Synthesis and characterization of NaGdF4:Nd³⁺@Ni Core@Shell nanoparticles with potential applications in anaerobic digestion

G. S. Aguilar-Moreno^a, T. Espinosa-Solares^b, J. M. Santos-Gaspar^b,

E. Montes-Ramírez^c, M. Á. Aguilar-Méndez^a, L. Martinez-Maestro^d, E. Navarro-Cerón^{e,*}

^a National Polytechnic Institute, Center for Research in Applied Science and Advanced Technology - Legaria Unit. Legaria no. 694, Col. Irrigación, Mexico City, C. P. 11500, Mexico

^b Chapingo Autonomous University, Department of Agroindustrial Engineering, Carretera México-Texcoco km 38.5, Texcoco, State of Mexico, C. P. 56230, Mexico

^c University of Guanajuato, Campus León, Division of Sciences and Engineering, Lomas del Bosque 103, Lomas del Campestre, León, C. P. 37150, Guanajuato, Mexico

^d Complutense University of Madrid. Av. Complutense s/n, Madrid, C. P. 28040, Spain

^eational Research Laboratory, and Agri-Food and Forest Service (LANISAF), Universidad Autónoma Chapingo, Department of Agro-industrial Engineering, Carretera México-Texcoco km 38.5, Texcoco, State of Mexico, C. P. 56230, Mexico

The NaGdF₄:Nd³⁺@Ni core@shell nanoparticles were synthesized and characterized. First, core@shell nanoparticles were synthesized using a solvothermal method to obtain the NaGdF₄:Nd³⁺ core with hexagonal phase; subsequently, a chemical reduction was performed to stimulate the growth of the Ni shell with cubic phase. NaGdF₄:Nd³⁺@Ni nanoparticles were characterized by transmission electron microscope, zeta potential, X-ray diffraction, scattered energy spectroscopy, UV-Vis, and photoluminescence emission spectra. The nanoparticles were round in shape, with mean sizes around 250 nm. The core@shell nanoparticles presented a homogenous composition and good stability. The photoluminescent emission of the nanoparticles was recorded at 1059 nm in the near-infrared spectral range; this band corresponds to the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ radiative transitions of Nd³⁺ ions. The synthesized nanoparticles, being hydrophilic, have potential for use in different areas, one of them could be in anaerobic digestion.

(Received May 18, 2023; September 11, 2023)

Keywords: Luminescent nanoparticles, Core-shell, Near-infrared, Nickel nanoparticles, Optical properties

1. Introduction

Nowadays, the effect of climate change due to pollution is one of the most relevant problems. Therefore, many countries have focused their efforts on reducing their dependence on non-renewable energy sources and, at the same time, on obtaining alternative fuels from biological resources [1]. Bioenergy production is one of the strategies aimed at reducing the emission of greenhouse gases and treating waste for generating energy [2].

Biogas is a secondary energy source that can be produced from different types of organic materials through anaerobic digestion (AD) [3]. Some of the most used materials for biogas production are, among others, sewage sludge, food waste, agricultural waste, and animal excreta [4].

^{*} Corresponding authors: nava_lice@yahoo.com.mx https://doi.org/10.15251/DJNB.2023.183.1093

1094

In order to enhance biogas production using animal excreta, many researchers have incorporated in AD processes micro-nutrients, such as Fe, Ni, Co, W, and Mo, that are considered decisive cofactors for methane formation in biochemical reactions [5]. However, the excessive use of micronutrients can inhibit the AD process [6].

With the nanotechnology revolution, it is possible to develop nanometric materials that improve biogas production in AD, and thus be able to incorporate small amounts that do not inhibit the process [7]. Different researchers have used metallic and magnetic nanoparticles (NPs) as trace metal additives in biogas production. Ajay et al. [8] reported that direct interspecies electron transfer, using conductive materials, has gained importance in the explanation of the influence of NPs on biogas and methane production. These authors concluded that Fe NPs showed a positive effect on AD, while Ag, Ce, CuO, and ZnO NPs showed a negative effect on biogas production. Abdelsalam et al. [9] found that Ni NPs generated the highest methane production in bovine slurry AD, compared to that obtained with Co, Fe, and Fe₃O₄ NPs. Chen et al. [10] studied two types of Ni NPs and reported that Fe₄NiO₄Zn and Fe₂NiO₄ NPs have negative and positive effects on AD activity, respectively. Abdallah et al. [11] used Ni-Co-Ferrite and Ni-Ferrite NPs, and observed an increase in biogas and methane production of 32.9 and 30.8 %, respectively, compared to the treatment without NPs. During the AD of microalgae biomass, Zaidi et al. [12] compared the influence of different concentrations of Ni (1 mg/L), Co (1 mg/L), Fe₃O₄ (10 mg/L), and MgO (10 mg/L) NPs, and observed that Ni NPs presented the highest hydrogen production (51.42 %, v/v); this fact becomes relevant in the AD of the consortia where hydrogenotrophic methanogenesis is more important.

In this context, our research group [2], by adding 20 mg/L of Fe₃O₄ NPs, increased the methane production rate by 73.89 %. This result was attributed to the fact that the NPs acted as electron carriers, improving biogas and methane production. However, despite the favorable response of NPs on biogas production, the action mechanisms of nanomaterials in AD are still unknown [13]. An alternative to demonstrate such mechanisms could be the use of luminescent NPs (LNPs), which can be housed in AD consortia. LNPs have a significant impact on the imaging of cells and microorganisms, both in vivo and in vitro [14]; because of that, they could be used to explore the interaction of different groups of microorganisms during the biogas production processes.

Recently, due to their optical properties, such as high photostability, sharp emission peaks, deep optical penetration, and low toxicity [15], research on rare earth LNPs and inorganic materials have drawn attention, as they are ideal candidates for bioapplications, such as labeling and image [16]. Inorganic nanomaterials doped with lanthanide ions have been widely used in biological and medical sciences (drug delivery and bioimaging), agriculture, and the optoelectronics industry [17]. An example of these materials is those based on gadolinium and doped with lanthanide ions, which can be used for bioimaging, illumination, temperature sensors, visualization devices, and as a catalyst [18, 19].

Compounds containing rare earths are known for their excellent optical properties, which can be attributed to their 4f electronic structure [20]. Yb^{3+} is the co-dopant and sensitizer most used in NPs doped with rare earths; however, Nd^{3+} is gaining interest as a sensitizer due to its absorption [21]. The replacement of the Yb^{3+} ion by Nd^{3+} allows changing the excitation range to 808 nm instead of 980 nm, which improves the penetration of biological material and minimizes the damage caused to biological tissues [22]. The excitation and emission wavelengths of Nd^{3+} are in the "optical transparency window" of cells and microorganisms, which is in the near-infrared (NIR) range of 700 - 1350 nm. [23]. That is, Nd^{3+} doped NPs can be excited in the first biological window (I-BW, from 700 - 950 nm) and emit in the second biological window (II-BW, from 1000 - 1350 nm). [24, 25].

Recently, NaGdF₄ has been used in nanomaterial preparation, as it has turned out to be an excellent host [26] due to its high photochemical stability, low photon energy (\sim 350 cm-1), high transparency in the UV-Visible and NIR regions, and high ability to mediate energy exchanges between lanthanide ions [27].

Considering the characteristics of NaGdF₄ and Nd³⁺ ions, several researchers have evaluated their properties and effects when mixing them with other materials. For example, Sengar and Narula [19] evaluated the photoluminescence and energy transfer mechanism of NaGdF₄@CaF₂:Eu³⁺ NPs

doped with Nd³⁺ and Yb³⁺, and found that the concentration of these lanthanides has a significant effect on emission intensity and energy transfer. Xi et al. [28] evaluated the toxicity and influence of NaGdF₄:Nd³⁺@Fe³⁺ NPs on microbial communities in a fermentation system and found that these NPs can serve as efficient biomarkers of exogenous electron carriers in bacteria.

To our knowledge, there are no reports on NaGdF₄:Nd³⁺@Ni NPs, which may have potential in several areas. According to various researches, Ni NPs have gained great importance in the last two decades due to their unique magnetic, chemical, and physical properties [29]; in addition, they present multiple potential applications as a catalyst [30], electrocatalyst, photocatalyst, biosensor, heat exchanger and antimicrobial [31]. Kumar et al. [32] point out that Ni NPs increase hydrogen production during dark fermentation, although their interaction with microorganisms is still unknown. On the other hand, Ahghari et al. [31] mention that Ni NPs have desirable characteristics for their use as magnetic mirrors, antibacterial activities, and magnetic properties.

Considering the above, the aim of this work was to synthesize a new nanomaterial with core@shell structure (NaGdF₄:Nd³⁺@Ni), to take advantage of its functionality, and to study its viability as LNPs. The initial proposal for the use of these NPs is in the AD study, due to the current importance of renewable energies. However, considering the multiple applications that Ni NPs and NaGdF₄:Nd³⁺ have, their combination could help in the identification and tracking of Ni NPs in different applications, and with this, the different processes could be better described and understood.

2. Materials and methods

The experiment consisted of two stages. The first one was the synthesis of NaGdF₄:Nd³⁺ NPs by the solvothermal method described by Navarro-Cerón et al. [24], and the second stage consisted in covering the synthesized NPs with Ni NPs to form the core@shell structure. Ni NPs were obtained by the chemical reduction method described by Aguilar-Méndez et al. [33], with some modifications. All reagents used were purchased from Sigma-Aldrich®. The purity of all rare-earth oxides was 99.99 %. Sodium fluoride, nitric acid, ethanol, hexane, stearic acid, sodium hydroxide, oleic acid, trisodium citrate dihydrate, hydrochloric acid, nickel chloride hexahydrate, sodium borohydride, and gelatin were of analytical grade. Deionized water (18 MΩ/cm) was used throughout the experiment.

2.1. Solvothermal synthesis of NaGdF₄:Nd³⁺ NPs

The nitrate powder was obtained by evaporating (at 80 °C) a solution containing 0.372 g of Gd_2O_3 (10 mmol), 0.1116 g of Nd_2O_3 (0.04 mmol), and 10 mL of nitric acid. The Nd^{3+} concentration was 4 mol% in relation to Gd^{3+} content. Then, 0.24 g of stearic acid (0.84 mmol) and 25 mL of hot ethanol were added to the obtained powder. The mixture was kept stirring for 30 min and a solution containing NaOH (0.224 g, 5.6 mmol, in 3 mL of water) was added dropwise. The resulting solution was refluxed for 30 min at 78 °C. Precipitates from the reaction mixture were centrifuged and washed four times, three using deionized water and one using ethanol. The rare earth stearate precursor was obtained, as a white powder, after the precipitates were dried at 60 °C for 12 h. Afterward, 0.432 g of precursor and 0.432 g of NaF (1.95 mmol) were dissolved in 2 mL of oleic acid (6.34 mmol), 1 mL of ethanol, and 7 mL of water. This mixture was stirred for 5 min, then it was transferred to an autoclave and treated with solvothermal for 48 h at 180 °C. Once the solution was cooled naturally at room temperature, the NPs were separated by centrifugation, washed four times with a solution of ethanol and hexane (1:1), and dried at 60 °C for 12 h.

2.1.1 Procedure for oleate molecules

To obtain water-dispersible NaGdF₄:Nd³⁺ NPs, a change of oleate molecules was performed by covering their surface with trisodium citrate. First, 60 mg of the hydrophobic NPs were dispersed in 5 mL of hexane, then 5 mL of 0.2 M trisodium citrate buffer was added, adjusted to pH 4 with concentrated HCl. This two-phase solution was stirred until a clear separation of the aqueous/organic phases could be observed. The aqueous phase of the solution, now containing the NPs, was isolated, and these were precipitated with acetone (1:5 aqueous:organic ratio) and centrifuged.

2.2. Chemical reduction synthesis of NaGdF₄:Nd³⁺@Ni NPs

Five mL of water-dispersible NaGdF₄:Nd³⁺ NPs, 15 mL of NiCl₂·6H₂O (0.1 M), and a solution containing the passivating agent (1 % gelatin) were mixed and heated at 60 °C. Once the desired temperature was reached, 750 μ L of sodium borohydride (NaBH₄) (0.2 M) was slowly added. The initial solution was transparent green, later it turned into a black colloidal suspension, which indicated the formation of Ni NPs. For some characterizations (such as UV-Vis and XRD), Ni NPs were synthesized with the same methodology, but without adding the NaGdF4:Nd³⁺ NPs, to make a better comparison between NaGdF₄:Nd³⁺@Ni and Ni NPs.

2.3. Nanoparticle characterization

To evaluate the change from hydrophobic to hydrophilic, the IR spectrum of the NaGdF₄:Nd⁺³ NPs was obtained in a spectrometer (Cary 630, Agilent Technologies, USA). For this, a drop of the solution was placed in the sampler, and it was measured in the wavenumber range of 500 to 4000 cm⁻¹. The size and morphology of the synthesized NPs were observed with a transmission electron microscope (TEM) (Tecnai G2 Spirit, FEI®, USA). For this, a drop of NPs solution was placed on a carbon-coated copper grid. This same grid was also observed in a high-resolution transmission electron microscope (HR-TEM). UV-Vis spectra were obtained using a spectrophotometer (VarioSkan Flash, Thermo Fisher Scientific®, USA), with a light source of Xenon flash lamp pulsed at 100 Hz, in an absorbance range of 300 to 800 nm. The optical properties of the NPs were measured in deionized water at a concentration of 0.09% v/v. The zeta potential and hydrodynamic diameter of the NPs were determined with a nanozetasizer (ZEN3600, Malvern Instruments, UK). To perform these analyses, the NPs were diluted to a concentration of 0.05% (v/v) with deionized water and sonicated for 20 min.

X-ray powder diffraction (XRD) measurements were made with a diffractometer (D8 Advance, Bruker®, Germany) with Cu K α (k = 1.5405 Å, 40 kV and 40 mA) radiation source, in the 2 θ range of 10 - 90°, with a step size of 0.05° and scanning speed of 3 s. The energy dispersive X-ray spectroscopy (EDS) of the NaGdF₄:Nd³⁺, NaGdF₄:Nd³⁺@Ni, and Ni NPs was performed with a scanning electron microscope (JSM-7800F, Jeol, USA), having a coupled brand silicon detector (X-Max 80, Oxford Instruments). For these characterizations, the colloidal suspensions were centrifuged at 7500 rpm for 30 min, and the precipitates were dried at 80 °C for 24 h. Finally, luminescence spectra were measured with a NIR Quest (Ocean Optics, Lithuania) detector and a laser diode of 808 nm (Roithner Lasertechnik) with an output power of 1500 mW, which was focused by a 20x objective lens and NA 0.4.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

The hydrophobicity change of NaGdF₄:Nd³⁺ NPs was confirmed by FTIR (Fig. 1). According to Himmelstoß and Hirsch [34], there are different techniques for oleate removal, although the most common method is assisted by an acid, such as sodium citrate. In this work, the acid used was trisodium citrate, and as can be seen, the change from hydrophobic to hydrophilic on the NPS surface was successfully carried out, thanks to the oleates removal carried out in the last step of the synthesis. This process was important, since to cover the luminescent NPs with Ni the NPs needed to be soluble in water. Furthermore, the potential use of core@shell NPs in AD requires that the NPs be dispersible in an aqueous medium.



Fig. 1. FTIR spectrum of NaGdF₄:Nd³⁺ NPs before (red) and after (blue) oleate removal.

According to Navarro-Cerón et al. [24], the FTIR bands in the hydrophobic sample correspond to the stretching and bending vibrations generated by the oleate molecules. Specifically, the peak observed at 2956 cm⁻¹ represents the asymmetric C–H stretching of CH₃, while the peaks at 2922 and 2854 cm⁻¹ correspond to the asymmetric and symmetric –CH₂ stretching vibrations, respectively, of oleate molecules [35]. The bands at 1459, 1377, and 725 cm⁻¹ correspond to symmetric stretching of the –COO, symmetric bending vibrations, and rolling vibration superimposition of CH₂, respectively [36]. In the hydrophilic sample, a band around 3300 cm⁻¹ can be observed, indicating the stretching vibration of the –OH group with a hydrogen bond [37]. Interestingly, no hydrogen-bonded –OH group was detected in the hydrophobic sample.

3.2. Morphological characterization

The NaGdF₄:Nd³⁺ and core@shell NPs were examined by TEM, and the results are shown in Fig. 2. The NaGdF₄:Nd³⁺@Ni NPs presented an almost spherical shape and monodispersity, with an average diameter of approximately 250 nm, with a size range of 100 - 450 nm (Fig. 2b). They were highly stable due to the type of biopolymer used as a passivating agent (gelatin) [38]. Fig. 2c shows the micrograph of NaGdF₄:Nd³⁺ NPs, before their coating with Ni NPs, which present a size distribution of 6.37 to 45.43 nm, and a characteristic grouping of this type of NPs [39]. From HR-TEM micrographic (Fig. 2d), it can be seen that the shell structure (Ni) is amorphous and much less dense than the core structure (NaGdF₄:Nd³⁺); furthermore, some crystal planes are conspicuously visible in the core structure. According to the micrographs, it can be stated that the core@shell NPs formation is not individual, rather the Ni NPs covered agglomerates of the NaGdF₄:Nd³⁺ NPs.



*Fig. 2. a) TEM image of NaGdF*₄:*Nd*³⁺*@Ni NPs, b) size distribution histogram of 100 NaGdF*₄:*Nd*³⁺*@Ni NPs, c) NaGdF*₄:*Nd*³⁺*WPs, and d) HR-TEM of NaGdF*₄:*Nd*³⁺*@Ni NPs.*

3.3 Optical properties

The UV-Vis spectra for Ni and NaGdF₄:Nd³⁺@Ni NPs using gelatine as a capping agent are presented in Fig. 3. The spectra show characteristic surface plasmon resonance for Ni NPs, with maximum absorption bands detected at 387 and 383 nm for Ni and core@shell NPs, respectively, which proves the Ni NPs formation. It has been reported that Ni NPs exhibited absorptions between 300 and 400 nm [40, 41]. The absorption peak is consistent with those of Din et al. [42], who obtained Ni NPs from chemical reduction using NaBH₄ as a reducing agent. Likewise, the calculations of Jaleh et al [43] estimate an absorption of 350 to 490 nm for the same type of NPs.



Fig. 3. UV-Vis spectra for Ni and NaGdF₄:Nd³⁺(@Ni NPs.

The absorption band of the core@shell NPs was slightly shifted, indicating a size difference, and that $NaGdF_4:Nd^{3+}$ in the core does not affect the optical properties of Ni. Din et al. [42] mention that the absorption band position depends on several factors, and that the thickness and size of the absorption peak are indicators of the dispersion and stability of the NPs.

3.4. Surface charge and hydrodynamic diameter

To determine the stability of the dispersed particles in solution, the surface charge was determined using the zeta potential. In this technique, as the absolute value of the zeta potential increases, the probability of NPs aggregation decreases [44]. In this work, gelatin passivated coreshell NPs were stable as reported by <u>Titus</u> et al. [45], since an average value of -27 ± 1 mV was obtained, with a hydrodynamic diameter of 520 nm.

3.5. Structural characterization

The diffraction pattern of Ni and NaGdF₄:Nd³⁺@Ni NPs is shown in Fig. 4. The peaks with Bragg reflections at 27.4°, 31.5°, 45.4°, 56.6°, 66.2°, 75.3°, and 84.1° correspond to NaCl according to ICSD 060280. This can be associated with a residual phase of colloidal suspension during the drying process. The X-ray diffractogram of the Ni NPs sample shows peaks with Bragg reflections at $2\theta = 31.5^{\circ}$ corresponding to NaCl and $2\theta = 45.5^{\circ}$ which correlates with the cubic phase of metallic Ni according to ICSD-64489/PDF-87-712 [46-47]. The Bragg peaks in the XRD pattern of the coreshell sample were in agreement with the hexagonal phase of NaGdF₄ (JCPDS card #27-0699) [49]. As expected, no significant change in the crystalline phase of NaGdF₄ is observed with the incorporation of Nd³⁺, because it occupies crystallographic sites of Gd³⁺, whose ionic radii are similar [50, 51].



Fig. 4. X-ray diffraction pattern: a) NaGdF₄:Nd³⁺(a)Ni NPs and b) Ni NPs.

3.6. Chemical composition

Energy dispersive X-ray spectroscopy (EDS) was applied to confirm the chemical composition and the approximate concentration of the prepared samples (Fig. 5). Through the elemental analysis mapping, the homogeneous distribution of the elements present in the NPs was observed. As shown in Fig. 5a, all elements of the NaGdF4:Nd³⁺@Ni core@shell NPs were detected. As it was expected, Ni was the element that was observed in greater abundance in these NPs, because it is covering the luminescent NPs. Figures 5b and 5c show the spectra of the NaGdF4:Nd³⁺ and Ni NPs; in both cases, a uniform distribution of the elements that make up the NPs was observed.



Fig. 5. EDS spectrum and mapping of the NPs: a) $NaGdF_4:Nd^{3+}$ @Ni, b) $NaGdF_4:Nd^{3+}$, and c) Ni.

3.7. Luminescence spectroscopy

The emission spectra of the NaGdF₄:Nd³⁺@Ni NPs can be observed in Fig. 6. The excitation at 808 nm (I-BW) fills the ${}^{4}F_{5/2}$: ${}^{2}H_{9/2}$ multiple levels of Nd³⁺, which then fills the ${}^{4}F_{3/2}$ state through non-radiative relaxation, from where the different near-infrared (NIR) emissions originate (II-BW). The emission spectra of the samples showed emissions at 1054 and 1330 nm, corresponding to transitions from the ${}^{4}F_{3/2}$ excitation level of Nd³⁺ ions to the lower ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ levels, respectively [52] (Fig. 6b).



Fig. 6. a) Photoluminescence emission spectra of $NaGdF_4:Nd^{3+}$ (Mi core (ashell NPs excited at 808 nm, and b) energy levels of Nd^{3+} .

4. Conclusions

The synthesized NaGdF₄:Nd³⁺@Ni NPs were developed with excellent chemical properties and stability, as shown in the different characterizations. The absorption spectra of the NPs indicate that the optical properties of Ni in the shell are not affected by the core. At the same time, the NPs present a Stokes shift, being excited in I-BW and emitting photoluminescence in II-BW. According to the results obtained, these NPs present a very good alternative for use in biogas production, not only as catalysts, but also as biomarkers to improve the understanding of biogas production during AD. Although this is only a proposal, since they could be applied in various areas.

References

[1] D. Deublein, A. Steinhauser, Biogas from waste and renewable resources: An introduction, Wiley-VCH Verlag GmbH & Co, Germany, 3-6, 2008; https://doi.org/10.1002/9783527621705 [2] G. S. Aguilar-Moreno, E. Navarro-Cerón, A. Velázquez-Hernández, G. Hernandez-Eugenio, M. A. Aguilar-Mendez, T. Espinosa-Solares, Renew. Energy 141, 204-213 (2020); https://doi.org/10.1016/j.renene.2019.08.111 [3] F. van Foreest, "Perspectives for biogas in Europe", Oxford Institute for Energy Studies, United Kingdom, 2012; https://doi.org/10.26889/9781907555633 [4] N. Scarlat, J. F. Dallemand, F. Fahl, Renew. Energy 129, 457-472 (2018); https://doi.org/10.1016/j.renene.2018.03.006 [5] M. S. Romero-Güiza, J. Vila, J. Mata-Alvarez, J. M. Chimenos, S. Astals, Renew. Sustain. Energy Rev 58, 1486-1499 (2016); https://doi.org/10.1016/j.rser.2015.12.094 [6] A. Schattauer, E. Abdoun, P. Weiland, M. Plöchl, M. Heiermann, Biosyst. Eng. 108, 57-65, (2011); https://doi.org/10.1016/j.biosystemseng.2010.10.010 [7] G. Baek, J. Kim, J. Kim, C. Lee, Energies. 11(107), 1-18 (2018); https://doi.org/10.3390/en11010107 [8] C. M. Ajay, S. Mohan, P. Dinesha, M. A. Rosen, Fuel. 277, 1-12 (2020); https://doi.org/10.1016/j.fuel.2020.118234 [9] E. Abdelsalam, M. Samer, Y. A. Attia, M. A. Abdel-Hadi, H. E. Hassan, Y. Badr, Renew. Energy 87, 592-598 (2015); https://doi.org/10.1016/j.renene.2015.10.053 [10] J. L. Chen, T. W. Steele, D. C. Stuckey, Sci. Total Environ. 642, 276-284 (2018); https://doi.org/10.1016/j.scitotenv.2018.05.373 [11] M. S. Abdallah, F. Y. Hassaneen, Y. Faisal, M. S. Mansour, A. M. Ibrahim, S. Abo-Elfadl, Fuel. 254, 1-8 (2019); https://doi.org/10.1016/j.fuel.2019.115673 [12] A. A. Zaidi, F. RuiZhe, Y. Shi, S. Z. Khan, K. Mushtaq, Int. J. Hydrog. Energy. 44, 14661-14670 (2019); https://doi.org/10.1016/j.ijhydene.2019.02.245 [13] Y. J. Lee, D. J. Lee, Bioresour. Technol. 292, 121926 (2019); https://doi.org/10.1016/j.biortech.2019.121926 [14] N. Bogdan, E. M. Rodriguez, F. Sanz-Rodriguez, M. C. de la Cruz, A. Juarranz, D. Jaque, Nanoscale. 4, 3647-3650 (2012); https://doi.org/10.1039/c2nr30982c [15] S. K. Gupta, K. Sudarshan, R. M. Kadam, Mater. Today Commun. 27, 102277 (2021); https://doi.org/10.1016/j.mtcomm.2021.102277 [16] H. Ma, J. Wang, X. D. Zhang, Coord. Chem. Rev. 448, 214184 (2021); https://doi.org/10.1016/j.ccr.2021.214184 [17] A. Ekner-Grzyb, J. Chmielowska-Bąk, A. Szczeszak, Plants. 10(6), 1187 (2021); https://doi.org/10.3390/plants10061187 [18] H. Thakur, R. K. Singh, A. K. Gathania, Mater. Res. Express. 8, 026201 (2021); https://doi.org/10.1088/2053-1591/abe221

[19] M. Sengar, A. Kumar-Narula, J. Solid State Chem. 295, 121913 (2021); https://doi.org/10.1016/j.jssc.2020.121913 1102

- [20] G. Sun, Y. Xie, L. Sun, H. Zhang, Nanoscale Horizons. 6, 766-780 (2021); https://doi.org/10.1039/D1NH00299F
- [21] E. Hemmer, A. Benayas, F. Légaré, F. Vetrone, Nanoscale Horizons. 1(3), 168-184 (2016); https://doi.org/10.1039/C5NH00073D

[22] Y. Xi, Z. Chang, X. Ye, H. Huang, Y. Huang, Q. Xiao, Nanoescale. 8, 1288 (2016); https://doi.org/10.1039/C5NR06106G

[23] D. Jaque, L. Martínez, B. del Rosal, P. Haro-González, A. Benayas, J. L. Plaza, Nanoscale. 6, 9494-9530 (2014); <u>https://doi.org/10.1039/C4NR00708E</u>

[24] E. Navarro-Cerón, D. H. Ortgies, B. del Rosal, F. Ren, A. Benayas, F. Vetrone, Adv. Mater. 27, 4781-4787 (2015); <u>https://doi.org/10.1002/adma.201501014</u>

[25] T. Wang, H. Zhou, Z. Yu, G. Zhou, J. Zhou, D. Huang, J. Phys. Chem. 18, 10113-10124 (2018); <u>https://doi.org/10.1021/acs.jpcc.8b00816</u>

[26] X. Li, F. You, H. Peng, S. Huang, J. Nanosci. Nanotechnol. 16(4), 3940-3944 (2016); https://doi.org/10.1166/jnn.2016.11818

[27] M. Xia, D. Zhou, Y. Yang, Z. Yang, J. Qiu, ECS J. Solid State Sci. Technol. 6(4), 41-46 (2017); <u>https://doi.org/10.1149/2.0031704jss</u>

[28] Y. Xi, Z. Chang, X. Ye, H. Huang, Y. Huang, Q. Xiao, Nanoscale. 8(3), 1288-1292 (2016); https://doi.org/10.1039/C5NR06106G

[29] N. D. Jaji, H. L. Lee, M. H. Hussin, H. M. Akil, M. R. Zakaria, M. B. Othman, Nanotechnol. Rev. 9(1), 1456-1480 (2020); <u>https://doi.org/10.1515/ntrev-2020-0109</u>

[30] R. G., Chaudhary, J. Tanna, N. V. Gandhare, A. R. Rai, H. S. Juneja, Adv. Mater. Lett. 6, 990-998 (2015); <u>https://doi.org/10.5185/amlett.2015.5901</u>

[31] M. R. Ahghari, V. Soltaninejad, A. Maleki, Sci Rep. 10, 12627 (2020). https://doi.org/10.1038/s41598-020-69679-4

[32] G. Kumar, T. Mathimani, E. R. Rene, A. Pugazhendhi, Int. J. Hydrog. Energy. 44(26), 13106-13113 (2019); <u>https://doi.org/10.1016/j.ijhydene.2019.03.131</u>

[33] M. A. Aguilar-Méndez, E. San Martín-Martínez, L. Ortega-Arroyo, G. Cobián-Portillo, E. Sánchez-Espíndola, J Nanopart Res. 13, 2525-2532 (2010); <u>https://doi.org/10.1007/s11051-010-0145-6</u>

[34] S. F. Himmelstoß, T. Hirsch, Part. Part. Syst. Charact. 36(10), 1900235 (2019); https://doi.org/10.1002/ppsc.201900235

[35] J. Premaratne, G. Priyadarshana, S. Gunawardena, A. de Alwis, Journal of Science of the University of Kelaniya 8, 33-48 (2013); <u>https://doi.org/10.4038/josuk.v8i0.7238</u>

[36] M. A. Poiana, E. Alexa, M. F. Munteanu, R. Gligor, D. Moigradean, C. Mateescu, Open Chemistry. 13(1), 689-698 (2015); <u>https://doi.org/10.1515/chem-2015-0110</u>

[37] N. J. Kuo, Y. S. Chen, C. W. Wu, C. Y. Huang, Y. H. Chan, I. Chen, W. Peter, Sci Rep. 6(1), 1-11(2016); <u>https://doi.org/10.1038/srep30426</u>

[38] M. A. Aguilar-Méndez, T. Espinosa-Solares, F. M. Guerrero-Toledo, D. Canseco-González, A. Velázquez-Hernández, G. S. Aguilar-Moreno, IET Nanobiotechnology 14, 94-97 (2020); https://doi.org/10.1049/iet-nbt.2019.0204

[39] B. del Rosal, A. Pérez-Delgado, M. Misiak, A. Bednarkiewicz, A. S. Vanetsev, Y. Orlovskii, J. Appl. Phys. 118, 143104 (2015); <u>https://doi.org/10.1063/1.4932669</u>

[40] D. Li, S. Komarneniw, J. Am. Ceram. Soc. 89, 1510-1517 (2006); https://doi.org/10.1111/j.1551-2916.2006.00925.x

[41] D. Muñetón-Arboleda, J. M. Santillán, L. J. Mendoza-Herrera, M. Fernández, P. Mendoza-Zélis, D. Muraca, J. Phys. Chem. 119, 13184-13193 (2015); https://doi.org/10.1021/acs.jpcc.5b03124

[42] M. I. Din, A. G. Nabi, A. Rani, A. Aihetasham, M. Mukhtar, Environ. Nanotechnol. Monit. Manag. 9, 29-36 (2018); <u>https://doi.org/10.1016/j.enmm.2017.11.005</u>

[43] B. Jaleh, M. J. Torkamany, R. Golbedaghi, M. Noroozi, S. Habibi, F. Samavat, Adv. Mat. Res. 403, 4440-4444 (2012); <u>https://doi.org/10.4028/www.scientific.net/AMR.403-408.4440</u>

[44] N. Rescignano, E. Fortunati, I. Armentano, R. Hernandez, C. Mijangos, R. Pasquino, J. Colloid Interf. Sci. 445, 31-39 (2015); <u>https://doi.org/10.1016/j.jcis.2014.12.032</u>

[45] D. Titus, E. Jebaseelan, S. M. Roopan, Green synthesis, characterization and applications of nanoparticles, Elsevier B.V., Netherlands, 2019; <u>https://doi.org/10.1016/B978-0-08-102579-6.00012-5</u>

[46] P. Srimaraa, T. Chevaprukb, P. Kumnorkaewc, T. Muangnapohc, P. Vas-Umnuaya, Materials Today 23, 720-725 (2020); <u>https://doi.org/10.1016/j.matpr.2019.12.264</u>

[47] X. Dong, S. Jiang, S. Khan, Z. Wu, J. Wang, C. Song, J. Sol-Gel Sci. Technol. 85, 520-528 (2018); <u>https://doi.org/10.1007/s10971-018-4597-y</u>

[48] R. I. Smith, J. E. Jørgensen, Acta Crystallographica, Section B 62, 987-992 (2006); https://doi.org/10.1107/S0108768106030023

[49] Q. Zhao, B. Shao, W. Lü, W. Lv, M. Jiao, L. Zhao, Dalton Trans. 44, 3745-3752 (2015); https://doi.org/10.1039/C4DT03619K

[50] X. Li, R. Wang, F. Zhang, L. Zhou, D. Shen, C. Yao, Scientific Reports 3, 3536 (2013); https://doi.org/10.1038/srep03536

[51] D. Ma, L. Meng, Y. Chen, M. Hu, Y. Chen, C. Huang, ACS Appl. Mater. Interfaces 7, 16257-16265 (2015); <u>https://doi.org/10.1021/acsami.5b05194</u>

[52] D. González-Mancebo, A. I. Becerro, T. C. Rojas, A. Olivencia, A. Corral, M. Balcerzyk, J Colloid Interface Sci. 520, 134-144 (2018); <u>https://doi.org/10.1016/j.jcis.2018.03.007</u>