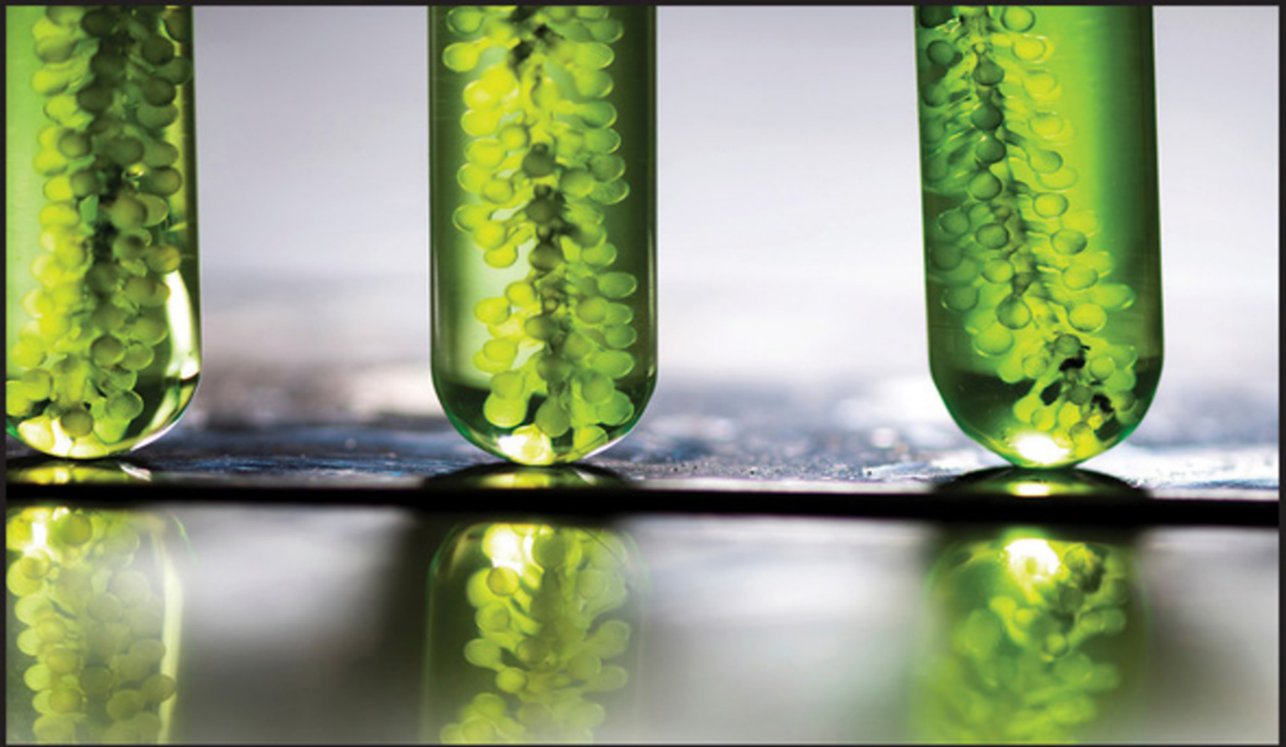

GREEN SYNTHESIS OF NANOMATERIALS FOR BIOENERGY APPLICATIONS

EDITED BY
NEHA SRIVASTAVA | MANISH SRIVASTAVA
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WILEY Blackwell

Green Synthesis of Nanomaterials for Bioenergy Applications

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Foreword

Bioenergy is a potential option to replace fossil fuels effectively and in a sustainable manner. Various known bioenergy options such as biohydrogen, biogas, biomethane, bioethanol, biomethanol, biobutenol, algal biofuels, and biodiesel are supposed to be very promising alternative renewable energy options for eliminating severe environmental issues. Significant efforts have been made to explore various bioenergy options and related technologies in practice. However, its commercial viability and symmetrical distribution are still a long way from practical implementation of bioenergy technologies. This book series explores the use of nanotechnology, which is grabbing the attention of the biofuels sector by playing the role of enhancer, to improve bioenergy production technology. Application of nanotechnology is emerging as new area for bioenergy production through its contribution as catalyst, enzyme, and microbial immobilizer. Nanomaterials have enormous potential for commercial markets and the industrial market is expected to grow and become more flexible in coming decades. Therefore, with an accelerating demand for viable and sustainable economic bioenergy production, the potential combination of bioenergy and nanotechnology area must be explored.

Green Synthesis of Nanomaterials for Bioenergy Applications is much needed contribution to this series and I am happy to write this positive and satisfactory message. The book contains nine chapters covering green synthesis and characterization of nanomaterials for cost-effective bioenergy applications. The current world scenario of bioenergy and application of nanotechnology in bioenergy production, different immobilization methods for enhancing bioenergy production, synthesis, and mechanism of nanomaterial for economic bioenergy production with green approach are presented and discussed in detail. The book presents a new horizon of advancement and sustainable solutions for the improvement of bioenergy production in the form of nanotechnology. These chapters suggest that the application of nanotechnology will play a major role in bioenergy production and they will serve as gems for those working in the relevant fields including scientists, researchers, teachers, and students.

I am taking the opportunity to congratulate Dr. Neha Srivastava [IIT (BHU) Varanasi], Dr. Manish Srivastava [IIT (BHU) Varanasi]), Prof. (Dr.) P.K. Mishra [IIT (BHU) Varanasi], and Dr. Viaji Kumar Gupta for their significant efforts in bringing about this publication in order to fulfill the needs of scientists, teachers, researchers, and students. My congratulations to all the editors for their contribution, devotion, and dedication in this endeavor. All the authors and editors of this book deserve sincere appreciation for their commendable achievements.

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1

Nanocatalysts and Biofuels

Applications and Future Challenges

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1.1 Introduction

The economy of the developing countries is entirely based on fossil fuels and variation in the price of fossil fuels. On the one hand, the demand for and consumption of fossil fuels are increasing every year because of an increase in population, rapid growth of the automobile sector, and industrialization. Energy consumption, economic growth, and population are interlinked. A recent estimate shows that crude oil, gas, and coal resources will be exhausted in the next five decades if production continues at current resource extraction rates (Behera and Varma 2019). On the other hand, increasing fuel demand, fluctuating fuel prices, uncontrolled population growth, global warming, and ill effects of environmental pollution will force us to search for an alternate ecofriendly fuel to fossil fuels. Among the renewable energy sources, biomass sources—namely plants, oils, and fats—are considered as feedstock to produce a variety of biofuels as future resources (Martini and Schell 2012).

Biomass feedstocks include all types of residues from the agricultural field and processing operations, wood processing industry wastes, forestry residues and branches, lignocellulosic feedstocks, organic fraction of municipal solid waste, and animal wastes, etc. The estimated annual global biomass production is 104.9 billion metric tons of carbon (Field et al. 1998). The annual photosynthesis yield in the world is ca. 720 billion tons of organic raw cellulose materials (Tong 2019) that have potential for conversion to biofuels.

Generally, biomass resources are playing an influential role in supplying food or fuel. Originally, the raw biomass materials were used for the production of heat and other energy requirements, which can make an essential contribution to satisfying the energy needs of society (Ruiz-Altisent 1994). Recently, biofuels production from biomass feedstocks is getting more attraction in developed/developing countries. The reasons for this interest are due to the reduction of foreign currency/crude oil imports, reduced dependence on crude oil,

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emissions from burning of fossil fuels, and their impact on the environment, i.e. air pollution as well as global warming, etc. To overcome the abovementioned environmental issues, biofuels can be promoted to replace conventional commercial diesel and petrol fuels in the transport sector. There are several biofuel technology pathways of production from various biomass feedstocks. To mitigate the greenhouse gas emissions, we have to start avoiding fossil fuels and/or promote the use of biofuels. Today, the biofuel industries are facing several challenges: specifically, poor supply chain and logistics, more expensive raw materials, higher costs for processing and production compared to petrofuels, low efficiency of the conversion process, and lack of supporting biofuel policies for promotions. Researchers are focused on improving the conversion efficiency of different biomass conversion methods, which can indirectly reduce the process cost and biofuel price. In conclusion, the economically viable biomass conversion technologies will reach commercial scales.

Recently, nanotechnology has been attempted to improve the overall performance of different biomass conversion systems, which, although in the research stage, have the potential to address the problems currently faced by the biofuel industries. In this chapter, the current research on application of nanocatalysts in the field of biofuels production is presented and their impact on product yield is also discussed.

1.2 Biofuels Production

Biofuel is a solid or liquid or gaseous fuel that can be generated from biomass feedstocks, which can replace (partially or wholly) conventional petrofuels. The biofuel production from feedstocks may be produced through biomass conversion methods. The biofuels can be produced in the form of liquid or gaseous or solid (Figure 1.1).

The kind of biofuel mainly depends on the process conditions used in the technology and nature of feedstock materials. The biofuel production technologies for biomass feedstocks have reached the fourth generation, depending on conversion methods and feedstocks used. The first generation deals with the production of biofuels using food crops, and technologies under this category are commercialized for biodiesel and bioethanol production. Feedstocks used for this generation include various carbohydrate and lipid sources for bioethanol and biodiesel production. The second generation deals with non-food crops for biofuel production. This generation's target is to produce bioethanol from all types of lignocellulosic feedstocks. The third generation focusses on production of biofuels (biodiesel/bioethanol) from microalgae. The fourth generation aims to produce biodiesel/bioethanol from genetically modified crops or microbial lipids. Among them, only the first generation for biofuel production from food crops is commercialized. Other generation technologies are still at the research and development stage.

Generally, there are three major biofuel production routes: thermochemical, biochemical, and chemical conversion methods. The thermochemical conversion technologies (TCCTs) deal with the conversion of feedstocks into biofuels using heat with or without air/oxygen, whereas biochemical conversion technologies (BCCTs) use microorganisms under aerobic or anaerobic conditions. The comparison of the BCCT and TCCTs on biofuels is presented in Table 1.1. The chemical conversion technologies (CCTs) are used to produce biodiesel from vegetable oil feedstocks. Biofuels are facing difficulty in selling at a commercial level; conventional fossil fuels are of higher calorific value and cheaper than biofuels. It is very

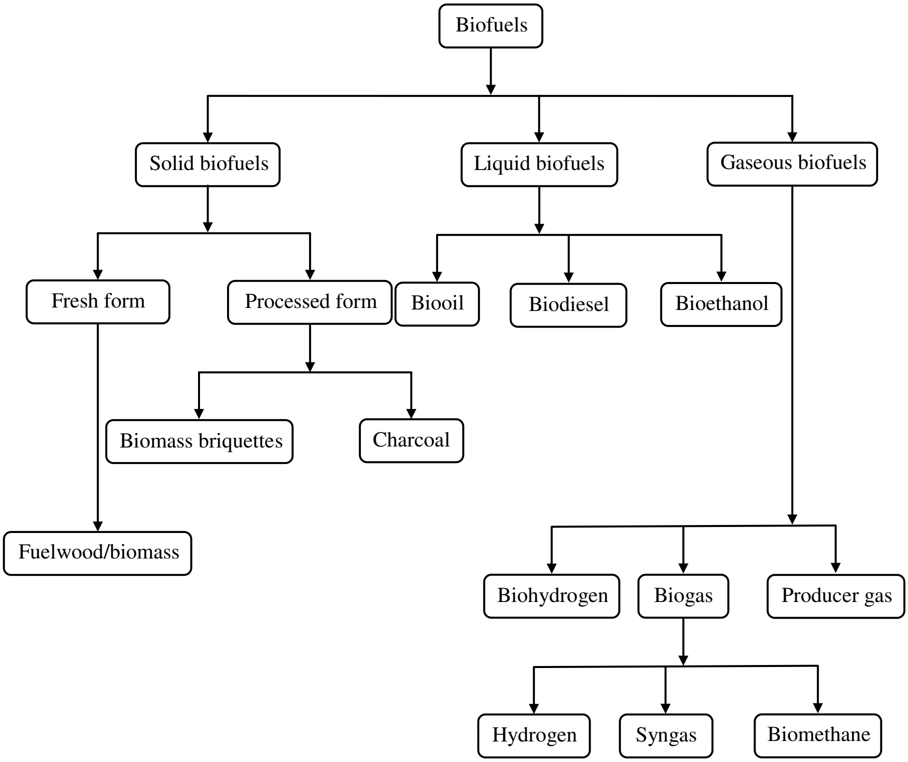

Figure 1.1 Types of biofuels production from various biomass feedstocks via different biomass energy conversion methods.

Table 1.1 Comparison of BCCTs and TCCTs for biofuel production.

S. No.	Parameters	BCCTs	TCCTs
1	Mode of action	Microorganisms	Heat
2	Maximum reaction temperature	< 60 °C	Up to 1200 °C
3	Products from biomass		
	a. Solid fuels	Not possible	Possible (e.g. charcoal)
	b. Liquid fuels	Possible (e.g. bioethanol)	Possible (e.g. biooil, biomethanol)
	c. Gaseous fuels	Possible (e.g. biogas)	Possible (e.g. syngas)
4	Suitable technology available for feedstocks with higher moisture content	Anaerobic digestion	Hydrothermal process
5	End products like multiple products	Acetone-Butanol-Ethanol (ABE)	Biocrude
6	Chemicals production from biomass feedstocks	Possible	Possible
7	Secondary products as soil amendments to maintain health	Biodigested slurry	Biochar
8	Reaction time	h to days	sec. to days

challenging to enhance the calorific value of biofuels and make them on par with fossil fuels. This may result in an increase of the production cost, which is a major challenge for scaling-up to a commercial level. Hence, the production costs should be brought down through technological breakthrough or government policies that provide support in the form of incentives and tax benefits to promote biofuels and protect the environment.

1.3 Role of Catalysts in Biomass Conversion

The biomass composition is one determining factor that prescribes the biofuels and biochemicals that can be produced from the biomass feedstocks via TCCTs, BCCTs, or CCTs. The yield of end products is varied when it comes to biomass types and reaction conditions used. The process conditions are determined by the catalyst types and quantity, reaction temperature, reaction pressure, reaction time, biomass compositions, and its properties. The catalyst has a significant influence in speeding up the reactions in the process and thus, the product yield. The catalysts are classified into four categories viz., homogeneous, heterogeneous, biocatalyst, and hetero-homogenized types (Philippot and Serp 2013). The strength and weakness of homogeneous and heterogeneous catalysts used in the chemical reactions are presented in Table 1.2. The catalyst selection for the biomass conversion

Table 1.2 Comparison of homogeneous and heterogeneous catalysts (Miessler and Spessard 1991; Farnetti et al. 2009; Chen 2014).

S. No	Parameters	Homogeneous	Heterogeneous
1	Nature of catalyst	The reaction occurs between the same type of catalyst and reactants	This catalysis uses the different type of catalyst to that of the reactants
2	Examples	Soluble organometallic or coordination compounds	Bulk metal or metal on a solid support
3	The type of catalyst used	Usually liquid	Mostly solid
4	Stability and degrading nature	Low	Comparatively high
	Thermal stability	Poor	Good
5	Reaction mechanisms	Easy to understand	Unknown and difficult to understand
6	Separation of catalyst from end products	Difficult	Easy
7	Applicability	Limited	Wide
8	Selectivity	High	Low
9	Active site	Well-defined	Poorly designed
10	Reutilization of catalyst	Difficult and costly	Simple and cheap
11	Neutralization	More amount of water required	Less in this case
12	Continuous processes	Limited	Possible
13	Corrosion	More	Less

process is based on different parameters such as low cost, high reactivity, efficiency and ecofriendliness, and reusability (Liu 2005). Limitations of heterogeneous catalysts used for biomass conversion are long reaction rates and low efficiency due to poor mass transfer or diffusion between the heterogeneous catalyst and reactants (Klaewkla et al. 2011).

1.4 Application of Nanocatalysts

The biomass conversion technologies are subjected to frequent changes with updating of latest conversion technologies in this field. Nanotechnology is one of new emerging sciences, which has application in different fields—namely biomedical applications, optic and electronic, sorbents, sensors, and catalysis—due to its merits over conventional catalytic conversion technologies (Ali Sinag 2018). Through nanotechnology nanocatalysts were developed by combining characteristics such as higher catalytic activities and easy recovery for homogeneous and heterogeneous catalysts respectively, which also has the higher specific surface area (Zuliani et al. 2018). Nanocatalysts can be made from low-cost metals, which must fulfill important properties such as high metal dispersion and stability (Chen et al. 2015). The properties of nanoscale materials can exhibit different from that of macroscale materials, and this offers unique applications for nanomaterials (Chaturvedi et al. 2012). The nanosized materials as nanocatalysts can be used directly or as solids supported with nanoparticles (Tong 2019). The properties of nanoparticles may be modified according to the requirements of varying conditions of the nanoparticle synthesis process (Pélisson et al. 2012; Akia et al. 2014). The usage of nanocatalysts can minimize the mass transfer resistance due to its large surface to volume ratios (Zuliani et al. 2018). Nanocatalysts also have a more comprehensive scope in the area of biomass conversion technologies for biofuel production from different biomass feedstocks.

1.4.1 Biomass Pretreatment

Lignocellulosic biomass feedstocks (LCB) are one of the possible candidates for promoting the bioeconomy for sustainable development. Pretreatment is one of the most crucial processes involved for turning LCB into liquid biofuels via the biochemical route. Downstream process selection is mainly based on biomass pretreatment used and by-products produced. The major obstacles in LCB-based liquid biofuels by larger scale units are costly, energy intensive, and complex processes involved in the pretreatment method. The barriers of first-generation biofuels can be partially overcome by effective utilization of LCB, which are inexpensive and readily available as waste. Cellulosic ethanol is much more cost-effective and has a higher net energy ratio than that of grain ethanol. Release of fermentable sugars from LCB for further processing remains challenging due to complex binding between lignin, cellulose, and hemicellulose compounds, which are closely linked with each other.

In comparison with sugar and starch crops, the lignin acts as a shield to protect carbohydrates in LCB and prevent the enzymatic hydrolysis and releasing fermentable sugars. Several biomass pretreatment methods such as physical, chemical, biochemical, or combined approaches have been tried for different LCB materials and are currently in the research and development stage. Pretreatment can be a costly process in LCB into biofuels conversion; it holds significant potential for efficiency improvement through advanced technologies. To achieve economic and environmental sustainability, the ideal pretreatment process should handle high solid loadings with minimal use of chemicals and energy. Existing catalysts have a number of problems such as inhibitors production, higher catalyst cost (enzyme), degradation of sugars, corrosion, low conversion efficiency, and biomass loading rates.

Recent studies have shown that the nanoparticles are performing better than conventional catalysts used in the biomass pretreatment (Pan et al. 2012; Duque and Eugenia 2013; Koo et al. 2017). Silica-coated magnetic nanoparticles (SiM NPs) with perfluoroalkyl sulfonic/alkylsulfonic were used to pretreat wheat straw. Ten percent of wheat straw hemicellulose was solubilized by nanoparticles; higher than that of the control (Duque and Eugenia 2013). Pan et al. (2012) reported that the titanium dioxide nanotube/leadoxide electrode performed better at treating kraft lignin due to its higher oxidative and increased surface area available for the reactions. Magnetite nanoparticles (Fe_3O_4 NPs) are also used to convert LCB to sugar. The enzymatic digestibility was enhanced by 177% and 87% for reed stem and paddy straw, respectively, under optimal conditions of H_2O_2 and Fe_3O_4 NPs. Advantages of the method are that NPs can be quickly recovered and recycled (Koo et al. 2017). Paramagnetic-based nanocatalysts are an attractive choice for depolymerization of cellulose into glucose monomer due to simplified catalyst separation using magnetic field (Guo et al. 2012; Lee et al. 2014).

1.4.2 Biochemical Conversion Route

In the case of biochemical conversion method, the microorganism of specific species or a consortium of microorganisms is used to convert the raw materials into biofuels. The two main methods falling under this category are anaerobic digestion and fermentation process. In the case of anaerobic digestion, the organic matter present in the biomass can be utilized by microorganisms to yield the biogas and biodigested slurry. The bioethanol can be produced by the fermentation process using different feedstocks. Bioethanol can then be added to gasoline to run a petrol engine. The problems associated with existing biochemical methods are higher production cost and low yield per raw materials used, i.e. low conversion efficiency. In the case of anaerobic digestion, the conversion rate for organic matter into biogas ranged from 30% to 40% (Faisal et al. 2019). This indicates maximum efficiency of conversion of biomass through present anaerobic digestion without catalyst, which can be further improved by adopting advanced technologies with suitable nanocatalysts. To increase the performance and yield of existing practices, the nanocatalysts can be introduced in the BCCTs.

1.4.2.1 Anaerobic Digestion

The moisture content of raw materials plays a significant role in the selection of appropriate biofuel production technology. In the case of biomass feedstocks with higher moisture content, anaerobic digestion is a preferable method than TCCTs. The biogas can be used for lighting, cooking, engine fuel, and electricity generation. The calorific value of the biogas depends on methane content (average CH_4:60%) and other impurities in the biogas, which can be improved by the removal of these impurities. The biogas with more than 90% methane content is called as biomethane. The details of nanocatalysts' applications to anaerobic digestion of different feedstocks for enhancing biogas and methane productions are shown in Table 1.3. In a recent study, it was observed that use of nanoparticles in the anaerobic

Table 1.3 Applications of nanocatalysts to enhance biogas production.

S. No.	Biomass feedstock used	Nanocatalyst used	Targeted biofuel	Yield	Reference
1	Mixed liquor volatile suspended solids	Fe nanocatalyst	Biogas	0.345 (l/g VS reduction)	Thiruselvi et al. (2018)
2	Cattle manure	Nanostructured SiC	Biogas	499 ml/g TS	Li et al. (2018)
3	Rice straw	Fe_3O_4 nanoparticle	Methane	129%	Khalid et al. (2019)
4	Slaughterhouse wastewater	Biosynthesized iron NPs	Methane	45%	Yazdani et al. (2019)
5	Poultry litter	12 mg/l Ni NPs	Methane	368 ml/g VS	Hassanein et al. (2019)
6	Waste-activated sludge	Fe^0	Methane	217.16 ml/g VSS	Wang et al. (2016)
7	Waste-activated sludge	Fe_2O_3	Methane	217.16 ml/g VSS	Wang et al. (2016)
8	Waste-activated sludge	Fe^0	Methane	70.6%	Su et al. (2013)
9	Sewage sludge	Ni (100 nm, 5–10 mg/kgVS)	Methane	Increased up to 10%	Tsapekos et al. (2018)
10	Domestic sludge	Zero valent iron	Methane	88%	Amen et al. (2017)
11	Raw manure (feces and urine)	2 mg/l Ni NPs	Biogas, Methane	614.5 ml/g VS, 361.6 ml/g VS	Abdelsalam et al. (2017a)
12	Manure	20 mg/l Fe_3O_4 magnetic NPs	Biogas, Methane	584 ml/g VS, 351.8 ml/g VS	Abdelsalam et al. (2017b)
13	Cattle dung slurry	Ni NPs	Biogas, Methane	1190.8 ml, 707.1 ml	Abdelsalam et al. (2016)
14	Cattle dung slurry	Co NPs (1 mg/l)	Biogas, Methane	1142.1 ml, 653.1 ml	Abdelsalam et al. (2016)
15	Cattle dung slurry	Fe NPs (20 mg/l)	Biogas, Methane	985.2 ml, 545.1 ml	Abdelsalam et al. (2016)
16	Cattle dung slurry	20 mg/l Fe_3O_4 NPs	Biogas, Methane	1154 ml, 703.3 ml	Abdelsalam et al. (2016)
17	Dairy cattle manure	500 mg/l TiO_2 NPs	Biogas, Methane	336.25, 192.31 ml/gVS	Farghali et al. (2019)
18	Wastewater sludge	Fe_3O_4 (7 nm, 100 ppm)	Biogas, methane	180%, 234%	Casals et al. (2014)
19	Microalgae Enteromorpha	Fe_3O_4 NPs, Ni NPs	Biogas, Biohydrogen	624 ml, 51.42% (v/v)	Zaidi et al. (2018)