6 Nanotechnology: An Application in Biofuel Production

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Abstract

Nanotechnology has been extensively studied for biofuel production. Fossil fuels are available in a limited amount on earth; therefore, it is needful to build up a new alternative to fulfill the requirement of energy sources in the near future. Biofuel such as biodiesel, biohydrogen, biomethanol, and bioethanol may replace the need for fossil fuel in the future. These fuels are produced from cost-effective and renewable sources such vegetable oils that come from different biological sources such as algal biomass, microbial biomass, and plant biomass. Nanomaterials have emerging applications in biofuel production due to their unique structural behavior such as small size (nanoscale size) of nanomaterials. These nanomaterials enhance biofuel production by improving the biosynthesis pathways. This manuscript mainly focuses on the various types of nanoparticles, synthesis methods of nanoparticles, and the emerging application of nanoparticles in biofuel production.

Keywords

Nanoparticles · Biofuel · Biodiesel · Biohydrogen · Bioethanol

6.1 Introduction

Fossil fuels such as coal, petroleum ions, and liquid petroleum gases are available in nature in a limited amount because these sources of energy are nonrenewable. These fuels have towering cost and cause several types of environmental pollutions such as air, soil, and water pollution. When fossil fuels burn, it produces energy and

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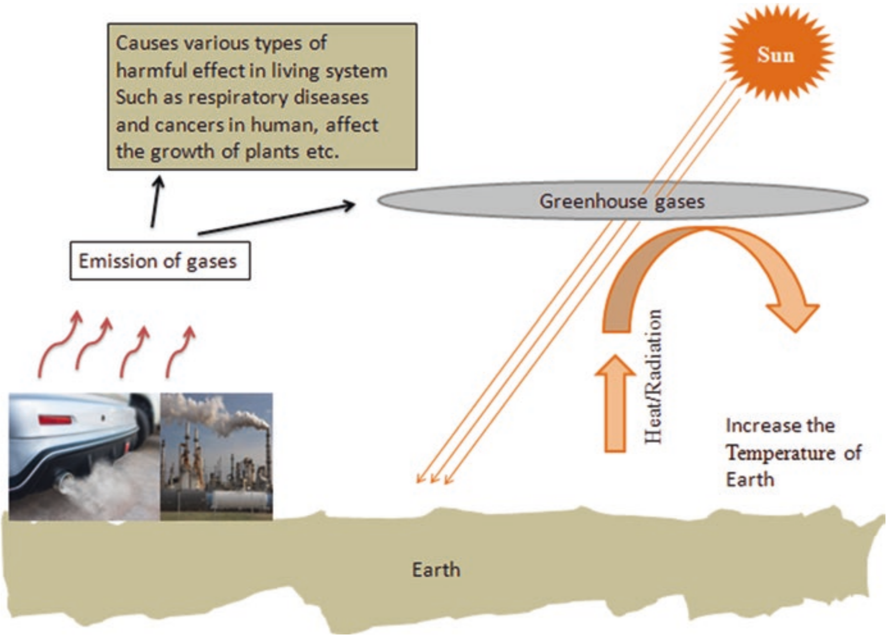

Fig. 6.1 Diagrammatic representation of the emission of gases during the burning of fossil fuel and the role of these gases in environmental pollution

various types of gases including carbon dioxide, sulfur dioxide, and other various types of gases. Carbon dioxide is the main greenhouse gas which maintains the earth temperature. Increase in the level of CO_2 causes increase in the temperature of the atmosphere which affects the distribution of living organisms (Fig. 6.1). Air pollution is main component of pollution which causes the depletion of the ozone layer. The ozone layer protects the earth from ultraviolet radiations. UV radiation causes various types of health effects in humans and other living organisms. Water pollution by these fuel waste materials is responsible for the addition of many types of toxic substances in the water sources which affect the distribution and life of living aquatic organisms. These wastes generated from these fuels also cause the loss of fertility in the soil. The availability of fossil fuel is limited, and after a certain time, these sources may be exhausted, making biofuel a potential candidate as an energy source. Therefore, biofuel production is very needful in the future as an alternative energy source (Palaniappan 2017).

Biofuel is referred to as energy sources generated from different types of biomass. These biomasses come from living organisms such as algae, bacteria, plants, and agricultural waste. Biofuel can terminate the demand for the fossil fuel in the future and minimize the environmental effects generated during the combustion of fossil fuel (Voloshin et al. 2015; Dragone et al. 2010; Demirbas 2009).

A recent approach for biofuel production is based on various types of microorganisms such as microalgae or cyanobacteria. Microalgae contain a huge amount of lipid which is used as raw material for biofuel production. The past few decades also

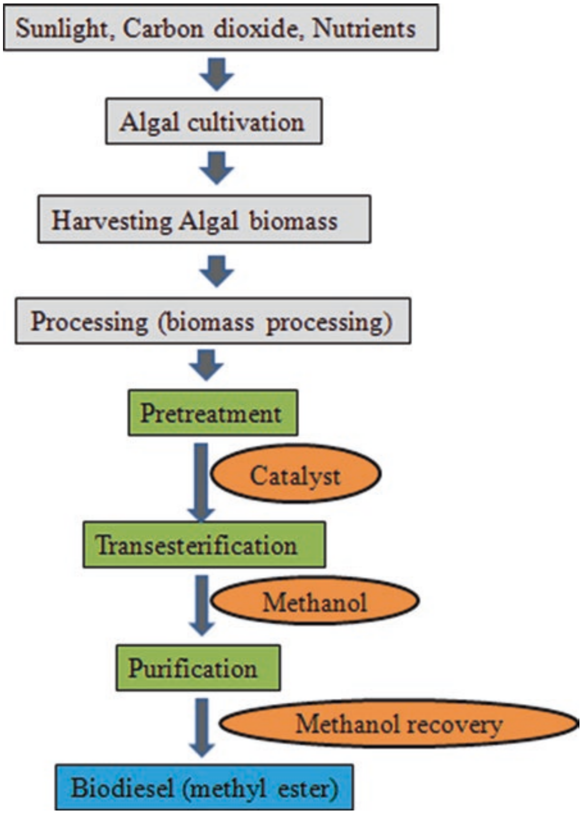

Fig. 6.2 Biodiesel production from algal cultivation

represent the production of biofuel from plant materials. Present research mainly focuses on the production of biofuel from microalgae. Plants and algae can synthesize sugar molecule by the process of photosynthesis. Photosynthesis is a process in which green plant and algae synthesize the carbon-based materials in the presence of environmental CO_2 and sunlight. Photosynthetic products require the growth of plant and production of biomass (Fig. 6.2). Plant and algal biomass are used as raw sources for the production of biofuel (Demirbas 2009; Heiman 2016; Babel and Kurniawan 2004; Barakat 2011).

Nanoscience and nanotechnology have also a great potential for remediation of various types of pollutants from contaminated water (Eccles 1999; Leung et al. 2000; Kurniawan et al. 2005; Rickerby and Morrison 2007; Brumfiel 2003). Nanostructures have more efficiency and fast adsorption rate compared to other conventional methods. Nanoparticles have a broad surface area due to the nano-range (small) particle size. Varieties of nanoparticles have been considered as an inexpensive and environmentally safe adsorbent material for adsorption of several types of contaminants such as toxic metallic pollutants and azo dyes. The few applications of nanotechnology in bioenergy production and wastewater treatment are given in Fig. 6.3 (Sadegh et al. 2016; Theron et al. 2008; Dil et al. 2017; Savage and Diallo 2005).

Nanotechnology has prospective applications in biofuel manufacturing industries. Biofuel is the best alternative option of energy source in the future. Nanoparticles have an important role in the production of biofuel such as enhanced production of biohydrogen methane, biodiesel, etc.

6.2 Classification of Biofuel

Biofuel is classified by the raw material used in its production and by its efficiency. Biofuel is mainly classified into two groups, namely, primary and secondary. The primary category of biofuel is classified as a natural biofuel source derived from plants, animal waste, forest, and crop residues. The second type of biofuel is directly synthesized from microorganism such as microalgae. The second type of biofuel is divided into four generations (the fourth generation is basically correlated with the third generation) (Fig. 6.3). The first generation of biofuel is produced from starch-rich materials such as sugarcane, wheat, oats, potato, sweet potato, corn, and animal fats. The second generation of biofuel is produced from various types of plant species, grass, and wood of plant. The third generation of biofuel is an advanced type of biofuel which is produced from microalgae and few microbial species. Many researchers are working in the field of biofuel production and are trying to improve the production of biofuel by the genetic modification in third-generation fuel-producing organism, known as the fourth-generation biofuel. The yield of biofuel production depends on the type of microorganism which has been selected for

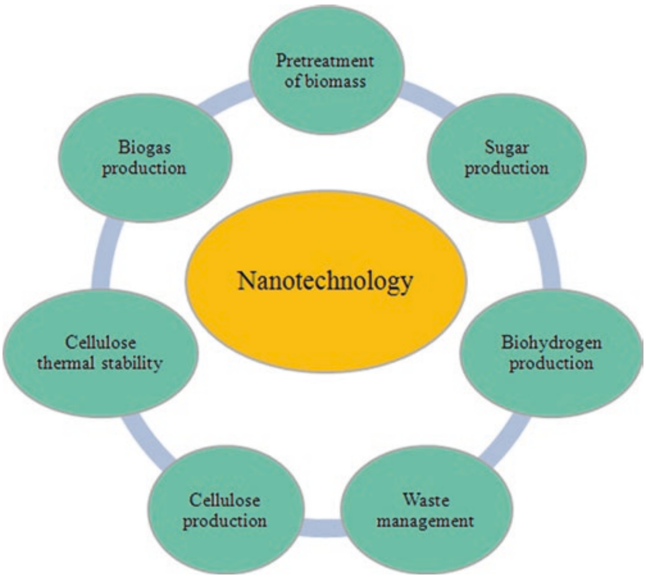

Fig. 6.3 Diagrammatic representation of application of nanotechnology in various fields

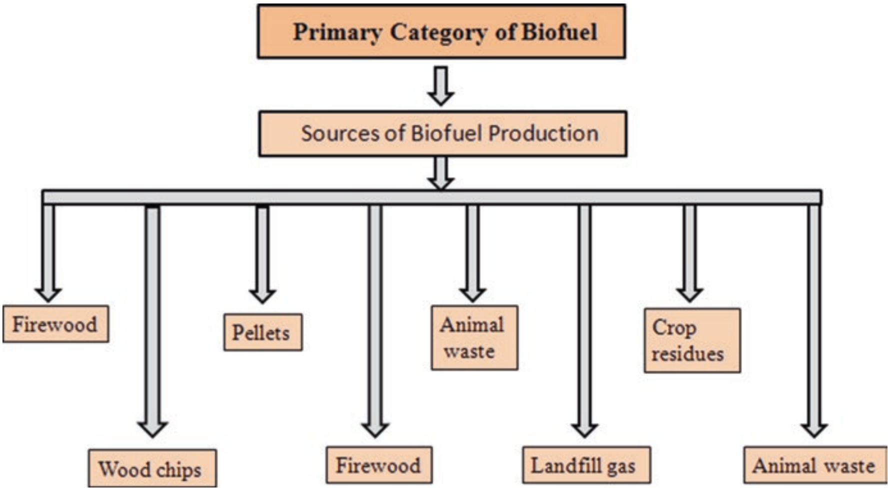

Fig. 6.4 (**a**) The primary category of biofuel and their sources of production. (**b**) The schematic diagram represents the second category of biofuel, generations of biofuel, and sources of biofuel production

biofuel production and optimum conditions required for the growth of the microorganism. Media compositions also affect the production of biofuel. Genetic engineering techniques are also used for the modification in genetic level which may be responsible for enhancing the production of biomass. These biomasses are used for the production of biofuel (Dragone et al. 2010; Abdelaziz et al. 2013). Various types of biofuels are shown in Fig. 6.4 (a and b).

6.3 Production of Biofuel

Biomass such as plant, algae, microbial biomass, and other waste materials is considered as suitable raw material for biofuel production. A variety of algal and microbial (fungal and bacterial) species are used for the production of bioethanol and biohydrogen. These products are partially mixed with fossil fuel (4–5%) in diesel and petrol engines. In the next few years, biofuel may be used as an additive in petroleum industry. Hence, biofuel can be considered as the best alternative of petroleum by-products (Ong and Bhatia 2010; Chanakya et al. 2013; Swain 2014). Pacific biodiesel is the first biodiesel plant commissioned in the United States in 1996, and this plant mainly focuses on biodiesel production from cooking oils. Biodiesel production was boosted after 2001 due to the price hike of petroleum oils. Biodiesel has many advantages like emission of less toxic waste, inexpensive, and independence from fossil fuels (Chanakya et al. 2013; Swain 2014).Various types of techniques and unit operations involved in biodiesel production (Fig. 6.5) are shown in Fig. 6.5.

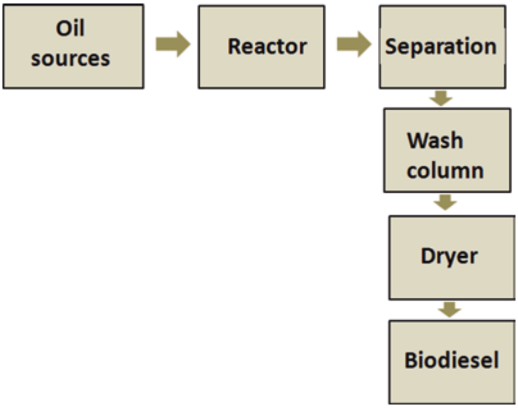

Fig. 6.5 Schematic diagram represents the stages of biodiesel production

6.3.1 Production Techniques for Biofuel

Biofuel production methods depend on the materials used for the production of biofuel, reactor types, reactor volume, and reactor parameters such as temperature, pH, mixing, etc. A variety of biological materials and production methods have been used for the production of biofuel processes. A few examples have been given in Table 6.1. Hydrotreatment is a technique in which vegetable oil and other lipid materials are used for biodiesel production purposes. It is a complex reaction process in which various types of reaction are involved (Swain 2014; Torres-Ortega et al. 2017).

6.3.2 Algal Biodiesel

Algae are the photosynthetic organisms which fix gaseous CO_2 in the form of algal biomass (Maeda et al. 1995). Algal biomass is considered as raw material for the bioenergy production. Microalga is the best alternative option for the production of diverse types of biofuel such as biohydrogen, bioethanol, biodiesel, etc. due to its high yield, fast growth rate, and high lipid and sugar contents and is easy to grow (cultivated on both arable and nonarable land) (Reddy et al. 2008). However, biodiesel production from microalgae is much expensive due to the tremendous requirement of energy source and maintenance of the growth condition for the cultivation of algal species. Algal biofuel production is a very complex process. A variety of mechanisms are involved in the production process (Fig. 6.6). Many researchers are working for the reduction of production cost and enhancement of the production of biofuel (Chanakya et al. 2013; Harayama 2012).

Table 6.1 Techniques of biofuel production and used raw materials for production processes

Raw material	Technique	Product	References
Vegetable oils	Transesterification	Biodiesel	Alptekin et al. (2014)
Animal fat waste	Transesterification, gas chromatography, bench-scale reactor	Ethylic biodiesel	CunhaJr et al. (2013a)
Lard oil	Transesterification, methanolysis	Biodiesel	Ezekannagha et al. (2017)
Microalgae	Full-scale photobioreactor	Biodiesel	Faried et al. (2017)
Bacteria (*Clostridium tyrobutyricum* JM1)	Immobilization and packed bed bioreactor	Biohydrogen	Singh et al. (2010)
Mixed culture (*Clostridium butyricum* and *Rhodopseudomonas faecalis* RLD-53)	Combined dark and photofermentation process	Biohydrogen	Singh et al. (2010)
Lignocellulosic materials and animal manure	Pretreatment techniques such as milling and extrusion and followed by microbial reaction in batch and continuous reactor	Biogas	Alptekin et al. (2014) and CunhaJr et al. (2013a)

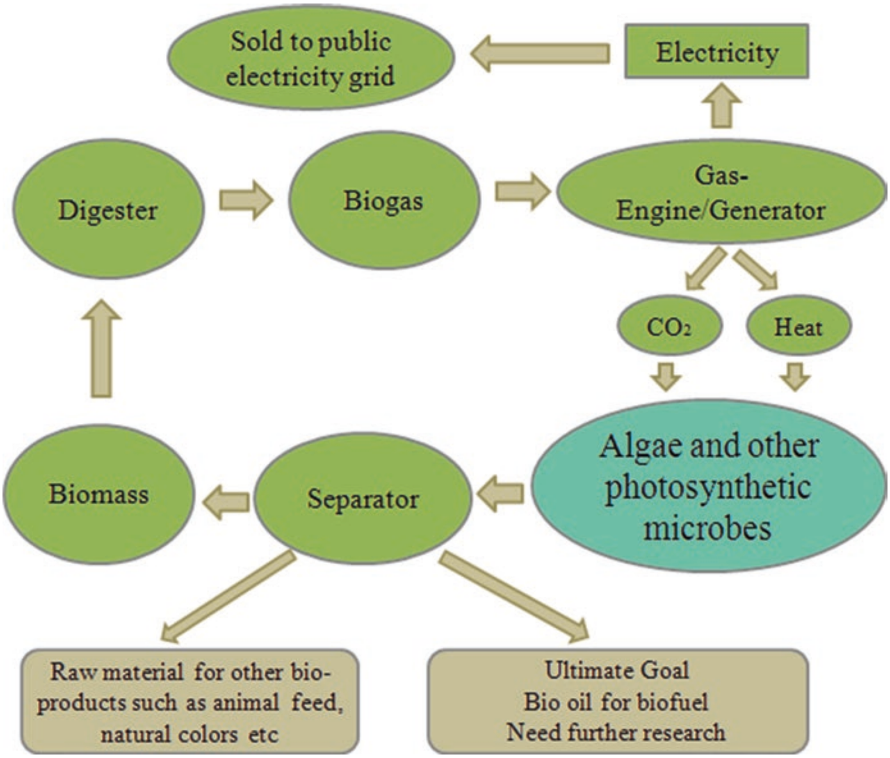

Fig. 6.6 The schematic diagram represents the processing of algae for the production of biofuel

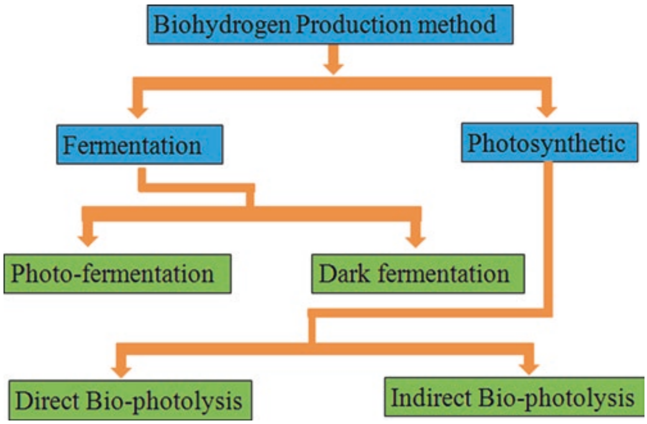

Fig. 6.7 The schematic diagram represents the various methods of biohydrogen production

6.3.3 Biohydrogen

Biohydrogen can be the best option of energy source in the future. It is an eco-friendly and cost-effective biofuel. Biohydrogen has many advantages compared to other fuels. It has high efficiency due to its high octane number. Nowadays, about 99% of hydrogen is generated from fossil fuels (Shaishav et al. 2013; Jo et al. 2006). Various conventional methods are available for hydrogen production such as electrolysis of water and coal gasification (Hsia and Chou 2014). These conventional methods have few disadvantages like requirement of high temperature (more than 840 °C) and environmentally unsafe processes (Shaishav et al. 2013; Hsia and Chou 2014). Electrolysis of water is an eco-friendly process but electricity for the production of hydrogen adds extra cost. Therefore, this process is possible where electricity is inexpensive because electricity covers the major cost (about 80%) of hydrogen production (Karthic and Shiny 2012). This manuscript is mainly focused on inexpensive and environmentally safe methods of biohydrogen production.

Biohydrogen is generated during the photolytic reaction in photosynthetic microorganisms such as microalgae and plants (Fig. 6.7). It also generated by fermentation process in anaerobic microorganisms. Various types of microorganisms have been studied for biohydrogen production such as *Chlamydomonas moewusii*, *Scenedesmus obliquus*, *Rhodobacter sphaeroides* (photosynthetic bacteria), and *Enterobacter aerogenes* (fermentative bacteria) (Fabiano and Perego 2002; Kars et al. 2006).

6.4 Synthesis and Properties of Nanomaterials

It is most important to know about the synthesis mechanism and basic properties of nanomaterials before discussing their use in the production of biofuel and waste management processes. A range of nanomaterials are available such as nanoparticles, nanotubes, nanosheets, etc. Two major methods have been used for the formation of different types of nanomaterials. The first is the top-down approach. In this method, bulk materials such as iron, gold, etc. are broken down into nanoscale-size particles. The second method is the down-up approach. In this approach, small-size particles come together and form nanomaterials (Biswas et al. 2012; Serrano et al. 2009).

Other methods are also used for the synthesis of nanomaterials. These methods include coprecipitation, laser ablation, self-assembly, and phase separation methods. These methods produce various types of nano-size particles. Nanomaterials produced as dry powder materials are used for suitable application (Yu and Xie 2012). A nanoporous gold particle from Au and Ag alloy foil dealloys in nitric acid at 25 °C (Qiu et al. 2008). This is considered as dealloying and thermal alloying method, respectively. In the coprecipitation method, nanomaterials are synthesized by precipitation in the presence of gravitational forces and magnetic field (Kalantari et al. 2012). Carbon nanotubes (CNTs) are synthesized by various methods. The arc discharge method is one of the best methods for the synthesis of good-quality nanotubes which require electricity and carbon sources (De Volder et al. 2013). The chemical vapor deposition method requires heat and carbon source for the synthesis of nanotubes also (Saifuddin et al. 2013). The electro-spinning technique is used for the production of nanofibers. This method requires a polymer solution, high-voltage electric supply, spinneret, and collecting plates (Bhardwaj and Kundu 2010; Sill and Recum 2008).

Nanosheets mainly are produced by thermal exfoliation technique. Nanographene sheets produced from graphite powder react with hard acids such as HNO_3, H_2SO_4, and HCl and heating at high temperature (1050 °C). Argon gas is also required in this process (Kishore et al. 2012).

After the synthesis of nanomaterials, another important process is surface functionalization. Surface functionalization is a process which enhances the property of nanomaterials. This process also provides many other properties to nanomaterials such as stability and biocompatibility. It also enhances the binding capacity of nanomaterials with various types of enzymes (Pavlidis et al. 2010).The functionalization method requires addition of functional groups with nanomaterials. The resources used for functionalization are biopolymers such as gelatin, carbohydrates, polypeptides, lipids, etc. A variety of synthetic polymeric materials are also used as functionalization materials (Wang et al. 2012). Adding the functional groups with nanomaterials responsible for the enhancement in the properties of nanomaterials provides different surface charges, provides a link between functional groups of more than one nanomaterial, and minimizes the pore entrance size which is also applicable for enzyme immobilization (Lee et al. 2009).

Nanomaterials have many different properties compared to other bulk materials. They have different electrical, heating conductivity, light reflection, and catalytic properties. These advanced properties of nanomaterials are responsible for the various applications of nanomaterials in drug delivery system, environmental engineering, and bioenergy production (Savolainen et al. 2016).

6.5 Application of Nanotechnology in Biofuel Production

Nanoparticles enhance the production of biofuel by increasing the catalytic reaction in the production process. Various types of nanomaterials have been reported for biofuel production (Ramsurn and Gupta 2013; Gordon and Seckbach 2012). This section of the chapter is mainly focused on the application of several types of nanoparticles and their role in the production of biodiesel, biohydrogen, bioethanol, biogas, and bioethanol.

6.5.1 Biohydrogen Production

Biohydrogen is produced from various types of microorganisms such as anaerobic bacteria, microalgae, etc. These microorganisms generate molecular hydrogen through various metabolic routes (Das et al. 2008). The biohydrogen production is extremely dependent on several ranges of parameters such as pH, temperature, retention time, and media compositions (Lukajtis et al. 2018; Nagaragan et al. 2017). It is also reported that nanoparticles enhance the production of biohydrogen in the microbial system by increasing the electron transfer rate in the microbial cell (Serrano et al. 2009; Ali et al. 2017; Zhang and Shen 2007).

6.5.1.1 Dark Fermentation for Production of Biohydrogen

Dark fermentative biohydrogen production is an inexpensive and eco-friendly process in which production of biohydrogen depends on various renewable feedstock and microbial species (Nagaragan et al. 2017). Different types of nanomaterials have application in the field of biohydrogen production. Gold (Au) nanoparticles (5 nm) enhance the substrate utilization efficiency by 56% and increase the yield of biohydrogen production up to 46% (Zhang and Shen 2007). Gold nanoparticles enhance the biohydrogen production due to their small size and large surface area which are responsible for the binding of microbial cells to active sites. Gold nanoparticles also enhance the activity of enzymes of biohydrogen synthesis machinery which is responsible for the production of biohydrogen.

Nanoparticles are beneficial to the microorganism when it uses the optimum concentration of nanoparticles. High concentration of silver nanoparticles inhibits the growth of microorganisms and decreases the production of biohydrogen. Silver nanoparticles are reported as an inducer for microbial biohydrogen production. It increases severalfolds the hydrogen production yield. Addition of silver nanoparticles enhances the substrate utilization up to 62% which is responsible for enhancing the biohydrogen production up to 2.48 mol H_2/mole substrate. These nanoparticles reduce the lag phase of bacterial and algal growth and activate acetic reaction. The acetic reaction is the main pathway for biohydrogen production (Zhao et al. 2013; Yang and wang 2018).

Silica nanoparticles have emerging application in the dark fermentation process for the production of biohydrogen. Silica nanoparticles combine with iron oxide and produce nanocomposite (Fe_3O_4@SiO_2) (detailed synthesis of composites is explained in Fig. 6.8). These newly synthesized nanocomposites/nanoconjugates

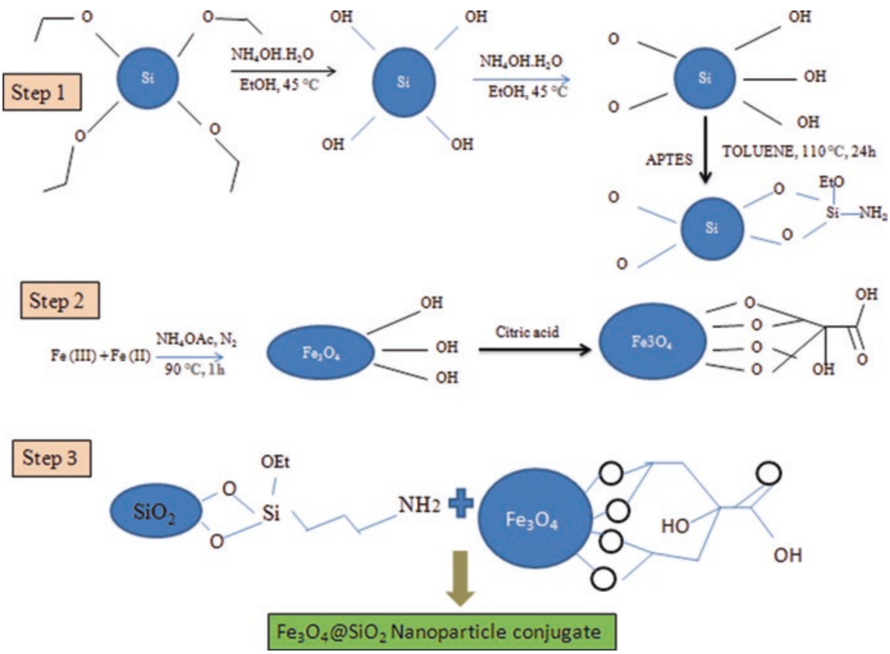

Fig. 6.8 The schematic diagram represents the synthesis of Fe3O4@SiO2 nanoparticle conjugate

have emerging application in biohydrogen synthesis due to more catalytic activity and stability. These nanomaterials are stable at high temperature and show a low level of toxic effects (Venkata et al. 2008; Abbas et al. 2014; Kunzmann et al. 2011).

6.5.1.2 Biohydrogen Production by the Photofermentation Process

Nanoparticles enhance the production of biohydrogen in photosynthetic microorganisms. The photosynthetic microorganisms used for the production of biohydrogen are microalgae, photosynthetic bacteria, etc. Addition of nanoparticles in growth medium enhances the growth, physiological process, photosynthetic efficiency, protein synthesis, lipid synthesis, and nitrogen metabolism in microbial species (Eroglu et al. 2013). Nanoparticles also enhance the activity of various enzymes which are involved in various applications such as glutamate dehydrogenase, glutamine synthetase production, etc. These microbial enzymes are also required for the metabolic activity of microorganisms (Yang et al. 2006; Mishra et al. 2014).

A variety of nanoparticles have been applied for biohydrogen production. The optimum concentration of Ag and Au nanoparticles enhances the photosynthetic activity of *Chlorella vulgaris* (Eroglu et al. 2013). Zerovalent nanoparticles also increase the activity of biohydrogen production by transfer of electrons from Fe° (Eq. 6.1) (Liu et al. 2012).

$$Fe + 2H^{+} \rightarrow Fe^{2+} + H_2 \tag{6.1}$$

6.5.2 Biogas Production

Biogas is an inexpensive and environmentally safe biofuel. Biogas is produced through various methods in which digestion of organic material takes place due to a variety of microorganisms (Romero-Guiza et al. 2016; Aryal et al. 2018). Biogas production occurs in many steps. The four important steps are hydrolysis (breakdown process), acidogenesis (alcohol production), acetogenesis (acetic acid production), and methanogenesis (production of methane gas) (Mao et al. 2015; Buitron et al. 2014; Sekoai et al. 2016). The hydrolysis step of biogas production contains conversion of large biomolecules (carbohydrates and proteins) into small sugar molecules and amino acids. The acidogenesis step produces hydrogen, CO_2, and alcohols from the products of the first hydrolysis step. Various types of pathways are involved in this process (Lochynsha and Frankowski 2018; Angelidaki et al. 2018). Acetogenesis pathways of biogas synthesis produce acetic acid and other constituents. The final step of these pathways generates methane gas by various methanogens. The growth of methanogens requires low hydrogen concentration in the growth medium (Khan et al. 2017; Leonzio 2016; Kadam and Panwar 2017).

Addition of nanoparticles has led to emerging results in the anaerobic condition. Nanoparticles act as an electron donor or acceptor and also enhance the activity of various enzymes which is responsible for biogas production (Romero-Guiza et al. 2016; Liu et al. 2013; Yang et al. 2013; Abdelsalam et al. 2016). Nanomaterials enhance the substrate utilization rate at various steps. Su et al. (Su et al. 2013) reported that adding the zerovalent iron nanoparticles ensures to improve the production of biogas from waste materials (Su et al. 2013; Karri et al. 2005).

6.5.3 Biodiesel Production

Biodiesel has much promising application in the future due to the emission of fewer pollutants, is eco-friendly, and is produced from edible as well as nonedible oils (De Araujo et al. 2013; Mohammadshirazi et al. 2014). Nonedible oils are considered as microbial oil and plants oil converted into biodiesel through various mechanisms. This process is considered as very beneficial because these nonedible oils are waste and are present in huge amount in nature (Rathore and Madras 2007; Bankovic Ilic et al. 2012).

Nanomaterials have promising results in biodiesel production. Nanoparticles enhance the catalytic reaction during transesterification, thereby improving the production of biodiesel (Chen et al. 2018; Lee et al. 2015). Chen et al. (2018) have reported that the biodiesel production yield was enhanced in the presence of Fe_3O_4/ZnMg(Al)O nanoparticles (Chen et al. 2018). Ca^{2+}doping in nanomaterials such magnetic nanoferrites has an emerging effect in biodiesel production. This process enhances the biodiesel production yield up to 85% from soybean cooking oils (Dantas et al. 2017).

Various researchers have reported that biodiesel production is also enhanced by using carbon-based nanoparticles. Carbon-based nanoparticles have been used as catalyst in various reactions such as transesterification of vegetable oils (Konwar et al. 2014; Zhang et al. 2014). Ion nanoparticles were incorporated on carbon nanotubes which are responsible for enzyme immobilization. Immobilization improves the efficiency of biofuel production and reduces the production cost. Nanostructure provides emerging immobilization support due to nanoscale size and large surface area. Microbial enzymes such as lipase from *Pseudomonas cepacia* are immobilized on the surface of nanoparticles and enhance the production of biofuel due to enhanced transesterification reaction (Goh et al. 2012).

Functionalization of the nanoparticle process also increases the production of biodiesel. Ion-silica nanoconjugates such as Fe_3O_4/SiO_2 have emerging application in biodiesel production. Nanoconjugates can increase the production of biodiesel up to 97.1%. In this process, various types of cooking and algal oils have been used. Algal oils have a high yield of production in the presence of these ion-silica nanocomposites (Chiang et al. 2015).

6.5.4 Bioethanol Production

It is one of the most important alternatives to fossil fuel. It is considered as an inexpensive and eco-friendly biofuel. Bioethanol has various advantages such as high evaporation enthalpy and high octane number (Saini et al. 2015; Sarkar et al. 2012; Limayen and Ricke 2012). Currently, bioethanol is produced from edible and nonedible vegetable oils, waste materials, and algal and bacterial biomass. Microalgae produced a large amount of bioethanol. Genetic engineering in microorganisms is also applied to improve production of bioethanol (Kuhad and Singh 1993; Balan 2014).

Various types of nanomaterials have emerging application in the production of bioethanol. Cherian et al. (2015) investigated that MnO_2 nanoparticles increase the bioethanol production by using sugarcane leaves. It catalyzes the mechanism of bioethanol production during various steps. In this process, sugarcane leaves are converted into bioethanol. MnO_2 nanoparticles provide the broad surface area which is responsible for the binding of enzymes on their active sites and causes the improvement in ethanol production (Cherian et al. 2015).

Bioethanol production using immobilized microbial cells on the surface nanoparticles has been reported in many literatures. Ivanova et al. (Ivanova et al. 2011) have investigated that yeast cells produced additional ethanol when immobilized on the surface of magnetic nanoparticles (Ivanova et al. 2011; Lee et al. 2011).

Lee et al. (2011) also reported that immobilized *S. cerevisiae* cells are responsible for more ethanol production. *S. cerevisiae* cells were immobilized on calcium alginate. These immobilized cells enhanced the bioethanol production yield up to 100% but production yield of suspended cells was 88%. In immobilization process, the cells can be reused up to several times and there are less chances of contamination. Therefore, immobilization is an emerging method used in microbial bioethanol production. Its application with nanotechnology can give better results at commercial-level bioethanol production (Galazzo and Bailey 1990).

6.6 Conclusion

This concludes that nanomaterials may play an important part in the enhancement of bioenergy production. Nanomaterials have promising application in biofuel production due to their small size, large surface area-to-volume ratio, and good catalytic properties which are responsible for enhancing the production of various types of biofuel such as biohydrogen, biodiesel, and bioethanol. This manuscript has described the synthesis of various types of nanomaterials and their application to enhance the production of biofuel. Recent trends on the use of nanotechnology in biofuel production were discussed in this chapter. From an up-to-date study in nanotechnology, the authors conclude that these approaches can be used in biofuel industries to enhance biofuel production and minimize the cost of biofuels due to unique structural properties of nanomaterials.

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