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RESEARCH ARTICLE

REVIEW ON RECENT ADVANCES IN TITANIUM DYE OXIDE NANOPARTICLES FOR DYE SENSITIZED SOLAR CELL APPLICATIONS.

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Abstract

Alternate energy source becomes a crucial for green energy solution against ever increasing demand. Dye Sensitized solar cell is another promising option toward green energy providing opportunity to explore natural dye extracts from plants. This review explores recent developments in the field of Dye Sensitized solar cell technology specifically with sensitizer synthesized from plants which are also found in India. Anthocyanin, betalain, chlorophyll and carotenoids are among the most common plant pigments explored as sensitizers. The review of different attempts on fabrication of natural dye based solar cells implies that titanium dioxide (TiO₂) nano particles can be used as photoanode, platinum (Pt) as counter electrode and iodine/iodide electrolyte. Plant pigments are highly pH sensitive and can alter solar cell performance based on its extraction method, concentration and its ability to anchor with photoanode. Stability of dye, absorption in near IR range and leakage of liquid electrolyte are few of the challenges ahead. However, natural dye is biodegradable and non-toxic having most of the extraction process harmless to environment. In addition, natural dye has the promising future as it is abundant.

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Introduction:-

Exhaustion of fossil fuels lead the world to shift from the conventional energy sources to renewable energy to meet the growing energy demand. Although the process is gradual but the potential of renewable energy was well talked in the past decade. Wind energy is effective, but due to the inconsistency of the blowing wind, it is not quite efficient. Unlike wind energy, solar energy has a fair amount of consistency. As a result, the conversion of solar energy into different forms was the core of the research for the recent past years [1].

Nanotechnology is a rapidly promising technology with vast potential in creating new materials with unique properties and to produce new and improved products for photo voltaic applications. The term nanoparticle refers to any small particle with all three dimensions less than 100 nanometres (nm) in size. It has a large surface area per unit mass. Titanium dioxide (TiO₂) nanomaterials are known for their numerous and different applications, which range from common products, such as sunscreens, to in advanced devices such as photovoltaic cells a series of environmental and biomedical applications such as photocatalytic degradation of pollutants, water purification, biosensing and drug delivery. The importance and variety of these applications have spur enormous interest and

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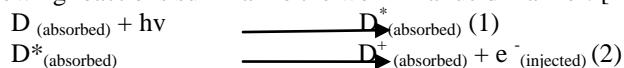
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large advances in the fabrication, characterization, and fundamental understanding of TiO₂ nanomaterials in the past decade [1-9]. Dye-sensitized Solar Cells (DSSCs) are promising devices for inexpensive, large-scale solar energy conversion. They are currently most efficient and stable excitonic photocells [10]. Central to this device is a thick TiO₂ nanoparticle that provides a large surface area for the adsorption of light harvesting molecules. The best solar energy conversion efficiency achieved till date is 12.4% [11]. This article presents a review on the literature available on fabrication, characterisation, properties, applications and commercialization of DSSCs.

Dye sensitized Solar Cell:-

Basic Principle:-

The basic operating principle for any TiO₂ DSSC consists of absorption, separation and collection. These parameters are optimized in different types accordingly to attain better efficiency. Thus, absorption occurs at the first step of the reactions in DSSC. Under illumination, sensitizer dye (D) absorbs a photon which leads to excited sensitizer state (D*). Photoexcitation of this sensitizer is then followed by the electron injection into the conduction band of the semiconductor (mesoporous). This takes the sensitizer to an oxidized state D⁺. With the electron donation from the electrolyte, containing a redox couple, the original state of the dye restored. Iodide/triiodide couple is the preferred and effective redox couple used. Iodide regenerates the sensitizer and it gets regenerated itself by the reduction of triiodide at the counter electrode. In this way the circuit gets completed by transferring electron via the external load. The following reactions summarize the work in a lucid manner: [12], [13]



The construction of a Dye Sensitized Solar Cell can be categorized as follows: [13]

- A mechanical support coated with Transparent Conductive Oxides.
- The semiconductor film, usually TiO₂
- A sensitizer absorbed onto the surface of the semiconductor
- An electrolyte containing a redox mediator
- A counter electrode is capable of regenerating the redox mediator.

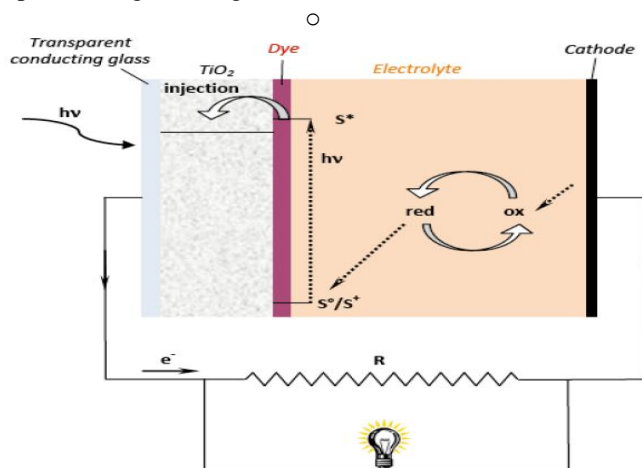


Fig1:- Schematic principle of a DSSC: photo excitation of the day (sensitizer, S) generates electrons which are injected into the conduction band of TiO₂.

In DSSCs, the function of light absorption and charge separation are isolated, unlike in the conventional silicon-based solar cells. Under light illumination, the interaction between the dye molecules and the photons cause their photo-excitation, thereby generating electron hole pairs. The electrons are injected into the conduction band of the semiconductor TiO₂. This can occur on a fast or ultrafast time scale on the order of picoseconds or hundreds of Femto seconds. The oxidized state of the dye containing the holes is rapidly reduced by the electrolyte, thus regenerating the dye. This prevents back transfer of electrons. The electrons travel through the semiconductor to the transparent electrode and the external load and eventually reach the counter electrode and regenerate the electrolyte [14].

Natural Dyes:-

Coumarin dye, merocyanine dye and polyene dyes have been designed successfully as organic-dye photosensitizers in DSSCs, and high solar energy to electricity conversion efficiencies of up to 8% under AM 1.5 irradiation have been attained. The lower performance of DSSCs based on organic dyes compared to those based on Ru complexes is probably due to the lower open-circuit voltage (V_{oc}) that is generated in the DSSCs based on organic dyes, rather than the performance of the short-circuit photocurrent density (J_{sc}), which is almost the same [17]. Natural sensitizers from plants are wide variety of flowers, leaves and fruits have been explored to extract natural sensitizer for solar cells, however scope of this review paper has been limited to sensitizers extracted from Indian plants in recent times. This study is also intended to identify Indian plants having potential to provide energy harvesting material.

Chromophores are responsible for the colour. Pigments can also be classified as natural, synthetic and inorganic based on its origin. Carotenoids provide yellow, orange and red colour to flowers and fruit. It absorbs visible light in the range of 470–550 nm usually not absorbed by chlorophyll. Carotenoids consist of eight isoprenoid units. They are classified as (i) Carotenes consisting carbon and hydrogen (ii) Oxycarotenoid or xanthophyll consisting carbon, hydrogen and oxygen. Primary Carotenoids are required for photosynthesis and secondary are found in fruits and flowers. Approximately carotenoid is produced 108 ton/year by nature [15]. Carotenoid molecules are very reactive and have quick degradation in presence of oxygen traces. Extraction of carotenoids is challenging as no optimal solvent is found which can completely avoid the degradation. Thin Layer Chromatography (TLC) can be used as one of the methods for separation being simple and economic. Absorption coefficient of carotenoids is 13 times higher than Ru based N-719 dye yet gives poor efficiency in DSSC due to poor dye regeneration [16].

Flavonoids can be grouped as anthocyanins, flavonols and proanthocyanidins. Anthocyanin has been widely explored as water soluble sensitizer rendering variety of colours from pink, red violet to dark blue. Its concentration varies from 0.1% to 1% dry weight in fruits and vegetables [17]. TLC is widely used to separate anthocyanin. Anthocyanin is most abundant and absorbs light at longest wavelength. Anthocyanin is affected by pH, aggregation and temperature among other factors. Betalains are water soluble pigment with orange and red colour. Betalains have high color strength than anthocyanin and hence maintains its color on mixing with other dyes [18]. They are stable in the pH range of 3–7 (Strack et al., 2003). The most important characteristics is the presence of carboxyl functional group ($-COOH$) that enables binding with TiO_2 photoanode. Betalains are grouped as betacyanins having maximum absorptivity of 535 nm and betaxanthins of 480 nm. Chlorophyll is the green colour pigment that is not stable in acid or base. They are abundant in nature and non-toxic. It has an advantage of tunable LUMO orbital by changing central metals for compatibility to conduction band of the photoanode[19].

Table 1:-Dye sensitized Solar Cell based different sensitizers.

Dye	Anode	Absorption peak (nm)	Electrolyte	Counter electrode	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
Canna indicall[20]	TiO_2	513	Iodide based	Pt	0.82	540	59	0.29%
Salvia splendens[20]	TiO_2	507	Iodide based	Pt	0.7	558	61	0.26%
Cowberry[20]	TiO_2	522	Iodide based	Pt	0.4	539	54	0.31%
Red cabbage[20]	TiO_2	550	Phthaloyl Chitosan: PEO NH4I+BMII	Pt	3.509	340	39	0.46%
Blackberry[20]	TiO_2	538.25	Iodide based	Pt	2.7	297	38	0.245%
Rose[21]	TiO_2	600	Iodide based	Pt	0.97	350	66.6	0.38%
Pomegranate leaves [21]	TiO_2	665	Iodide based	Pt	2.09	560	52	0.597%
Mallow[21]	TiO_2	513	Iodide based	Pt	0.69	600	55	0.215%
Annatto [21]	TiO_2	570	Iodide based	Pt	1.1	590	59	0.37%
Tamarind[21]	TiO_2	410	Iodide based	Pt	0.18	610	56	0.48%
Banana[21]	TiO_2	400–550	Iodide based	Pt	0.78	300	45	0.21%
Pumpkin[22]	TiO_2	400–550	Iodide based	Pt	0.02	300	50	0.006%

Henna[22]	TiO ₂	400–550	Iodide based	Pt	0.199	503	0.476	0.052%
Musa[22] acuminata (Banana flower)	TiO ₂	400–550	Iodide based	Pt	0.485	556	0.557	0.168 %
Cherry[22]	TiO ₂	543	Iodide based	Pt	1.89	555	49	0.49%
Black Grapes[22]	TiO ₂	520	CuSCN	Pt	1.19	449	50	0.59%

Preparation of TiO₂ DSSC:-

The process of construction of solar cells begins with two glass plates coated with indium tin oxide (ITO). Glass in itself is non-conductive and hence the thin semiconducting layer of ITO allows charge to flow. The plates are first tested to find the conductive side of the glass. This conductive side is then covered with the other required materials. A uniform coating of titanium dioxide is applied to the conductive side of one plate using a glass rod. The TiO₂ matrix is approximately 10–30 nm in diameter enabling a greater surface area for adsorption [23].

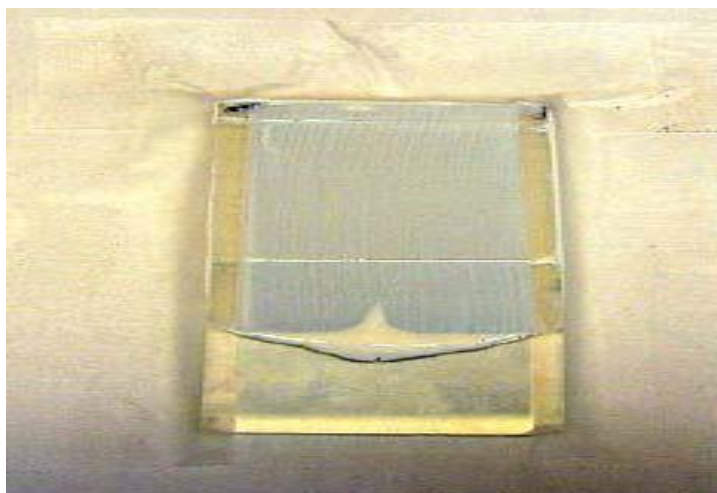
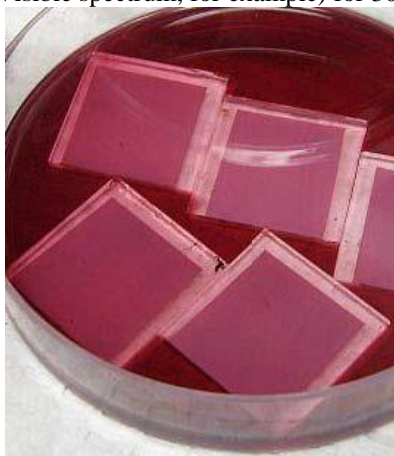
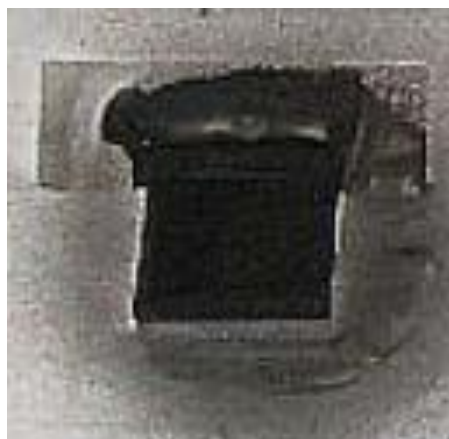


Figure 2:- ITO Glass with TiO₂ substrate.

The plate is then placed above a Bunsen burner for about 10–15 minutes to allow TiO₂ bind to the plate. This process called sintering which allows a three dimensional networks of about 10 to 30 nanometres thick to be achieved and thus favour electron flow. Following the sintering process, the plate is allowed to cool and is then placed in a bath of a dye solution (Ru535 bis-TBA, a Ruthenium-based pink dye which peaks at 384 and 530 nm in the UV-Visible spectrum, for example) for 30 minutes[24].



(a)



(b)

Figure 3:- a) TiO₂-coated cells are soaked in dye solution (Ruthenium – 535) b) cells after spraying of carbon as counter electrode.

The increased surface area of TiO_2 nanoparticles permits a greater amount of dye molecules to be absorbed, which in turn translates into an increased flow of electricity. The amounts of electrons allowed to flow through the system are dependent upon the number of dye molecules present in the cells themselves. After absorption of the dye, the plate is placed under a heat gun for drying and then sprayed with an even coating of the counter electrode (carbon or platinum). Finally, it is again dried using a heat gun (reaching approximately 120°C). This process may be repeated until the total number of desired cells is obtained. The individual pieces of glass are sandwiched together (conductive sides touching) and secured with binder clips [25].

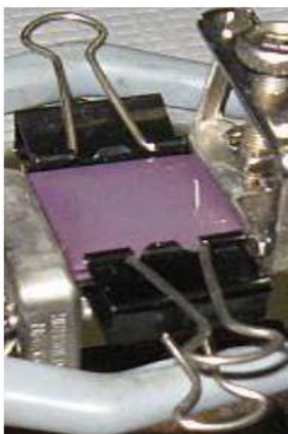


Figure 4:- Dye-sensitized TiO_2 coated solar cells

Preparation of TiO_2 Nanoparticles:-

Physical quantities including high ion exchange capability, high surface area due to their open mesoporous nature, proton conductivity and relative stability [25]. TiO_2 nanoparticles having high efficiency, low cost, non toxic, environmental friendly, corrosion resistance material. It is frequently used in paint, white pigments, and sun-blockers. The key factors are exceptional biocompatibility and even more unique ionic and electronic properties of this oxide. They have wide band gap semiconductor with suitable band gap positions that enable to be used in solar cells and photocatalytic reactions [26]. TiO_2 nanoparticles photocatalyst require a large amount of catalyst, difficulty in catalyst recycling and problematic agglomeration of TiO_2 nano crystals into large particles [27]. Although immobilized TiO_2 is the overall photocatalytic activity has been compromised due to the reduction of surface area and limitation in mass transfer [28]. In order to enhance photocatalytic activity and facilitate catalyst separation after photocatalytic reaction, one-dimensional (1D) nanostructured materials such as nanotubes, nanowires and nanorods have been investigated. Besides, charge recombination probability within TiO_2 nanoparticles also increases due to the presence of defects, surface states and grain boundaries which act as electron trapping sites [29].

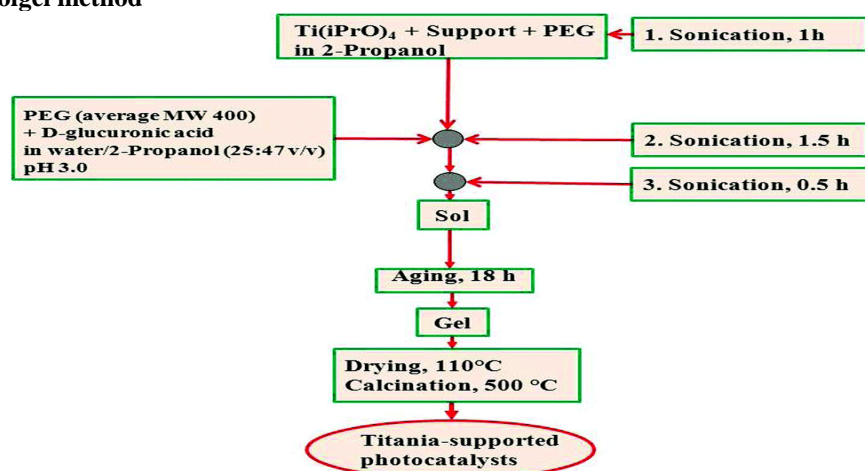
Synthesis of TiO_2 nanotubes:-

Sol-gel Method:-

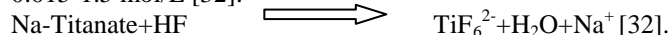
The sol-gel is an important template assisted technique used for the synthesis of TiO_2 anatase phase. In sol-gel process, a colloidal suspension or a sol is formed from the hydrolysis and polymerization reaction. Ching-Hsun et al. explained that ZnO nanoparticle seed solution was spin coated onto TiO_2 by glass substrate, then that substrate immersed in Zinc Nitrate and methenamine aqueous solution at 80°C for 24 hrs to grow TiO_2 nanorods [30]. Dye extraction is an important activity in sol-gel process. Betanin is used by S. Ananth et al. for pure TiO_2 . Titanium isopropoxide mixed with distilled water and 2-Propanol was the other precursor solution. Finally white precipitate was formed. Efficiency of the solar cell was 68% [31].

Table 2:- Sol-gel method.

S.No	TiO ₂ morphology	Particle size	Phase	Precursors
	Titanium alkoxides, 445°C, 2 hr	3.8-9.2 nm	Anatase	Halide precursorsers [32].
	Conventional sol-gel method, Titanium isopropoxide, 500°C, 30 mins	1.5-20 nm	Anatase	30 ml isopropanol [33].
	Surfactant wrapping sol gel method, Titaniumisopropoxide, 35 mg acid treated(raw), 500°C, 30 mins	0.88-35 nm	Anatase	0.5 wt% sodium dodecylbenzene sulfonate, 20 ml ethonol [34].
	β- tricalcium and Hydraxapatite (from animal bone)	3-5 nm long	Anatase	NaCl and distilled water [35].
	Cuo-TiO ₂ -xN _x nanoparticles	56.8 nm	Anatase	CO ₂ Conversion [35].

Flow chart for solgel method**Figure 5:-** Flow chart for preparation of TiO₂ nanoparticles using sol-gel method**Hydrothermal/solvothermal Method:-**

This technique is an important tool for advanced nanostructured material processing. Nanoparticles are prepared by steel pressure vessel called autoclave under controlled temperature can be elevated above the boiling point of the water/organisms. There are several hydrothermal methods are their conventional, ultrasonic assisted and microwave assisted. Kunyang chen et al. explained that 1 g of TiO₂ immersed in NaOH(50ml of 10mol/L) hydrothermal related 180°C for 12 hr.40ml of acid solution (HNO₃,H₂SO₄ or CH₃COOH). The concentrations of HF, HCl and HNO₃ 0.015-1.5 mol/L [32].



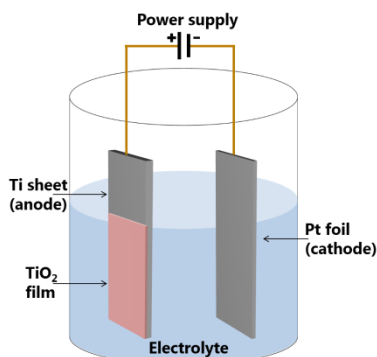
Another method to produce 2g of TiO₂ nanoparticles+100ml of NaOH(10mol/L). This mixture refluxed for 24hrs/40°C. After filtration white product treated with 0.1mol/L of HCL & distilled water (PH level less than 7). Finally Nanoparticles was dried at room temperature and calcined at 300°C for 1hour.finally prepared nanotubes range between 300-800 nm in length and 15-30 nm in diameter [14]. 10-15 NaOH 16-72 Teflon lines autoclave at110-180°C, the precipitate washed with deionized water and dispersed in HCl. This method is used to preparing ceramic materials like ZrO₂, CeO₂ and Fe₂O₂ [33].

Table 3:- Hydrothermal method.

Auxiliary methods	Conditions for hydrothermal reaction	Dimensions of nanoparticles
Conventional hydrothermal [35]	5 g TiO ₂ powder in 10 M sodium hydroxide (NaOH), 50 °C, for 20 h	Washing with 0.1 M nitric acid (HNO ₃) Average = 9 nm, Average Di = 6 nm, Interlayer spacing = 0.7 nm (2–4 walls) L = 0.3–3.0 nm, Specific surface area = 423 m ² /g.
Ultrasonication-assisted hydrothermal [33]	150 mg TiO ₂ powder in 30 mL of 10 M NaOH	Mixture was sonicated at 280 W for 60 min 110 °C for 4 h , Acid washing with 0.1 M HNO ₃ , Average Do = 5 nm, Wall thickness = 1.3 nm, L = 200–3 nm.
Microwave-assisted hydrothermal [32]	0.5 g TiO ₂ rutile in 25 ml of 10 M NaOH,	Acid washing with 0.1 M HNO ₃ ,Di = 3–5 nm, Do = 8–10 nm, L = 100–500 nm.

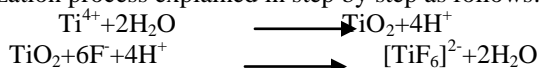
Electrochemical Anodization:-

Electrochemical anodization technique is a relatively simple, cheap and effective technique to fabricate highly ordered TiO₂ nanotubes.

**Figure 6:-** Electrochemical Anodization technique

Titanium di oxide nanoparticles were first prepared by Zwilling et al. in 1997 using chromic acid and hydrofluoric acid. The potential difference between anode and cathode was 0 to 5V. The specimen was treated in several voltages and different times between 0 to 55 mins. HF solution fluorine plays an important role in antidote, oxidation and dissolution process happens finally porous alumina growth happened [35].

The anodization process explained in step by step as follows: oxide barrier layer formed



The growth of nanotubes is related to the diffusion of F⁻ ions through the oxide layer and diffusion of [TiF₆]²⁻.

Table 4:- Electrochemical anodization technique.

Anodization categories	Types of (i) titanium (ii) electrolytes	Conditions anodization	Dimensions of nanotubes
Hydrofluoric acid (HF) based electrolytes (first generation) [32].	(i) Titanium foil (thickness: n.d.) (ii) 0.5–3.5 wt.% HF aqueous solution	Voltages: 10–40 V Duration: 20 min to 6 h D = 60 nm L = 250 nm, (i) Titanium foil (thickness: 0.2 mm)	D = 40–110 nm, L = 1 m S _v
Water-based electrolyte containing fluoride ion (second generation) [33].	(i) Titanium foil (thickness: 0.2 mm) (ii) 3 wt.% of ammonium fluoride (NH ₄ F) in 1 M sodium sulfate (Na ₂ SO ₄) solution	Voltages: 20V Duration: 30 min to 3h D = 90 nm L = 0.7–2.5 m Wall thickness = 20 nm (i) Titanium foil (thickness: 0.5 mm) (ii) 0.5 wt.% sodium fluoride in 1 M Na ₂ SO ₄ Voltages: 20 V Duration: 2 h	Pore diameter = 75 nm, Surface area = 94 cm on 4 cm sample

Characterisation of Titanium dioxide nanoparticles:-

Morphological characterisation of TiO₂ film by X-ray diffraction chromatography and scanning electron microscopy. Figure 6(a) shows the XRD pattern of sol-gel TiO₂ nanoparticles at 450°C, which indicates a mixture of the anatase and rutile phases. The XRD pattern of TiO₂ nanoparticles shows prominent anatase peaks at (101), (004), (200) and prominent rutile peaks at (110) and (101). Figure 6(b) shows the XRD patterns of Titanium dioxide nanoparticle nanotubes (TNT) films prepared at hydrothermal temperature at 150°C for 12 h. The TiO₂ nanoparticles were observed to be transformed into the anatase phase by the hydrothermal method. As it can be observed from the corresponding XRD patterns [Figure 6(b)], the TNTs possess a highly crystallised anatase structure without any impurity phase. In the TNTs, the rutile peaks indicate that the transformation to anatase is complete.

FE-SEM images of the TiO₂ sol-gel nanoparticles and the TNTs prepared at hydrothermal temperatures are shown in Figures 7(a) and 7(b). The diameter of the TiO₂ nanoparticles prepared by the sol-gel method is consistently about 25 nm. Figure 7(b) shows an FE-SEM image of the sample anatase TNTs which were grown at 150°C for 12 h and exhibit a pure tube-like structure. The length of the TNTs is several micrometers, their diameter is approximately 50 to 100 nm, and they are very uniform, quite clean, and smooth-surfaced. A DSSC with a light-to-electric energy conversion efficiency of 4.56% was achieved under a simulated solar light irradiation of 100 mW/cm². The DSSC based on a TiO₂/TNT combination at the optimal weight percentage (10 wt.% TNT) showed better photovoltaic performance than the cell made purely of TiO₂ nanoparticles [35].

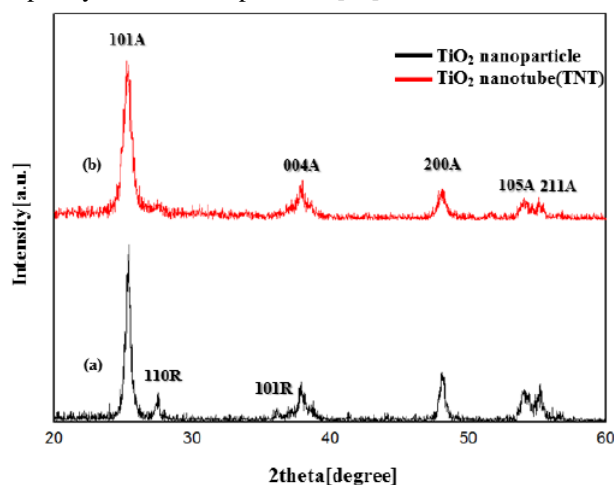


Figure 7:- XRD patterns of (a) TiO₂ nanotube (TNT) and (b) TiO₂ nanoparticles.

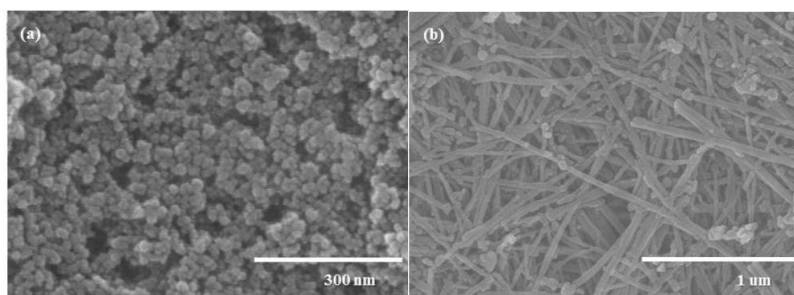


Figure 8:- FE-SEM images of TiO₂ nanoparticles and TNT films, (a) TiO₂ nanoparticles made by sol-gel method (b) TNT films made by hydrothermal method at 150°C for 12 h

Conclusion:-

DSSCs are attractive because they are made up of cheap materials that do not need to be highly purified and can be printed at low cost. DSSCs are unique compared with almost all other kinds of solar cells in that electron transport, light absorption and hole transport are each handled by different materials in the cell. Increasing the module efficiencies of DSSCs to more than 14% would relax the ultralow-cost constraints, thus providing substantial incentive to create laboratory-scale devices with efficiencies greater than 15%. The relatively slow increase in

record values for DSSCs over the past ten years left the impression of a performance ceiling, which is partially justified given that conventional iodide- and ruthenium-based and natural dye added DSSCs have a realistic maximum possible efficiency of little more than 13%. The loss-in-potential can realistically be reduced to 500 mV by better matching the energy levels at the heterojunction, using more strongly absorbing dyes in thinner films and further inhibiting recombination losses, pushing efficiencies to 19% with a dye capable of absorbing out to 920 nm. Finally, although a number of initial studies into the development of DSSC modules, a thorough understanding of the overall lifetime degradation mechanism of new natural DSSC cell and module designs require a great deal of further investigation.

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