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Titanium Dioxide Nanoparticles Biosynthesis for Dye Sensitized Solar Cells application: Review

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Abstract The synthesis of metallic nanoparticles is an active area of academic, application research as well and nanotechnology. Different chemical and physical procedures that are currently used for synthesis of metallic nanoparticles present many problems. These problems include generation of hazardous by-products, use of toxic solvents, and high energy consumption. Biological synthesis of nanoparticles by bacterial, fungi, yeast, and plant extract is the best alternative to develop cost effective, less labor, non-toxic using more green approach, environmentally benign nanoparticles synthesis to avoid adverse effects in many nanomaterials applications. Among the various metal oxide nanoparticles, titanium dioxide nanoparticles have wide applications for dye-sensitized solar cells, in air and water purification, due to their potential oxidation strength, high photo stability and non-toxicity. Till now, titanium dioxide (TiO_2) is the cornerstone semiconductors for dye-sensitized (DSSC) nanostructured electrodes for dye-sensitized solar cells. This paper reports an overview of synthesis of TiO_2 nanoparticles by biological means for dye-sensitised solar cell application.

Keywords: *titanium dioxide, dye-sensitized solar cells, green chemistry, biosynthesis, nanoparticles*

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1. Introduction

Nanoparticles have unique catalytic, optical, magnetic and electrical properties due to their nano-scale dimensions [1]. Metal oxide nanoparticles such as tin oxide, iron oxide, zinc oxide and titanium are very attractive and play a significant role in various device applications [2,3].

They are also widely used in medicinal fields, electronics, sensors, optics, catalysis, photoelectrochemical devices, drug delivery, biosensors, bio-imaging, antimicrobial activities, food preservation and photonics.

TiO_2 is one of the semiconductors that are mostly used in DSSC.A DSSC is a device for the conversion of visible light power into electricity based on the sensitization of wide band gap semiconductors such as TiO_2 [2,4]. Till now, TiO_2 is the cornerstone semiconductor for dye-sensitized nanostructured electrodes for DSSC. Due to the non-toxic, easily available and low cost characteristics, TiO_2 has been the mostly preferred semiconductor for the photoelectrode [4].

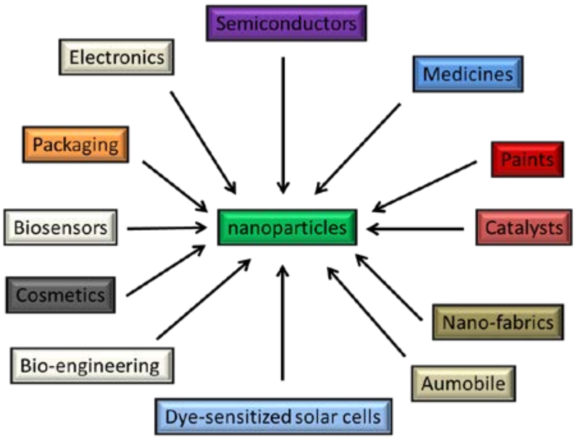

Figure 1. An overview of nanoparticles applications

DSSC are relatively new class of low-cost solar cells that belong to the group of thin film solar cells. They are very promising compared to silicon based solar cells as they are made from low-cost materials, and do not need sophisticated methods and apparatus to be manufactured

[2,5]. DSSC contains several components: a conducting glass substrate, a mesoporous semiconductor film, a dye sensitizer, an electrolyte or mediator solution with a redox couple as well as counter electrode [2,5,6].

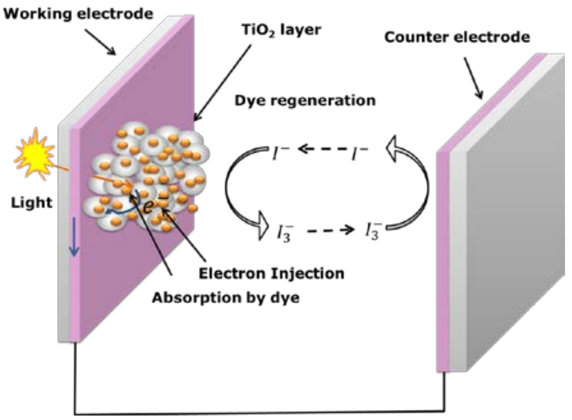

Figure 2. A schematic diagram of a dye-sensitized solar cell [2]

There are so many different materials used in the literature review for DSSC components. But, since its invention in 1991 over many years ago, the components of the state-of-the art dye-sensitized solar cell did not change a lot relatively [5]. The development has concentrated on the one hand to the change of the properties of the original components, such as the morphology and the surface properties of the TiO_2 electrode [7,8]. This paper reviewed on the application of TiO_2 for DSSC as well as the biosynthesis of TiO_2 nanoparticles by biological means.

2. DSSC and TiO_2 Nanoparticles

2.1. Brief History of DSSC

The historical background of DSSC began in 1839 when the French Physicist Edmond Becquel discovered the photovoltaic effect on which the DSSC operating principle is based [9,10]. He was doing experiment on illuminated electrode metal in an electrolyte. While he was immersing the two platinum electrodes in an illuminated solution containing a metal halide salt, he realized that there was an electric current between these two electrodes [11,12,13]. In 1873, the photovoltaic effect in selenium was observed by Willoughby Smith [14].

In 1883, the first solar cell made of a selenium/gold junction with an efficiency of about 1 % was reported by Charles Fritts [12]. This American inventor, Charles Fritts described this cell in detail for the first time six years later [15]. The theory behind the photovoltaic phenomenon was first described by Albert Einstein in 1904, who won the Nobel Prize in 1921 [12,15]. The first “Silicon” solar cell was invented by Russell Ohl in 1940 and reported in 1941 [14]. Fourteen years later, it was discovered that the improvement of the efficiency of solar cells can be achieved by doping silicon with certain impurities up to 6% by Gerald Pearson, Calvin Fuller, and Daryl Chapin of Bell Laboratory. This discovery led to a practical application in space craft as early as in 1958 [14,11].

Actually, there is an interesting convergence of photography and photoelectrochemistry because both phenomena are based on a photoinduced charge separation in a liquid-solid interface. Before being aware of such similarities and following the experiment developed by Becquerel, Vogel discovered that silver halide emulsions sensitized by a dye resulted in an extended photosensitivity to longer wavelengths in 1873 [9]. Four years later, J. Moser was the first to report the dye-sensitized photovoltaic effect [12,16]. Gerischer and Tsubomura together with their co-workers in 1960, discovered dye sensitization of wide band gap semiconductors where they used ZnO as the semiconductor and different dyes such as rose bengal as photosensitizer [17].

From that time, several attempts were made to use dye-sensitized photoelectrochemical cells to convert sunlight into electricity. However, the efficiency of those devices was very low, well below 1 %, mainly due to the poor light harvesting and instability of the dyes employed. O’Regan and Grätzel described for the first time a three dimensional (bulk) heterojunction applied to the fabrication of DSSC. This new device was based on the use of semiconductor films consisting of nanometer-sized TiO_2 particles, together with newly developed charge-transfer dyes. These authors report an astonishing efficiency of more than 7 % [5]. The DSSC and its inventor, Prof. Michael Grätzel, have received prestigious awards, including the Balzan Prize in 2009 and the 2010 Millennium Technology Prize, the largest technology prize in the world [18].

Several companies have accepted the challenge to bring DSSC technology “from the lab to the fab" (Dyesol, G24i, Sony, Sharp, and Toyota, among others) [13].The facile assembly functional cells sensitized with berry juice can be assembled by children within fifteen minutes, the large choice of colors, the option of transparency and mechanical flexibility, and the parallels to natural photosynthesis all contribute to the widespread fascination for DSSC [5,13,19].

In 2013, the drastic improvement in the performance of DSSC has been made by Professor Michael Grätzel and co-workers at the Swiss Federal Institute of Technology (EPFL). They have developed a state solid version of DSSC called perovskite-sensitized solar cells that is fabricated by a sequential deposition leading to the high performance of the DSSC. This deposition raised their efficiency up to a record 15% without sacrificing stability [20]. The authors believe that this will open a new era of DSSC development, featuring stability and efficiencies that equal or even surpass today’s best thin-film photovoltaic devices.

2.2. TiO_2 Nanoparticles for DSSC Application

The standard DSSC technology based on a liquid electrolyte and glass substrate are made of a transparent conducting glass electrode coated with porous nanocrystalline titanium dioxide (nc-TiO_2); dye molecules attached to the surface of the nc-TiO_2; an electrolyte containing a reduction-oxidation couple such as iodide and triiodide ions $(I^-/I_3^-)$and a counter electrode coated by a catalyst [2,5,17].

The semiconductor, typically a metal oxide, is responsible for providing the surface for dye adsorption, for collecting electrons from the excited dye and for conducting them towards the external circuit [5]. The band gap of the semiconductor should be greater than 3 eV in order to let the light pass through the semiconductor easily [11]. In solution under irradiation, oxide semiconductor materials have good stability. Stable oxide cannot absorb visible light because they have relatively wide band gaps. To be able to absorb light, wide band gap oxide semiconductor materials (e.g. TiO_2, ZnO and SnO_2) are sensitized with photosensitizers that are able to absorb visible light [2,5,21].

A great number of common wide energy band gap semiconductors have been reviewed but anatase TiO_2 is the most used [5,22]. In addition to TiO_2, other semiconductors used in porous nanocrystalline electrodes include for example: ZnO, CdSe, CdS, WO_3, Fe_2O_3, SnO_2, Nb_2O_5, and Ta_2O_5 [11,23,24,25,26].

Till now, TiO_2 is the cornerstone semiconductor for dye-sensitized nanostructured electrodes for DSSC. Due to the non-toxic, easily available and low cost characteristics, TiO_2 has been the mostly preferred semiconductor for the photoelectrode [25,26].

3. Green Chemistry Approach

The synthesis of metal and metal oxide nanoparticles using green biological methods are favor for the synthesis comparing to physical and chemical methods that are very expensive, environment polluting, consuming more energy, sophisticated process, and time consuming process. Green methods are cost-effective, environmental friendly and easy process [1].

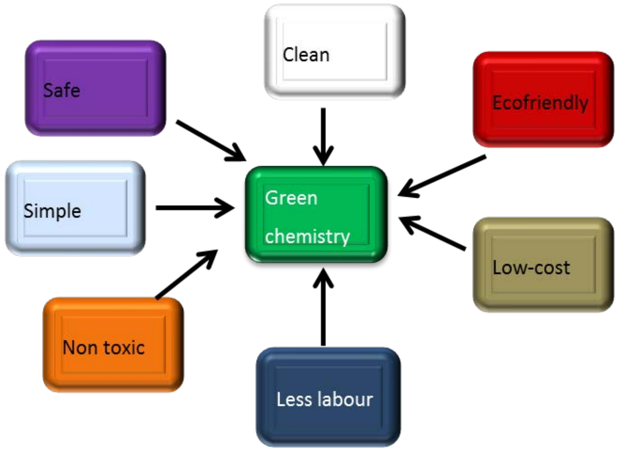

Figure 3. Green chemistry advantages

Green chemistry is based on twelve principles [27].

1. Pollution Prevention: It is batter to prevent waste than to treat or clean up waster after it has been created.

2. Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Synthesis: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals: Chemical products should be designed to affect their desired function while minimizing their toxicity.

5. Safer Solvents and Auxiliaries: The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Design for Energy Efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives: Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. Real-time analysis for Pollution Prevention: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

These are the twelve principles that are used in green chemistry, also called sustainable chemistry which in philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.

4. Biosynthesis of TiO_2 Nanoparticles

The biological method provides a wide range of resources for the synthesis of nanoparticles due to the use of biological agents like bacteria, fungi, actinomycetes, yeast and plants. The rate of reduction of metal ions using biological agents is found to be much faster and also at ambient temperature and pressure conditions [28]. Plant extracted TiO_2 nanoparticles synthesis has led to a remarkable progress in a green synthesis protocol for many nanoparticles synthesis.


Catharanthus roseus
Solanum trilobatum
Annona squamosa
Eclipta prostrata
Hibiscus rosa-sinensis
Calotropis gigantean

Figure 4. Some types of plant that are used for TiO_2 biosynthesis

Due to the diversity of plants, nanoparticles synthesis from plants has known an interesting subject across the world as different plant species are being rapidly investigated and used in nanoparticles synthesis [29].

Table 1 reports some of TiO_2 nanoparticles extracted from biological sources to date.

Table 1. Biosynthesis of TiO2 nanoparticles from biological sources

Plants extracts			
Extracts source	*Particle size*	*Shapes*	*Reference*
Nyctanthes arbor-tristis leaf	*100–200 nm*	*Spherical*	[1]
Solanum trilobatum	*70 nm*	*Spherical*	[30]
Annona squamosal	*40-60 nm*	*Spherical*	[31]
Catharanthus roseus leaf	*25–110 nm*	*Clustered and irregular Spherical*	[32]
Calotropis gigantean	*10.52 nm*	*Spherical, Oval*	[33]
Jatropha curcas	*25–50 nm*	*Spherical*	[34]
Eclipta prostrate	*49.5*	*Spherical*	[30]
Bacterium			
Propioni bacterium	382 nm	Smooth spherical	[35]
Aeromonas hydrophilia	28-54 nm	Spherical, uneven	[1]
Planomicrobium sp.	8.89 nm	Irregular, spherical	[36]
Lactobacillus subtilis	8-35 nm	Spherical	
Bacterium bacillus subtilis	66-77	Spherical, oval	[37]
Fungii and yeast			
Yeast	8-35 nm	-	[38]
Aspergillus flavus	62-74 nm	Oblate spherical	[1]

The above tables (Table 1) report some of typical examples of biological sources of TiO_2. Due to the biodiversity of plant, bacteria and fungi, TiO_2 with different particle sizes can be extracted easily in a lot of amount.

4.1. Synthesis of TiO_2 Nanoparticles Using Plants

TiO_2 nanoparticles were prepared by Maura et al. [3] from the leaves of plants *B. variegata* and stem of *T.cordifolia* [3]. The precursor that has been used was of titanium (IV) chloride (TiCl4). The solution of prepared plant extracts was made using ethanol. To prepares TiO_2 nanoparticles, amount of titanium (IV) Chloride solution was added on the extracts solution under stirring process till obtaining the composite residue(plant extract/ TiO_2). The characterisation of the sample was done on the obtained powder after drying the residues at 70^oC. The calculated average crystallite sizes for of TiO_2 nanoparticles from *T. cordifolia* were ~ 8 to 10 nm while the ones for TiO_2 from *B. variegata* were in the range of ~ 6 to 20 nm. It was reported by Maura et al. that antibacterial activity against *E.faecalis* and *E. coli.* can be improved by plant extract/TiO_2 composites [3].

M. Sundrarajan and S. Gowri synthetized TiO_2 nanoparticle from leaves of nyctanthes arbor-tristis in 2011. The finest powder that was obtained by grinding and sieving dried leaves was mixed with ethanol in order to extract ethanolic leaf extracts. Titanium tetraisoproxide was used precursor for TiO_2 nanoparticles synthesis from ethanolic leaf extracts of nyctanthes arbor-tristis. The obtained TiO_2 nanoparticles were spherical in shape and their sizes were ranging from 100 nm to 150 nm [39].

The TiO_2 nanoparticles were synthetized from Petals of *Hibiscus-rosa-sinensis* flowers that were dried under shadow [40]. The extracts solution was done using dried petals and water at 70°C for 2 hrs. The preparation of TiO_2 nanoparticles from the filtrate (flower extract) was done using 0.5 M titanium oxysulfate solution and extracts solution [40]. From the stirred solution for three hours, the centrifugation was used to separate the formed TiO_2 nanoparticles. The calculated average size of TiO_2 nanoparticles synthesized by green route using the Scherrer's formula ($d = 0.89\lambda/\beta\cos\theta$) was found to be 7 nm and 24 nm [40].

4.2. Synthesis of TiO_2 Nanoparticles Using Bacteria

Titanium dioxide nanoparticles were synthetized from B. subtilis cells. The method used for the culture of B. subtilis cells is well described by Kirthi et al. [37]. The obtained culture was treated by a precursor ($TiO(OH)_2$ to produce TiO_2 nanoparticles. The synthesized TiO_2 nanoparticles were spherical and their sizes were 66-77 nm [37].

The synthesis of TiO_2 nanoparticles was successful done using Lactobacillus sp. [41]. Different culture solutions were prepared in using Lactobacillus, distilled water, and $TiO{\cdot}(OH)_2$ solution as a precursor. The obtained TiO_2 nanoparticles were almost spherical and their sizes ranged from 8-35 nm [1]. The calculated mean particle size for biosynthesized TiO_2 nanoparticles were 24.63 ± 0.32nm. The average particle sizes for *Lactobacillus* sp.was estimated to be of the order of 30nm [41].

TiO_2 nanoparticles were also synthesized from *Lactobacillus sp.* of curd [42]. The filtrate was prepared using the same methods [43] with only small modifications. The obtained TiO_2 nanoparticles sizes were ranging from 20 – 50 nm. A higher concentration of bacterial mediated biological source was reported to favour the formation of spherical TiO_2 nanoparticles which are efficient in dye removal.

4.3. Synthesis of TiO_2 Nanoparticles Using Yeast and Fungii

The synthesis of TiO_2 nanoparticles was also successfully done from baker's yeast by W. He et al. [38]. The culture solution of yeast cells was prepared using 30 mL of glucose aqueous solution at room temperature. The formation of uniform bioemulsion was observed after stirring the solution 30 minutes. In stirring the bioemulsion, a solution of 10 mL of TiCl4 and 20 mL of HCl was added. The obtained white precipitate after maintaining the stirring process for 24 hours was cleaned, and then dried to obtain the final sample for analysis. The particle sizes of the obtained nanocomposite were ranging from 10nm to 12 nm [38].

The synthesis of TiO_2 nanoparticles was successful done using baker's Yeast [41]. Different culture solutions were prepared in using Yeast cells, distilled water, and $TiO{\cdot}(OH)_2$ solution as a precursor. The obtained TiO_2 nanoparticles were almost spherical and their sizes ranged from 8-35 nm [1,41]. The calculated mean particle size for biosynthesized TiO_2 nanoparticles was 12.57±0.22nm. The average particle size was estimated to be of the order of 18nm [41].

A salt precursor (bulk TiO_2) at a concentration of 10^{-3}M was used for the biosynthesis of TiO_2 nanoparticles from extracellular enzyme obtained by A. flavus TFR 7 in an aqueous solution **[44]**. In order to develop fungal ball of mycelia, the culture was kept on shaker at 150 rpm at 28°C for 72 hours. The TiO_2 nanoparticle sizes were 12–15nm. The synthesized TiO_2 nanoparticles from extracellular enzymes were reported to enhance crop production as plant nutrient fertilizer [44].

5. Application of TiO_2 Nanoparticles

TiO_2 is a non-toxic white pigment for use in manufacture of paints, plastics, paper, ink, rubber, textile, cosmetics, leather, and ceramics. TiO2 is also widely employed as a pigment to provide whiteness and opacity to products such as coatings, sunscreen, foods, medicines, and most toothpaste [3,44,45].

Due to their unique chemical, physical, and biological properties, TiO_2 nanoparticles are widely used in paints, printing ink, rubber, paper, cosmetics, and sunscreens, car materials, cleaning air products, industrial photocatalytic processes, and decomposing organic matters in wastewater [30].

TiO_2 is one of the most widely used material in the field of photocatalysis, gas and humidity sensors, self-cleaning, photo electrochemical cells, protective coatings on optical elements, bioanalytical chemistry and solar cells [3]. TiO_2 is the cornerstone semiconductor for dye-sensitized nanostructured electrodes for DSSC because it is the non-toxic, easily available and low cost characteristics.

5. Conclusion

There is a need of further investigation on the biosynthesis mechanism TiO_2 nanoparticles because they have potential applications in coming years. Green synthesis of TiO_2 from biological source is the best way to use in order to get enough amount of TiO_2 for dye sensitized solar cells as well as other different applications. The use of biological sources such as plant, bacteria, fungi and yeast for the production of TiO_2 nanoparticles is low cost, simple and environmental friendly process.

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