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Nanoparticles: Application in Biofuel Production Processes

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Abstract: *Biofuels are progressing rapidly as alternative renewable energy sources because of their non-polluting traits and their low cost compared to fossil fuels. However, the main focus is the use of novel techniques to maximize the yields in order to effectively commercialize biofuel. Nanotechnology is an enormous and intensifying field of research owing to its broad area of application in various fields, particularly in the biomedical and pharmaceutical fields. The various unique properties of nanoparticles have attracted the scientists to investigate their role in biofuel production processes. The application of nanoparticles in biofuel production is still in infancy stage. The present review analytically discusses the different studies that have been carried out to explore the role of nanoparticles in biofuel production i.e. in the production of biohydrogen, biogas, biodiesel and bioethanol. The review also deals with the nanomaterials characterization techniques.*

Keywords: *Nanoparticles, Biohydrogen, Biodiesel, Bioethanol, Biogas*

I. INTRODUCTION

Nanotechnology is a promising science with wide-ranging applications including disease therapy, cosmetics, clothing, fuel catalysts, renewable energy, food products and home appliances. Nanotechnology also play a key role in various kinds of refining and manufacturing procedures, including construction products, wastewater treatment, nanovirus graphene and water filtration (Ghoranneviss et al., 2015). Nanotechnology is expected to enhance the "green technology" for sustainable development. It is expected that nanotechnology could play a crucial role in the extension of renewable energy commercialization leading to development of new technologies in storage, capture and transmission of energy (Drexler et al., 1991). For instance, carbon nanotube inventions were used for applications in automotive parts, energy storage, thin-film electronics, coatings and so forth (Baucher et al 2013, Lourtioz et al., 2016). Currently, researchers are involved in synthesizing various types of nanomaterials because of its probable use in industry and science. For instance biocompatible nanomaterials are used directly with natural resources to work or to stay in touch with live organisms (Yousaf et al., 2008; Nikalje et al., 2015; Khan et al., 2017). The term nanometers include various types of nanostructure materials which contain at least one dimension in the nanometer range. Nanostructures include, zero dimension nanostructures like ceramic nanoparticles, semiconductor and metal; One-dimension nanostructures such as nanorods, nanowires, and nanotubes; two dimension nanostructures such as quantum well structures. Apart from this individual nanostructure, pieces of these nanostructures form high dimension arrays, super lattice and assemblies (Ghoranneviss et al., 2015). The properties of resources with nanometer dimensions are very dissimilar from atoms and bulk materials. This is mostly because of the nanometer size of the resources which constitute them: (i) high surface energy; (ii) large fraction of surface atoms (iii) abridged flaw, which is not present in the respective bulk materials (iv) spatial confinement (Cao 2004). The most important focus of researchers is to design new multifunctional nanoparticles platform for tissue / cell specific targeting, co-delivery of synergistic drug combinations, continuous or triggered drug delivery. The present review analytically discusses the different studies that have been carried out to explore the role of nanoparticles in biofuel production i.e. in the production of biohydrogen, biogas, biodiesel and bioethanol. The chapter also deals with the nanomaterials characterization techniques.

II. NANOMATERIALS

Nanomaterials properties are different and often better than their traditional counterparts available in polycrystalline form because they are dependent on microelectronic that is determined by grain size, crystallographic orientation, chemical composition, atomic structure, dimension, and coordination number. Due to fine grain dimensions, significant quantities of atoms in the nanometer are located on grain boundaries which give them special properties. Nanoparticles, due to their smaller size and a large surface to volume ratio, show attractive new properties which contain nonlinear optical behavior, enhanced diffusivity, high specific heat, increased mechanical strength, magnetic behavior and electric resistivity etc.

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Nanoscience and nanotechnology deals with the area of characterization, synthesis, exploration, and application of nanostructure materials (Huaizhi and Yuantao, 2001, Guisbiers et al., 2012). Properties of nanomaterials are classified into five and they are; Mechanical, Thermal, Biological, Optical, and Chemical properties. For the production and dispensation of nanostructures and nanomaterials, the following challenges must be met; a good surface to volume proportion to the energy, each and every nanoparticle should have same chemical composition, uniform size distribution, desired size, morphology, and microstructures that overall result in preferred physical properties, As the time value prevents nanostructure and nanomaterials from Ostwald being thick or thick by the pile (Guisbiers et al., 2012).

Most of the current nanoparticles and nanomaterials are placed in four material based categories. (i) Carbon-based nanomaterials mainly composed of carbon and they are found in shapes like shells, hollow tubes, or ellipses (Iijima, 1991, Reilly, 2007). Carbon nanotubes (CNTs), Carbon Black, Fullerenes (C₆₀), Carbon Nanofiber, Carbon Onion and Graphene (GR) are included under the category of Nanomaterials based on carbon. Chemical vapor deposition, laser isolation and arc discharge (except carbon black) are significant production process for the manufacture of these carbon-based materials. (Huaizhi and Yuantao, 2001, Kulkarni, 2015, Kumar and Kumbhat, 2016). (ii) Inorganic based nanomaterials contain metal oxide and metal nanoparticles. These nanomaterials can be produce in metals such as silver and gold nanoparticles, metallic oxides such as titanium oxide and zinc oxide nanoparticles and semiconductors such as ceramic and silicon (Callister, 1997, Gupta et. al.,2019). (iii) Organic-based nano-materials include organic or non-inorganic-based nanomaterials, most of the nanomaterials made of organic matter. The use of self-combination interaction of non-co-ordinator and molecule for design, organic nanomaterials, to the desired structures such as liposomes, dendrimers , Helps in converting polymerase, micelles nanoparticles (Kulkarni,2015 Gleiter,1989). (iv) Composite-based nanomaterials: Composite are nanomaterials, NSMs, and NPO, which are with a phase on the dimension that can either connect nanoparticles to other nanoparticles or nanoparticles, which are joint with large or bulk type materials or more complex Structures, such as a metal structure Metal-based, composite can be any combination of carbon-based or organic-based nanomaterials, including ceramic, metal or polymer bulk material. Various morphology of nanomaterials are depicted (Born and Wolf, 2003, Shionoya and Yen,1999, Kumar and Kumbhat, 2016).

In addition to classification based on content and dimension nanoparticles can also be classified as synthetic or natural depending on their origin; (i) Natural nanoprticles are available in nature either through anthropogenic activities or biological means. Naturally occurring nanomaterials are present in the spheres of the Earth (i.e., the lithosphere, the atmosphere, and the hydrosphere, even in the biosphere) despite of human activity. Earth is made of nanomaterials which are naturally present in the Earth's shell, such as the atmosphere, in which the entire hydrosphere, the lithosphere, the troposphere, the lakes, the ocean, the groundwater, the rivers, and the hydrothermal vents are involved in special steps of development. Magma, rocks, soil or lava, and biosphere, which includes humans including microbes and high organisms (Hochella et al.,2015, Sharma et al.,2015). (ii) Synthetic nanomaterials are generated by engine exhaust, smoke and mechanical grinding, or synthesized by biological, chemical, physical or hybrid methods. The question of risk estimation plan has arisen in current days because engineers have increased their use in composites and then consumer products and industrial applications This is very helpful in predicting the behaviors of engineered nanometers in various conditions (Jeevanandam et al.,2018). At present, various resource related to probable applications are used for the production of engineered nanometers (Wagner et al., 2014).

III. SYNTHESIS OF NANOMATERIALS

In general, bottom-up and top-down are two main approaches for nanomaterials synthesis.

1) *Top-Down*: size reduction from bulk materials.

2) *Bottom-up*: material synthesis from atomic level.

Top down route is included in specific solid-state processing. This route is based on with bulk materials and makes it smaller. Thus breaks large particles by using physical processes such as grinding, crushing or milling. Mainly, this route is not mentioned above to create similar content and with very high energy consumption, very small particles are very difficult to realize. The biggest problem with the top-down approach is the inefficiencies of the surface structure. Physical properties of such incompetence and the effect of nanomaterials and nanostructures will have significant impact on the surface chemicals. It is well known that top-down techniques can cause significant crystallographic damage to processed patterns. (Arole and Munde et al.,2014).

The bottom-up approach refers to the creation of a material from below: Cluster-by-cluster, atom-by-atom or atom-by-atom. This route is often used to prepare nanoscale materials with the ability to produce, resize and produce similar shapes. It effectively covers chemical synthesis as well as regulates the reaction of particulate growth. Although the bottom-up approach is not new, it plays an important role in the formation and processing of nanostructure and nanometer. (Arole and Munde et al.,2014).

Planning Environment-friendly Economic Processes To better control the particle size, quantity, quality, morphology, accuracy on the synthesis of nanoparticles has always been a challenge for researchers (Hahn et al.,1997). The selection of synthesis technology can be an important factor in determining the effectiveness of photovoltaic as a study (Figure 1). There are several technique of synthesizing titanium dioxide, such as combustion synthesis, (Köhler et al.,2018) gas-phase methods, (Xu et al.,2018, Wang et al.,2005) microwave synthesis and hydrothermal, (Cheng et al.,1995, Yin et al.,2001) which was discussed in great detail.

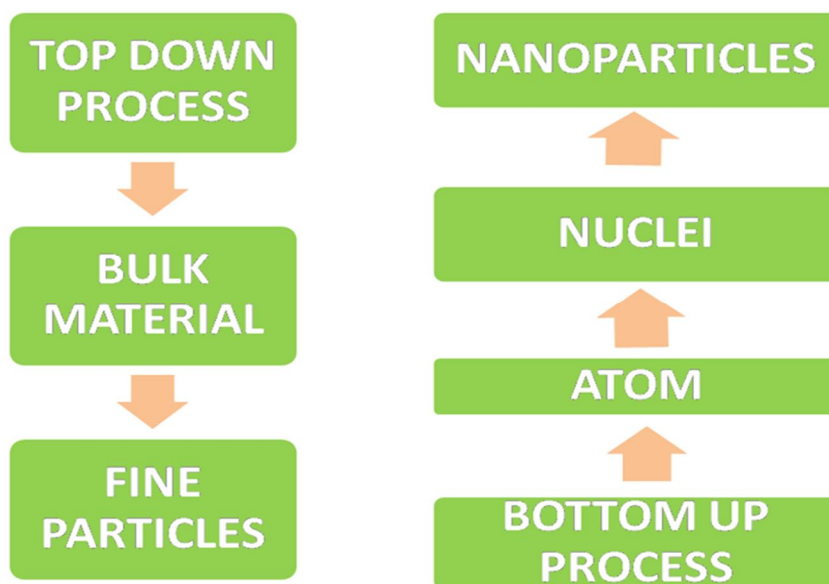


Figure 1 Approaches for the synthesis of nanoparticles (Adapted and modified).

A. Hydrothermal Synthesis

Hydrothermal synthesis is mainly done in a pressure vessel which is autoclave with response in aqueous solution. The temperature in the autoclave is move up above the boiling point of water while reaching the saturated temperature (Table 1). Hydrothermic synthesis is extensively used for the grounding of titanium oxide nanoparticles, which can easily be achieved through hydrothermal treatment of a titanium precursor's peptized precipitate with water (Yang et al.,2001). Hydrothermal method may be useful for controlling particle morphology, surface chemistry, grain size and crystalline phase through the reaction temperature, connector, solution, solvent properties, structure, pressure and time of aging (Carp et al.,2004).

B. Combustion Synthesis

Combustion synthesis leads to excessive crystalline particles with large surface areas (Nagaveni et al.,2004). During this process, during the combustion, the temperature attain around 650 degrees Celsius for one or two minutes, so that the material becomes crystalline (Nagaveni et al.,2004). Since the time is so short, hence the angle to rutile the infection is stopped.

C. Gas Phase Methods

The gas phase method is mentioned above for the production of thin films. Gas vapor can be done physically or chemically by chemical vapor deposition, which is a extensively utilize industrial method which is in short term (Jones and Chalker et al.,2003). During the process, titanium dioxide is shaped by the decomposition of a precursor of a chemical reaction. Physical vapor statement is one more thin film techniques. The film is made from the phase of gas, but without the chemical transition from the precursor to the product (Choy et al.,2003). Titanium dioxide, a concentrated beam of electrons for thin films, heats up the titanium dioxide material. The electrons are heated by a current with the tungsten wire. It is known as electron beam evaporation. In titanium dioxide films deposited with e-beam evaporation, CVD has better characteristics of increased films such as conductivity, lubrication, crystallization and pollution (Krol et al.,1997). Lower TiO₂ powder is necessary for the required conduction of electron beam on TiO₂.

D. Microwave Synthesis

Various titanium oxide materials have been synthesized using microwave disintegration. Crowway eliminates the use of high temperature calcination for extended periods of time and allows rapid transcription synthesis of crystalline titanium oxide nanometry (Corradi et al.,2005). Using microwave radiation, Coradi et al created colode titanium oxide nanoparticles suspension within 5 minutes (Guobin et al.,2005). High quality rutile rods were developed in the form of a combination of microwave synthesis and hydrothermal, while titanium oxide hollow and open-end nanotubes were synthesized through Routile crystals and anathesis in NaOH Solutions (Wu et al.,2005).

Table 1: Different Synthesis methods via different Characterization

S.No.	Types of synthesis	Advantage	Disadvantage	References
1.	Hydrothermal synthesis	1.High quality and greater sized crystals produced. 2. Nano-materials having higher vapor pressure can also be synthesized.	1.High cost of equipment. 2.Inability to monitor crystal formation in the growth process.	Kim et al., 2014
2.	Combustion synthesis	1.Low energy input. 2.Use of single equipment. 3.No inert gas & vacuum required. 4.High purity products.	1.Higher amount of carbon presence in final product. 2.products look sponge-like & highly porous.	Yeh, 2016
3.	Gas Phase Methods	1.Flexibility in structure & size of grains. 2.Materials to be put in grains & matrix can be chosen.	1.Coalescence and agglomeration of NPs is observed as very rapid quenching takes place.	Méndez-Rojas et al., 2018
4.	Microwave synthesis	1.Heat direct to the reaction & not vessel ; thus time saving. 2.Clean product formation. 3.Higher yields & versatility in reaction conditions.	1.Expensive equipment set-up. 2.Reaction monitoring not possible.	MIKROVALOV et al., 2011

IV. CHARACTERIZATION OF NANOMATERIALS

After the nanoparticles have been synthesized, there is a need to characterize them to know the various details related to their size, chemical bondings, topography and concentrations. Various tools and techniques have been used to characterize the nanoparticles some of them like UV-Vis spectroscopy, XRD analysis, FTIR, DLS, AFM, Energy Dispersive X-Ray Spectroscopy, SEM and TEM are being described here in detail.

A. UV-Vis Spectroscopy

UV-Visible Spectroscopy involves spectroscopy of photons in the UV-visible area as well as it uses visible light near UV and near-infrared ranges. In this field of electromagnetic spectrum, molecules pass through electronic transmissions. In this area of the electromagnetic spectrum, molecules pass through electronic transit (Lo et al., 2009). UV-Visible Spectrophotometer is mainly used to measure transparency or opaque and liquid absorption or transmission in liquid concrete. By sending a ray of light through this sample and doing so, then the remaining light is monitored in a detector. In the case of UV-Visible Spectrophotometer, the light is in wavelength of 800-200 nanometers, examining electronic transition in the sample. It is difficult to reach Wavelength less than two hundred nanometers because the oxygen starts to absorb light under the wavelength. When the light passes through the sample, some of the molecules in the sample will absorb the light on the various wavelengths of this spectrum, depending on their structure and chemical brand (Perkampus et al.,1992). For illustration, AgNPs generate a particular absorbance peak between 400 and 450 nm (Anandalakshmi et al.,2016), while zinc oxide nanoparticles have an absorbance peak between 355-380 nm (Gupta et al.,2018), due to the excitation mode of the surface Plasmon, which vary depending on the size of the nanoparticles.

B. XRD Analysis

XRD is a non-destructive type of analytical technique that provides valuable information about bonded angles, unit cell-dimensions, chemical composition, natural and manufactured materials of crystallographic structure, such as crystalline material mesh structure (Thodeti et al.,2016). XRD is based on X-ray theory of constructive related samples which should be crystalline. X-rays produced through CRT and are filtered simultaneously and are then guided and directed (Lo et al.,2009). The interactions that occur in this way create creative interventions based on the rules of the Bragg's, which interferes with the difference between the phenomena of radiation and the difference of the diffraction angle. X-ray powder diffraction is rapidly analytical technique, which is mainly used for the phase detection of crystalline material, as well as providing information on nuclear vacuum and unit cell amplitude (Bunaciu et al.,2015). X-rays are produced by cathode ray tubes, which are filtered to produce monochromatic radiation, are blown to focus and samples are directed and directed (Figure 2).

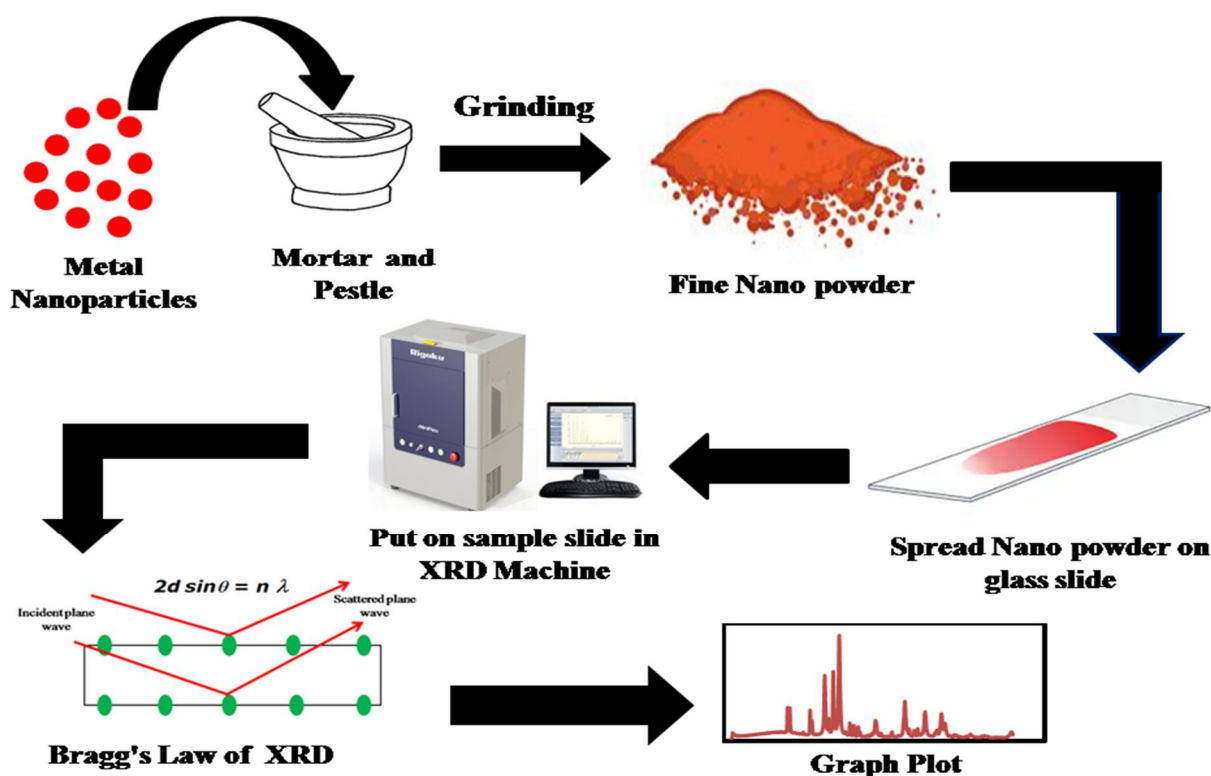


Figure 2: Sample preparation of XRD.

C. FTIR Analysis

Fourier-transform infrared spectroscopy is done to identify functional groups on nanoparticles. By using Fourier-transform infrared spectroscopy analysis, a solid gas or liquid infrared emission spectrum, Raman, photoconductivity or absorption can be calculated. Spectrums signify the fingerprint of nanoparticles, which has absorption in the air. Which are analogous to the frequency of vibration between nanoparticles in nanoparticles (Faraji et al.,2010). Since, there is a unique combination of atoms in each type of nanoparticles. Therefore, we identify functional groups within nanoparticles on the basis of Fourier-transform infrared spectra (Chauhan et al.,2012). It can help to facilitate the synthesis of nanoparticles using Green Technology. The number of functional groups present in the nanometer can be determined by the size of spectrum peaks. Transmission spectra for nanoparticles are obtained from the formation of thin crystal clear bromide pellets (Gupta et al.,2013). This contains the amount of interest. The KBR mixture is kept in one. Before making the bullet, vacuum lines and pellets are kept in the vacuum line before use again. After purifying the transmission spectra background and dry air, a reference is accurate in relation to the empty sample (Figure 3). With the application of modern software tools, quantitative analysis of nanoparticles has been completed within a few seconds (Prasad et al., 2011, Priya et al.,2011)

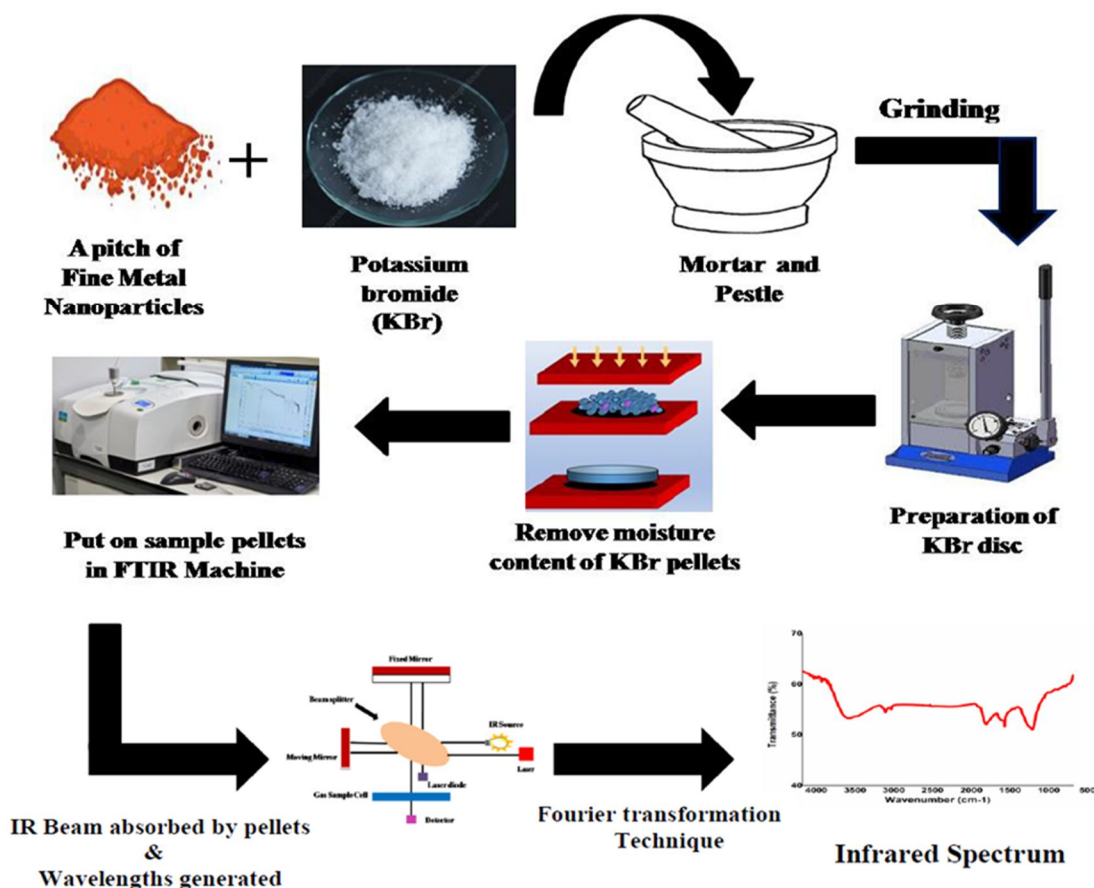


Figure 3: sample preparation FTIR.

D. DLS Analysis

The Dynamic light scattering is known as another photon correlation spectroscopy. Particles are one of the fastest formations and one of the most popular methods. Dynamic light scattering is used primarily to measure the size of Brownian nanoparticles in colloidal suspensions (Chauhan et al.,2012 Jaeger et al.,1991). When, a monochromatic ray of light is directed at the absorption of sphere-shaped particles in Brownian motion, then the doppler effect take place. When the light collides with moving particles, from which the value associated with particle size changes the wavelength of the inward ray of light. Therefore, Dynamic light scattering enables calculation of size distribution, as well as the speed of nanoparticles in the medium, can be calculated by measuring the spread of the particles (Saxena et al.,2010).

E. AFM Analysis

Atomic force microscopy is used to perform morphology of bimolecular and nanoparticles. Contrasting TEM and SEM, Atomic force microscopy produces 3D (three-dimensional) images. In order that height and particle quantity can be calculated. This method is capable of ultra-high resolution for particle size and is based on the physical suspension of samples at the submicron level using the test tip (Mucalo et al.,2002, Vesenska et al.,1993). Using Atomic force microscopy, evaluation of quantitative information about individual nanoparticles and groups of particles such as morphology, surface texture and size can be calculate by the help of seeding-based image processing (Chauhan et al.,2012). AFM can be done in a liquid or gas medium. For this technique, a small quantity of nanoparticles is spread over a glass wrapped on an AFM stub, as well as dehydrated with nitrogen gas at 25 °C. To enable interpretation of data, about 6 to 10 images can be taken for a only sample. Creates a topographic chart of the sample founded on the forces between the sample surface and the device tip, which are scanned in contact mode (Muhlen et al.,1996). On the basis of Sample Specific Properties, the probes are on the surface in non-contact mode and check starts. Atomic force microscopy is to create an image of a non-conductive sample without any whitespace treatment for the main advantage, as well as to create an image of nanostructure and delicate biological (65,68).

F. EDX Analysis

Energy-dispersive X-ray spectroscopy is an analytical technique used to describe the chemical symptom or radical analysis of the sample (Thodeti et al.,2016). This is one of the variants of X-ray fluorescence spectroscopy, Depending on the substance and the interaction between electromagnetic radiation, hitting the charged particles and analyzing the X-ray emitted by the reaction in the case (Prasad et al.,2011).

Its specialization ability are due to the bulky part of the basic theories that every element has a single atomic structure that allows X-rays, which are characterized by the identification of the atomic structure of an element to each other (Ali et al.,2011). To stimulate X-ray emissions from a specimen, a sample focuses on sampling being charged to charged particles like protons or electrons or a high beam of a beam of X-rays.

During relaxation, the discrete energy level or electrons in the nucleus within the sample are grounded electrons in the electron shell. Event beam can stimulate an electron in an electron solution while making an electron-hole, it extracts it from the solution where the electron was. An electron then fills the hole from an external high energy cell and the dissimilarity between energy between the high energy cell and the inferior energy cell can be released as X-rays. The energy and the number of X-rays produce from a sample can be calculated by an energizing spectrometer. Since the energy of X-rays are the characteristics of energy between the atomic structure and two shells of that element from which they were emitted. This permits measuring the elemental structure of the sample (Patra et al.,2014).

G. SEM Analysis

A scanning electron microscopy is a type of electron microscopy that scans a sample by scanning the electron's elevated energy insurance in a linear scan pattern (Pal et al., 2011). The electrons interact with the atom, which creates sample output signals containing information about topography, sample surface structure and other properties like electrical conductivity. (Thodeti et al.,2016). SEM can produce very high-resolution images of the sample surface, revealing the details of less than 1 to 5 nanometers in size. Due to the very narrow electron beam, a micrograph of SEM has a large depth of dimensional presence area to understand the surface structure of a sample (Gupta et al., 2013; Jores et al., 2004). Under the vacuum, electrons generated by a source are accelerated into one gradient area.

The beam passes through electromagnetic lenses, which focus on samples. As a result of this bombing, different types of electrons are emitted from the sample. A detector caters the secondary electrons, as well as an image of the sample surface compared to the intensities of these secondary electrons compared to the scanning electron beam. Finally, the image displays on a monitor (Thodeti et al., 2018).

The data collected in most applications is much more than a previously selected area of the sample surface, and after that, a 2D image is generated which shows different spatial variations. With a spatial resolution of 50-100 nanometers, conventional beams with a magnification range of 20X-30000X can scan areas that vary in width from 1 cm to 5 micrometers (Prashanth et al., 2011). SEM also has the ability to analyze specific points, which EDX can be seen during operation, which help in determining the chemical composition of the respective sample (Priya et al.,2011).

H. TEM Analysis

A transmission electron microscopy is done; (A) To create an image of the plane and diffraction in the focal plane behind the objective lens, (B) to concentrate the electron beam on the sample of two or three condenser lenses (C) increase the image or diffraction pattern on the screen for some intermediate lenses (Thodeti et al., 2016). If the samples are thin (<200 nanometers) and is formed of elements of light chemicals, they present very little contrast when the image is concentrated (Chauhan et al.,2012, Prasad et al.,2011, Saxena et al.,2010).

If diffraction is formed by several diffraction phases then each of them can be differentiated by selecting one of the beams with its detachable diaphragm. To do this, the event beam should be tilted so that the object is placed on the lens axis to avoid the axial axis aberration of the tectonic beam.

This mode is called dark field mode. DF and BF modes are used for imaging materials on the nanometer scale. To obtain the symmetry of its lattice and to calculate its Inter planner distance, a crystal permit is based on the SAED and micro diffraction patterns. It is usually useful to confirm the identification of one phase after assumptions (Profeta et al.,2005, Mallikarjuna et al.,2011, Vahabi et al.,2011).

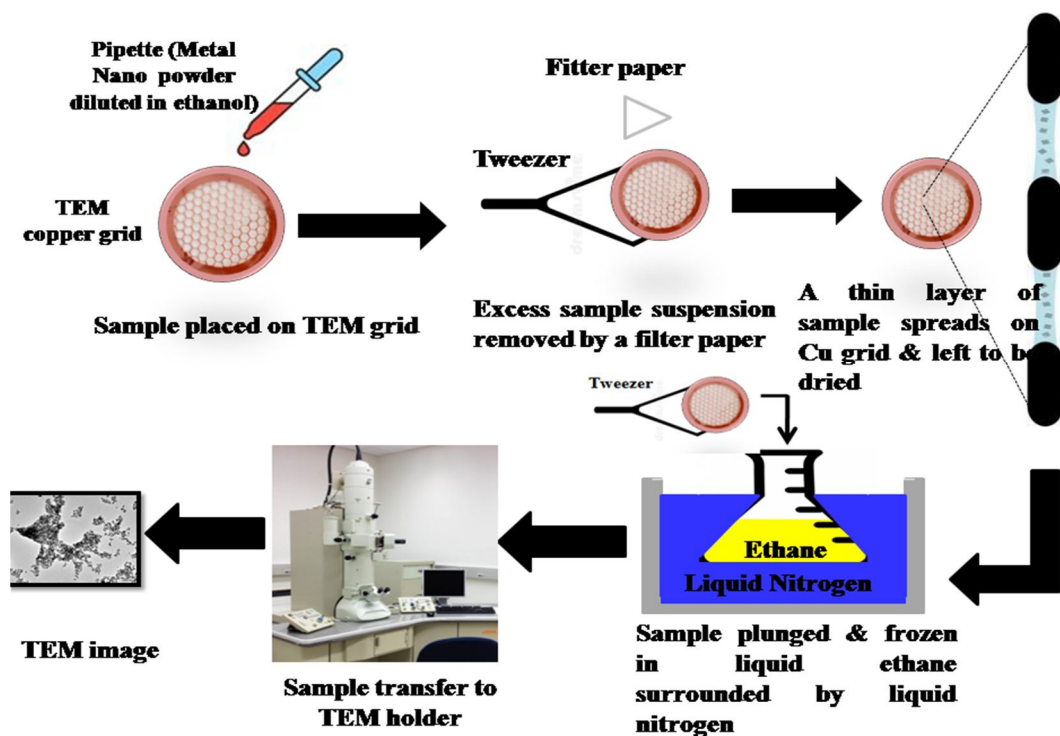


Figure 4: sample preparation TEM.

V. APPLICATION OF NANOPARTICLES IN BIOFUEL PRODUCTION

Because of the positive impacts on the metabolic reactions of the bioprocesses, the use of nanoparticles is gaining importance in biofuel manufacturing processes. In biofuel manufacturing processes, various nanomaterials such as nanofibers, nanotubes and metallic nanoparticles were recorded (Ramsurn and Gupta, 2013, Sharma et al., 2020). It has also been demonstrated that nanoparticles can boost the activity of microorganisms by increasing electrons transfer in metabolic processes. Several metals (nanoparticles) have been reported to enhance the dark- fermentative biohydrogen production (Rai et al., 2014). Zhang and Shen (2007) reported improvement in the substrate utilization efficiency by 56% by adding 5 nm gold nanoparticles. This stimulatory effect of gold nanoparticles on biohydrogen-production is due to the large surface-area-to-volume-ratio for bacteria to bind in active sites of molecules. Zhao et al.,(2013) explored the impacts of silver nanoparticles on the dark fermentative biohydrogen production in anaerobic batch reactors. They reported the addition of silver nanoparticles enhanced the substrate conversion ultimately lead to a maximum biohydrogen yield. They suggested that nanoparticles reduced the lag phase of the inoculum and favored the acetic acid pathway i.e., the main biohydrogen producing pathway. Nanoparticles were also used in Photo- fermentative biohydrogen production to observe the effect. Dolly et al. (2015) utilized co-cultures of *Rhodobacter sphaeroides* NMBL02 and *Escherichia coli* NMBL04 to evaluate the impact of iron nanoparticles on the production of biohydrogen. They reported 20% increase in biohydrogen yield by the addition of iron nanoparticles. Nanoparticles were also used to enhance the activity of photosynthetic microalgae producing biohydrogen. Studies showed the implementation of nanoparticles in algal biotechnology boost the development of biomass and physiological functions in microalgal species such as photosynthetic activity, nitrogen metabolism and protein levels (Eroglu et al., 2013). Silver nanoparticles and gold nanorods enhanced the photosynthetic activity of *Chlorella vulgaris* in batch processes (Eroglu et al., 2013). TiO₂ nanoparticles were also used to enhance biohydrogen production rate by 50 % in photosynthetic *Rhodobacter sphaeroides* NMBL02 (Pandey et al., 2015).

The supplementation of nanoparticles has shown promising results in anaerobic digestion processes, particularly in biogas production by increasing the hydrolysis of organic matter (Romero-Guiza et al., 2016, Gupta et al.,2020). This higher conversion was attributed to the large surface-area-to-volume-ratio provided by the nanoparticles for microorganisms to bind in active sites of molecules, ultimately results into enhanced biochemical processes (Ahmad et al., 2018). Gonzalez-Estrella et al. (2013) studied the impact of eleven nanoparticles on methanogenic activity using anaerobic granular sludge as an inoculum. It was found that CuO and ZnO showed high inhibitory effects on methanogenic species. Luna-delRisco et al., (2011) investigated the effect of CuO and ZnO nanoparticles on biogas production using cattle manure.

The use of nanoparticles has appeared as a new technology that can be used to achieve efficient biodiesel production (Chen et al., 2018). It was shown that the inclusion of nanoparticles during the transesterification phase increases the catalytic effectiveness. The impacts of $\text{Fe}_3\text{O}_4/\text{ZnMg}(\text{Al})\text{O}$ magnetic nanoparticles on biodiesel production using microalgal oil were assessed by Chen et al. (2018). The catalyst showed outstanding magnetic responsiveness and a high area-to-volume ratio that favored biodiesel production, resulting in a high efficiency of 94%. In addition, after seven cycles, the conversion of biodiesel was above 82 percent and the nanocatalyst could be recovered. Tahvildari et al. (2015) investigated the impacts of nanocatalysts of CaO and MgO on the production of biodiesel from waste cooking oil. Experimental findings have shown that the use of both nanocatalysts has maximized the output of biodiesel production. As a result, yield of 98.95 percent was achieved using 0.7 g of CaO and 0.5 g of MgO nanoparticles at a methanol-to-oil ratio of 7:1, a reaction time of 6 h. Dantas et al. (2017) reported Cu^{2+} doping in magnetic nanoferrites ($\text{Ni}_0.5\text{Zn}_0.5\text{Fe}_2\text{O}_4$) during the methyl transesterification of soybeans oil enhanced biodiesel production yield of 85%. The implementation of nanoparticles in biodiesel manufacturing guarantees that the method is economically feasible because catalyst regeneration and reusability outcomes in elevated effectiveness of biodiesel conversion as documented various studies Chiang et al., 2015; Bet-Moushoul et al., 2016).

Enhancement in bioethanol production using nanoparticles is also under investigation by various groups across the world. Cherian et al. (2015) cellulase was immobilized in MnO_2 nanoparticles to study the conversion of sugarcane leaves to bioethanol. The immobilized cellulase was able to hydrolyze cellulosic materials over a wide range of temperatures and pH, resulted into high bioethanol yield (21.96 g/L). It was also reported that enzyme retained 60% of catalytic activity, even after five cycles. β -galactosidase immobilized in SiO_2 nanoparticles for the hydrolysis of whey resulted in high bioethanol yield of 63.9 g/L. The immobilized β -galactosidase was reused up to 15 times during hydrolysis, without major loss in catalytic activity (Beniwal et al., 2018). Enzyme β -glucosidase involved in bioethanol production, when immobilized in Fe_3O_4 nanoparticles showed a binding efficiency of 93% and more than 50% of catalytic activity after 16 cycles (Verma et al., 2013). Immobilized cells of *S. cerevisiae* using magnetic nanoparticles showed a high bioethanol production rate with a productivity of 264 g/L.h during the fermentation process (Ivanova et al., 2011).

VI. CONCLUSION

It is evident from the various studies that Biofuel production could be enhanced by utilizing nanoparticles. This promising approach has the potential to address the problem of low yield of biofuels. A number of organisms as pure or mixed cultures were reported to produce biofuel in the presence of nanoparticles from various organic materials. However, their efficiencies in production varied considerably with the type and concentration of nanoparticles. Many technical obstacles need to be resolved in order to speed up their implementation in biofuel production processes. For example, the nanoparticle utilized should be nontoxic to microorganisms, less expensive, and should be environmentally friendly. Further studies related to exact mechanism of nanoparticles interaction with the microorganisms during biofuel production is required.

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