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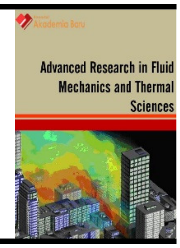

Nanoparticles: A Review on their Synthesis, Characterization and Physicochemical Properties for Energy Technology Industry

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ABSTRACT

In this paper, an overview about nanoparticles (NPs), their synthesis, characterizations, thermal properties and applications is discussed. Specific morphology, size and magnetic properties of NPs can be controlled by NP synthetic techniques. NPs have a size range of between 1-100 nm. This tiny structure will cause NPs to have a large surface area that correlates with their physical and chemical properties. They can be classified into different classes based on their properties, shapes or sizes. The different groups include fullerenes, metal NPs, ceramic NPs and polymeric NPs. The physicochemical properties of NPs are the main characteristics used in determining the specific functions among the various applications of NPs. Due to their characteristics; they are widely used in various applications including the energy technology industry, medical, imaging and environmental applications. However, some NPs have disadvantages such as environmental toxicities which will be taken into account for further improvements.

1. Introduction

Nanoparticles (NPs) are materials produced via nanotechnology method. According to Laurent [1], NP physical properties, with size of less than 100 nm, include various types of materials with particular substances. NPs are divided broadly into various categories based on their sizes, morphologies and chemical compositions. These groups or categories include carbon-based NPs, metal, ceramic, semiconductor, lipid-based and semiconductor NPs. Nanoparticles have enormous surface-to-weight ratio and they have special properties that differ from the parent material. Variance dimension on NP structure leads to the divergent of physiochemical properties which will be discussed in this review. For example, Figure 1 shows the scanning electron microscope (SEM) and

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transmittance electron microscope (TEM) images of mesoporous and nonporous methacrylate-functionalized silica (MA-SiO_2). Lee *et al.,* [2] reported that, mesoporosity imparts additional characteristics in NPs which can be employed for drug delivery. NPs are complex molecules of materials by themselves. They comprise three component-structured layers as shown in Figure 2.

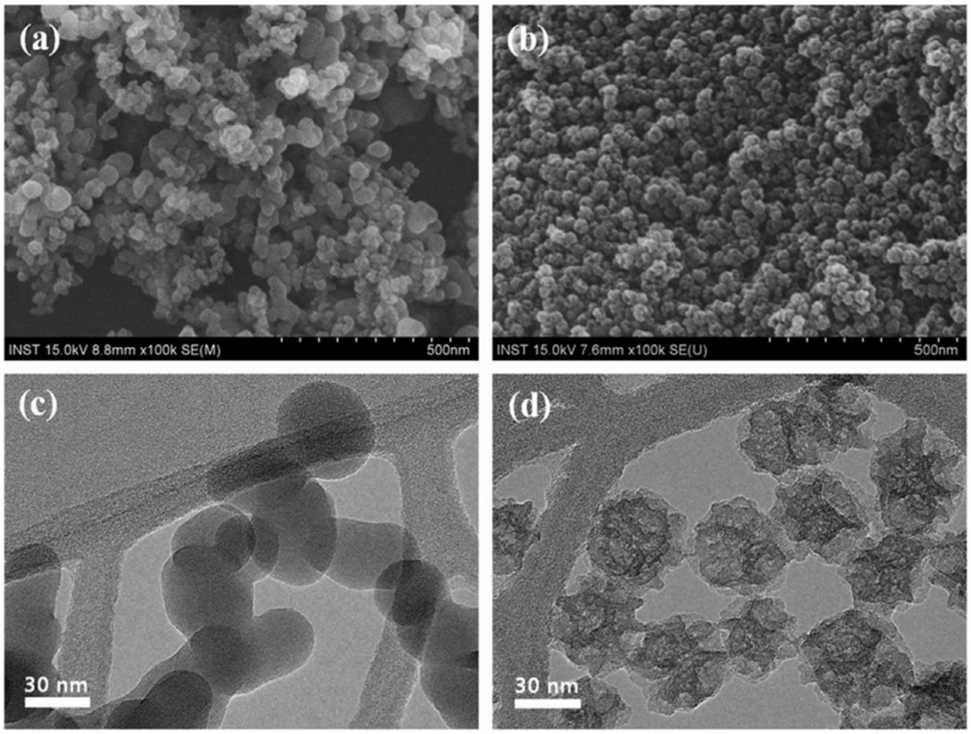

Fig. 1. FE-SEM micrographs of (a) nonporous MA-SiO_2 NPs and (b) mesoporous MA-SiO_2 NPs. TEM images of (c) nonporous MASiO_2 NPs and (d) mesoporous MA-SiO_2 NPs [2]

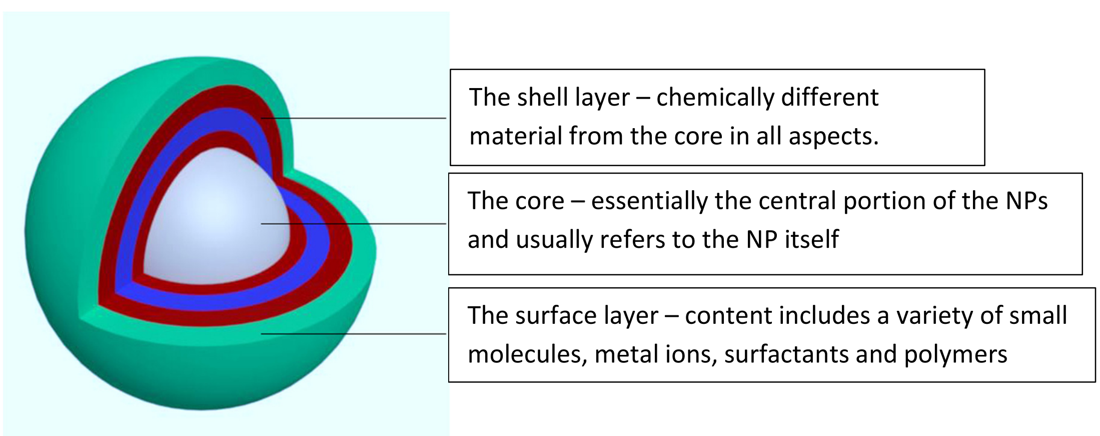

Fig. 2. Schematic of nanoparticle component-structured layers [3]

1.1 Classification of NPs

In order to classify the elements of NPs, four factors will be considered, which consist of types of NPs, their chemical properties, morphologies and sizes. However, NPs are mainly divided based on their chemical characteristics and physical properties as the majority of the stated properties would affect the effectiveness of NP application. The classification of NPs is simplified as in Figure 3.

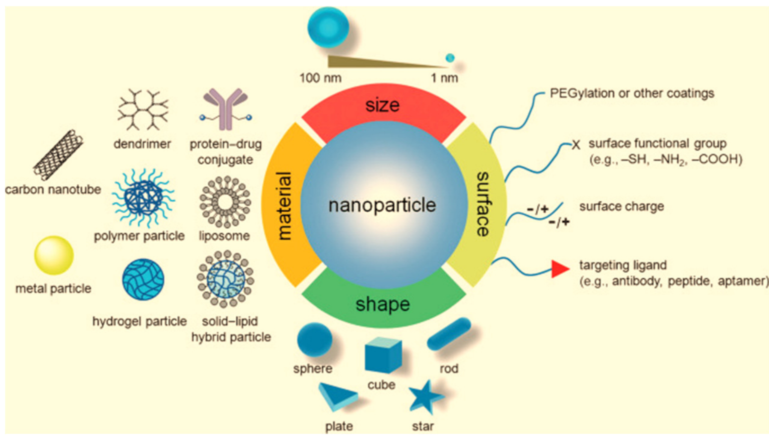

Fig. 3. Major classification of NPs [4]

2. Synthesis of Nanoparticles

The synthesis of NPs is classified into two methods which are the bottom-up and top-down syntheses as shown in Figure 4 below. The approach is further divided into various subclasses based on the operation, reaction condition and adopted protocols. This can be illustrated briefly by the synthesis of graphene oxide (GO) nanoparticles. The GO nanoparticles were synthesized to improve stability and dispersibility in electrochemical sensor application due to their excellent and exceptional thermal, mechanical and electrical properties [5].

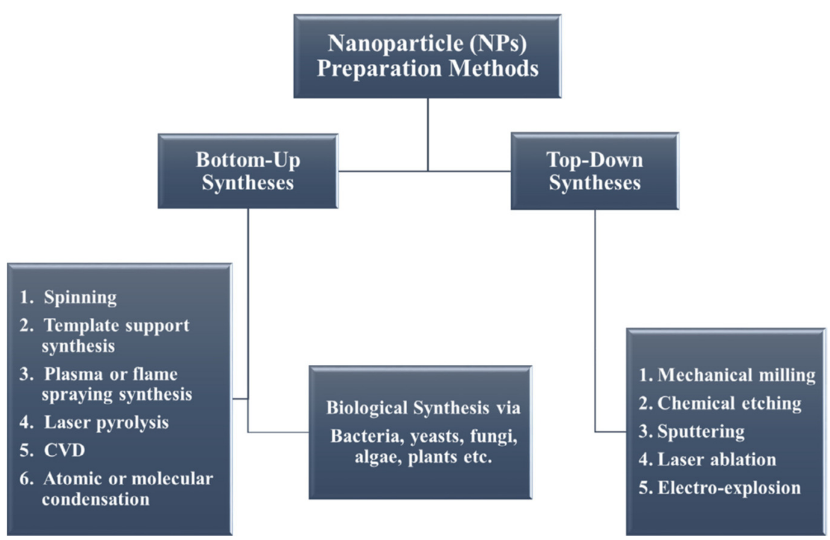

Fig. 4. Typical synthesis methods for NPs [6]

The effectiveness of the synthesis methods was exemplified in a report by Saleh *et al.,* [7], using fluorine doped tin oxide (FTO) material. The material was prepared by using bottom-up synthesis which employed nebulizer spray and electro-spinning techniques. The result showed that the spray technique enhanced the electrical and optical properties of the FTO films which can be implemented in solar energy applications especially as heat mirrors for solar collector.

2.1 Preparation of NPs

Synthetic polymers, proteins and polysaccharides are among the materials used in producing NPs. The preparation of NPs depends on factors discussed in the classification of NPs above. The NP preparation factors are shown in Figure 5 [8]. The size of NPs is determined between 1-100 nm depending on the optimum size which is applicable for the related applications. On the other hand, surface characteristic is slightly related to the morphology of the NP itself. Divergent in structure, dimension and surface area would lead to the different properties of NPs. Thermo-physical properties and chemical reactivity are common properties in considering NPs as catalyst agents. In addition, intrinsic and optical properties of NPs are also implemented in variance applications.

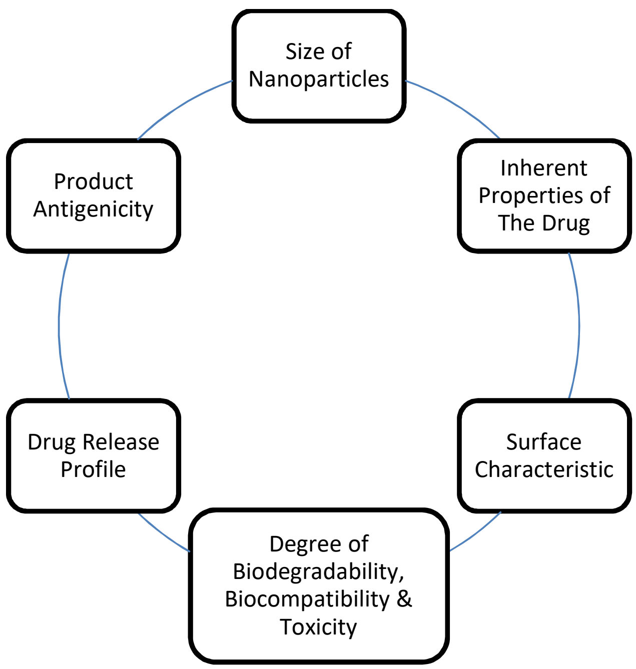

Fig. 5. Factors in NPs preparation

Apparently, there are three common methods in the preparation of NPs, which are dispersion of preformed polymers, polymerization of monomers and ionic gelation or coacervation of hydrophilic polymers. In this review, the dispersion of preformed polymers method is prioritized to be discussed as below.

Practically, biodegradable NPs are usually made via poly (lactic acid) (PLA); poly (D,L-glycolide), (PLG); poly (D, L-lactide-co-glycolide) (PLGA) and poly (cyanoacrylate) (PCA), [9-11] by using the dispersion of preformed polymers method. This method can be classified into different techniques simplified as follows.

2.1.1 Solvent evaporation method

Figure 6 shows the steps for preparing NPs by using the solvent evaporation method. For the present research, the polymer concentration, stabilizer type and concentrations and homogenizer speed were found to affect the particle size [12]. According to Zambaux *et al.,* [13], a high-speed homogenization or ultrasonication may result in the production of small-sized particles.

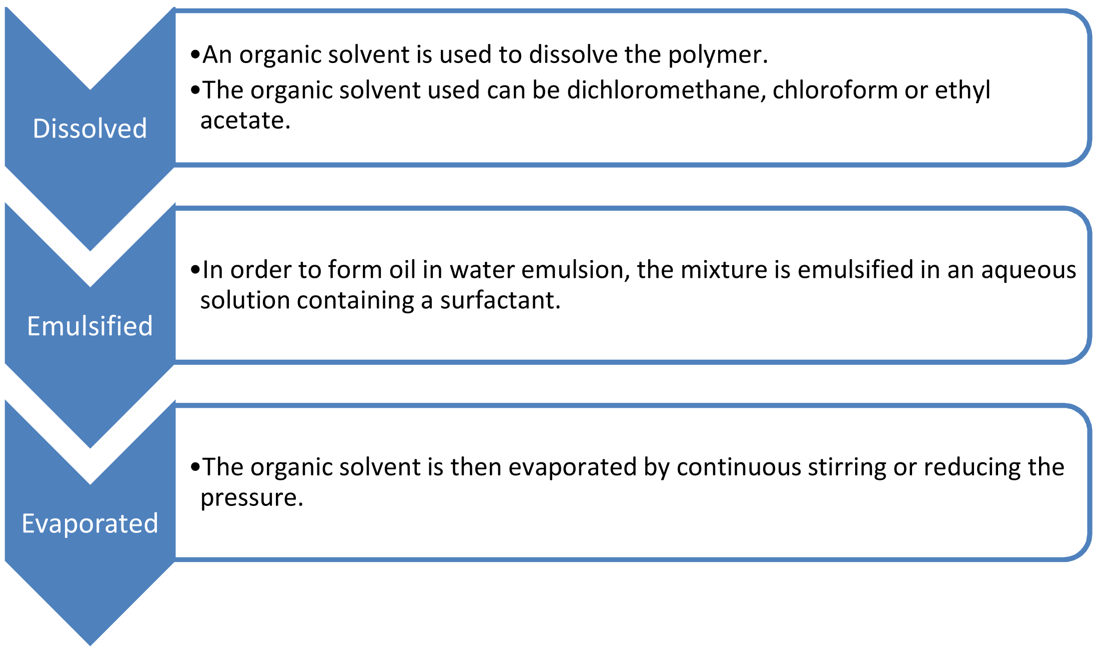

Fig. 6. Simplified steps for solvent evaporation method

2.1.2 Spontaneous emulsification or solvent diffusion method

Spontaneous emulsification or solvent diffusion method is an improved version of the solvent evaporation method [14]. This method is initiated by an oil phase, which forms a homogeneous mixture solution containing water and organic solvent. Then, the formation of tiny particles occurs as a result of the spontaneous emulsification of solvent. This is an effect of interfacial turbulence created between the two phases of mixture. Particle size decrement can be attained by increasing the concentration of water-miscible solvent.

Both methods can be applied in either hydrophobic or hydrophilic drugs. In addition, other methods, as reported by Reverchon and Adami [15], such as supercritical fluid technology and particle replication in non-wetting templates (PRINT) as addressed by Rolland *et al.,* [16], have also been defined in the literature for NP preparation. However, recent researchers are interested to have infinite control of particle size, shape and composition, which would be the guidelines for the future mass production of NPs in the industry.

3. Nanoparticles Characterization

Currently, there are four different characterization techniques for the analysis of various physicochemical properties of NPs as explained in Table 1 below.

Table 1
Characterization techniques for NPs

Characterization Technique	Summary
Morphological	NP properties are always influenced by morphology. Various techniques for morphological characterization, scanning electron microscope (SEM), polarized optical microscopy (POM) [17] and Transmission electron microscope (TEM) [18] are the common microscopic techniques used during characterization.
Structural	In structural characterization technique, infrared (IR), X-ray diffraction (XRD) [19], energy dispersive X-ray (EDX), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and Zeta size analyzer are some of the important methods used to study the structural properties of NPs such as the nature and composition of bonding materials.
Particle size and surface area	According to Kestens *et al.,* [20], the characterization techniques include XRD, SEM, atomic force microscope (AFM), TEM, and dynamic light scattering (DLS). However, SEM, TEM, XRD and AFM can give better ideas about particle size while the Zeta potential size analyzer/DLS is commonly used to find the NP size at an extremely low level.
Optical	Optical characterization is widely used in photocatalytic applications as the mechanism of photochemical processes. These characterizations are based on the famous beer-lambert law and basic light principles [21]. Furthermore, this technique is important in obtaining the absorption, reflectance, luminescence and phosphorescence properties of NPs. Ultraviolet–visible (UV–Vis), photoluminescence (PL) and the null ellipsometer are widely deployed as optical instruments, to study the optical properties of NP materials. Moreover, the UV/vis-diffuse reflectance spectrometer (DRS) is a fully equipped device that is used to measure the optical absorption, transmittance and reflectance.

The characterization techniques stated above employ techniques such as X-ray diffraction (XRD), particle size analysis, X-ray photoelectron spectroscopy (XPS), infrared (IR), SEM, TEM, and Brunauer–Emmett–Teller (BET). The evidence of NP characterization can be clearly seen in the case of microgel characterization as reported by Rifa'i *et al.,* [22]. Characterization techniques using SEM showed the morphology of microgel images, while Fourier-transform infrared spectroscopy (FTIR) was used to determine the chemical structure and confirm the crosslinking of microgels.

4. Nanoparticles Physicochemical Properties

The physicochemical properties of NPs are classified as a large surface area, mechanically strong, optically active and chemically reactive; making the NPs unique and in demand for various applications. In this review, the NP thermal properties are discussed in the following sections.

4.1 Nanoparticles Thermal Properties

As metal NPs possess thermal conductivities that are higher than those of fluids in solid form, they are expected to exhibit significantly enhanced thermal conductivities compared to those conventional heat transfer fluids. Fluids that encompass NPs, known as nanofluids, are produced by dispersing the nanometric scales solid particles into liquid such as water, ethylene glycol or oil. Therefore, nanofluids are expected to perform a desirable thermal conductivity property. A larger total surface area becomes a better heat transfer as it takes place at the surface of the particles. Besides that, the stability suspension will also be influenced by the total surface area of NPs [23]. Recently, it has been demonstrated that, nanofluids that consist of CuO or Al_2O_3 NPs in water or ethylene exhibit advanced thermal conductivity [24]. In a similar case in Malaysia, Lee [25] showed that, the use of NPs in water heat exchanger was significant in affecting the optimal efficiency by adding 1.5% volume fraction of copper (Cu) or alumina (Al_2O_3) in water-based nanofluids.

4.1.1 Grain boundaries and size effects in effective thermal conductivity

A correlation of effective thermal conductivity (ETC) between grain size, single crystal phonon mean free path (PMFP) single crystal thermal conductivity, and the Kaptiza thermal resistance was proposed by a theoretical model [26]. The studies reported on the relative importance between grain boundaries (GBs) and size effects on the ETC of nanocrystalline diamond as the subject. The results showed that the increase in grain size would lead to weaker GBs and size effects. However, the size effects became stronger on thermal conductivity than the GBs effects.

5. Nanoparticles in Energy Harvesting

Research found that only 9% of renewable energy is consumed to fulfill the energy demand as shown in Figure 7. This will affect the level of greenhouse gas emission and global warming due to increasing atmosphere temperature. Therefore, it is necessary to find alternative ways in renewable energy supply.

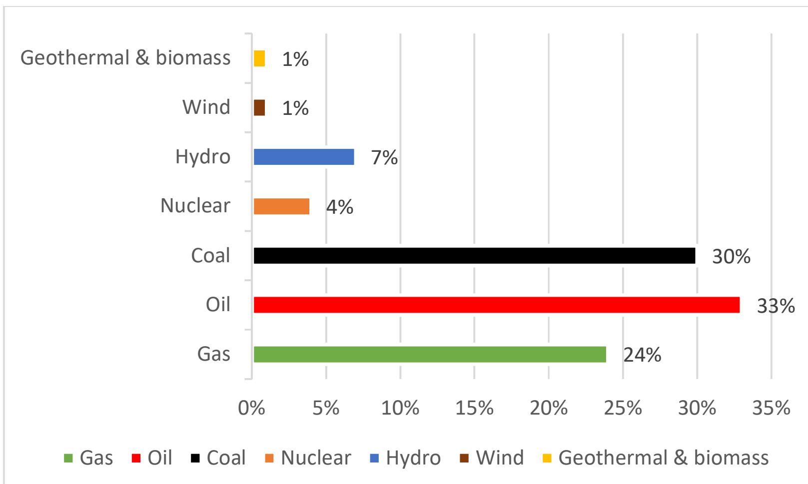

Fig. 7. Global energy consumption in 2013 [27]

NPs have a large surface area, good optical behavior and catalytic nature. These characteristics make NP the best alternative way in renewable energy supply. The applications of NPs are as follows:

- ✓ NPs are widely used especially in photocatalytic application to generate energy from photo electrochemical (PEC) and electrochemical water splitting [28].
- ✓ Besides water splitting, electrochemical CO_2 reduction to fuel precursors, solar cells and piezoelectric generators also offer advanced options to generate energy [29].
- ✓ NPs are also used in energy storage applications to reserve the energy into different forms at nanoscale level [30].
- ✓ Recently, with the creation of nanogenerators, mechanical energy can be converted into electricity using piezoelectric, which is an unconventional approach to generate energy. Figure 8 shows some energy generating devices and uses of NPs.

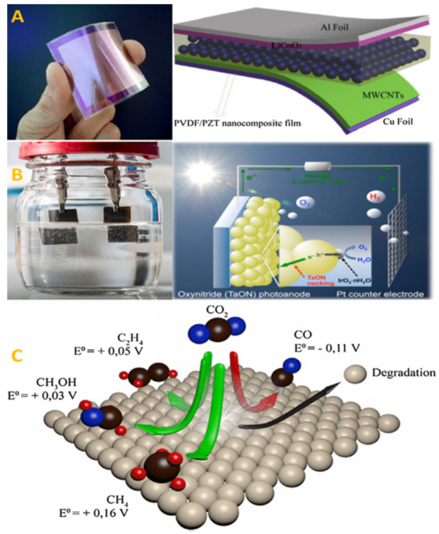

Fig. 8. Energy generation approaches from (A) Piezoelectrics actuators, (B) Water splitting, and (C) CO_2 reduction [31]

6. Toxicity of Nanoparticles

Although NPs have advantages such as smaller size, high reactivity and great capacity, they could also bring potential harmful effects on both human and the environment. The lethal and toxicology effects of NPs can be explained where the tiny particles can enter organisms during ingestion or inhalation and can translocate within the body to various organs and tissues. Toxicological studies with magnetic NPs are available, but limited. According to Navarro *et al.,* [32] common Ag NPs are being used in numerous consumer products. Thus, this will lead to the release of dissolved Ag into the aquatic environment and exert toxic effects on aquatic organisms including fish, algae, bacteria, etc. Moreover, the respiratory system of the living creature represents the main target for potential toxicity of NPs because apart from being the portal of entry for inhaled particles, it also receives the entire cardiac output [33].

7. Conclusions and Recommendations

In this review, an overview about NPs, their synthesis, characterizations, thermal properties and applications was discussed. The tiny size of NP causes it to possess a large surface area, which appoints it to be the best candidate for various applications. Besides, photocatalytic applications also reap the benefits of optical properties that are also dominant with NP size. The specific morphology, size and magnetic properties of NPs can be controlled by the NP synthesis techniques.

Based on the review, some recommendations can be made for future works regarding the reaction parameters of NPs synthesis methods. Parameters such as temperature, pressure, time, and pH can be the important factors in controlling the physical structure of NP materials. As a result, optimization and specific characteristics of a product can be attained. In addition, the invented synthesis method will be the route for the property study of specific characterization techniques. On the other hand, there are some disadvantages of NP usage that are related to health hazards if it is used without control and discharged to the natural environment, which should be considered in future studies.

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