

Clean Energy Production Technologies
Series Editors: Neha Srivastava · P. K. Mishra

Manish Srivastava
P. K. Mishra *Editors*

NanoBioenergy: Application and Sustainability Assessment

Clean Energy Production Technologies

Series Editors

Neha Srivastava, Department of Chemical Engineering and Technology, IIT (BHU)
Varanasi, Varanasi, Uttar Pradesh, India

P. K. Mishra, Department of Chemical Engineering and Technology, IIT (BHU)
Varanasi, Varanasi, Uttar Pradesh, India

The consumption of fossil fuels has been continuously increasing around the globe and simultaneously becoming the primary cause of global warming as well as environmental pollution. Due to limited life span of fossil fuels and limited alternate energy options, energy crises is important concern faced by the world. Amidst these complex environmental and economic scenarios, renewable energy alternates such as biodiesel, hydrogen, wind, solar and bioenergy sources, which can produce energy with zero carbon residue are emerging as excellent clean energy source. For maximizing the efficiency and productivity of clean fuels via green & renewable methods, it's crucial to understand the configuration, sustainability and techno-economic feasibility of these promising energy alternates. The book series presents a comprehensive coverage combining the domains of exploring clean sources of energy and ensuring its production in an economical as well as ecologically feasible fashion. Series involves renowned experts and academicians as volume-editors and authors, from all the regions of the world. Series brings forth latest research, approaches and perspectives on clean energy production from both developed and developing parts of world under one umbrella. It is curated and developed by authoritative institutions and experts to serves global readership on this theme.

Manish Srivastava • P. K. Mishra
Editors

NanoBioenergy: Application and Sustainability Assessment



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Manish Srivastava
Department of Chemical Engineering and
Technology
Indian Institute of Technology (BHU)
Varanasi, Uttar Pradesh, India

P. K. Mishra
Department of Chemical Engineering and
Technology
Indian Institute of Technology (BHU)
Varanasi, Uttar Pradesh, India

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Preface

This book entitled, *NanoBioenergy: Application and Sustainability Assessment*, provides ecofriendly nanomaterials as green catalysts to enhance biofuels. Nanomaterials work as catalysts in various steps of different biofuels production options in order to improve the productivity of the bioenergy. Nevertheless, synthesis cost of the nanomaterial may be the hindrance to limit the biofuels production process. Therefore, green synthesis of nanomaterial may play a potential role to improve sustainability of overall biofuels process. Based on this concept, this book has been divided into nine focused chapters in which Chaps. 1 and 2 explore feasibility and applications of nanomaterial to improve biofuels production. Whereas Chaps. 3 and 4 deal with the possibility of nanomaterial application in gaseous biofuels and biosynthesis of nanomaterial through microbial process. Further, Chaps. 5 and 6 are focused on green synthesis of iron nanomaterial for biohydrogen and other biofuels applications while Chaps. 7, 8, and 9 discuss green synthesis of nanomaterials using waste biomass and microbial cultures and contributions of nanomaterials in microbial fuel cells application. The book certainly sets a potential milestone that overcomes the high production cost and low productivity issues related to waste to bioenergy production.

Varanasi, Uttar Pradesh, India

Manish Srivastava
P. K. Mishra

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The editors are thankful to all the academicians and scientists whose contributions have enriched this volume. We also express our deep sense of gratitude to our parents whose blessings have always prompted us to pursue academic activities deeply. It is quite possible that in a work of this nature, some mistakes might have crept in text inadvertently and for these we owe undiluted responsibility. We are grateful to all authors for their contribution to this book. We are also thankful to Springer Nature for giving this opportunity to editors and Department of Chemical Engineering and Technology, IIT (BHU) Varanasi, Uttar Pradesh, India, for all technical support. We thank them from the core of our heart.

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Editors and Contributors

About the Editors



Manish Srivastava is currently working as SERB-Research Scientist in the Department of Chemical Engineering and Technology IIT (BHU), Varanasi, India. He has worked as DST INSPIRE faculty in the Department of Physics and Astrophysics, University of Delhi, India during June 2014 to June 2019. He has published 46 research articles in peer-reviewed journals, edited 8 books for publishers of international renown, authored several book chapters, and filed one patent. He worked as a postdoctoral fellow in the Department of BIN Fusion Technology, Chonbuk National University, South Korea from August 2012 to August 2013. He was an assistant professor in the Department of Physics, DIT School of Engineering, Greater Noida, from July 2011 to July 2012. He received his PhD in Physics from the Motilal Nehru National Institute of Technology, Allahabad, India, in 2011. Presently, he is working on the synthesis of graphene-based metal oxide hybrids and their applications as catalysts. His areas of interest are synthesis of nanostructured materials and their applications as catalyst for the development of electrode materials in energy storage, biosensors, and biofuels production.



P. K. Mishra is currently Professor and Head in the Department of Chemical Engineering and Technology, Indian Institute of Technology (BHU), Varanasi, India. He has authored/co-authored over 60 technical papers published in reputed national/international journals and supervised more than 20 doctoral students. He has received several awards and honours and has 5 patents with 1 Technology Transfer. He is Fellow of Institution of Engineers India. He has received several awards and honours at National/International levels.

Contributors

Ghufran Ahmed ICMR Rajendra Memorial Research Institute, Patna, Bihar, India

Shanthipriya Ajmera Department of Microbiology, Palamuru University, Mahabubnagar, Telangana, India

Zeenat Arif Department of Chemical Engineering and Technology, Indian Institute of Technology (BHU), Varanasi, India

Debashree Borthakur Assam Don Bosco University, Guwahati, Assam, India

Ramesh Chandra Department of Zoology, S S College, Shahjahanpur, Uttar Pradesh, India

Sai Prashanthi Govumoni Department of Microbiology, St. Pious X Degree and PG College for Women, Hyderabad, Telangana, India

P. Kumar Department of Chemical Engineering and Technology, Indian Institute of Technology (BHU), Varanasi, India

Sachin Kumar Punjab Agricultural University, Ludhiana, Punjab, India

Kundan Kunal ICMR Rajendra Memorial Research Institute, Patna, Bihar, India

Jyoti Mishra Department of Chemistry (Environmental Science and Technology Program), ITER, Siksha 'O' Anusandhan (Deemed to be) University, Bhubaneswar, Odisha, India

P. K. Mishra Department of Chemical Engineering and Technology, Indian Institute of Technology (BHU), Varanasi, India

B. S. Naveen Prasad Chemical Engineering Section, Engineering Department, University of Technology and Applied Sciences (Salalah College of Technology), Salalah, Oman

M. Noorjahan Department of Chemistry, Palamuru University, Mahabubnagar, Telangana, India

Dharm Pal Department of Chemical Engineering, National Institute of Technology Raipur, Raipur, Chhattisgarh, India

Gaurav Kumar Pandit Department of Botany, Patna University, Patna, Bihar, India

Dhruti Sundar Pattanayak Department of Chemical Engineering, National Institute of Technology Raipur, Raipur, Chhattisgarh, India

Sindhura Podduturi Telangana Social Welfare Residential Degree College for Women, Warangal, Telangana, India

Souvik Roy Post-Graduate Department of Biotechnology, St. Xavier's College (Autonomous), Kolkata, West Bengal, India

Tanvi Sahni Punjab Agricultural University, Ludhiana, Punjab, India

Naresh Kumar Sahoo Department of Chemistry (Environmental Science and Technology Program), ITER, Siksha‘O’Anusandhan (Deemed to be) University, Bhubaneswar, Odisha, India

B. Saikat Chemical Engineering Section, Engineering Department, University of Technology and Applied Sciences (Salalah College of Technology), Salalah, Oman

Loveleen Kaur Sarao Punjab Agricultural University, Ludhiana, Punjab, India

Sreedevi Sarsan Department of Microbiology, St. Pious X Degree and PG College for Women, Hyderabad, Telangana, India

Naresh K. Sethy Department of Chemical Engineering and Technology, Indian Institute of Technology (BHU), Varanasi, India

Shanvi Department of Botany, Patna University, Patna, Bihar, India

Veer Singh School of Biochemical Engineering, IIT (BHU), Varanasi, Uttar Pradesh, India

S. Sivamani Chemical Engineering Section, Engineering Department, University of Technology and Applied Sciences (Salalah College of Technology), Salalah, Oman

J. Immanuel Suresh Department of Microbiology, The American College, Madurai, Tamil Nadu, India

Ritesh Kumar Tiwari Department of Botany, Patna University, Patna, Bihar, India

Diksha Verma Punjab Agricultural University, Ludhiana, Punjab, India

Manisha Verma School of Biochemical Engineering, IIT (BHU), Varanasi, Uttar Pradesh, India

Chapter 1

Application of Nanomaterials for Renewable Energy Production



Gaurav Kumar Pandit, Ritesh Kumar Tiwari, Shanvi, Manisha Verma, Veer Singh, Kundan Kunal, Ghufran Ahmed, and Ramesh Chandra

Abstract The ever-increasing demand for energy due to the rapidly increasing industrialization and urbanization compels the research community to devise ways to transition from non-renewable sources of energy to renewable energy sources. The burning of fossil fuels is the primary source of energy that we are utilizing today. Apart from the fact that it is not sustainable and is likely to diminish by 2050 (if we continue using it at the same rate), it also poses severe adverse threats to the environment due to harmful greenhouse gases (GHGs). Thus, we must look for ways to utilize renewable energy in ways so that it can fulfill our energy demands without causing harm to the environment. The efficiency of production and storage of renewable energy needs to be enhanced. Nanotechnology is one such field that is being explored and studied extensively lately due to its practical applications in renewable energy. This chapter discusses the primary classification of nanomaterials and their applications in various renewable energy generation and storage, such as solar energy, hydrogen energy.

Keywords Non-renewable energy · Renewable energy · Fossil fuels · Nanotechnology · Solar energy · Wind energy · Hydrogen energy · Hydrogen economy

G. K. Pandit (✉) · R. K. Tiwari · Shanvi
Department of Botany, Patna University, Patna, Bihar, India

M. Verma · V. Singh
School of Biochemical Engineering, IIT (BHU), Varanasi, Uttar Pradesh, India

K. Kunal · G. Ahmed
ICMR Rajendra Memorial Research Institute, Patna, Bihar, India

R. Chandra
Department of Zoology, S S College, Shahjahanpur, Uttar Pradesh, India

1.1 Introduction

Energy is very crucial for the holistic progress of any country (Stern 2011; Barnes et al. 2011). The energy demand increases exponentially due to the rapid increase in industrialization and urbanization (Graham 2009; Mazur 1994). The significant portion of energy that we are utilizing today comes from the burning of fossil fuels. But the burning of fossil fuels has many deleterious effects on the environment attributed to the release of harmful greenhouse gases (GHGs). It also adversely impacts human health (Kataki et al. 2017). It is cited as the primary contributor to the increasing global warming. As stated by the US Energy Information Administration, the all-consuming of fossil fuels in 2016 caused a substantial 76% of the US greenhouse gas emissions. Also, fossil fuels are representatives of non-renewable sources of energy; that is, they cannot be utilized sustainably. If we continue using fossil fuels at the same pace for our energy needs, it is reported that we will fall short of this energy source by 2050 (Satyanarayana et al. 2011; Demirbas 2009). Thus, it is very imperative that we look for other sources of energy having some of the essential attributes of sustainability and minimal harmful effect on the environment. Renewable sources of energy are the potential alternatives having the characteristics above. Renewable energy is any energy source that can fulfill the existing energy demands without compromising the energy needs of the future as well. In other words, they are a form of a sustainable source of energy. Renewable energy sources such as solar energy, hydrogen energy, wind energy, geothermal energy, and biomass energy have the potential to generate electricity, heat, and light, which can be utilized for various purposes without having deleterious impacts on the environment. Nowadays, much interest and research have been attentive on the practice of Nanotechnology in the renewable energy field. Nanotechnology is basically the science of materials in the nanoscale (diameter having less than 100 nm mostly). Nanomaterials, owing to their very small size, confer many technological and engineering advantages for the parts or equipment associated with renewable energy generation. Various beneficial aspects of nanomaterials have been explored in renewable energy generation, such as wind energy, solar energy, hydrogen energy, etc., and efforts are being made to transition the use of nanotechnology for renewable energy production to a commercial scale. Let us know more about the use of nanotechnology in renewable energy generation.

1.2 Classification of Nanomaterials

Nanomaterials can be classified according to various parameters. Broadly, they can be classified into (Mageswari et al. 2016): (1) Nanoparticles, (2) Nanoclays, and (3) Nanoemulsions.

1.2.1 Nanoparticles

Nanostructures and composites are the two forms in which nanoparticles can exist. Their size range from 1 to 100 nm (Hasan 2015). They can be of various shapes, sizes and can be composed of different types of materials. Based on the materials they are composed of, nanoparticles can be (Mageswari et al. 2016; Jeevanandam et al. 2018; Ealia and Saravanakumar 2017)

1.2.1.1 Organicnanoparticles

These nanoparticles are favorable choices for drug delivery. Some of the characteristics which make them a favorable candidate for this purpose are: (1) They are biodegradable; (2) They are not toxic by nature; (3) Some of them form a hollow core and are called nanocapsules. They are believed to be sensitive towards light and heat (Tiwari et al. 2008), such as liposomes and micelles; (4) Suitable for targeted drug delivery. Besides their general characteristics such as morphology, size, etc., their field of application is also determined by their drug-carrying capacity, drug delivery system (whether encapsulated or adsorbed) as well as stability. Some examples are liposomes, ferritin, micelles, and dendrimers.

1.2.1.2 Inorganic Nanoparticles

They do not contain carbon. They comprise metal and its oxides-based nanoparticles.

1.2.1.3 Carbonnanoparticles

It consists of carbon entirely. Examples: Fullerenes, carbon nanofibers, carbon nanotubes (CNT), etc.

1.2.2 Dimension-Based Nanomaterials Classification

The nanomaterials classification based on dimension is achieved by considering the pattern of the electron trail alongside the various dimensions in the nanomaterials. Pokropivny and Skorokhod proposed this system of classification in 2007 (Pokropivny and Skorokhod 2007). Based on the dimension, nanoparticles can be of different types (Jeevanandam et al. 2018; Mageswari et al. 2016):

1.2.2.1 0D

In these types of nanomaterials, the electrons movement is enmeshed in all three dimensions, or they are confined within the dimensionless space. Examples are fullerenes, molecules, metal carbides, etc.

1.2.2.2 1D

The electrons movement in this type is restricted in one dimension, in the X-direction. Examples include nanotubes, filaments, fibers, etc.

1.2.2.3 2D

The movement of electrons is confined in the X-Y plane. Examples- Layers.

1.2.2.4 3D

The movement of electrons can occur along the X, Y, and Z directions (Siegel 1993).

1.2.3 Classification Based on the Origin of Nanomaterials

1.2.3.1 Natural

They are naturally present in the Earth's sphere, i.e., atmosphere comprising of hydrosphere, lithosphere, troposphere, and even the biosphere. It is noteworthy to mention here that the biosphere includes all the microorganisms and the higher organisms, which include humans (Sharma et al. 2015; Hochella et al. 2015). Either natural processes or some sort of anthropogenic activity serves to produce these nanomaterials.

1.2.3.2 Synthetic

They are fabricated or engineered and are generated by processes that may be physical, biological, chemical, or hybrid methods such as mechanical grinding, etc. One of the significant challenges with these nanomaterials is difficulty in assessing whether the current knowledge is sufficient in forecasting their behavior or if they exhibit any environment-related activity that is distinct from the nanomaterials occurring naturally (Wagner et al. 2014).

1.2.4 *Nanoclays*

They are the other types of nanomaterials, the preparation of which exploits the hydrophilic or charged characteristics of clay molecules. The charged groups can be ammonium, aryl/alkyl, phosphonium, or imidazolium, either in the aqueous or solid-state. X-ray diffraction, gravimetric analysis, Fourier transform infrared (FTIR) spectroscopy, and inductively coupled plasma can be used for chemical characterization.

1.2.5 *Nano-Emulsion*

These types of nanomaterials are in the form of soft materials and are generated by dispersing the solid materials, droplets, and polymers in the viscous liquid. It is generally synthesized by using either of the two methods:

1. High-energy emulsification includes microfluidizer, ultrasonication, and high-pressure homogenization.
2. Low energy emulsification includes techniques like phase inversion temperature, solvent displacement, and phase inversion composition.

The given figure (Fig. 1.1) shows the general classification of nanomaterials.

1.3 Synthesis of Nanomaterials

The route for the synthesis of nanomaterials can be physical, chemical, or biological (Mageswari et al. 2016).

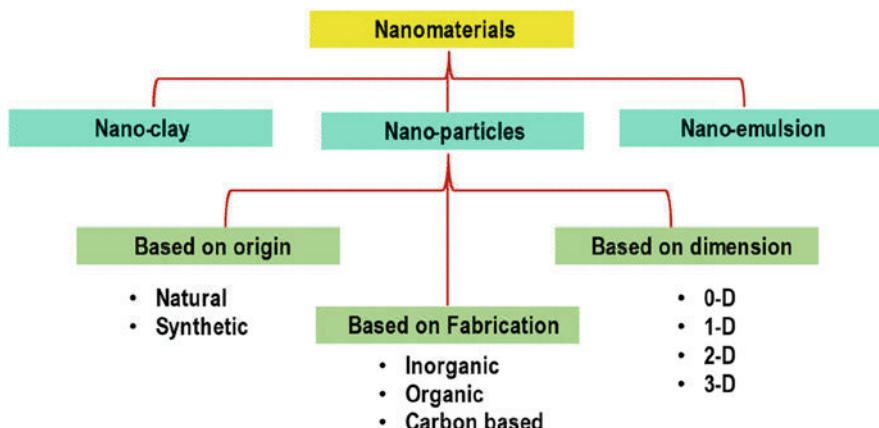


Fig. 1.1 Types of nanomaterials

1.3.1 *Physical Methods*

These include physical techniques to synthesize nanomaterials. One of the main advantages of physical methods over chemical methods is that nanomaterials have a uniform distribution as they are devoid of solvents. Some of the techniques include:

1.3.1.1 *Laser*

It uses Transmission Electron Microscopy to emit high-energy electron beams and irradiate surfaces to synthesize nanomaterials of various forms. Examples are carbon nanocapsules, nanotubes, etc.

1.3.1.2 *Arc-Discharge*

Two methods, including higher frequency plasma and direct current arc plasma, can be applied for this technique. This is mainly used to synthesize fullerenes.

1.3.1.3 *Combustion*

In this technique, the activation energy barrier is overcome by the heat generated during the exothermic reaction. It is fast and has the potential to form a wide range of ceramic oxides.

1.3.1.4 *Evaporation–Condensation*

In this technique, first, the metals, ceramics, or alloys are allowed to evaporate and react with each other using gases. Later, they are subjected to condensation, leading to the formation of nanomaterials.

1.3.1.5 *Laser Ablation Method*

This is an advanced technique that allows for the controlled synthesis of nanomaterials with respect to the composition and size of particles. In this, the target is subjected to vaporization followed by controlled condensation with well-defined pressure and temperature parameters. It can be used to synthesize various nitrides, carbides, and metal oxides at the nanoscale.

1.3.2 *Chemical Methods*

These methods allow for the extensive quantity synthesis of nanomaterials in a controlled manner (Hyeon 2003). There are many methods for synthesizing nanomaterials by chemical means (Chaki et al. 2015; Umer et al. 2012; Anbarasu et al. 2015; Yu et al. 2009).

1.3.2.1 *Chemical Reduction*

It is the most applied technique for the synthesis of nanomaterials in the form of colloids. It involves the chemical reduction of inorganic as well as organic reducing agents.

1.3.2.2 *Oxidation*

The process of oxidation can be used to form nanomaterials of alloys, metals, or oxides, either in water or some other organic solutions.

1.3.2.3 *Microemulsion*

It involves the separation between two immiscible phases in space, that is, between reducing agent and metal in two-phase aqueous organic systems. Quaternary ammonium salts are used to mediate the interface between two phases. Stabilization of the clusters of the metal is achieved as the stabilizer molecules are capped in the non-polar aqueous medium, which is then transferred to the organic phase.

1.3.2.4 *Sol-Gel Process*

In this method, the first formation of sol is achieved by dispensing precursors in suitable solvents, which upon drying, are put in solid (gels) to form a polymeric network. When the gel is subsequently dried to be subjected to operations such as sintering and calcination, ceramic products are formed. Other chemical synthesis methods include polymerization, microwave-assisted synthesis, UV-initiated photo-reduction, irradiation, etc.

Some drawbacks of physical and chemical methods of nanomaterial synthesis (Mageswari et al. 2016; Hebbalalu et al. 2013):

1. Complex protocols.
2. High operational costs.
3. The presence of minor toxic components makes their biological use questionable.

Table 1.1 Synthesis of nanomaterials using various biological agents

Biological agent	Examples	Types of nanoparticles
Plants	<i>Azadirachta indica</i> , Lemon grass, <i>Garcinia mangostana</i> , etc.	Gold, Silver, Copper, Aluminum oxide, etc.
Bacteria	<i>E.coli</i> , sulfate-reducing bacteria, <i>Bacillus subtilis</i> , etc.	Cadmium sulfide, Magnetite, Titanium oxide, etc.
Fungi	<i>Aspergillus flavus</i> , <i>F.oxysporum</i> , <i>Agaricus bisporus</i> , etc.	Silver, Lead sulfide, Zinc sulfide, Silver, etc.
Yeast	<i>Saccharomyces cerevisiae</i> , Extremophilic yeast, <i>Yarrowia lipolytica</i> , etc.	Titanium oxide, Manganese oxide, Gold, Silver, etc.
Actinomycetes	<i>Rhodococcus</i> sp., <i>Nocardiopsis</i> sp., <i>S. albidoflavus</i> , etc.	Gold, Silver, etc.

1.3.3 Biological Synthesis

Biological production of nanomaterials is more environment-friendly and thus preferred more over physical and chemical modes (Hebbalalu et al. 2013; Sastry et al. 2003; Kruis et al. 2000; Ahmad et al. 2003).

The given table (Table 1.1) enlists some of the biological agents with examples for the synthesis of nanoparticles.

1.4 Nanomaterials: Applications in Renewable Energy

The advancements in nanotechnology, together with the fact that nanomaterials hold several benefits to be applied for renewable energy, have in all opened a new domain of research. Some of the attributes of nanomaterials that make them a preferred choice for various renewable energy applications are (Hussein 2015):

1. They provide greater capacity for energy storage and efficiency for lighting and heating.
2. The energy so generated with the use of nanotechnology can help curtail pollution.

The nanomaterials, having their one or more dimensions at the nanoscale, tend to disobey conventional rules of physics and thus express remarkable properties compared to their larger entities. Some of the advantageous features and potential benefits they show at the nanoscale are their strength, electrical conduction capacity, and reactivity increase.

1.4.1 *Solar Energy*

Solar energy is one of the primary sources which can be harnessed to produce renewable energy. The sunlight that is reflected on the Earth's surface annually surpasses the total resources that we use. It is noteworthy to mention here that the sunlight of 1 h equates to more than the total energy consumed annually (Vayssieres 2009). Thus, it is of utmost relevance to utilize this most excellent energy source to meet the energy requirements efficiently and inexpensively. There are two ways by which we can use solar energy (Ghasemzadeh and Shayan 2020; Esmaeili Shayan et al. 2020):

1. To directly produce electricity utilizing sunlight.
2. Solar thermal energy can be used in high-temperature power plants to generate electricity. Or for ventilation in houses and processing of hot water when used in low-temperature power plants.

Nanotechnology can be used to improve heat and electricity generation. Nanotechnology can be exploited to increase the efficiency of solar cells in many ways (Sarbu et al. 2017):

1. Nanotechnology can be used to enhance the storage of solar power.
2. The efficiency of solar cells can be boosted using nanowires.
3. Sunlight absorption and retention can be enhanced.

1.4.1.1 *Improved Absorption and Capture of Solar Energy*

Nanomaterials having the capacity to emit and capture light such as Silver, gold, or quantum dots, and fluorescent nanofibers may be employed to advance the functioning of solar cells (Esmaeili Shayan and Najafi 2019). Based on their dimensions, these nanoparticles can absorb different wavelengths and become excited. After this these nanoparticles emit the absorbed energy in the form of radiation with a different wavelength or from the earliest one. Owing to their photoelectric properties, which help in the conversion of solar light to electricity, however, they tend to absorb wavelengths that are beyond the visible spectrum. A fascinating improvement of 64% in the performance of solar energy is observed when projected simulating the quantum-based cell theory. Quantum dots of silver sulfide and silver selenide tend to immensely enhance the response of the solar cell to light. It has been observed that almost a 4% increase in the production of electrical energy is seen with these quantum dots when compared to routine pigment-sensitive cells. Hence, such quantum dots are very relevant to increase the efficiency of solar cells.

1.4.1.2 Nanofluids

Nanofluids, owing to their high heat transfer coefficient in heat exchangers or engines, serve to rise the economy and performance. Many businesses and academic institutes are adopting solar batteries and heaters.

1.4.1.3 Photocatalysts

These are stable semiconductors generating an electron-hole pair as they collect photons, thus interfering with the molecules at the surface level. Some of the advantages of nano-photocatalysts with respect to solar cells are:

1. The performance of the solar cells can be enhanced dramatically as the absorption of light can be improved attributed to their property of absorbing specific light spectra.
2. The absorption of sunlight and the performance of the solar cells also get improved as they render a clean atmosphere free from air pollutants and obstacles to light. This is due to their anti-dust, self-cleaning, and anti-steam properties.
3. They also help in improving the energy-transfer capacities.

1.4.1.4 Nanotechnology in the Storage of Power

Nanotechnology is also being increasingly used for the storage of power. Many factors such as environmental conditions, including temperature, hours, photoperiod, and atmospheric patterns, tend to impact solar power generation systems production, rendering the consistent supply of output not feasible in such cases (Achkari and El Fadar 2020). Owing to the fact that the ordinary or conventional batteries have certain loopholes such as inefficient capacity, heavyweight and poor performance and therefore, Lithium batteries are in trend nowadays (Walker 2013). Lithium-ion batteries utilize organic solvents for the purpose of electrolytes instead of gas used in conventional batteries. But liquid electrolytes have strong electrical resistance, and nanomaterials are being utilized to increase the electrolyte's efficiency. Nanotechnology aims to boost the conductivity by sixfolds by adding powers in the form of nanoparticles (silicon oxide, zirconium oxide, etc.) to non-aqueous electrolytes.

The given figure (Fig. 1.2) displays some of the general approaches in which nanotechnology can be applied in solar energy sector.

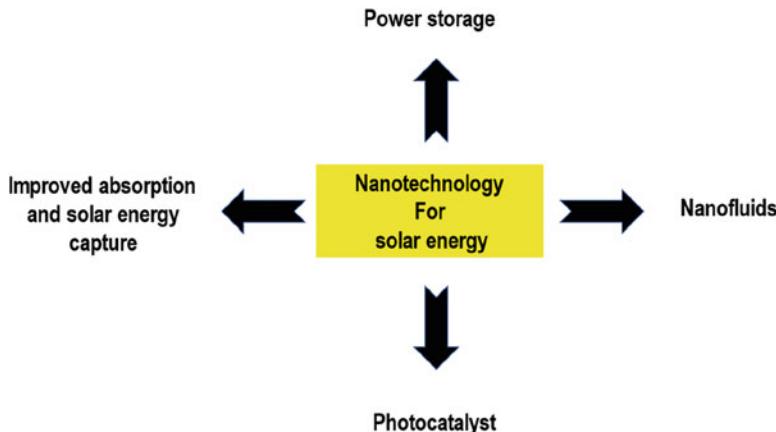


Fig. 1.2 Approaches for nanotechnology applications in solar energy

1.4.2 *Renewable Hydrogen Energy and Use of Nanotechnology*

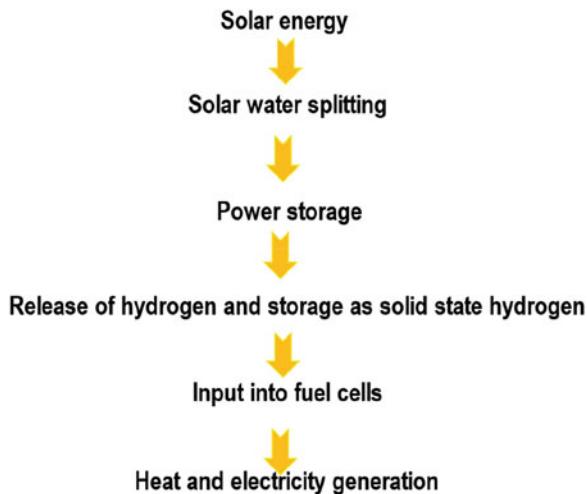
Hydrogen energy is also being explored as a clean source of renewable energy for it only produces water upon consumption in fuel cells. Solar water splitting has been considered as one of the most efficient ways of producing hydrogen energy. The hydrogen so produced can then be utilized by fuel cells for the generation of electricity, with water being the only emission. This also paves the way for the effective utilization of solar energy and its conversion (Mao et al. 2012). For the purpose of ensuring efficient and optimum utilization of solar energy for hydrogen energy production, the efficacy of solar water splitting systems must be increased. Also, the storage capacity and performance of fuel cells should be enhanced to make hydrogen energy the primary contributor to the prospective renewable energy-based economy.

The given figure (Fig. 1.3) shows the general framework for production of hydrogen energy using solar water splitting-

1.4.2.1 **Nanomaterials-Based Electrodes for Photo-Electrochemical Water Splitting**

Water splitting by photo-electrochemical (PEC) means been the fascinating way of hydrogen energy production amongst other techniques. Fujishima and Honda first pioneered Solar energy-induced splitting of water in PECs, wherein they used TiO_2 anode and Pt cathode to generate oxygen and hydrogen, respectively (Fujishima and Honda 1972). In this system, once the anodes are irradiated by sunlight, and if the irradiated energy has energy larger than its bandgap, then electrons are generated in

Fig. 1.3 A general framework for hydrogen energy production using solar water splitting



the conduction band, and holes are generated in the valence band respectively (Chen et al. 2010). As a result of this, water gets oxidized at the TiO_2 anode liberating oxygen, and the photogenerated electrons are transferred to the Pt cathode to produce hydrogen. However, oxygen production at the photoanode is kinetically limited for splitting of water in the PEC process, and so, nanostructured photoanodes were designed for PEC water splitting leading to the production of oxygen. TiO_2 , which is the most widely used semiconductor for PEC-based water splitting, has a very large bandgap of almost 3.2 eV (Chen and Mao 2007; Ni et al. 2007). This renders the TiO_2 anode inefficient and incapable of absorption of light in the visible and infrared range. Thus, photoanodes were designed to introduce either a donor or acceptor level in the forbidden gap to narrow the bandgap of TiO_2 . This makes the photoanode TiO_2 sensible to visible light (Chen et al. 2010; Chen and Mao 2007). For instance, a TiO_2 doped nanocrystalline film showed a more excellent efficient water splitting phenomenon with 11% accounting for total energy conversion and 8.35% of photoconversion efficiency, attributed to the enhanced capability to absorb visible light (Khan et al. 2002). The morphology of TiO_2 is also of considerable importance since the morphology impacts the capability of transfer of charge. TiO_2 nanotube arrays were designed and examined by Grimes and co-workers for water splitting by PEC, and it was found that they render more efficient charge separation owing to their architecture (Rani et al. 2010; Mor et al. 2005, 2007). The photoelectric conversion efficiency of almost 16.5% could be obtained under UV illumination when nanotubes of 24 μm in length were fabricated electrochemically in an ethylene glycol-based electrolyte (Mao et al. 2012).

1.4.2.2 Nano-Photocatalysts and Hydrogen Production

Bard in 1979 designed a photocatalytic water splitting system based on the concept of photoelectrical splitting of water. He utilized particles or powders of semiconductors as photocatalysts (Bard 1979). Electrons and holes photogenerated at the conduction and valence bands, respectively, are transferred to photocatalysts, where they participate in a redox reaction leading to oxygen and hydrogen production.

Some of the fundamental characteristics to be considered for photocatalysts are (Mao et al. 2012):

1. Relevant band gaps and structures to ensure optimum absorption of sunlight are needed to drive oxygen and hydrogen production.
2. Efficient transferability of holes and electrons.
3. High catalytic reactivity of surface for half-reactions.

Extensive research and efforts have been put in the past decades to meet the specific requirements and ensure efficient generation of hydrogen from water (Chen et al. 2010; Shen et al. 2011; Osterloh 2008; Shen and Mao 2012; Maeda and Domen 2010).

1. Surface Layer Disorders

As mentioned earlier, TiO_2 is the most widely studied photocatalyst, but it has a wide band gap, limiting its absorption efficiency. To narrow its bandgap, doping with ions is done, but this also has a drawback. The energy levels created by doping can then act as recombination centers for photoinduced charges and deleteriously impact the photocatalytic activity of doped TiO_2 (Chen and Mao 2007). To circumvent this issue, a new approach of surface layer disorder was envisioned for the enhanced absorption of solar energy by TiO_2 nanocrystals (Chen et al. 2011). Surface disordered black TiO_2 nanocrystals obtained by hydrogenation of anatase TiO_2 nanocrystals at 200 °C for a duration of 5 days in 20.0- bar H_2 atmosphere, produced hydrogen at a constant rate. The hydrogen production rate so observed (10 mmol $\text{h}^{-1} \text{g}^{-1}$ of photocatalysts) and efficiency as close to 24% of solar energy conversion is almost two times greater than most semiconductor photocatalysts' yield (Chen et al. 2010). This observation is attributed to the efficient energy harvesting from UV to near infrared by the surface disordered black TiO_2 and the retardation in recombination of charge (Mao et al. 2012).

2. Cocatalysts

Loading of cocatalysts onto photocatalysts is considered as an efficient strategy for optimal water splitting due to increased photocatalytic activity for the formation of hydrogen or oxygen. Different materials have been developed as proficient cocatalysts in the past few decades, such as sulfides and oxides of metal, transition metals, etc.