CHAPTER 1

Introduction to Green Nanostructured Photocatalysts

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1.1 Introduction

1.1.1 General Background

Fossil fuel-based sources of energy, such as coal, oil, and natural gas, have been used to meet the world's energy demands for centuries; however, overproduction and overconsumption of these fuels have created many known and unknown concerns. Knowledge about the sources of mineral fuel, including nuclear energy, are also inadequate in terms of long-term waste disposal and lack of technology.[1] Fossil fuel-based energy systems have a huge impact on the environment and are considered to be the major cause of global warming as well as air, soil, and water contamination and pollution. Because of dramatic economic development, population growth, environmental and health concerns, and increasing demands on clean energy sources, many countries have been seeking to find alternative energy sources to replace fossil and mineral-based fuels.[1–3] These new sources of

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energy should be renewable, minimize/eliminate concerns, and, at the same time, be inexpensive and affordable by many nations of the world.

Renewable energy is usually defined as clean energy, which mainly comes from natural sources such as sunlight, rain, tides, wind, waves, biomass, and geothermal heat, and can be naturally replenished in a shorter period of time without harming the Earth. Solar energy is one of the greatest sources of renewable energy for meeting the world's demand because of its enormous magnitude – approximately 10^5 terawatts.[2] The current energy consumption of the world is about 12 terawatts; this represents only 0.01% of the total amount of the Sun's energy that reaches the Earth's surface. This energy could be generated from an area $10^5\,km^2$ in size that is installed with solar cells working at 10% efficiency. However, today, many energy conversion systems can easily pass the 10% energy conversion levels.[2–4]

Even though energy from the Sun is one of the most widely considered renewable energy sources, new studies need to be conducted to address some concerns with solar energy, such as harnessing incident photons, lowering production costs, enhancing efficiency, storing energy, eliminating waste materials, eliminating health and environmental risks, dealing with seasonal changes, addressing the lack of technology, and so on.[4–8] Nanotechnology is an emerging technology that could address these concerns by using innovative strategies.

1.1.2 Nanotechnology in Energy Systems

Nanotechnology is the development of materials, components, devices, and/or systems at the near-atomic level or nanometer scale. One of the dimensions of nanotechnology is between 1 and 100 nm.[9] This technology mainly involves fabricating, measuring, modeling, imaging, and manipulating matter at the nanoscale. Nanotechnology consists of highly multidisciplinary fields, including chemistry, biology, physics, engineering, and some other disciplines. For more than two decades, significant progress has been made in designing, analyzing, and fabricating nanoscale materials and devices, and this trend will continue for a few more decades in various fundamental studies and in research and development fields.[10]

Nanomaterials are the major building blocks of solar energy conversion devices and have been applied in the following three ways:[2]

(a) the assembly of molecular and clusters of donors–acceptors mimicking photosynthesis
(b) the production of solar fuel using semiconductor-assisted photocatalysis
(c) the use of nanostructured semiconductor materials in solar cells.

Among the nanostructured solar energy conversion systems and devices, binary and ternary metal oxides are the most widely used and have a promising future in this field.[2–4]

Even though several books have been published on renewable energy, solar cells, solar conversion, and solar fuels, very few books have been published on green photo-active nanomaterials and their major applications. Most books cover a broad spectrum of photocatalysts, including metal oxides and non-metal oxides. However, this book introduces and summarizes the fundamentals of harnessing solar energy using nanomaterials, synthetic approaches to green photo-active nanomaterials and their applications in designing artificial photochemical systems for solar energy conversion, and microorganisms found in solar energy conversion up until the present time. It describes the natural photosynthetic system in plants, the mechanisms involved in photosynthesis, and how components contribute to this sophisticated orchestration. Relevant cell biology as well as variations of the process used by plants in hot and dry environments are also discussed. The potential for biomass to contribute to meeting humanity's growing need for sources of energy is described, and a context is provided to frame efforts in mimicking natural photosynthesis in order to generate energy.

This book also focuses on applications of organic and inorganic nanomaterials utilized for fuel production from carbon dioxide and biomass, removal of contamination, water splitting, modeling, and health and environmental aspects of these green photo-active nanomaterials.

1.1.3 Environmental Considerations

Industrialization has significantly increased gas emissions and suspended particulate concentrations, and these concerns will likely continue for the next few decades, in turn further worsening the quality of air, soil, and water in the world and jeopardizing human life over the long term. Methane, carbon dioxide (CO_2), and nitrogen oxide (NOx) are the primary greenhouse gas sources involved in global warming and climate change, so reducing these emissions is now a worldwide challenge. Microorganisms (*e.g.*, microalgae, bacteria, viruses, fungi, and molds) can be an effective way of addressing some of these concerns. Nanomaterials can also offer structural features for reducing CO_2 and other emissions in an environmentally friendly manner.[11]

Combining microorganisms with nanomaterials can effectively capture greenhouse gasses from the atmosphere and convert them into carbon sources for the production of biomass and biofuels for industrial and household heating, transportation, agriculture practices, and many other uses. Also, plants can naturally absorb CO_2 emissions and other contamination for their growth media and reduce toxicity levels. As an outcome of this cycle, concentrations of specific pollutants in the air, soil, and water can be significantly decreased. Carbon dioxide contains an abundant source of carbon, which supports the growth of microbial species and plants in the environment, and can be biochemically transformed into biomass and renewable energy sources to meet the world's demands.[12–14]

1.2 Photo-active Nanomaterials

Some binary and ternary metal oxides are photoactive and are used for photocatalytic activities in solar cells, water splitting, and other solar-driven reactions. Synthetic methods for binary and ternary metal oxide photocatalysts emphasize green reaction processes. The advent of green, facile, and benign methods of producing these nanomaterials is necessary to comply with modern environmental concerns. An important aspect for such green methods is low temperature, fast reaction rate, and reduced toxic agents. The second chapter of this book highlights new techniques to produce photo-active nanomaterials in order to minimize the use and generation of hazardous substances during the manufacturing process. Such techniques include hydrothermal approaches along with the polymer gel method, chemical precipitation technique, solvothermal method, ultrasound sonication, and hybrid synthesis method. For example, even though several methods are currently available, such as solid state reactions, the polymerizable complex method, and the hydrothermal method, titanium dioxide (TiO_2) is usually synthesized *via* sol–gel methods. Typically, particles synthesized by soft methods, including the polymerizable complex and sol–gel methods, provide higher performance than those synthesized using a solid state reaction because of the small particle size, shape, and good crystallinity.[2]

The band gaps of metal oxides with d^0 metal ions are usually formed from O 2p orbitals and *n*d orbitals from a metal cation, which are more negative than the zero potential of hydrogen ions. The band gaps of metal oxides are usually in the ultraviolet (UV) range. Powdered titania photocatalysts cannot split water without modification, such as a platinum (Pt) cocatalyst.[2–4] Hydrogen production experiments have been conducted using a TiO_2 photocatalyst with a band gap of 3.2 eV under different conditions, including pure water, vapor, and an aqueous solution including an electron donor with the assistance of a cocatalyst. Sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) have been used to split water with a loaded Pt. Under UV irradiation, the efficiency of titania doped with other metal ions is considerably improved.[3]

Zirconium dioxide (ZrO_2) with a band gap of 5.0 eV is a photocatalyst that can split water without a cocatalyst under UV irradiation owing to the position of its high conduction band. Photocatalytic activity of ZrO_2 decreased when it was loaded with cocatalysts, such as Pt, copper (Cu), gold (Au), and ruthenium oxide (RuO_2). It is likely that the height of the electronic barrier of the semiconductor band metal impeded electron transport and stopped further molecular water-splitting reactions. Nevertheless, photocatalytic activity improved with the addition of Na_2CO_3.[2]

Niobium pentoxide (Nb_2O_5) with a band gap of 3.4 eV is not active without any modification under UV irradiation. It decomposes water efficiently in a mixture of water and methanol after being loaded with a Pt cocatalyst. Its higher photocatalytic activity under UV irradiation was observed as assembled mesoporous Nb_2O_5. Tantalum pentoxide (Ta_2O_5) with a band gap of

4.0 eV is also a well-known photocatalyst. It can produce a small amount of hydrogen and no oxygen without any modification. Ta_2O_5 loaded with nickel oxide (NiO) and RuO_2 shows great photocatalytic activity for generating both hydrogen and oxygen. The addition of Na_2CO_3 and a mesoporous structure of the catalyst showed enhanced photocatalytic activity. Nanostructured vanadium dioxide (VO_2) with a body-centered cubic (BCC) structure and a large optical band gap of 2.7 eV demonstrated excellent photocatalytic activity in hydrogen production from a solution of water and ethanol under UV irradiation. It also exhibited a high quantum efficiency of 38.7%.[2] Additionally, all of the metal oxides with d^{10} metal ions (Zn^{2+}, In^{3+}, Ga^{3+}, Ge^{4+}, Sn^{4+}, and Sb^{5+}) are effective photochemical water-splitting catalysts under UV irradiation.[3]

Even though binary metal oxides with d^0, d^{10}, and f^0 metal ions show efficient photocatalytic activity, their ternary oxides have been widely studied and proven to have the same photocatalytic effects. For instance, strontium titanate ($SrTiO_3$) with a band gap of 3.2 eV and potassium tantalite ($KTaO_3$) with band gap of 3.6 eV photoelectrodes can be photoactive without an external bias because of their high conduction bands. These materials can be employed as powder photocatalysts for solar cells and water splitting. Domen and co-workers studied the photocatalytic performance of NiO-loaded $SrTiO_3$ powder for water splitting. A reduction in hydrogen gas (H_2) is responsible for the activation of the NiO cocatalyst for H_2 evolution. Then, subsequent oxygen gas (O_2) oxidation to form an NiO/Ni double-layer structure provides a further path for the electron migration from a photocatalyst substrate to a cocatalyst surface. The NiO cocatalyst prevents the back reaction between H_2 and O_2, which is totally different for Pt.[2–4] The enhanced photocatalytic activity of $SrTiO_3$ was also reported using a new modified preparation method or suitable metal cation doping (*e.g.*, La^{3+}, Ga^{3+}, and Na^{+}).

Many ternary titanates are efficient photocatalysts for water splitting under UV irradiation. The H_2 evolution of photocatalysts of sodium titanate $Na_2Ti_3O_7$ (layered crystal structure), potassium titanate $K_2Ti_2O_5$ (layered crystal structure), and potassium titanate $K_2Ti_4O_9$ (layered crystal structure) from aqueous methanol solutions in the absence of a Pt cocatalyst was reported. The quantum yield of materials studied for H^+-exchanged $K_2Ti_2O_5$ reaches 10%. The method of catalyst preparation also shows a different activity. Barium titanate ($BaTiO_3$) with a band gap energy of 3.22 eV and perovskite crystal structure prepared using a polymerized complex method has high photocatalytic activity in comparison with materials prepared by the traditional method because of the smaller size and larger surface area.[2]

Calcium titanate ($CaTiO_3$) with a band gap energy of 3.5 eV and perovskite crystal structure loaded with Pt showed good photocatalytic activity under UV irradiation. The activity of $CaTiO_3$ doped with a zirconium ion (Zr^{4+}) solid solution was further increased. Quantum yields were reported to be up to 1.91% and 13.3% for H_2 evolution from pure water and an aqueous ethanol solution, respectively. A number of lanthanum titanate perovskites (including La_2TiO_5, $La_2Ti_3O_9$, and $La_2Ti_2O_7$) with layered structures were reported with much higher photocatalytic activities under UV irradiation than bulk $LaTiO_3$. The photoactivities of $La_2Ti_2O_7$ doped with barium (Ba), strontium (Sr), and (calcium) Ca was improved sufficiently. The lanthanum titanate perovskite $La_2Ti_2O_7$ (band gap energy of 3.8 eV) prepared using a polymerized approach showed higher photoactivity than when the traditional solid-state method was used.[2]

Biological materials used as templates, such as bacteriophages, offer environmentally friendly synthesis and organization of functional materials at the nanoscale, where there is an efficiency of energy transfer by increasing the probability of the energy transfer groups being precisely positioned. A biological system such as M13 viruses presents a rational design and assembly of nanoscale catalysts based on biological principles (which are required for the water-splitting reaction) for the production of oxygen and hydrogen gas driven by light.

1.3 Microorganisms in Energy Mitigations

Recent studies have indicated that nanotechnology materials and processes could be applied to microorganism growth processes to potentially improve biological biomass production from the atmosphere. This technology can significantly enhance biodiesel production and biomass conversion rates. It can also improve enzyme immobilization, lipid accumulation and extraction, enzyme loading capacity, nanoscale catalysis activity, storage capacity, separation and purification rates of liquid from other liquids and solids, and bioreactor design and applications.[11–14]

Microorganisms such as bacteria, viruses, algae, molds, and fungi are living creatures and have survived in extreme environmental conditions for millions of years. They usually deposit fat, lipids/oil, glucose, starch, and other hydrocarbons and organic substances in their bodies that can be extracted and converted into useful products.

Bacteria are a single-cell form of life, and each individual cell is unique. They often grow into different colonies; however, each bacteria cell has its own independent life. New bacteria are reproduced by a process known as cell division. It is estimated that more than 3000 species of bacteria are living in totally different environments and conditions. Nevertheless, some of them are found only in a very specific environment, thus requiring specialized types of food, temperature, and light.[11]

A virus is a small infectious organism that can only replicate inside living cells of other cells and organisms. They can infect all kinds of animals, bacteria, plants, and so on. Unlike bacteria, viral populations do not grow through cell division since they are acellular, instead they use the machinery and metabolism of a host cell to produce multiple copies of themselves and then assemble inside those cells. To date, approximately 5000 viruses have been scientifically described in detail. A group of scientists has recently announced that they can successfully modify a virus to split water molecules, which can be an efficient and non-energy-intensive method of producing H_2.

These scientists genetically modified a commonly known, harmless bacterial virus in order to assemble the components for separating water molecules into H_2 and O_2 molecules, in turn yielding a fourfold boost in production efficiency. This novel process mimics plants that use the power of sunlight to make chemical fuel for their growth. In this research, the scientists engineered the virus as a kind of biological scaffold to split a water molecule.[12]

Algae comprise several different species (2800) of relatively simple living organisms that are found all over the world, capturing light energy through photosynthesis and converting inorganic/organic substances into simple sugars and other substances using photon energy. Algae can be considered the early stage of simple plants, and some are closely related to more complex plants as well. Some algae also appear to represent different protist groups (large and diverse groups of eukaryotic microorganisms), alongside other organisms that are traditionally considered more animal-like (*e.g.*, protozoa). Therefore, algae do not represent a single evolutionary direction but rather a level of organization that may have developed several times in the early history of microorganism life on the earth's crust.[13]

Some microorganisms usually require the following conditions for their growth:

- pH of 5–9 (lower pH may be seen)
- presence of organic substances (waste water, city waste, leaves)
- temperature between 4 °C and 40 °C; sulfur-, iron-, copper-, zinc-, cobalt-, and manganese-rich conditions;
- the presence of carbon and CO_2, nitrogen, phosphoros, oxygen, hydrogen, and sunlight (more sunlight, less UV rays).

As an example, the growth conditions of microorganisms found in Yellowstone National Park, which is an extremely hot, and mineral- and ion-rich environment, are totally different than the growth conditions of similar species that live in coastal and lake areas.[14]

Botryococcus braunii, a green algae with a pyramid-shaped planktonic structure, is one of the most important algae in biotechnology. These algae colonies are held together by a lipid biofilm and are usually found in tropical lakes, rivers, and creeks. They will bloom in the presence of dissolved inorganic phosphorus and other nutrients in a growth condition. *B. braunii* has great potential for algae farming because it produces hydrocarbons, which can be chemically converted into different fuels. It has been estimated that up to 86% of the dry weight of this alga can be composed of long-chain hydrocarbons, and some of its useful hydrocarbon oils can be found outside of the cell. *B. braunii* can convert 61% of its biomass into oil, which drops to only 31% under different conditions. It grows best between 22 °C and 25 °C, and is a great choice for biofuel production.[12]

Recently, nanotechnology-associated studies have been conducted on microorganisms to increase the efficiency of their growth and rates of fuel conversion. Nanotechnology probes tap into algae and bacteria cells to extract electrical energy. It has been postulated that *Chlamydomonas reinhardtii*, a single-cell alga, might be an ideal cell for energy harvesting. This new study demonstrated the feasibility of collecting high-energy electrons in steps of the photosynthetic electron transport chain prior to the downstream process. However, cells usually die after a period of time because of leaks in the membrane where the nanoscale electrodes penetrate into the body of the cell.[14]

1.4 Environmental Health and Safety

Nanomaterials have outstanding electrical, optical, mechanical, magnetic, quantum mechanical, and thermal properties. Because of these unique properties, a variety of nanoscale materials, such as nanoparticles, nanofibers, nanocomposites, nanotubes, and nanofilms, all of which are considered to be the next generation of materials, have been utilized in several different industries worldwide.[8] It has been stated that nanomaterials are already found in more than 1500 different products/processes, including solar cells, water-splitting reactions, bacteria-free cloths, concrete, sunscreens, car bumpers, tennis rackets, toothpastes, polymeric coatings, wrinkle-resistant clothes, and various electronic, optical, diagnostic, and sensing devices.

Recently, several studies have focused on photo-active nanomaterials for renewable energy generation from solar energy. However, some exposure of workers during large-scale nanomaterial production is inevitable, even when incidents of unusual release do not occur. It is necessary to determine the degree of exposure that can cause major health impacts. The toxicities of photo-active nanomaterials are among the most studied in nanotechnology because of their numerous applications in both energy and medical fields. The risk of exposure is greatest to workers in the nanotechnology field, but others would also be vulnerable, such as following the environmental release of nanomaterials during consumer product use, transportation, storage, *etc.*[1]

Nanomaterials are more reactive and potentially more damaging than bulk-scale materials of the same composition because of their high surface area-to-volume ratio. Testing with a variety of organisms to determine the impact of nanoparticle characteristics on toxicity has yielded inconsistent results, but some generalizations can be made. Smaller nanomaterials tend to be more toxic than larger nanomaterials. Fibrous or rod-like nanoparticles of any composition tend to be more hazardous than spherical or agglomerated nanoparticles. For TiO_2, the crystalline phase may influence the degree or mode of toxicity, but both rutile and anatase nanoparticles can cause toxic reactions at nanoscale. As the nanoparticle concentration increases, toxicity tends to increase, unless particles aggregate, which tends to reduce toxicity significantly. Nevertheless, aggregations may reduce the efficiency of solar energy conversion systems. Some tests indicate that the size of nanoparticles has less effect on toxicity than the material itself. Nanoparticle surface charge can impact toxicity and may prevent contact with cells if they share a surface charge.

The variables that affect nanoparticle toxicity continue to be refined, but impacts remain difficult to predict. The risk-control method involving nanomaterials entails a chain of assessment, planning, implementation, and corrective action, which is repeated in order to minimize employee exposure to unwanted nanoparticles, thus allowing them to work in acceptable environments.[15] The three main categories of risk control are engineering techniques, administrative measures, and personal protection.[8] Table 1.1 shows this hierarchy applied to nanoparticle assessment.

Engineering controls, such as design, elimination/substitution, isolation/confinement, and ventilation seem to be more effective than the administrative measures (*e.g.*, information/training, work procedures, cleaning and equipment, personal hygiene, and work periods). Personal protective equipment, such as respiratory protection, and skin and eye protection, is less effective than other elements of the hierarchy.[8] Once the conditions of the engineering techniques are satisfied, then workers can reduce the possibility of contact and potential risk. This also shows the effectiveness of these three categories relative to the overall risk-control hierarchy.[15,16] Table 1.2 summarizes some properties of nanoparticles currently used by

Table 1.1 Risk control hierarchy applied to nanoparticles.

Risk control hierarchy	Actions	Effectiveness
Engineering techniques	Design Elimination/substitution Isolation/confinement Ventilation	+
Administrative measure	Information/training Work procedures Cleaning and equipment Personal hygiene Work periods	↓
Personal protective equipment	Respiratory protection Skin, eye, and other protections	−

Table 1.2 Some concerns capable of influencing nanomaterials toxicity.

Primary concerns	Secondary concerns
Number of particles	Surface shape and geometry
Specific surface area	Solubility/dissolution
Size and granulometric distribution	Clustering/agglomeration
Concentration	Crystalline structures
Chemical compositions	Surface oxidation
Surface properties	Surface hydrophobicity/hydrophilicity
Zeta potential	Manufacturing techniques
Functional groups	Inertness/reactivity
Oxidative stresses	Biocompatibility/biodegradability
Free radicals	Metal and alloy, ceramic, polymer, composite
Cell viability	Dispersion/settlement
Surface coverage	Impurities and defects

various industries. Overall, more effort needs to be conducted in the field to minimize/eliminate the toxicity of nanomaterials used for photocatalyst purposes.

1.5 Contents of This Book

This book summarizes the most recent developments in the field of photoactive green nanomaterials, as well as their recent applications in solar energy conversion, mitigation of contamination, water splitting, health and environmental aspects, modeling, CO_2 emissions reduction, and nano and biological systems, in order to address some concerns of climate change and global warming. The following chapters will be included in this book, all of which were written by world-renowned authors in their fields:

Chapter 1: Introduction to Green Nanostructured Photocatalysts
Chapter 2: Fundamentals of Sunlight–Materials Interactions
Chapter 3: Green Nanomaterials Preparation: Sustainable Methods and Approaches
Chapter 4: Natural Photosynthesis System
Chapter 5: Bioinspired Photocatalytic Nanomaterials
Chapter 6: Hybrid Molecular–Nanomaterial Assemblies for Water-Splitting Catalysis
Chapter 7: Hierarchical Nanoheterostructures for Water Splitting
Chapter 8: Nanophotocatalysis in Selective Transformations of Lignocellulose-derived Molecules: A Green Approach for the Synthesis of Fuels, Fine Chemicals, and Pharmaceuticals
Chapter 9: Photocatalytic CO_2 Conversion to Fuels by Novel Green Photocatalytic Materials
Chapter 10: Hybrid Inorganic and Organic Assembly System for Photocatalytic Conversion of Carbon Dioxide
Chapter 11: Biological Systems for Carbon Dioxide Reduction and Biofuel Production
Chapter 12: Organic Reactions using Green Photo-active Nanomaterials
Chapter 13: Hierarchical Nanoheterostructures: Double Layer Hydroxide-based Photocatalytic Materials
Chapter 14: Health and Environmental Aspects of Green Photo-active Nanomaterials
Chapter 15: Risk Assessments of Green Photo-active Nanomaterials
Chapter 16: Energy Harvesting from Solar Energy Using Nanoscale Pyroelectric Effects

1.6 Conclusions

Fossil fuels, such as coal, oil, and natural gas, have been heavily utilized by many developed and developing countries. Because of their overproduction and consumption, fossil fuel-based energy systems have had a dramatic impact on the environment and on health, causing global warming as well as air, soil, and water contamination and pollution. Inspiration from the natural environment can be an option for solving these problems. By mimicking photo-active green nanomaterials found in nature, we can create light-harvesting assemblies, devise new methods for synthesizing fuels, and develop tools to synthesize novel functional materials for solar cells, water-splitting units, pollution control devices, and so on. Photo-active green nanomaterials can be more reactive, and potentially more damaging, than bulk materials of the same composition because of their high surface area-to-volume ratio. The properties of these nanomaterials should be determined prior to any photocatalytic applications.

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