Indian Journal of Chemistry
Vol. 63, March 2024, pp. 263-268
DOI: 10.56042/ijc.v63i3.6308

Structural characterization and supercapacitor application of green synthesized Fe_2O_3 nanospindles using *Palmyra palm* extract

R Reshma, K M Govindaraju, S Chandra, J Raffiea Baseri, D Ragavi, P Subashini & J Manikandan*

Department of Chemistry, PSG College of Arts & Science, Avinashi Road, Civil Aerodrome Post, Coimbatore 641 014, Tamil Nadu, India

E-mail: manijegan@gmail.com

Received 19 October 2023; accepted (revised) 22 February 2024

Iron oxide nanospindles (IONSs) have been synthesized by greener route assisted with *Palmyra palm* (PP) extract. The synthesized IONSs have been characterized by FTIR, XRD, EDAX, SEM and TEM techniques. FT-IR results confirmed the nanosystem formation and the presence of the phytochemical constituents on the surface of prepared nanosystems. XRD analysis confirmed the crystalline state of synthesized iron oxide nanospindles with the size of about 7.76 nm. Morphological analysis of the iron oxide nanoparticles from SEM and TEM results reveal the spindle like morphology. Working electrodes fabricated from the active material Fe_2O_3 nanospindleshave been studied through CV, GCD and EIS techniques to investigate their electrochemical behaviour.The prepared Fe_2O_3electrode shows good electrochemical properties with maximum specific capacitance of 350.66 F/g and very low charge transfer resistance of 0.81Ω.

Keywords: Iron oxide, nanospindles, *Palmyra palm*, electrochemical studies

There has been a demand for clean, sustainable, ecofriendly and efficient energy storage devices/technologies due to the increase in energy demand and decrease in fossil/conventional fuels[1,2]. This becomes worsening in the forthcoming days as the energy requirement is enormously increasing every day. Considering the environmental issues related to fossil fuels, focus is given for the development of useful and effective technologies to fulfill the needs in many fields. One such technology is nanotechnology which has emerged as one of the most hopeful technologies, using nanomaterials with enhanced performances for a variety of applications[3]. The applications of nanomaterials have a new dimension in interdisciplinary applications such as electrochemical devices, sensors, healthcare equipments and drugs[4]. They play a vital role in variety of gadgets such as, super capacitors, electronic appliances, surface coatings, energy storage devices, sports equipments and textile materials[5]. Numerous physical and chemical methods are employed in designing nanomaterials that could be used for biomedical applications, biosensors, electronic gadgets, *etc*. Super capacitor is one of the important gadgets that have gained much attention due to its potential advantages over batteries[6].

For the past few years, research is intensified in the field of super capacitors due to their advantages such as high energy density, excellent charge discharge rate, long cycle life, improved stability and a wide range of applications in portable electronics, power backup systems and hybrid electric vehicles[7]. Super capacitors are differed from batteries and other conventional capacitors in such a way that they have high charge and energy density[8,9]. An important aspect which decides the performance of a super capacitor depends on the electrode material used in it. When compared to carbon based materials, transition metal oxides that include MnO_2, Co_3O_4, NiO, and Fe_2O_3 are widely used as electrode materials in the field of super capacitors owing to their high energy density and stability[10]. Considering the factors like cost, nontoxic nature and availability of raw materials, metal oxide nanomaterials have been widely used as alternate materials for electrochemical devices[11]. Among the metal oxides, Fe_2O_3 nanosystem is the choice of our interest for super capacitor applications due to its variable valency, eco-friendly, low cost and abundance[12]. Since iron oxide nanoparticles possess magnetic properties, they are widely used in various fields namely gas sensing, magnetic recording, medicine and an electrode material[13]. In recent years,

synthesis of nanoparticles from plant extracts (*via* green route) gainmuch attraction owing to its many advantages over other physico-chemical methods. This way of preparing materials involves less reagents, less energy requirement, simple infrastructure, cost effective and eco-friendly[14,15].

Palmyra palm is a member of the *Aceraceae* family also known as *Borassus flabellifer* L., can be found from Western Africa and Madagascar to Eastern Indonesia, India and Papua New Guinea[16]. This fan-shaped tree is a dioecious plant that takes roughly 15–30 years to reach a height of 30 meters and a base of 1.5 meters. The *Palmyra palm* tree provides employment to more people because of its every part of this plant is valuable[17]. The nutritional analysis of *Palmyra palm* sprouts revealed the presence of 7.29% crude fiber, 8.54% protein, and 23.53% carbohydrate[18]. *Palmyra palm* sprout extract contains wide variety of active biomolecules and can be used to feasibly produce nanomaterials with no cost and environmental impact. The main aim of this work is to prepare Fe_2O_3 based electrode material in the form of nanospindles through a ecofriendly green route.

Materials and Methods

Chemicals and plant material

The chemicals $FeCl_3.6H_2O$ and NH_4OH of AR grade were purchased from Merck India Private Limited and used as received. The edible sprouts of *Palmyra palm* were picked from the fields in and around Irumbupalam village located in Namakkal district of Tamil Nadu, India. The sprouts were dried, powdered and stored at 4°C. The extract of *Palmyra Palm* sprouts was prepared by Soxhlet extraction method using ethanol.

Synthesis of Iron Oxide nanospindles

The IONSs were synthesized by simple co-precipitation method as mentioned in Fig. 1. In a 100 mL beaker, ammonia solution was heated along with the ethanolic extract of *Palmyra palm* sprouts at 80°C. To this, hot solution of 0.1 M metal precursor was added drop wise under vigorous stirring for about 20 minutes. Colour of the mixture turned to dark brown from yellow which indicates the formation of iron oxide nanomaterial. The formed black precipitates of IONSs were magnetically separated, washed thoroughly with distilled water until no traces of NH_4OH. Centrifuged particles were dried in a hot air oven for 1 hour at 90°C and stored in an air tight container.

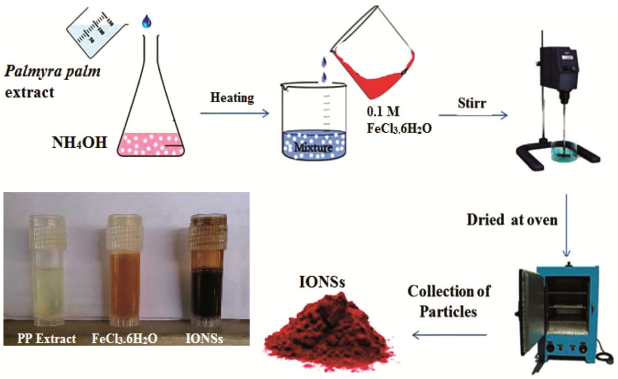

Fig. 1 — Scheme of preparation of Iron oxide nanospindles (IONSs)

Characterization techniques

Synthesized iron oxide nanospindles were studied for physiochemical properties by various characterization techniques. Surface functionalization of biomolecules on the iron oxide surface was studied by FTIR for the range of 4000 cm^{-1} to 400 cm^{-1}. The XRD patterns were recorded with Cu Kα radiation of wavelength 1.5406 Å, to study the crystalline nature of the synthesized nanospindles. Surface morphology, elemental composition and particle size distribution of the prepared nanospindles were analyzed by SEM, EDAX and TEM techniques respectively.

Electrochemical measurements

The electrochemical performance of the synthesised Fe_2O_3nano particles were evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopic (EIS) techniques in 3M KOH electrolyte. In a three-electrode electrochemical system, the Ag/AgCl as reference electrode and the platinum foil as the counter electrode and graphite sheet loaded with Fe_2O_3nanospindles was used as the working electrode.

The working electrode was fabricated by mixing the active material Fe_2O_3 with acetylene black and polyvinylidine difluoride (PVDF) at mass ratio of 80:10:10 respectively. The above materials were mixed thoroughly to form homogeneous thick slurry by adding N-methylpyrrolidone (NMP) solvent and ground well until it became a fine paste. A well cleaned graphite sheet of 1 cm x 1 cm was served as substrate holder for the prepared paste of sample. Furthermore, the obtained paste was coated on the well cleaned graphite substrate followed by drying at 60°C and cooled to room temperature. By weighing, the active mass loading on working

electrodes is averagely found to be 1.4 mg/cm^2. All the electrochemical measurements were carried out by CH instrument model CHI 600E. The specific capacitances and energy densities were calculated from CV and GCD curves using relation (1),

$$C = \frac{I}{\Delta v \times m} \quad \ldots(1)$$

Where, I (mA) is the average current obtained by integrating CV, Δv is the voltage difference at discharge time and m (mg/cm^2) is the mass of the active material. Specific capacitance can also be calculated from the galvanostatic discharge curves using the equation (2),

$$C = \frac{I \times \Delta t}{m \times \Delta v} \quad \ldots(2)$$

Where, I (mA) is the discharge current, Δt (s) the time needed for discharge, Δv is the voltage difference at discharge time and m (mg/cm^2) is the mass of the active material.

Results and Discussion

FTIR analysis

FTIR analysis of the *Palmyra palm* sprouts extract and the green synthesized IONSs is given in Fig. 2. Plant extract shows the peaks at 3319 cm^{-1} correspond to the -OH and -NH groups of terpenoids, alkaloids and polyphenols present in the plant material, the peak at2972 cm^{-1} is probably due to stretching bands in alkanes. The band at 1408cm^{-1}represents the presence of -C-C stretching due to the presence of aromatic compounds in the extract. The peak at 1106 cm^{-1} is ascertained to the -C-H stretching of terpenoids[19]. The peak around 1019 cm^{-1}reveals the -C-O stretching vibration of alcohols and broad band at 1700 cm^{-1}corresponds to -C=O stretching bands of carboxylic functional groups.

FTIR spectrum of plant mediated IONSs shows a strong stretching vibration of -OH group at 3356 cm^{-1}, -C-H stretching at 2924 cm^{-1}. The band appears at the 1610 cm^{-1} and 1377 cm^{-1} corresponds to the -C=O and -C-O stretching vibrations respectively. The strong and broad absorptions located at 500-700 cm^{-1} are due to the vibrations of-Fe=O. A strong sharp band at 599 cm^{-1} corresponds to Fe-O stretching and indicates the synthesis of stable iron oxide[20,21]. The results prove the successful encapsulation of biomolecules of *Palmyra palm* sprout extracts on the IONSs surfaces.

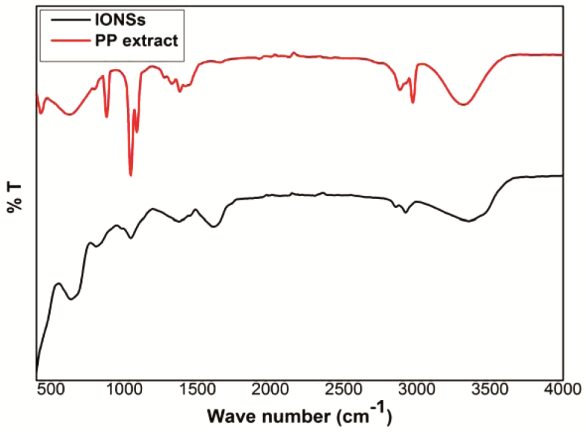

Fig. 2 — FTIR spectrum of Palmyra palm extract and Iron oxide nanospindles synthesized using plant extract

XRD analysis

The crystalline nature and crystallite size are calculated from XRD pattern. Fig. 3 shows the XRD pattern of biofunctionalized synthesized iron oxide nanoparticles. X-ray diffraction reveals the formation of nanostructured iron oxide. The shift in the peak position of biofunctionalized nanoparticles are attributed to the influence of interaction between nanoparticles with biomolecules. The diffraction peaks and their uniform d spacing allow us to specify the crystal structure of the prepared nanomaterials.

The powder X-ray diffraction (PXRD) pattern having prominent peaks from (111), (220), (311), (222), (440), (422), (511) and (440) which are in accordance with the rhombohedral α-Fe_2O_3 with JCPDS No: 00-001-1053 [22]. For the green synthesized IONSs the average particle size was calculated as 7.76 nm using Debye Scherrer's formula. Presence of the noises in the XRD spectrum confirms the presence of biomolecules on the surface of the nanomaterial.

SEM and EDAX analysis

SEM image of the IONSs in Fig. 4 clearly shows that the prepared Fe_2O_3 nanoparticles have uniform

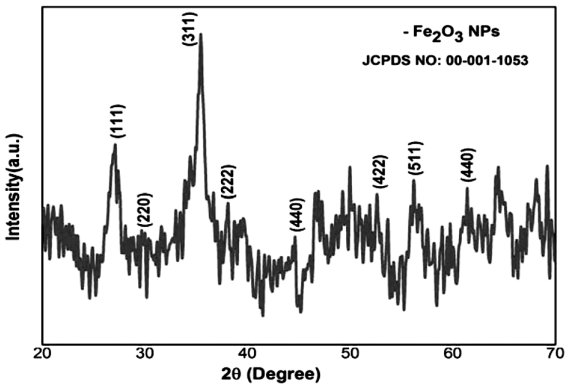

Fig. 3 — XRD pattern of green synthesized IONSs

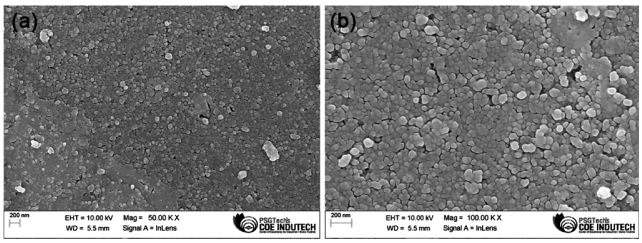

Fig. 4 — SEM images of prepared IONSs

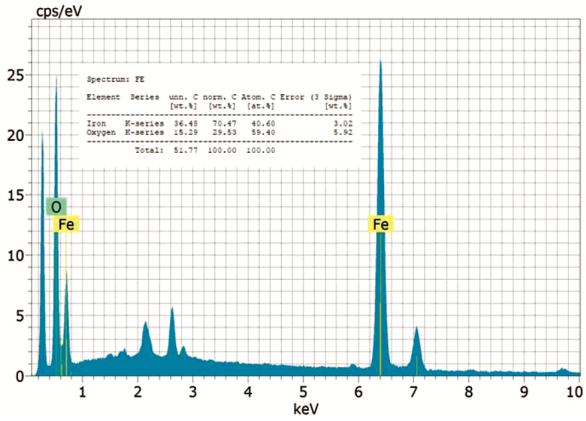

Fig. 5 — EDAX spectrum of IONSs

size distribution with less agglomeration. The shape possessed by the particle is witnessed as spindle like morphology. Fig. 5 elucidates the elemental composition of the prepared sample. The peak position and their intensity reveal the type of element present and % of the element in the sample respectively. The peaks observed for our sample confirm the presence of iron, oxygen, carbon and hydrogen. The presence of carbon, hydrogen is ascertained to the presence of biomolecules on the surface of the prepared nanospindles.

TEM analysis

The TEM analysis was carried out to witness the size and shape of green synthesized iron oxide nanospindles using *Palmyra palm* sprouts extract. TEM picture of iron oxide nanospindlesclearly shows that the nanomaterial is exclusively composed of crystals with a uniformly distributed spindles like structure. TEM results confirm a very narrow size distribution of iron oxide nanospindles (Fig. 6). The average dimension of the monodispersed nanospindles are 7.5 nm of width and 30 nm of length.

Electrochemical measurements

The CV curves of working electrode made of Fe_2O_3nanospindles recorded at different scan rates

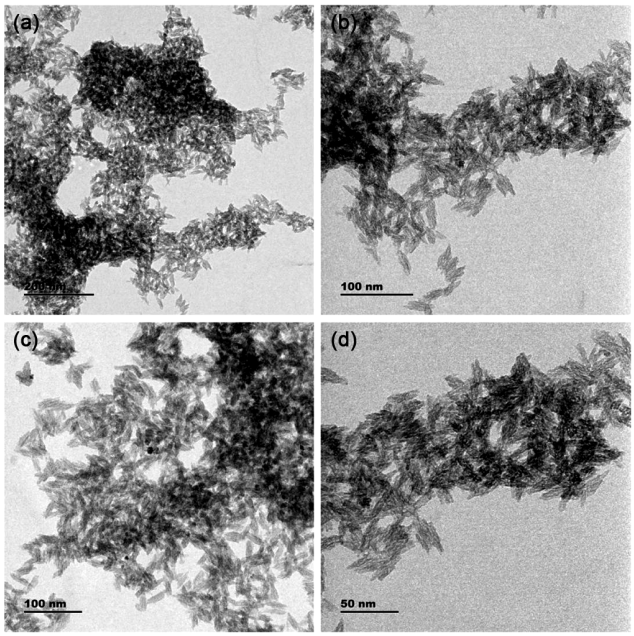

Fig. 6 — HRTEM images of prepared IONSs

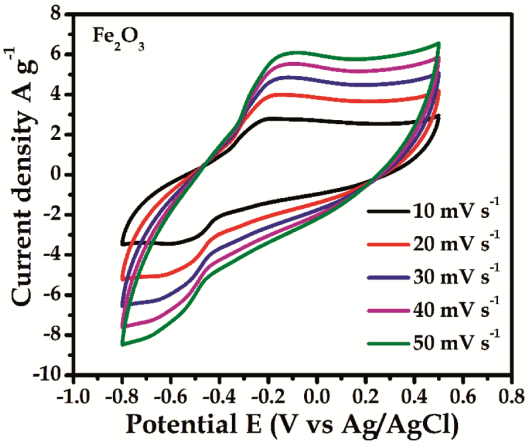

Fig. 7 — CV curve of Fe_2O_3 nanospindles at different scan rates

were shown in Fig. 7. It retains the shapes of the curve even for high scan rate to establish good rate of charge/discharge capability.The prepared Fe_2O_3 nanomaterials show a very good electrochemical properties and a high specific capacitance of 350.66 F/g at 1 A/g. The position of the redox peaks in cyclic voltammetry shift to cathodic region with the increasing scan rate. It is realized as rapid redox reactions take place at the electrode/electrolyte interface.Moreover, the internal resistance of the electrode causes decrease in the specific capacitance of Fe_2O_3 nanospindles with increased scan rate.

Galvanoststic charge discharge measurements were performed at constant current density, to study

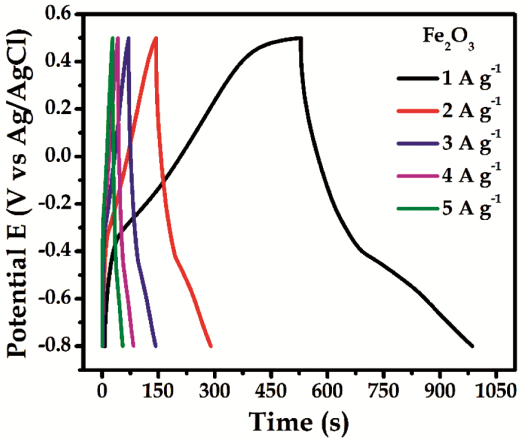

Fig. 8 — Charge-discharge profile of Fe_2O_3 nanospindles at different current densities

Table 1 — Specific capacitance of Fe_2O_3 nanospindles at various current densities of 1, 2, 3,4 and 5 A g^{-1}

Current density (A/g)	Applied Current (mA)	Time (s)	Voltage (V)	Mass loading (mg)	Specific capacitance (F/g)
1	0.0014	455	1.3	1.4	350.66
2	0.0028	144	1.3	1.4	222.01
3	0.0042	72	1.3	1.4	166.52
4	0.0056	41	1.3	1.4	126.74
5	0.007	29	1.3	1.4	112.69

the influence of electrochemical properties on the prepared nanospindles of Fe_2O_3. The electrode made of Fe_2O_3nanospindles gives a symmetric charge discharge curves, which reveals the good double layer capacitor performance. It is obvious that nonlinear nature of the current because of Faradaic redox reactions takes place between electrode and the electrolyte.

Fig. 8 shows a characteristic charge–discharge curve for the Fe_2O_3 nanospindles at various current densities. The Fe_2O_3 provides the maximum specific capacitance value of 350.66 F/g at 1 A/g is originated from the presence of the high surface area of the nano Fe_2O_3 spindles which facilitates the electrochemical process leading to the good conductivity and better ion intercalation. At high current rate, the specific capacitance is decreased due to the poor synchronization of ion movement between the electrodes. Table 1 clearly indicates the capacitance of Fe_2O_3 at 1 A/g current density. It was chosen this current density because of its higher capacitance ability over other current density value. This is attributed to the increased conductivity of Fe_2O_3, which promotes ion diffusion in the host material.

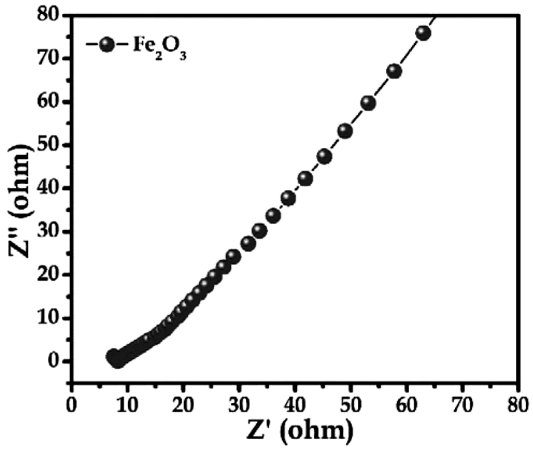

Fig. 9 — Nyquest plot of Fe_2O_3 nanospindles

The EIS experiments were conducted to study the fundamental electrochemical behaviour of prepared electrode materials. The enhanced capacitive performance of Fe_2O_3 nanospindles may also be correlated through the low resistance observed by EIS. The Nyquist plot depicts variation of real and imaginary parts of the impedance from high to low frequencies, which also gives the information about the interfacial properties of prepared electrode. The Nyquist plot of the as-prepared sample in Fig. 9, shows very low charge-transfer process occurring at the electrode/electrolyte interface and a straight line in the low frequency region is attributed to Warburg impedance. The charge transfer resistance is generally caused by the Faradaic reaction and the double layer capacitance on the nanostructures' surface[23]. From the figure, the measured R_{ct}value was found to be 0.81Ω indicates a very low charge transfer resistance and good capacitive behaviour of the prepared Fe_2O_3 nanospindles.

Conclusion

Iron nanoparticles were successfully synthesised using eco-friendly, rapid, simple and low-cost approach through a greener route using *Palmyra palm* sprouts extract. Due to the phytochemical constituents present on the surface of the nanoparticles, the stability of the IONSs fabricated was observed to be superior to chemically synthesised nanoparticles. Synthesised IONSs were studied using FTIR, XRD, EDAX, SEM and TEM techniques. SEM images of the biosynthesized IONSs at different magnifications showed that the particles were less aggregated and having a smooth surfaces. The TEM images revealed the nanoparticles were spindle structured with the

sizes in the range of 7.76 nm. The X-ray diffraction analysis reveals that the synthesized nanoparticles were crystalline in nature and capped with the biomolecules.The presence of high surface area of Fe_2O_3nanospindlesmay facilitate the electrochemical process leading to the good conductivity and better ion intercalation.The prepared electrode materials exhibit a very good electrochemical property with high specific capacitance of 350.66 F/g. Thishigh capacitive performance of Fe_2O_3 nanospindlescan also be correlated through the very low charge transfer resistance.

References

1 Zhao Y, Jiafeng H, Meizhen D, Depeng Z, Xiang W & Baodan L, *J Energy Chem*, 45 (2020) 67.
2 Liu H, Zhao D, Liu Y, Hu P, Wu X and Xia H, *Chem Eng J*, 373 (2019) 485.
3 Baig N, Kammakakam I & Falath W, Mat Adv, 2 (2021) 1821.
4 Patel P, Nandi A, Jha E, Sinha A, Mohanty S, Panda P.K, Mishra S, Verma S.K and Suar M, MagnNanopart-Based Hyb Mat, 12 (2021) 33.
5 Shahriar S, Shahed B, Sophie L, Forrest M L, Pieter S&Morteza M, ChemSoc Rev, 41 (2012) 6.
6 Brousse T, Bélanger D, Chiba K, Egashira M, Favier F, Long J, Miller J R, Morita M, Naoi K, Simon P & Sugimoto W, Materials for Electrochemical Capacitors, (Springer Handbooks, Springer Berlin, Heidelberg) (2017) 495.
7 Xu B, Zheng M, Tang H, Chen Z, Chi Y, Wang L & Pang H, Nanotechnology, 30 (2019) 20.
8 Wang G, Zhang L & Zhang J, ChemSoc Rev, 41 (2012) 797.
9 Li B, Zheng M, Xue H and Pang H, Inorg. Chem. Front. 3 (2016).
10 Jana S K, Rao V P & Banerjee S, ChemPhys Lett, 593 (2014) 160.
11 Verma S K, Thirumurugan A,Panda P K, Patel P, Nandi A, Jha E, Prabakaran K, Udayabhaskar R, Mangalaraja R V,Mishra Y K, Akbari-Fakhrabadi A, Morel M J, Suar M, & Ahuja R, 12 (2021) 100131.
12 Nithya V D & Arul N S, J Mat Chem A, 4 (2016) 28.
13 Reddy M V, Yu T, Sow C H, Shen Z X, Lim C T, Subba Rao G V &Chowdari B V R, AdvFunct Mater, 17 (2007) 2792.
14 Singh A, Gaud B&Jaybhaye S, Mat Sci Energy Technol, 3 (2020) 232.
15 Morales-Díaz A B, Juárez-Maldonado A, Morelos-Moreno Á, González-Morales S & Benavides-Mendoza A, *Rev Mexicana De Ciencias*, 7 (2017) 5.
16 AmanAnkita, SenguptaSamik, Prasad M, Sinha S & Kumari S, *J PharmacogPhytochem*, 7 (2018) 459.
17 Murthy G N, Ramana K T V, Raju M S &Vengaiah P C, *J Res ANGRAU*, 43 (2015) 58.
18 Sahni C, Shakil N A, Jha V & Gupta R K, *J Pharm Phytochem*, 3 (2014) 58.
19 Danbature W L, Shehu Z, Adam M M& Mohammed B A, *Jurnal Ilmiah Biologi*, 8 (2020) 126.
20 Devatha C P, Jagadeesh K &Patil M, *Env Nanotech Mon Manage*,9(2018). (https://doi.org/10.1016/j.enmm.2017.11.007)
21 Herrera-Becerra R, Zorrilla C, Rius J L &Ascencio J A, *Appl Phys A*, 91 (2008) 241.
22 Sun L, Han X, Liu K, Yin S, Chen Q, Kuang Q, Han X, Xieb Z & Wanga C, *Nanoscale*, 7 (2015) 9416.
23 Ahmadi F &Ghasemi S, *J Mat Sci Mat Elec*, 29 (2018) 9067.