers the promising characteristics for potentially low cost polymer based solar cells.

Polymeric gel electrolyte is considered as a compromise between liquid electrolytes and hole conductors and it has attracted the researcher for the stabilized electrolyte synthesis. To enhance the exciton splitting process, modification of donor-acceptor is required. Quantum confinement can be tailored by changing the particle size by utilizing the tunable narrow band gap semiconductor nanoparticles. The inorganic quantum dots CdS, CdSe, and CdTe are aligned using the bimolecular linker. An exciting discovery is innovated for the multi exciton generation by treating the TiO₂ surface with N₂. Eventhough hybride solar cells show low efficiency, the simple processability and cost efficient techniques are attracted much attention. However, to meet a required efficiency for commercial applications the PV systems with atleast 25% light to line electricity have to be developed.

REFERENCES

- [1] A.E.Becquerel; C.R.Acad.Sci., 9, 561 (1839).
- [2] M.Green; Progr.Photovolt., 9, 123 (2001).
- [3] Serap Gu'nes, Niyazi Serdar, Sariciftci; Inorganica Chimica Acta, **36**, 581 (**2008**).
- [4] K.Hashimoto, H.Irie, A.Fujishima; J.Appl.Phys., 44, 8269 (2005).
- [5] M.Graetzel; Progr.Photovolt.Res.Appl., 8, 171 (2000).

Physical CHEMISTRY An Indian Journal

Review

- [6] H.Halme; Ph.D. Thesis, Espoo (Finland), (2002).
- [7] H.Hoppe, N.S.Sariciftci; J.Mater.Res.Soc., 19, 7 (2004).
- [8] J.Rotalsky, D.Meissner; Sol.Energ.Mat.Sol.Cells., 63, 37 (2000).
- [9] M.Hagfeldt, Gra'tzel; Acc.Chem.Res,. 33(5), 269 (2000).
- [10] G.Sauve, M.E.Cass, G.Coia, S.J.Doig, I.Lauermann, K.E.Pomykal, N.S.Lewis; J.Phys.Chem.B., 104, 6821 (2000).
- [11] A.S.Polo, M.K.Itokazu; Coord.Chem.Rev., 248, 1343 (2004).
- [12] G.R.A.Kumara, M.K.Okuya, S.Murakami, V.Kaneko Jayaweera, K.Tennakone; J.Photochem. Photobiol.A: Chem., 164, 183 (2004).
- [13] Li Zhang, Yunhui Shi, Shengjie Peng, Jing Liang, Zhanliang Tao, Jun Chen; J.of Photochem. and Photobiology A: Chem., 197, 260 (2008).
- [14] Jifu Shi, Jing Liang, Shengjie Peng, Wei Xu, Juan Pei, Jun Chen; Solid State Sciences, 1-6 (2008).
- [15] Kim Yoon, Ki Y Lee; J.Vac.Sci.Technol.A, 25, 1219 (2007).
- [16] Y.Kim, B.Yoo, R.Vittal, Y.Lee, N.G.Park, K.J.Kim; J.Power Sources., 17, 914 (2008).
- [17] Weidmann Dittrich, Konstantinova Lauermann, Uhlendorf F.Koch; Sol.Energy Mater.Sol.Cells., 56, 153 (1999).
- [18] Pan Maschhoff, Diebold Madey; J.Vac.Sci. Technol.A, 10, 2470 (1992).
- [19] B.O.Aronsson, J.Lausmaa, B.J.Kasemo; Biomed. Mater.Res., 35, 49 (1997).
- [20] S.Gan, Y.Liang; Surf.Sci., 459, 498 (2000).
- [21] SujuanWu, Hongwei Han, Qidong Tai, Jing Zhang, Sheng Xu, Conghua Zhou, Ying Yang; Journal of Power Sources, 182, 119 (2008).
- [22] J.Xia, N.Masaki, K.Jiang, S.Yanagida; Chem. Commun., 138 (2007).
- [23] Beomjin Yoo, Kyungkon Kima, Seung Hoon Lee, Won Mok Kim, Nam-Gyu Park; Solar Energy Materials & Solar Cells, 92, 873 (2008).
- [24] Ito Seigo, M.Shaik, Zakeerudiin, Robin Humphry-Baker, Paul Liska, Paphae'l Charvet, PascalComte, Mohammad K.Nazeeruddin, Peter Pe'chy, Masakazu Takata, Idetoshi Miura, Satoshi Uchida, MichaelGra'tzel; Adv.Mater., 18, 1202 (2006).
- [25] Sarmimal Hore, Carmen Vetter, Rainer Kern, Herman Smit, Andreas, Hinsch; Solar Energy Mater.Solar Cells, 90, 1176 (2006).
- [26] E.William Vargas; J.Appl.Phys., 88, 4079 (2000).
- [27] Zhong-Sheng Wang, Hiroshi Kawauchi, Takeo

Kashima, HironoriArakawa; Coord.Chem.Rev., 248, 1381 (2004).

- [28] Hyung-Jun Koo, Jihee Park, Beomjin Yoo, Kicheon Yoo, Kyoungkon Kim, Nam-Gyu Park; Inorganica Chimica Acta, 361, 677 (2008).
- [29] M.B.Wang, P.Kang, Wang, Qiu, Y.Sol; Energ. Mat.Sol.Cells, 90, 549 (2006).
- [**30**] A.F.Nogueira, C.Longo, M.A.De Paol; Coord. Chem.Rev., **248**, 1455 (**2004**).
- [31] K.Tennakone, G.R.R.A.Kumara, A.R.Kumarasinghe, K.G.U.Wijayantha Sirimanne; Semicond. Sci.Tech., 10, 1689 (1995).
- [32] G.R.R.A.Kumara, A.Konno, G.K.R.Senadeera, P.V.V.Jayaweera, Dbra De Silva, Tennakone; Sol.Energ.Mat.Sol.Cells, 69, 195 (2001).
- [33] K.Tennakone, G.K.R.Senadeera, Dbra De Silva, Kottegoda; Appl.Phys.Lett., 77, 2367 (2000).
- [34] P.R.Sirimanne, T.Jeranko, P.Bogdanoff, S.Fiechter, H.Tributsch; Semicond.Sci.Tech., 18, 708 (2003).
- [35] G.R.A.Kumara, A.Konno, K.Shiratsuchi, J.Tsukahara, Tennakone; Chem.Mater., 14, 954 (2002).
- [36] B.O.Reagan, F.Lenzmann, R.Muis Wienke; Chem.Mater., 14, 5023 (2002).
- [37] G.R.A.Kumara, S.Kaneko, M.Okuya, K.Tennakone; Langmuir., 18, 10493 (2002).
- [38] D.Bach, U.Lupo, Comte, P.Moser, J.E.Weissortel, J.Salbeck, Preitzer Gra'tzel; Nature, 395, 583 (1995).
- [39] J.Kru'ger, R.Plass, L.Cevey, M.Piccirelli, M.Gra'tzel; Appl.Phys.Lett., 79, 2085 (2001).
- [40] L.Schmidt Mende, M.Gra'tzel; Thin Solid Films, 500, 296 (2006).
- [41] Kru'ger, R.Plass, M.Gra'tzel, H.J.Matthiek; Appl. Phys.Lett., 81, 367 (2002).
- [42] A.F.Nogueira, C.Longo, M.A.De Paoli; Coord.Chem. Rev., 248, 1455 (2004).
- [43] M.Armand, J.R.Maccallum, C.A.Vincent; Polymer Electrolyte Reviews, Elsevier, London, (1987).
- [44] B.O.Regan, M.Gratzel; Nature, 353, 737 (1991).
- [45] A.F.Nogueira, J.R.Durrant, M.A.De Paoli; Synth. Met., 61, 135 (2000).
- [46] G.K.Shankar, G.K.Mor Varghese, O.K.Grimes; J.Mater.Res., 19, 2989 (2004).
- [47] S.Haque, E.Palomores, H.M.Upadhyaya, L.Otley, R.J.Otter, A.B.Holmes, J.R.Durrant; Chem. Commun., 24, 3008 (2003).
- [48] G.K.Mor Varghese, M.O.K.Paulose, K.Shankar, C.Grimes; A.Sol.Energy Mater.Sol.Cells, 90, 2011 (2006).

Physical CHEMISTRY An Indian Journal



- [49] C.O.Too; Synthetic Metals, 123, 53 (2001).
- [50] S. Yanagida, G.K.R. Senadeera, K. Nakamura, Kitamura, T.Y. Wada; J. Photochem. Photobiol. A., 166(1-3), 75 (2004).
- [51] J.K.Mwaura, X.Y.Zhao, H.Jiang, K.S.Schanze, J.Reynolds; R.Chem.Mater., 18(26), 6109 (2006).
- [52] G.Benco, B.Skarman, R.Wallenberg, A.Hagfeldt, V.Sundstrom, A.P.Yartsev; J.Phy.Chem.B., 107, 1370 (2003).
- [53] Karthik Shankar, K.Gopal, Mor, E.Haripriya, Prakasam, K.Oomman, Varghese, A.Craig Grimes; Langmuir, 23, 12445 (2007).
- [54] S.Megahed, B.Scosati; Interface, 4, 34 (1995).
- [55] F.Cao, G.Oskam, P.Searson; J.Phys.Chem., 99, 17071 (1995).
- [56] Elias Stathatos, Yongjun Chen, Dionysios, D.Dionysiou; Solar Energy Materials & Solar Cells, 92, 1358 (2008).
- [57] S.McDonald, G.Konstantatos, S.Zhang, P.W.Cyr, E.J.D.Klem, Levina, H.Sargent; Nat.Mater., 4, 138 (2005).
- [58] T.Taguchi, X.T.Zhang, I.Sutanto, K.Tokuhiro, T.N.Rao, H.Watanabe, T.Nakamori, Uragami, M. Fujishima; A.Chem.Commun., 19, 2480 (2003).
- [59] K. Tennakone, G. Kumara, I.R.M. Kottegoda, P.S. Perera; Chem. Commun., 15, (1999).
- [60] G.Ramakrishna, A.K.Singh, D.K.Palit, H.N.Ghosh; J.Phys.Chem.B., 108, 1701 (2004).
- [61] R.Plass, S.Pelet, J.Krueger, M.Gratzel, U.Bach; J.Phys.Chem.B., 106, 7578 (2002).

- [62] K.S.Leschkies, R.Divakar, J.Basu, Enache-Pommer, J.E.Boercker, C.B.Carter, U.R.Kortshagen, D.Norris, E.S.Aydil; Nano Lett., 7 (2007).
- [63] C.Levy-Clement, R.Tena-Zaera, M.A.Ryan, Katty, A.Hodes; AdV.Mater., 17, 1512 (2005).
- [64] I.Robel, M.Kuno, P.V.Kamat; J.Am.Chem.Soc., 129, 4136 (2007).
- [65] S.Somasundaram, C.R.Chenthamarakshan, N.R.de Tacconi, Y.Ming, K.Rajeshwar; Chem.Mater., 16, 3846 (2004).
- [66] R.J.Ellingson, M.C.Beard, J.C.Johnson, P.R.Yu, O.I.Micic, A.J.Nozik, A.Shabaev, A.L.Efros; Nano Lett., 5, 865-871 (2005).
- [67] M.Califano, A.Zunger, A.Franceschetti; Nano Lett., 4, 525-531 (2004).
- [68] Tzarara Lo'pez-Luke, Abraham Wolcott, Li-ping Xu, Shaowei Chen, Zhenhai Wen, Jinghong Li, Elder De La Rosas, Z.Jin Zhang; J.Phys.Chem.C., 112, 1282 (2008).
- [69] X.B.Chen, C.Burda; J.Phys.Chem.B., 108, 15446 (2004).
- [70] Istva'n Robel, Vaidyanathan Subramanian, Masaru Kuno, V.Prashant, C.Kamat; Published on Web, 31st January, (2006).
- [71] X.X.Liu, Z.G.Jin, S.J.Bu, T.Yin; J.Sol-Gel Sci. Technol., 36, 103 (2005).
- [72] J.Nowotny, T.Bak, M.K.Nowotny, L.R.Sheppard; J.Phys.Chem.B., 110, 18492 (2006).
- [73] H.Gerischer, M.Lubke; J.Electroanal.Chem., 204, 225 (1986).
- [74] Schmidt Mende, M.Gra'tzel, Thin Solid Films, 500, 296 (2006).