



NANOSTRUCTURED TiO_2 AND THEIR ENERGY APPLICATIONS-A REVIEW

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ABSTRACT

Environmental sustainability and reliable energy sources are major challenges facing the world in the 21st century. Ironically, the solution to these taunting problems may lie in something small. Nanomaterials with attractive chemical and physical properties are being explored for potential uses in energy and environmental applications. Nanostructured Titanium dioxide (TiO_2) has gained considerable attention in the energy and environment sectors due to their brilliant prospects in photo catalysis, solar cells, environmental pollution treatment and its use in solar water splitting for the production of H_2 . There are many processing techniques such as; the Sol gel (SG), the hydro-thermal (HT), the solvo-thermal (ST) and chemical vapor deposition (CVD) which are used in the production of nanostructured TiO_2 for the applications stated above. This review aims at examining the general characteristics of nanostructured TiO_2 and its application in dye sensitized solar cells, photocatalytic splitting of water and solid state hydrogen storage devices. The analysis is meant to demystify the anxiety associated with the application of nanomaterials in solving everyday challenges in the energy and environmental sectors.

Keywords: nanostructured TiO_2 , energy, photo catalysis, sol gel, hydrogen gas.

INTRODUCTION

The main energy source all over the world is fossil fuel which comprises of oil, natural gas and coal. The Energy Information Administration (EIA) of the United States government has quoted that, about 10% of the world's marketed energy consumption is from renewable energy. This 10% comprises of solar, geothermal, hydropower, wind, nuclear, biomass and biofuel with the remaining 90% coming from fossil fuels (Chang *et al.*, 2010). These fossil fuels cause a lot of problems such as global warming, depletion of the ozone layer and the destruction of the bio and geo spheres to the environment. With the world energy consumption expected to increase by 71% from 2003 to 2030, a fact that for the next two to four decades, fossil fuels are likely to remain the primary source of energy in the world and the world fossil fuels are being consumed more rapidly than they are being created, there is the pressing need for alternative energy sources that are both renewable and environmentally benign (Mao *et al.*, 2007, Chang *et al.*, 2010; Elano *et al.*, 2009).

Renewable energy sources such as wind, solar, geothermal, hydropower, biofuel and biomass provides a much cleaner and environmentally benign source of power. Nevertheless, these alternative energy production sources are still limited due to their high production cost and low energy conversion efficiency (Elano *et al.*, 2009). The low energy conversion efficiency can be improved through nanotechnology. Nanotechnology, which is the manipulation and control of matter on the dimension of approximately 1 to 100 nm, where unique phenomena enables novel application, has what it takes to help solve

the world energy crises. Nanomaterials provide unique properties which cannot be provided by equal volume and shape of its corresponding bulk material; a phenomena termed nano effect. Nano materials exhibit distinct size dependent properties which can make a strong impact on energy conversion and storage (Chang *et al.*, 2010).

Extensive research efforts dedicated to TiO_2 nano materials have been most fascinated with the discovery of the phenomenon of photocatalytic water splitting on TiO_2 electrodes by Fujishima *et al.*, in 1972. A lot of research on TiO_2 nanomaterials which include nanoparticles, nanorods, nanowires and nanotubes has been widely carried out. The movement of electrons and holes in semiconductor nanomaterials is governed by the well-known quantum confinement, the transport properties related to phonons and photons, and these three key parameters are largely affected by the size and geometry of the materials, and the specific surface area and surface to volume ratios increases dramatically as the size of material decreases. TiO_2 which is a semiconductor utilizes these size dependent properties in the conversion of solar energy. The high surface area brought about by small particle size is beneficial to most TiO_2 -based devices as it facilitates reaction/interaction between the devices and interacting media which mainly occurs on the surface and depends on the surface area (Chin *et al.*, 2010). McEvoy *et al.*, in 2006 reported that, dye sensitized nanocrystalline solar cells require a sufficient optical density of the absorbing structure. This leads to the use of nanocrystalline materials for the TiO_2 semiconductor, which provides an extended surface area, sufficient dye, chemisorbed as a monomolecular layer and can be retained on a given area



of electrode to provide absorption to the incident light. This high surface area is also required in the photocatalytic splitting of water for the production of H_2 , which is a much cleaner source of energy and also for solid state uptake of H_2 . Oxide structures of TiO_2 nanotubes has been recently used to store up to 2 wt% H_2 at room temperature and 6 MPa (Mao *et al.*, 2007). That is nanostructured TiO_2 can be used to provide a much cleaner and environmentally benign energy due to the unique properties it possess as a semiconductor and also as a nanomaterial.

Structural and thermodynamic properties of nanostructured TiO_2

Titanium dioxide (TiO_2) is a naturally occurring oxide of Titanium. The unique properties of TiO_2 is directly connected to its crystal structure which is also related to its processing method. TiO_2 has three phases of crystal structures namely: anatase, rutile and brookite. The most commonly seen phases are anatase and rutile, which are also the phases that are utilized as a photocatalyst. The anatase phase exhibits a high photoactivity which is promising for the envisaged applications in the generation of H_2 by decomposing water with solar energy. A problem in the application of anatase as a photocatalyst is the large band gap energy of 3.2 eV, which shows photocatalytic activity under ultraviolet (UV) irradiation of wavelength less than 387 nm. Rutile on the other hand has been reported to have band gap energy of 3 eV by Shu *et al.*, in 2005, Yin *et al.*, in 2003^a, "a", Wang *et al.*, in 2003, Yin *et al.*, 2003^b, Sclafani *et al.*, in 1996 and Kormann *et al.*, in 1988. The unit cell structures of these commonly seen phases are shown in Figures 1 (a-b). These two structures can be described in terms of chains of TiO_6 octahedral, where each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions. Anatase which is a tetragonal mineral with pseudo-octahedral habit has octahedral shape and is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are larger, whereas the Ti-O distances are shorter than those in rutile. In the rutile structure, each octahedron is in contact with

10 neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while, in the anatase structure, each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner). These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO_2 . In reality, the crystal structure of TiO_2 nanoparticles is dependent largely on the preparation method (Chin *et al.*, 2009).

Of all the phases mentioned above, rutile is stable at high temperature (for bulk TiO_2) while anatase and brookite are common in fine grained (nano-scale) natural and synthetic samples. Anatase seems to be the most stable phase when the size of the nanoparticles is below 50nm. The transformation from one phase to the other is dependent on the processing temperature. Anatase can be transformed to rutile at processing temperatures greater than 973 K. This was confirmed by Kitano *et al.*, 2008, who synthesized a highly active TiO_2 with rutile structure using Radio Frequency Magnetron Sputtering with substrate temperature of 873 K. XRD analysis showed that, the TiO_2 produced at temperature less than 873 K has anatase crystal structure. In a study conducted on the phases of TiO_2 , the prepared TiO_2 nanoparticles have anatase and/or brookite structures, which transformed to rutile after reaching a certain particle size. Once rutile was formed, it grew much faster than anatase (Chin *et al.*, 2009; Xiaobo *et al.*, 2007).

By analyzing the energetics of the TiO_2 polymorphs by high temperature oxide drop melt solution calorimetry, it has been shown that the energetically stable regions cross over between the three phases as shown in Figure-1(c) (Xiabo *et al.*, 2007). The dark solid line represents the phases of the lowest enthalpy as a function of specific surface area. Rutile is energetically stable for surface areas 592 m^2/mol (7 m^2/g or particle sizes 200 nm). Brookite, also common in nano-scale natural and synthetic samples, is energetically stable from 592-3174 m^2/mol (7 - 40 m^2/g or particle sizes 200 - 40 nm) and while anatase is energetically stable for greater surface areas or smaller sizes 40 nm (Xiabo *et al.*, 2007).

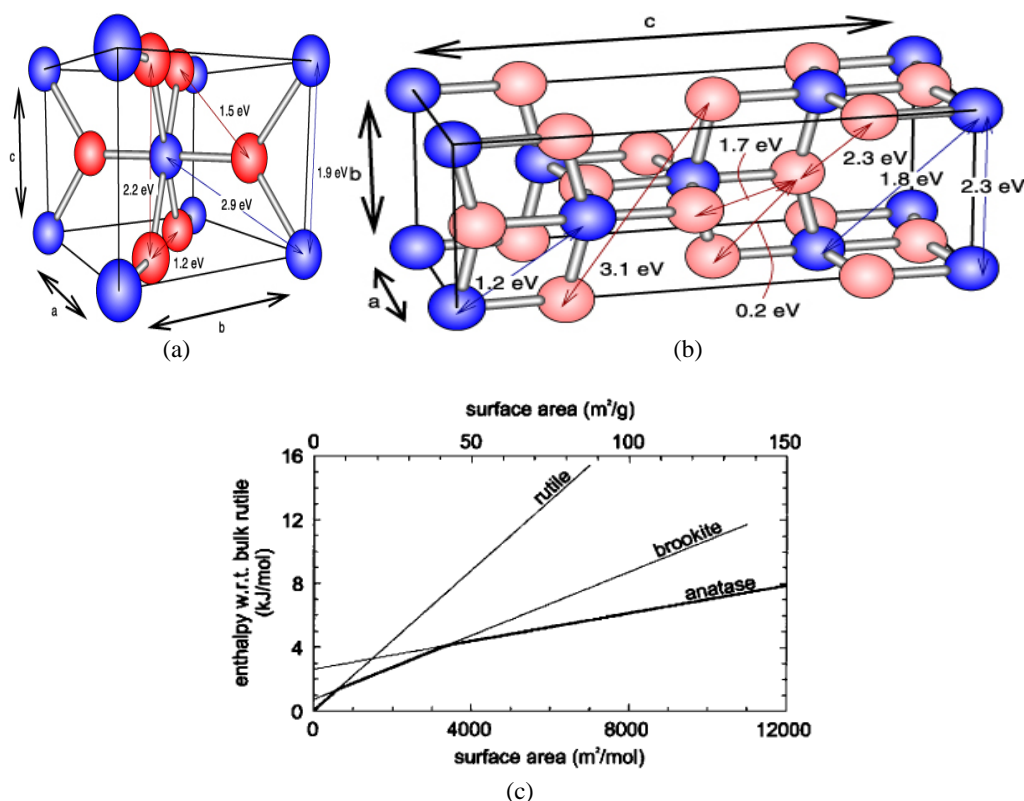


Figure-1. Lattice structures of (a) Rutile and (b) Anatase TiO₂ (Blas *et al.* 2011), (c) Enthalpy of Nanocrystalline TiO₂.

Synthetic methods for TiO₂ nanostructures

Different nanostructures such as nanotubes, nanoparticles and nano-films exist for TiO₂ and as a result, there exist different processing methods. The common among them includes sol gel, hydro-thermal, solvo-thermal and chemical vapour deposition.

Sol gel method

Sol-gel process has attracted a considerable interest since the mid 1970's and forms the most important liquid precursor route for the production of simple or complex oxides. The sol gel method is a versatile process and can be used to process a variety of materials. In this method, a solution of metal compounds or a suspension of very fine particles in a liquid (referred to as a sol) is converted into a highly viscous mass. In a sol gel processing of nanostructured TiO₂, the hydrolysis of a titanium alkoxide followed by condensation lead to the formation of TiO₂ inorganic framework. This frame work which mainly consists of Ti-O-Ti chains is developed though alcoxolation which is favored by low content of water, with low hydrolysis rates and excess titanium alkoxide in reaction mixture. Three dimensional polymeric skeletons with close packing are resulted from the development of Ti-O-Ti chains since each Ti is coordinated with four O atoms (Chin *et al.*, 2009 and Xiaobo *et al.*, 2007).

Sol-gel synthesis is well noted for the production of TiO₂ films and coatings. A slight modification of the processing precursor and conditions can lead to the production of different nanostructured TiO₂ with unique properties. Natalie *et al.*, 2004 synthesized a mono-dispersive Titania coating by controlled acid hydrolysis using Titanium Tetra-Iso-propoxide in Iso-propanol. They also succeeded in the production of mesoporous TiO₂ by sol-gel synthesis under a different processing technique.

Highly crystalline anatase TiO₂ nanoparticles with different sizes and shapes could be obtained with the polycondensation of titanium alkoxide in the presence of tetramethylammonium hydroxide. In a typical procedure, titanium alkoxide is added to the base at 2°C in alcoholic solvents in a three-neck flask and is heated at 50-60°C for 13 days or at 90-100°C for 6 h. A secondary treatment involving autoclave heating at 175°C and 200°C is performed to improve the crystallinity of the TiO₂ nanoparticles (Xiaobo *et al.*, 2007).

Sue *et al.*, in 2009 reported on sol-gel synthesis of linear Sn-doped TiO₂ (TDT) nanostructures with high aspect ratios. These binary metal-oxide nanostructures are readily accessed by treating titanium isopropoxide with appropriate quantities of acetic acid in heptane to generate linear macromolecules that form nanofibers upon calcination. Scanning and transmission electron microscope imaging of the nanofibers revealed diameters in the 10-20 nm range and lengths in excess of 1 mm.



Elemental mapping by SEM-EDS techniques indicated a homogenous distribution of Tin (Sn) ions throughout the linear TDT structures. Powder X-ray diffraction data indicated that pure TiO_2 nanostructures are anatase when calcined at 500°C , but showed a propensity to adopt the rutile phase at progressively higher Sn concentration.

Hydro-thermal method

Numerous publications have reported the processing of different nanostructured TiO_2 using hydro-thermal method. Hydro-thermal synthesis is normally conducted in autoclaves under controlled temperature and/or pressure with the reaction in aqueous media. Alkaline aqueous medium such as NaOH has been used in the hydrothermal processing of TiO_2 nanotubes with inner and outer diameters of 5 and 10 nm, respectively (Takashi *et al.*, 2008 and Bavykin *et al.*, 2006). Temperature, the volume of the aqueous medium used and the pressure in the vessel influences the whole production process. Temperatures higher than the melting point of the aqueous medium can be used. TiO_2 nanoparticles have been prepared by hydrothermal reaction of titanium alkoxide in an acidic ethanol-water solution. In this process, Titanium tetraisopropoxide (TTIP) was added in drops to a mixed ethanol and water solution at a very low pH with nitric acid, and reacted at 240°C for 4 hours. The TiO_2 nanoparticles obtained by this process were mainly anatase phase with particle sizes between 7-25 nm (Xiaobo *et al.*, 2007).

Recent work has shown that, it is possible to prepare nanocrystallites of the different polymorphs of TiO_2 by manipulating the pH of the aqueous media. Titanium isopropoxide and nitric acid mixture under vigorous mixing in hydrothermal process was adopted in the preparation of 20 nm rutile nanocrystallites (Aruna *et al.*, 2000). In another process, a mixture of brookite, rutile and anatase were obtained by hydrothermal processing of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ under acidic conditions using HCl (Yanagasiwa *et al.*, 1999). Hengbo *et al.* in 2001 on the other hand with amorphous TiO_2 produced anatase and rutile TiO_2 nanocrystallites in the presence of HF and nitric acid, respectively. It can be deduced from the above statements that, the precursor as well as pH have dramatic effect on the final morphology of the TiO_2 nanomaterial produced by the hydrothermal process.

Solvo-thermal method (ST)

The solvo-thermal method is similar to the hydrothermal method except that the solvent used here is non-aqueous. That is the precursor solution is usually made up of an organic solvent. This makes it possible for processing temperature to be elevated much higher than in the hydrothermal method because a variety of organic solvent with high boiling points can be chosen. The solvo-thermal method normally has a better control than hydrothermal methods of the size, shape distributions and the crystallinity of TiO_2 nanoparticles.

In this method, the solvent, pH, the precursor composition, solvo-thermal temperature and reaction time

has an impact on the crystal morphology that results Bao-Mei *et al.* and Shu *et al.*, in 2005. Yang *et al.* (2009) reported that, the fraction of rutile phase in the resulting product that is dependent on the ratio of the starting precursors in the solvent. With the synthesis of nanostructured TiO_2 from Titanium tetrachloride (TiCl_4) and Tetrabutyl titanate, $\text{Ti}(\text{OBU})_4$ mixture based on Benzene-water interfaces, the fraction of the rutile phase in the product increased with the starting molar ratio of TiCl_4 and $\text{Ti}(\text{OBU})_4$. They also reported that, at a much lower temperature, the product is made up of a mixture of rutile and anatase. At a higher solvothermal temperature, the anatase phase transformed into a rutile phase, resulting in a pure product made up of only rutile (Kitano *et al.*, 2008).

Solvo-thermal method has been used to synthesize anatase TiO_2 nanosheets with dominant {001} facets. The main precursor in this process was Titanium tetrafluoride (TiF_4). Hydrochloric acid was used to adjust the pH of deionized water and TiF_4 by dissolving all into a solution under vigorous stirring. About 14.5 ml of the TiF_4 solution, 13.38 ml of 2-propanol and 0.5 ml of hydrofluoric acid was then fed into an autoclave. The resulting product was mainly made of anatase TiO_2 single crystals (Yang *et al.*, 2009).

Chemical vapor deposition (CVD)

Chemical vapor deposition is a well-established material processing technique used in most processing industries. It is a process by which reactive molecules in a gas phase are transported to a surface at which they chemically react and form a solid film. Vapor deposition processes usually take place within a vacuum chamber. CVD is similar to physical vapor, the only difference being that, no chemical reaction occurs in the later. Different forms of materials such as single thin films, nanoneedles, coatings, monoliths and composites can be attained with CVD (Ding *et al.*, 2001 and Boras *et al.*, 2009). The precursor molecules enter the reactor by the help of a carrier gas. Some of the carrier gases that have been used in the processing of nanostructured TiO_2 by CVD are O_2/N_2 , He, N_2 , Ar and H_2 . The temperature of these carrier gasses has enormous effect on the CVD process. The substrate on which the deposition is made can be solid particles, porous solids, alumina, glass (Bin *et al.*, 2007) etc. For photo catalysis, the substrate is usually made of glass or another conducting material; which can be a semiconductor. The substrate temperature and its surface morphology are very important for the deposition. A lower substrate temperature can slow down the rate of deposition but will result in a much finer grain size. A higher substrate temperature on the other hand will result in a much larger grain size, and the deposited material will decompose if the substrate temperature is higher than the decomposition temperature of the deposited material.

There exist modified forms of CVD, some of which are plasma enhanced chemical vapor deposition (PECVD), metal-organic chemical vapor deposition (MOCVD), and low pressure chemical vapor deposition



(LPCVD). All these modifications have their own unique advantages. MOCVD allows easy mass production, excellent crystallinity, good mechanical stability and good adhesion of films (Jun *et al.*, 2005 and Wu *et al.*, 2002).

PECVD has been used to produce thick crystalline TiO_2 films with grain sizes below 30 nm as well as TiO_2 nanoparticles with sizes below 10 nm. These were achieved by pyrolysis of TTIP in a mixed Helium/Oxygen atmosphere, using liquid precursor delivery. Deposition of the cold areas of the reactor resulted in the formation of amorphous TiO_2 nanoparticles with high surface to volume ratio after being annealed at high temperature (Chin, 2009).

MOCVD has also been used to grow TiO_2 nanorods on fused silica substrates using titanium acetylacetonate as a precursor molecule. The reaction conditions had a great effect on the phase and morphology of the TiO_2 nanostructures produced. For example, at 630 and 560°C under a pressure of 5 Torr, single-crystalline rutile and anatase TiO_2 nanorods were formed respectively, while at 535°C under 3.6 Torr, anatase TiO_2 nano-walls composed of well-aligned nanorods were formed (Xiaobo *et al.*, 2007).

Additional synthesis method for TiO_2 nanostructures are physical vapor deposition (PVD), Sol method, direct oxidation method, sonochemical method, electrodeposition, microwave method etc.

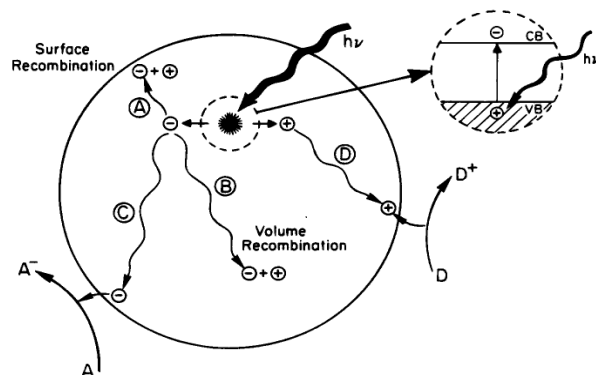


Figure-2. Schematic photoexcitation in a solid followed by de-excitation events (Linsebigler *et al.*, 1995).

Titanium dioxide as a semiconductor

The unique photocatalytic properties of TiO_2 can be attributed to the unique properties inherent in semiconductors. Semiconductors possess a void energy region called band gap where no energy levels are available to promote recombination of an electron and holes produced by photoactivation in the solid, a structure that makes it different from metal where the valence band and the conduction band overlaps. Excitation, which occurs by the absorption of energy, leads to the transfer of electrons from the valence band to the conduction band when the absorbed energy is greater than the band gap energy which has been reported as 3.2 eV for anatase. As will be discussed later, the size of the semiconductor as well as the processing method affects the band gap energy

value. Once excitation occurs across the band gap there is a sufficient lifetime, in the nanosecond regime, for the created electron-hole pair to undergo charge transfer to adsorbed species on the semiconductor surface from solution or gas phase contact. If the semiconductor remains intact and the charge transfer to the adsorbed species is continuous and exothermic the process is termed heterogeneous photocatalysis (Linsebigler *et al.*, 1995). This heterogeneous photocatalytic property of nanostructured TiO_2 gives it a self-cleaning property and the ability to be used in environmental purification.

The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductors is the generation of electron-hole pairs in the semiconductor particles. The magnified section of Figure-3 shows the excitation of an electron from the valence band to the conduction band initiated by light absorption with energy equal to or greater than the band gap of the semiconductor.

The electrons and holes can migrate to the surface of the semiconductor. The electron transfer process is more efficient if the species are preadsorbed on the surface. While at the surface the semiconductor can donate electrons to reduce an electron acceptor (usually oxygen in an aerated solution) (pathway C); in turn, a hole can migrate to the surface where an electron from a donor species can combine with the surface hole oxidizing the donor species (pathway D). This mechanism is used in photocatalytic splitting of water for the production of H_2 . The electron at the surface can also flow in an external circuit, where it can be used to generate electric power. A complete utilization of the above mechanism has not been achieved due a phenomenon called electron-hole recombination which can occur and usually occurs after the photo excitation. This is described in pathway B. Modification of the structure of TiO_2 by processing methods and doping has been adopted to decrease this unwanted phenomenon (Linsebigler *et al.* (1995).

A major setback in the use of nanostructured TiO_2 as a photocatalytic material despite its unique properties is the fact that, a band gap of 3.2eV makes it impossible to absorb light in the visible light spectrum. That is TiO_2 semiconductor can only absorb light in the UV range which only makes up about 4% of the total light spectrum (Ni *et al.*, 2007 and Cowan *et al.*, 2010).

Low photoenergy conversion of nanostructured TiO_2 materials

Despite the unique photocatalytic properties of nanostructured TiO_2 materials, low photoenergy conversions have been recorded in dye sensitized nanocrystalline solar cells (DNCSs) and in the production of H_2 by photocatalytic splitting of water. Graetzel (2003) reported a solar energy to current efficiency of up to 10%. Henrik *et al.* (2001) in an attempt to develop DNCSs at room temperature recorded as low as 5.2 % solar energy to current conversion. Hinsch *et al.* (2001) on the other hand reported an efficiency of 5.5%, when MgI_2 was added to the electrolyte in a DNSC. Two major reasons that were



attributed to these low efficiency values were electron-hole recombination and high band gap energy of the TiO_2 material which made absorption of energy in the visible spectrum impossible.

Although Bolton *et al.* (1985) had reported through thermodynamic calculations that it is possible to store 12% of the incident solar energy in the form of H_2 after considering reasonable losses in the electron transfer step, such high solar energy conversion to H_2 has not been realized up to date. Kitano *et al.* (2008) reported a solar energy conversion of 0.1% from the initial rate of H_2 evolution while Justin *et al.*, reported ~1 % quantum yield when they splitted water into H_2 and O_2 using a dye sensitized TiO_2 film. Maeda *et al.* (2008) reported a quantum yield of about 6% at a wavelength of 420 nm. The main reasons attributed to these low quantum yield and efficiencies were electron-hole recombination and high band gap energy of TiO_2 .

A lot of research being conducted lately is therefore aimed at improving the efficiencies of DNSCs and photocatalytic water splitting process. The main target is to reduce the electron-hole recombination and decrease the energy band gap of nanostructured TiO_2 by modification of processing steps. That is different processing methods has been developed to synthesize nanostructured TiO_2 with low band gap energy and low electron-hole recombination.

Overcoming the high energy band gap of nanostructured TiO_2

The structure of a material has a direct effect on its properties and performance. As depicted in Figure-4, the structure can be modified by choosing a suitable processing technique. The best way to address the high band gap of the nanostructured TiO_2 materials is to adopt different processing methods. That has been the goal of most researchers.

Shahed *et al.* (2002) tried to address this problem by synthesizing chemically modified n- TiO_2 by thermal pyrolysis. In their work, thermal hydrolysis of Ti metal in the presence of CO_2 and steam in a natural gas flame (flame temperature of 850°C with controlled amount oxygen was carried out). Structural analysis of the thin films produced by this method depicted the presence of mainly porous rutile phase which is known to have low band gap energy. The measured band gap energy of the synthesized TiO_2 thin films was 2.32 eV which is below the 3.2 eV for the referenced n- TiO_2 and was able to absorb light below 535 nm. The reference n- TiO_2 used in their study was made of both rutile and anatase phase. Alexandrescu *et al.* (2004) reported that, the fraction of the rutile phase is dependent on the nature of the oxygen precursor used in the pyrolysis. It is therefore possible to choose an Oxygen precursor that will lead to the synthesis of mainly rutile phase and therefore able to absorb light in the visible spectrum.

Application of stress along the soft crystal direction of TiO_2 can lead to a remarkable reduction in the band gap energy. Tavares *et al.* (2008) reported that for

strain less than 5%, the photocatalytic activity of TiO_2 thin film increased dramatically. Shibata *et al.* (2003) also reported that, for anatase TiO_2 film with tensile stress, its photocatalytic activity increased by 5 times. Wan *et al.* (2010) calculated the band gap energy using first principle band structure calculations and reported that, the band gap energy of the anatase phase can be effectively reduced by applying stress along a soft direction [001]. Their calculated band gap was 1.88 eV, which was less than the experimental values of 3.2 eV.

Negaveni K. *et al.* (2004) also synthesized anatase TiO_2 with reduced band gap energy by solution combustion method. Nanosize anatase TiO_2 was obtained by the combustion of aqueous solutions containing stoichiometric amounts of $\text{TiO}(\text{NO}_3)_2$ and fuels such as glycine. A UV-Vis spectroscopy analyses showed that, band gap energy as low as 2.21 eV can be attained by solution combustion method. Narrowing of the band gap energy has been reported in nanocrystalline TiO_2 films doped with N, C and S, with carbon-doped TiO_2 as one of the best in terms of band-gap width. The most common method of producing a carbon-doped TiO_2 films is by direct oxidation of the Ti metal in the flame of a burner (Jong *et al.*, 2006, Brborini *et al.*, 2005 and Yu *et al.*, 2005).

The lower band gap energy obtained in the paragraphs above cannot be achieved with some processing methods such as hydrothermal process and sol gel synthesis. Sergio V. *et al.* (2010) synthesized titanium dioxide nanoparticles by sol gel synthesis using Teraisopropyl orthotitanate (TIOT) and reported band gap energy of 3.27 eV. Vijayalakshmi *et al.* (2012) compared the band gap energy of TiO_2 nanoparticles prepared by sol gel synthesis and hydrothermal method. Their study showed that, the TiO_2 nanoparticles prepared by Sol gel synthesis had particles size of 7 nm and band gap energy of 3.54 eV, while the hydrothermal method produced TiO_2 nanoparticles with particle sizes of 17 nm and band gap energy of 3.43 eV.

It can be deduced that, the choice of processing method for the nanostructured TiO_2 has a direct impact on the band gap energy. To be able to address the high band gap energy problem, there is the need for in-depth studies to be done on developing new processing methods for nanostructured TiO_2 .

Overcoming electron-hole recombination of nanostructured TiO_2

As already mentioned, one of the major problems affecting the efficiency of photocatalytic activities of nanostructured TiO_2 is electron-hole recombination. Different authors have used different methods to reduce this unwanted phenomenon in TiO_2 nanomaterials. Some of these methods are outline in this section.

Most of the processing methods adopted involve incorporating of another material into the nanostructured TiO_2 . Ag/ TiO_2 nanocomposite has been generated by incorporating Ag nanoparticles into TiO_2 film. This nanocomposite recorded a remarkable increase in



photocatalytic activity. The increase in photocatalytic activity was attributed to the suppressing of the electron-hole recombination, which was caused by the metal-semiconductor contact (Jinxia *et al.*, 2012). This may be as a result of the donation of Ag free electrons, which combined with the holes created in the TiO₂, preventing the excited electrons from recombining with the holes.

Addition of electron donors to the nanostructured TiO₂ has also been adopted. These electron donors sometimes referred to as sacrificial reagents or hole scavengers are mostly organic compounds. These electron donors react irreversibly with the photo-generated valence band holes therefore suppressing the electron-hole recombination. Since electron donors are consumed in photocatalytic reaction, continual addition of electrons is required to sustain the process (Ni *et al.* 2007).

Incorporating of Carbon nanofiber into nanostructured TiO₂ has also been tried. This hybrid TiO₂-Carbon nanofiber nanostructure was fabricated by Metal-Organic chemical vapor deposition. XRD analysis of the nanostructure revealed the presence of anatase TiO₂. Photoluminescence spectra taken at room temperature showed the absence of Photoluminescence emission which showed that the electron-hole recombination in the TiO₂ is completely quenched in such a core-shell hybrid structure (Jianwei *et al.*, 2008).

Application of stress along the soft direction of anatase TiO₂ does not only decrease the band gap energy, it also suppresses the electron hole recombination. Kamei *et al.* (2005) reported that anatase film under epitaxial strain could enhance the electron-hole charge separation. One major issue is the reports by other researchers that, the photo electrochemical activity of the nanostructured TiO₂ is reduced when stress is applied (Wan *et al.*, 2010, Miyamura *et al.*, 2008 and Nambara *et al.*, 2007).



Figure-3. Processing, structure, property and performance relationship of materials.

Energy applications of nanostructured TiO₂

The dramatic increase in energy demand and the growing pressure to address environmental concerns have triggered the development of alternative energy and sustainable environmental technologies. Wade Adams, in his energy TED (Technology, Entertainment and Design) talk in 2010 stated that, the world energy consumption is expected to increase to about 60 terawatts in 2050. He also stated that, more energy is produced from the sun in an hour than what the entire human race on earth consumes in a year. There is therefore the need to take a much closer look into the mechanisms that can be used to make good use of the energy supplied by the sun. Of the various renewable energy options, solar energy stands out as the most ultimately sustainable choice in terms of its availability and vast potential. In the past decades, nanostructured materials have emerged as unique building blocks to construct light energy harvesting assemblies. A

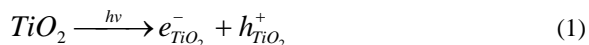
large number of published papers on possible methods of solar energy transfer, such as solar cells hydrogen energy production by photocatalytic water splitting, have already been published (Hu *et al.*, 2010), while a few papers have reported possible use of TiO₂ nanotubes as solid state hydrogen storage material.

Photocatalytic water splitting

Hydrogen has a higher chance of becoming the most environmentally acceptable fuel of the future because it is an excellent source of clean energy. Also it has a high calorific value, nonpolluting and forms water as a byproduct during use. One promising method of producing hydrogen is photocatalytic water splitting. Nano-sized TiO₂ photocatalytic water splitting into H₂ and O₂ has great potential for low cost and environmentally friendly solar-hydrogen production to support the future hydrogen economy (Chin, 2009 and Ni *et al.*, 2007). The principle of water splitting using TiO₂ photocatalyst can be summarized as follows; When TiO₂ absorbs light with energy larger than the band gap, electrons and holes are generated in the conduction and valence bands respectively. The photo-generated electrons and holes cause redox reactions. Water molecules are reduced by the electrons to form H₂ and oxidized by the holes to form O₂, leading to overall water splitting.

Mechanism of TiO₂ semiconductor photocatalytic water splitting for hydrogen production

The electronic structure of a semiconductor plays a key role in semiconductor photocatalysis. Unlike a conductor, a semiconductor consists of valence band (VB) and conduction band (CB). Energy difference between these two levels is said to be the band gap. Without excitation, both the electrons and holes are in valence band. When semiconductors are excited by photons with energy equal to or higher than their band gap energy level, electrons receive energy from the photons and are thus promoted from VB to CB. For semiconductor TiO₂, the reaction is expressed as:



The photo-generated electrons and holes can recombine in bulk or on surface of the semiconductor within a very short time, releasing energy in the form of heat or photons. Electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidize the reactants adsorbed by the semiconductor. The reduction and oxidation reactions are the basic mechanisms of photocatalytic hydrogen production and photocatalytic water/air purification, respectively. Both surface adsorption as well as photocatalytic reactions can be enhanced by nano-sized semiconductors as more reactive surface area is available (Ni *et al.*, 2007).

For hydrogen production, the CB level should be more negative than hydrogen reduction level while the VB should be more positive than water oxidation level for



efficient oxygen production from water by photocatalysis. The photocatalytic hydrogen production by TiO_2 is shown in Figure-4. Theoretically, all types of semiconductors that satisfy the above-mentioned requirements can be used as photocatalysts for hydrogen production. However, most of the semiconductors, such as CdS and SiC, that cause photocorrosion, are not suitable for water-splitting. Having strong catalytic activity, high chemical stability and long lifetime of electron/hole pairs, TiO_2 is the most widely used photocatalyst.

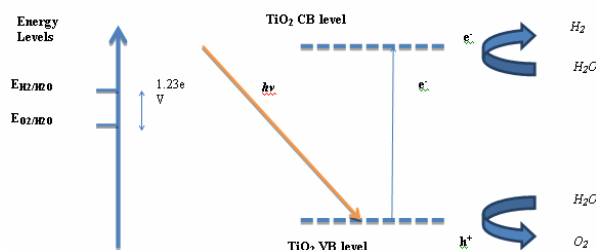


Figure-4. Photocatalytic hydrogen production by TiO_2 .

Presently, the energy conversion efficiency from solar to hydrogen by TiO_2 photocatalytic water-splitting is still low, mainly due to the following reasons (Chin, 2009, Ni *et al.*, 2007 and Serano *et al.*, 2009):

- **Electron-hole recombination:** CB electrons can recombine with holes very quickly, and release energy in the form of unproductive heat or photons.
- **Fast backward reaction:** decomposition of water into hydrogen and oxygen is an energy increasing process, therefore recombination of hydrogen and oxygen to produce water can take place easily.
- **Inability to utilize visible light:** the band gap of TiO_2 is about 3.2 eV and only UV light can be utilized for hydrogen production. How to overcome these challenges has already been dealt with in the previous section.

Water splitting photoelectrochemical (PEC) cell

Though there have been a lot of modifications to the PEC cell used for water splitting, the main set up is the same with some variations to the electrode materials. Some of the PEC has been produced with pure nanocrystalline TiO_2 (Cowan *et al.*, 2010), while others have been produced by chemically modifying TiO_2 by controlled combustion of Ti metal in a natural gas flame. Some have also modified the process by using a dye sensitized nanostructured TiO_2 (Khan *et al.*, 2002 and Youngblood, 2009). All these modifications are meant to increase the water splitting efficiency.

Cowan *et al.*, (2010) developed a PEC cell and subsequently used it to split water. In their study, nanocrystalline TiO_2 film to be used as an electrode was prepared on conductive Fluorine doped Tin Oxide (FTO) glass. The films were prepared by spreading the TiO_2 colloidal paste onto the surface of the FTO glass and left to dry in air for 20 minutes. Electrolyte solutions were

prepared from Milli-Q-Water and NaOH, and degassed with Argon prior to transfer under an argon atmosphere to a custom built gastight PEC cell. The cell consisted of two compartments separated by nafion membrane. The nanocrystalline-electrode was mounted with the substrate FTO facing the UV excitation source behind a borosilicate glass window in the first compartment alongside Ag/AgCl reference electrode (Youngblood *et al.*, 2009). A Pt flag counter electrode was mounted in the second compartment. The PEC cell for water splitting is shown below in Figure-5 (Kitano *et al.*, 2008). Kitano *et al.*, (2008) also reported the production of hydrogen using a highly active TiO_2 photocatalyst. In their report, the TiO_2 thin films were prepared by radio frequency magnetron sputtering (RF-MS) deposition method. This method lead to the synthesis of nanostructured TiO_2 films which were able to absorb visible light by manipulating the substrate temperature. A UV-VIS transmission spectra showed a lower transmittance when the substrate temperature was 873 K, depicting a higher absorbance in the visible spectrum. The TiO_2 phase present at this temperature is most likely to be a rutile phase which has lower band gap energy. The TiO_2 electrode prepared by this film was mounted on an H-type container filled with water. These thin films photocatalysts were found to have enough potential for the separate evolution of H_2 and O_2 from water under sunlight irradiation. The PEC cell used is shown in Figure-6.

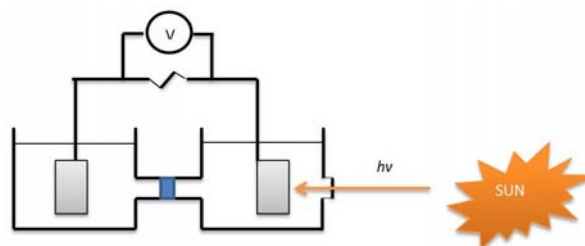


Figure-5. Schematic PEC cell for water splitting.

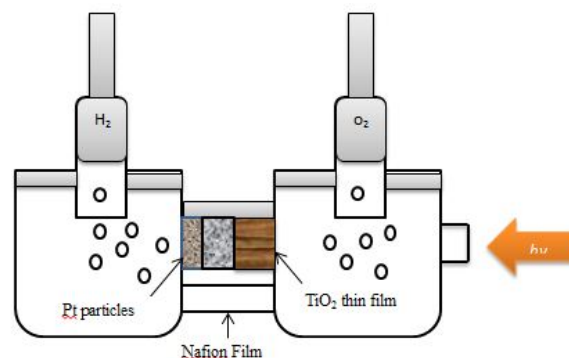


Figure-6. Schematic PEC cell used by Kitano *et al.*, (2008).

The TiO_2 side was immersed in 1M NaOH aqueous solution and the Pt side was immersed in 0.5 M H_2SO_4 aqueous solution. Under visible light, water could



be decomposed separately into H_2 and O_2 with a good linearity against the irradiation time. Figure-7 shows the effect of irradiation time of light from the sunlight gathering system on the amount of evolved H_2 (on the Pt side) and O_2 (from the TiO_2 side). Changes in the relative intensity of the sunlight along with the irradiation time are also shown in the Figure-7.

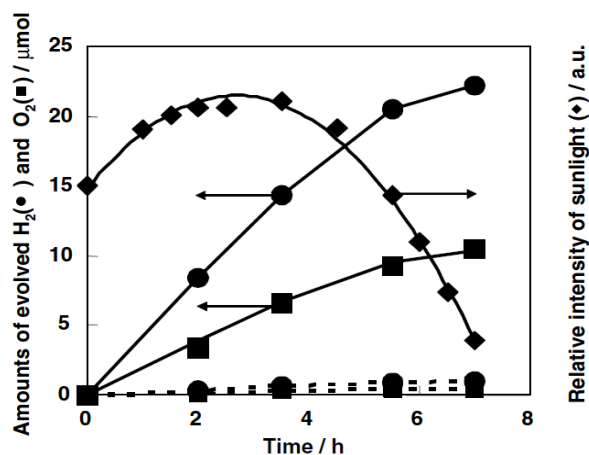


Figure-7. Amount of H_2 and O_2 evolved as a function of time.

The efficiency of the solar energy conversion was estimated to be 0.1% from the initial rate of the H_2 evolution. The decline in the observed evolution rates of H_2 and O_2 can be attributed to the decline in the intensity of sunlight according to Kitano *et al.*, (2008).

Instead of using a pure nanostructured TiO_2 as the working electrode in the PEC, Jong *et al.* (2006) used a carbon doped TiO_2 nanotube arrays with high aspect ratio as the working electrode. They reported that, this C/ TiO_2 nanocomposite had band gap energy of 2.22 eV, which is very low compared to the pure TiO_2 nanotube. This made it possible to harvest light in the visible light spectrum and the result was a conversion efficiency of 0.55% when the set up was used to split water into H_2 .

Water splitting into H_2 has also being carried out with visible light using a dye-sensitized TiO_2 film. The dye facilitates the injection of electrons into the conduction band of the TiO_2 ; therefore the most important stage is the excitation of the dye electrons. In this particular set up, the photoanode was a mesoporous TiO_2 electrode and the dye is a monolayer of sensitizer capped $IrO_2 \cdot nH_2O$ particles. A quantum yield of approximately 1 % was attained when the photocatalytic splitting of water into H_2 was carried out. The low quantum efficiency was attributed to the slow electron transfer from the $IrO_2 \cdot nH_2O$ nanoparticles to the oxidized dye (Justin *et al.* “a” and “b”, 2009).

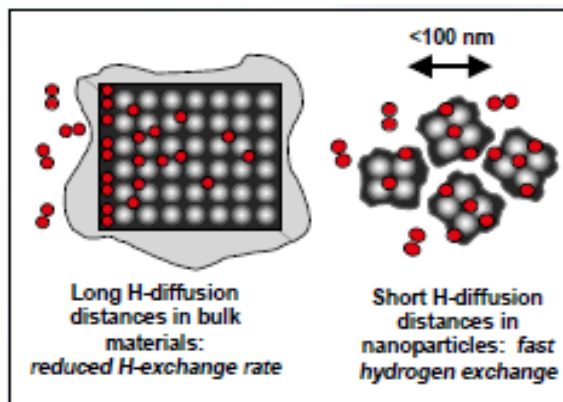
Solid-state hydrogen storage

As already mentioned, one of the most promising source of energy is hydrogen. This is due to the fact that, it has a high calorific value, it is nonpolluting and forms

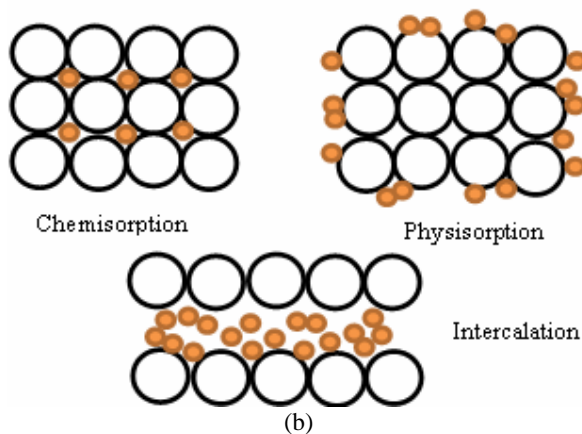
only water as a byproduct when in use. The energy produced from the sun can be converted and stored in the form of hydrogen. The US department of energy’s gravimetric hydrogen storage target for the year 2015 is 9 wt% (Sunita *et al.*, 2007). A major problem for this target is the development of high capacity and safe hydrogen storage materials. Hydrogen storage approaches currently being examined includes compressed hydrogen gas, cryogenic gas and liquid hydrogen, metal hydrides, high surface area adsorbents, and chemical or physical hydrogen storage media (that is chemically or physically bonding hydrogen to a suitable solid-state material). Of all these methods, solid-state hydrogen storage has the highest volumetric density of hydrogen and is also the convenient and safest method for storing and distributing hydrogen for transportation systems (Mao *et al.*, 2007).

Solid-state hydrogen storage mechanism

Due to the unique properties of nanomaterials which includes; high surface to volume ratio, high aspect ratios for nanotubes, high surface area, improve kinetics by increasing diffusivity and reducing reaction distance (Figure-8a), nanomaterials are able to provide high storage capacity compared to their bulk counterparts.



(a)



(b)

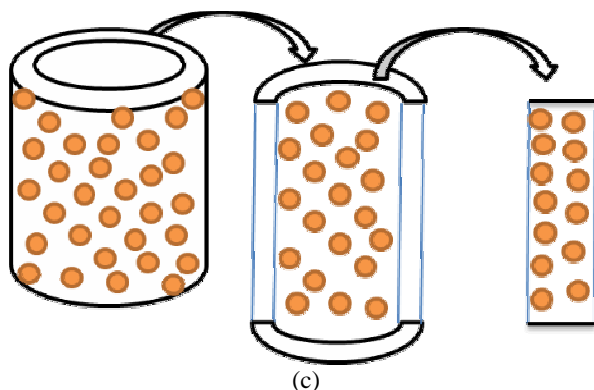


Figure-8(a-c). Bulk vs Nano particles (Sunita *et al.*, 2007), mechanisms for H₂ intake and schematic depiction of advantageous use of nanotubes for energy storage.

The mechanisms of solid-state hydrogen storage in nanomaterials include chemisorption, physisorption and intercalation (for tubular nanostructures). Intercalation is when the hydrogen molecules fill the space between the tubular layers of the nanomaterials and the layers remain associated. This method is common for carbon nanotubes and TiO₂ nanotubes. Physisorption involves the adsorption of hydrogen molecules on the surface of the nanomaterial mainly through Van der Waals forces. On nanoscale, Van der Waals forces are not negligible and are mainly made up of Keesom interactions, Debye interaction and London Dispersion forces. For the chemisorption mechanism, the hydrogen molecules dissociates and chemically bonds to the lattice of the solid nanomaterial. Upon desorption, the elemental hydrogen recombines to form the hydrogen molecule.

Nanostructured TiO₂ as a hydrogen storage material

Since the beginning of research into the possible use of nanostructured TiO₂ as a possible hydrogen storage material by Lim *et al.*, in 2005, only TiO₂ nanotubes has been used so far as an experimenting material. Hydrogen molecules can be either physisorbed/chemisorbed in the open interstitial pore spaces or on the surfaces of the tubes or intercalate between the various layers of the TiO₂ for multi-walled nanotubes. In other words, a very high surface area is available for the hydrogen molecule to interact with the nanostructured TiO₂. To increase the hydrogen uptake capacity of the TiO₂ nanotubes, the synthesized nanotubes should possess high aspect ratio (L/D), that is the length of the nanotubes should be significantly larger than its diameter. This allows for more interaction between the hydrogen molecules and the TiO₂ nanotube and hence more hydrogen can be stored. Double walled TiO₂ nanotube is used as an example in Figure-8c to illustrate this point. In principle, metal oxides that possess a larger interstitial spacing than the diameter of a free hydrogen molecule ($d=0.4059$ nm) may be possible candidates for host materials to accommodate guest hydrogen molecules. TiO₂ nanotubes demonstrate this

because of their large interlayer spacing, $d = 0.72$ nm (Fangyi *et al.*, 2006).

So far the hydrogen storage capability of two different categories of nanostructured TiO₂ has been studied and they include situations where pure TiO₂ nanotubes were used for the study and also where the TiO₂ nanotubes impregnated with Carbon nanotubes were used. Lim *et al.*, (2005) reported the room-temperature hydrogen uptake by TiO₂ nanotubes and the mechanism of the uptake. They synthesized the TiO₂ nanotubes which looks much like a multiwalled carbon nanotubes by hydrothermal process and had outer diameter of about 10 nm and length that varies from 200 nm to >1 μ m. They found that, at a pressure of 6 MPa and at room temperature, the synthesized nanotubes were capable of storing up to 2 wt% H₂, which was higher than the 0.8 wt% storing capacity of the bulk form of TiO₂. They speculated that, about 75% of the stored H₂ was physically adsorbed while the remaining 25% was chemically adsorbed and can be desorbed only at temperatures above 120°C.

Bavykin *et al.*, in 2005 reported on reversible storage of molecular hydrogen by sorption into multilayered TiO₂ nanotubes exactly 6 months after Lim *et al.* (2005) released their paper. They reported that it is possible to store about 2 wt% H₂ at 0.1 MPa and temperature range of 80-125°C. Their TiO₂ nanotubes had a better storage capacity than that reported by Lim *et al.* (2005) so far as the storage pressure is concerned. Their multiwalled nanotubes had an internal diameter of 2-20 nm and a tube length of 0.5 to 10 μ m. The walls consisted of more than two layers with a spacing of 0.72 nm, which made it possible for H₂ molecules to intercalate between the layers.

The differences in the storage capacities reported by these two authors can be attributed to two reasons. First, the nanotubes synthesized by the two authors had different aspect ratios, with Bavykin *et al.* (2005) nanotubes having a higher aspect ratio than those of Lim *et al.* (2005). The high aspect ratios allows for a higher uptake of H₂. Secondly, Lim *et al.* (2005) did not state in their paper whether or not their synthesized nanotubes were single walled or multiwalled. Obviously, a multiwalled nanotube will have a higher H₂ uptake than a single walled nanotube due to possible intercalation of hydrogen molecules between the layers of the nanotube.

Impregnation of Carbon nanotubes (CNT) into TiO₂ nanotubes for hydrogen storage has also been investigated. Mishra *et al.* (2008) reported that, material consisting of multiwalled carbon nanotube and larger TiO₂ nanotube arrays, prepared by CVD is efficient for reversible hydrogen storage. Their TiO₂ nanotubes arrays had 60 nm diameter and 2-3 μ m length while the multiwalled carbon nanotubes were of a few μ m in length and 30-60 nm in diameter. The uptake of H₂ by the CNT-TiO₂ nanotubes at 298 K and 77 K were 1.04 wt% at 2.2 MPa and 2.5 wt% at 2.5 MPa respectively. They reported that about 90% of the stored hydrogen was by physical adsorption. The 1.04 wt% at 298 K and 2.2 MPa is more



than the H₂ storage capacity of 0.4 wt% reported by Rather *et al.* (2009) at 1.8 MPa and 298K. At identical conditions, the TiO₂ nanotubes alone showed only 2.0 wt% H₂ storage at 77K and 0.9 wt% at 298K while the CNT showed 0.4 wt% H₂ storage.

It can be deduced from the above that, the 6 wt% H₂ storage target for 2010 set by the US energy Department has not been attained not to talk about the 9 wt% target for 2015, which is only 2 years from now. There is therefore the need to continue researching into this area to find out new materials with higher hydrogen storage and also improve on existing materials.

Dye sensitized solar cells (DNSCs)

Dye sensitized solar cells, first disclosed by O'Regan and Grätzel in 1991 have promised to provide "leapfrog" in solar cell cost effectiveness and the field has attracted an increasing number of academic and industrial research teams. Also, dye-sensitized nanocrystalline solar cells (DNSCs) have been intensively studied during the last decade. Certified solar power efficiencies of 10.4 % and stability data with lifetime expectancies of at least 10 years for outdoor use have been achieved in the laboratory (Tulloch *et al.*, 2004 and Lingstrom *et al.*, 2001).

Tulloch *et al.* (2004) reported that, the three key features of a dye solar cell are:

- **Photoelectrochemical:** charge separation occurs at the interface between the titania, a wide band gap semiconductor, and distinctly different material, the electrolyte.
- **Nanoparticulate:** the surface area of the titania film is about 1000 times its apparent area. This result in high surface to volume ratio and therefore more solar energy can be harvested.
- **Dye-sensitized:** the dye adsorbed as a monolayer to the titania is the primary absorber of light. This makes it possible to harvest light in the visible spectrum.

Fabrication of dye-synthesized nanocrystalline solar cells

The fabrication of a typical DNSCs starts with two sheet of glass (conducting glass) coated with a transparent layer of fluorine-doped tin oxide. One plate is coated with a thin layer of colloidal TiO₂ paste consisting of particles with sizes in the 20–40 nm range. The film is sintered in air at 400°C to produce a mesoporous layer with porosity of around 50% (Peter, 2007). The mesoporous film can be produced from a hydrothermally processed TiO₂ colloid and also by sol-gel processing. The conducting glass coated with TiO₂ is then sensitized by adsorption of a dye such as cis-bis (isothiocyanato) bis (2, 2-bipyridyl-4, 4-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium or some of the newly developed organic dyes. A lot of factors need to be taking into consideration when developing the dye. The dye should have a high absorption co-efficient across the visible spectrum so that the electrons in the dye can be excited by the absorbed solar energy. Also, for attachment to the

semiconductor surface, the dye molecule should be chemisorbed to the substrate. To facilitate this chemisorption, carboxylate or phosphonate groups, which bind strongly to titanium sites in the oxide, are integrated into the dye molecule (McEvoy *et al.*, 2006).

The second glass plate is coated with a thin film of platinum by sputtering or by electrochemical deposition. The two plates are sandwiched together with a hot melt polymer gasket, and an electrolyte consisting of the iodide/tri-iodide redox couple in a suitable solvent is filled through a small hole drilled in the platinum coated plate, which is then sealed. The fabrication steps and schematic representation of DNSC are depicted in Figures 9 and 10.

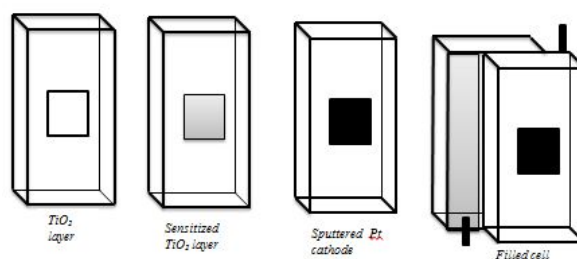


Figure-9. Fabrication of dye sensitized mesoporous solar cell (Peter, 2007).

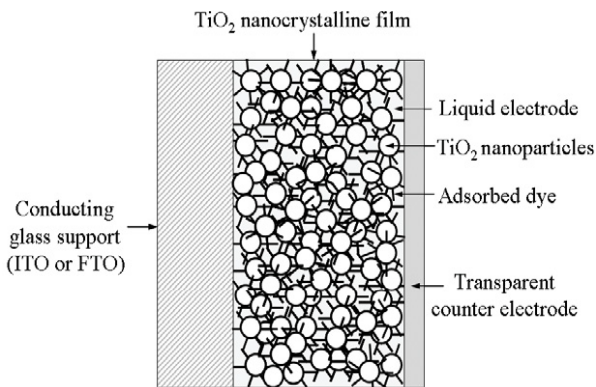


Figure-10. Schematic illustration of structured DNSC (Chin, 2009).

Operation principles of dye- sensitized nanocrystalline solar cell

So far, it can be stated that, the heart of the DNSC is a nanocrystalline mesoporous TiO₂ film with a monolayer of the charge transfer dye attached to it surface (Gratzel, 2003). An incident light from the transparent electrode side arrives at a dye retained on the surface of the transparent semiconductor surface and excites the dye. This results in ultra-fast electron injection into the conduction band of the TiO₂. The injected electrons move through the network of interconnected oxide particles by a random walk process until they reach the conducting glass substrate (Peter, 2007 and Murai *et al.*, 2010). That is the injected electrons form a current in an external circuit reaching a cathode in contact with the redox electrolyte.



The original state of the dye is subsequently restored by electron donation from the electrolyte. The regeneration of the dye by the iodide intercepts the recapture of the conduction band electrons by the oxidized dye. The iodide is regenerated in turn by the reduction of tri-iodide at the counter-electrode, the circuit being completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. Overall the device generates electric power from light without suffering any permanent chemical transformation (Peter, 2007 and Gratzel, 2003). Figure-11(a) presents the schematic of the operation of the DNSCs and the summary of the regeneration process is shown in Figure-11(b).

New method of making dye-sensitized nanocrystalline solar cells at room temperature

Lindstrom *et al.* (2001) has developed a new method that can be used to make dye sensitized nanocrystalline solar cells at room temperature. In their method, two different substrates, one made of a conducting glass and the other, plastic (Polyethylene terephthalate (PET based)) were coated with the TiO_2 nanomaterial to form the compressed TiO_2 electrode. The counter-electrodes were made from glass and plastic substrate. For the glass substrate, it consisted of thermally platinized conducting glass. They studied two different

kinds of counter electrodes (one made with porous carbon and the other, porous-platinized SnO_2) with plastic substrate. The compressed TiO_2 electrodes were sensitized by submerging the substrate with the deposited film for 2 hours in a dye bath consisting of 0.5 M cis-bis(isothiocyanato) bis (2, 2-bipyridyl-4, 4-dicarboxylato) ruthenium (II) bis-tetrabutylammonium. The electrolyte consisted of 0.5 mM LiI, 0.5 M I_2 and 0.5 M *t*-butylpyridine in methoxypropionitrile (Lingstrom *et al.*, 2001).

Figure-12(a) presents the I-V curves for plastic sandwiched cells. The counter electrode consisted of platinized SnO_2 powder pressed on a conducting plastic substrate. The electrodes were synthesized without any heat treatment. The overall cell efficiency was 4.9%. This low cell efficiency value was attributed to the series resistance losses in the conducting plastic layer.

When a counter electrode manufactured by pressing carbon powder mixture on a conducting plastic substrate was used, a remarkable current was obtained as was depicted in Figure-12(b). The results can be compared to the performance of an amorphous silicon glass module (Lingstrom *et al.*, 2001). This implies that, the DNSCs produced better results when a carbon counter electrode was used. The readings for the graphs were taken under indoor room illumination conditions. The writers were able to demonstrate the possibility of producing TiO_2 porous film for DNSCs at room temperature.

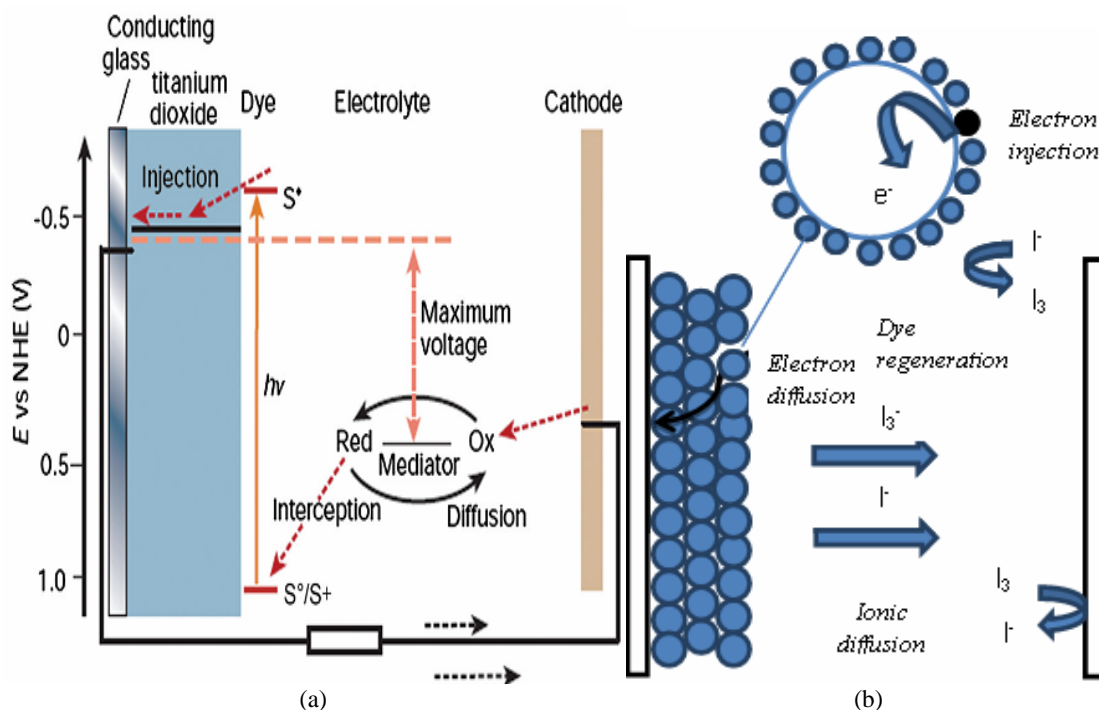


Figure-11(a-b). Schematic of the operation of DNSC and Regenerative cycle in DNSC (Gratzel 2003).

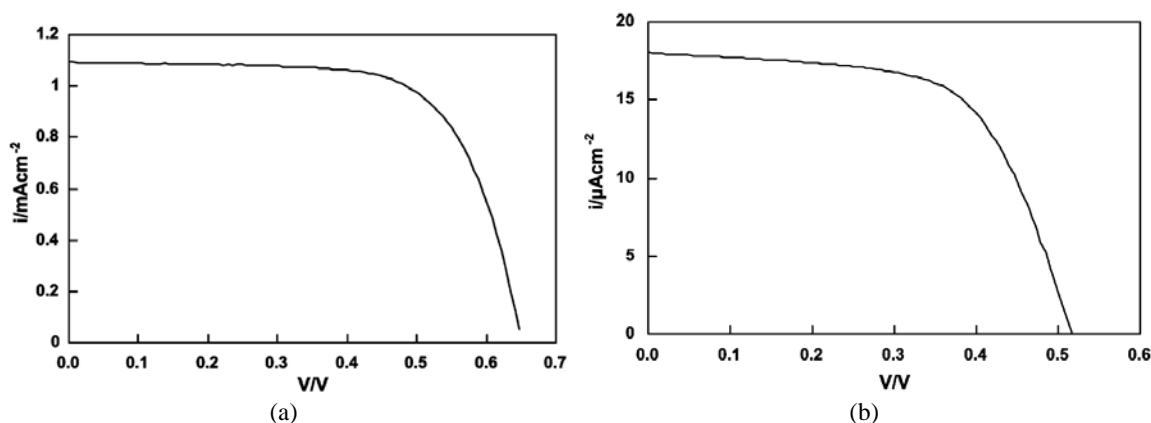


Figure-12(a-b). I-V curves for platinized SnO₂ electrode and C-powder electrode.

DNSCs scalability issues

One of the major problems affecting the scalability of the DNSCs is its low efficiency compared to the conventional monocrystalline silicon solar panels which have efficiency as high as 24%. The 10.4% reported by Kitano *et al.* (2008) results is far below the efficiency values recorded from amorphous and multicrystalline solar cells, which are around 12% and 16%, respectively. The low efficiency values have been attributed to electron-hole recombination. Most of the work on DNSCs are therefore still on the laboratory scale. The main hurdle is how to overcome this electron-hole recombination and the synthesis of modified titanium electrode which will enhance the efficiency and also a dye which will increase the solar harvesting process. In other words, the scalability of DNSCs is dependent on the material science on the nanometric scale, and on molecular engineering to provide dyes with energetics, chemical kinetics and adsorption match to the solar spectrum.

The need to overcome the limitations of the DNSCs is necessary since it will provide a low cost energy compared to the conventional Silicon solar panels. Also, the efficiency of the conventional silicon solar cells falls off rapidly with increasing temperature whereas the sensitized one remains constant (McEvoy *et al.*, 2006) and therefore, there will be no need to worry about variations in energy output.

CONCLUSIONS

Nanostructured TiO₂ has a lot of unique properties which makes it one of the prospective materials that will make it possible to address the energy problems that the world will encounter in the near future. From the review, it is worth emphasizing that, solving the visible light harvesting problem by synthesizing nanostructured TiO₂ with minimum band gap is not enough. Detailed molecular engineering studies need to be conducted to synthesize new dye sensitizers to improve the existing efficiency values registered by DNSCs. An improvement on the existing water splitting photocatalytic process will also help address the energy problem. The quantum yields being recorded are too low, which has made scalability of

the process impossible. Tackling the electron-hole recombination problem and reducing the redox back reaction for the water splitting process can help improve the quantum yield. The solid state hydrogen storage capacity of nanostructured TiO₂ also needs to be improved in order to meet the set target for hydrogen storage.

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