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A Study on the Role of Titanium Oxide for Solar Cell Applications

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Abstract
Basic need of modern civilization is energy and its production from fossil fuels causes hazardous effect on the environment. This motivates to use the clean energy sources. Solar energy has best potential to fulfill the energy demand in future. Sunlight is not only the most plentiful energy resource on earth, but it is also one of the most versatile, abundantly available and free of cost throughout on the planet, converting readily to electricity, fuel and heat without emitting pollutant elements.
The time line of solar energy research shows the development of photovoltaic technology. The way of conversion of sun energy into electrical energy divides the photovoltaic technology into different generations.

Keywords: Solar Energy, titanium oxide, photovoltaic technology

1. Introduction
The energy plays the most crucial role in the modern human civilization. Mankind uses the fossil fuels as energy source from millions of years. Presently, most of the energy demand (upto 90%) is fulfilled from the fossil fuels in the form of coal, natural gases, petroleum product etc. The burning of theses fuels emits the gases like CO_2, CH_4, NOx, sulphur etc. and remains their residuals in an environment. These gases are also known as greenhouse gases.
The greenhouse gases traps the infra-red radiation within the earth's atmosphere, thereby increasing the "global" atmospheric temperature (approximately 4°C of earth temperature will increase in this century). During the past few decades, all nations have become extremely concerned with the effect of global warming.
The emission of these gases depends on the use of the fossil fuels and cut down the dependency on fossil fuels is one solution to reduce effect of global warming. Dependency on renewable energy sources in power sector is a need of the universe, since fossil fuel resources are rapidly depleting and responsible to emission of greenhouse gases.
The transformation of energy policies is not individual government effort but world-wide political issue. The several nations have been transfer their energy policies; towards utilization of clean energy sources instead of use of fossil fuels.
Clean energy sources will play vital role in the future which includes: wind, geothermal, biomass, tidal and hydroelectric etc. out of these none of the technology is scalable to fulfill future energy demands. Only solar energy is having potential to fulfill the energy demand in future. For a scale, consider; sun provides 130 TW energy daily. Current global energy consumption occurs at the rate of 13.5 TW, projected to rise to 40.8 TW in $_2$050.
Today, in just one hour, the sun provides enough power to supply our energy needs for an entire year which is available free of cost. In the universe and particularly country like India, an average intensity of solar received is $_2$00 MW/km (megawatt per square kilometer) with $_2$50-3$_2$5 sunny days in year. Hence, solar energy is having capacity to fulfill the energy demand of urban civilization without harming the environment.
Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium with chemical formula TiO_2. Recently, scientific and research community have shown their great interest to synthesize titanium dioxide (TiO_2) for device grade applications because of its excellent properties such as easily available, nontoxic, safe, environmental friendly and cheap.

These advantages make TiO_2 beneficiary towards number of device grade applications such as, energy harvesting, hydrogen production, photonics, sensors, cancer treatment and water purification. TiO_2 has been available in three different structure types: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic).

1.1 Review of related literature

Gratzel *et al.* 2011 [1] have reported DSSC with nano-porous TiO_2 film used as photoanode that provides high surface area for the adsorption of dye molecules, act as widow layer and receives charge carrier from excited dye molecules and achieved 7% efficiency and increased efficiency further 4%. Many groups have reported various TiO_2 nanostructures morphology with various dye molecules for the DSSC application.

Although the DSSC concept is comparatively simple, a lot of disputes still remain. Because, charge generation and injection from the dye is most efficient when the dye is coated in a monolayer upon the surface of the nano-structured TiO_2.

However, the deposition of the dye molecules proceeds via self-assembled chemisorptions and gets aggregated. This can obstruct to transfer electron from the dye to the TiO_2 as well leading to charge carrier recombination as a result of intermolecular quenching.

In addition, the excited dye molecules can be quenched by the oxidised redox species in the electrolyte, thereby reducing the performance of the cell. Another drawback of using dyes is that the photocatalytic properties of the TiO_2 under UV light make the organic dyes more susceptible to degradation than inorganic materials.

The stability of dye molecules is major issue in DSSC which enforce us to search new types of absorber/sensitizer. Hence, nanostructured solar cell is an immerging as an alternative to conventional solar cell technology, which works on similar principle of DSSC. Where, the device constructed with inorganic narrow band gap semiconducting material either in the form of thin absorber layer or quantum dot layer as a light harvester instead of dye.

The conventional inorganic semiconductors can absorb over broad wavelength range (i.e. the material will absorb photons $\geq$ Eg of the semiconductor), whereas dye molecules are known to display a Gaussian (bell shaped) type absorption profile, hence reducing the absorption of light in the DSSC.

The pioneering work in nanostructured solar cells was initiated by Konenkamp *et al.* 2012 [2] where the anatase porous TiO_2 film act as photoanode and provides high surface area for the adsorption of absorber layer, also; electron can be recombined much faster.

Ernst et al 2011 have synthesized nanostructured TiO_2 film by spray pyrolysis technique and further forms heterostructure with II-VI compound for ETA solar cell application.

In 2011, Earnst et al. explains the concept of ETA solar cell with CdTe as an absorber layer of on porous TiO_2 and achieved 1.17% efficiency. Tennakone et al has constructed photovoltaic cell by using TiO_2 nanoporous and achieved 0.13% efficiency. Recently, Itzhaik et al reported 3.37% efficiency of ETA solar cell by introducing In_2S3 buffer layer between porous TiO_2 and absorber layer of Sb_2S3.

It is to coat extremely thin film consisting of nanoparticles onto wide band gap TiO_2 towards solar cells application as a low cost alternative to conventional solar cell technology.

Konenkamp *et al.* 2012 [2] have put forward the idea of ETA solar cell concept, which has an ability to overcome the problems faced by DSSC. ETA cell works on the similar principle of DSSC but monolayer of dye is replaced by extremely thin film of inorganic metal chalcogenide absorber layer consisting of nanoparticles or quantum dots (QD's). The semiconducting inorganic materials (CdS, CdSe, Bi_2S3 and Sb_2S3) are more stable than dye molecules. Also one can tune their electrical and optical properties according to their size.

2. Research Study

All of these crystalline forms of TiO_2 occur in nature as mineral, but only rutile and anatase have been able to be synthesized in pure form. The review in this filed suggest that most stable phase of TiO_2 are anatase and rutile, extensively studied by research community in entire world.

Synthesis and applications of TiO_2 toward solar cell application Titanium dioxide has important material since ancient time, where it can be used as white pigment. In early $_2$0th century, the commercial productions of TiO_2 has been widely used in sunscreen, paints, toothpaste many other. There was a report on the photo bleaching of dyes by TiO_2 both in vacuum and in oxygen in 1938.

Recently, various forms of TiO_2 have been synthesized in the form of powders, thin film and nano-crystals as a nano-particles, nano-tubes, nano-fiber, nano-belts and nano-rods etc. by number of synthesis techniques.

Among new materials being developed for solar cells, photo-catalytic and other applications, TiO_2 remains one of the most promising materials, due to its low cost, chemical inertness, eco-friendly nature and photo stability.

Several excellent properties of TiO_2 are available such as chemical inertness, superior light scattering characteristics, thermodynamic stability, better charge transport, lower conduction band edge position, large band gap, easily process in laboratory etc. These properties make it suitable for the PEC cell application.

Table 1: The structural properties of different TiO_2 morphology

Compound	Rutile	Anatase	Brookite
Formula	TiO_2	TiO_2	TiO_2
Molecular weight (g/mol)	79.89	79.89	79.89
Molecules per unit cell (Z)	2	4	8
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Most stable surface	(110)	(101)	---
Unit cell parameters a (Å) b (Å) c (Å) Unit cell volume	 4.58 4.58 2.95 62.07	 3.78 3.78 9.78 136.25	 9.184 5.447 5.145 257.38
Electron effective mass	9-13 m_e	~1 m_e	--
Mobility of electron in thin film form	0.1 cm^2/Vs	0.1-0.4 cm^2/Vs	--
Molar volume	18.693	20.156	19.377
Density (g/cm^3)	4.2743	3.895	4.123
Band gap (eV)	3.02	3.2	3.1
Refractive index ⊥ to c axis ‖ to c axis	 2.60 2.89	 2.55 2.48	 2.57 2.69
Dielectric constant ⊥ to c axis ‖ to c axis	 89 173	 31 48	78
Cationic radius (Ti^{4+}) (Å)	0.605	0.605	0.605
Anionic radius (O^{2-}) (Å)	1.36	1.36	1.36

In current photovoltaic technology, the cost per watt is mainly high, because most of the efforts and cost required to obtaining pure Silicon. Hence, commercially available cells are not affordable for large scale energy production compared with the available resources. The cost per watt can be lowered by two ways, either lowering the manufacturing cost or increasing the amount of power output for the same cost.

The current photovoltaic devices have reached to their maximum theoretical and practical efficiencies and may not be possible to further increase in the efficiencies and reduce the processing cost. Till today, different types of solar cells are available based on Si, GaAs, CdS/CdTe, chalcopyrite, organic solar cells.

So, many co-workers are working to search an efficient low cost device which has ability to fulfill both conditions as low production cost and higher conversion efficiencies. In this concerned, DSSC's have been attracting a lot of interest due to their high-energy conversion efficiency and low production cost.

In 2011, the highest certified efficiency value reported by Gratzel was more than 11%. But, thereafter; none of the remarkable improved in efficiencies is not reported for DSSC devices. Also, DSSC suffering from some additional problems like dyes degradation in UV light and life of PV cells, cost of the high efficient metal complex dyes. Hence, there is prevailing need to search for low cost new materials synthesized by low cost chemical techniques and use these materials to construct the solar cell.

3. Significance of the study

The fabrication of sensitizer material on the entire surface of TiO_2 electrode has a prime importance. In practices, it is a very difficult to coat the TiO_2 surface by sensitizer without blocking any pores of TiO_2 network from top to bottom of TiO_2 film. Here, we made emphasis on the wet chemical synthesis route namely, chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR).

Number of reports are available for the synthesis of individual inorganic (narrow band gap) semiconductor material with various morphologies but not reported for the layer heterostructures. By controlling the nucleation and growth kinetics to avoid precipitation in the reaction, the blocking of the porous network of TiO_2 can be avoided and it is difficult task without using linker/ligand molecules.

4. Conclusion

In the present investigation, we have used simple wet chemical synthesis route and successfully deposited quantum to nano size particles of sensitizer material onto surface of TiO_2 nanoparticles without using linker/ligand molecules and by controlling the reaction kinetics such as concentration, deposition time, number of immersions, solvent and complexing agent.

Here, the current investigation is based on the synthesis quantum to nano particles of CdS, CdSe, Bi_2S3 and Sb_2S3 as the extremely thin absorber layer consisting of nano particles onto porous TiO_2 at room temperature. The synthesized layer hetero structures were used as a photo anode in extremely thin film consisting of nano particles for solar cell application.

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