

Metal nanoparticles as emerging catalysts: A mini review

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Received 28 October 2020; revised 07 December 2020; accepted 08 December 2020; available online 28 December 2020

Abstract

Green chemistry is the pragmatism of a set of principles, which eliminate the use or production of hazardous substances in the design, development, synthesis and applications of chemical harvest. Accordingly, green synthetic techniques aim at hazard reduction as the recital criteria, whilst designing new chemical processes/methods. Catalysis lies at the heart of all chemical processes and hence, nanocatalysts with particle size dependent material engineering are of significant interest towards green chemistry and clean energy applications. In addition to particle size, nanostructured catalysts are exceedingly shape and/or morphology sensitive and their catalytic performance depend largely on their shape and morphology. Besides, nanocatalysts empowered with colossal surface areas, excellent recycling potential and efficient recovery characteristics are heralded as new process candidates with expanding catalytic capabilities. Accordingly, recapitulation of the synthesis of several new types of chemical entities is using nano-catalysts in the heterocyclic ring formation and some other important functionalization.

Keywords: Catalysis; Catalytic Applications; Characterization; Green Synthesis; Nano-Catalyst.

How to cite this article

Veeranna R., Shivamurthy P., Chandrashekaraiyah M., Kundachira Subramanni N., Madanahalli Ankanathappa S., Khanum S., Ranganatha Venkataravanappa L. Metal nanoparticles as emerging catalysts: A mini review. *Int. J. Nano Dimens.*, 2021; 12(2): 90-97.

INTRODUCTION

Catalysis is a significant and widely investigated subject both in fundamental and industrial chemistry. It further plays an essential part in various aspects' like production of energy, industrial chemistry and environmental remediation with removal of pollution or contaminant from soil, water and sediments. In present situation more than 60% of chemical products and 90% of chemical processes in globe are significantly dependent on catalysis. This scope will progressively increase to convince

our ever-growing demands for the sustainable processes with improved atom economic impacts and inferior environmental conflicts [1].

Any reactions favored by catalyst have a great attention with the aim of finding meaningful applications in the pharmaceutical and fine chemical industries. The continued growth of green, sustainable and economical chemical processes is one of the major challenges in chemistry. Besides, traditional need for competent and selective catalytic reactions, that will transform raw materials into valuable chemicals and significant pharmaceuticals. However,

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green chemistry is also struggle for waste and hazardous material reduction, atomic efficiency and high rates of catalyst revival. In this view, nanostructured materials are attractive agents as heterogeneous catalysts for a variety of organic transformations, particularly they meet the purpose of green chemistry. Researchers have made significant contributions in synthesis of well-defined nanostructured materials in recent years like ZnO [2, 3], BiVO₄, BiWO₄ [4], CeO₂ [5, 6], ZnFe₂O₃ [7]. These novel approaches have allowed the rational design and synthesis of highly energetic and selective nanostructured catalysts by scheming the structure and composition of the active nanoparticles further by manipulating the interaction between the catalytically active nano particle species and their support. In additional, metal nanoparticles are believed to be likely agents for catalysis due to their relatively large surface area per volume or weight unit as compared with bulk metal. This means heterogeneous metal nanoparticles catalysts classically function on metal surfaces. The heart of the catalytic chemistry is centered on the design of catalysts in which metal, metal oxide, metal complexes and so forth are certainly the most vibrant for several paramount reactions in modern chemistry [8].

Catalysis is significant due to the unique capabilities of catalysts in accelerating chemical reactions by reducing the energy barrier of their transition states and in controlling reaction pathways toward selective synthesis of target products[9]. The activity and selectivity of nanocatalysts can be rationally tuned by changing their chemical and physical properties, such as size, shape, composition, and morphology. Consequently, nanocatalyst-involved reactions have experienced exponential growth in chemical manufacturing [10], energy harvesting [11], conversion and storage [12], and environmental protection [13, 14].

In this review, the properties and functions of nanocatalysts are first discussed to provide insights into the fundamental relationships between the activity, selectivity, and recyclability of the nanocatalysts and their structures and compositions. Then, the methods of the state-of-the-art for synthesis of metal nanoparticles and supported metal nanoparticles with controllable sizes, shapes, and surface structures are summarized. In conclusion the recent advances of nano catalysis in different organic transformations,

new energy conversion, and environmental remediations are also reported.

NANOCATALYST: SIZE, SHAPE AND SURFACE CHEMISTRY

Researchers have not collectively settled on a precise definition of nanomaterials, but agree that they are partially characterized by their tiny size, measured in nanometers. A nanometer is one millionth of a millimeter approximately 100,000 times smaller than the diameter of a human hair.

Nano-sized particles exist in nature and can be shaped from a variety of products, such as carbon or minerals like silver, but nanomaterials by definition must have at least one dimension that is less than approximately 100 nanometers. Most nanoscale materials are too small to be seen with the naked eye and even with conventional lab microscopes. Materials engineered to such a small scale are often referred to as engineered nanomaterials, which can take on unique optical, magnetic, electrical, and other properties. These developing properties have the potential for great impacts in electronics, medicine, and other fields.

Materials at this scale are characterized by significantly different properties than molecules, atoms, or bulk items. Because of this, the field of nanoscience was coined to address this comparatively novel scientific field. Although the concept of this scientific area is not new, modern-day science is constantly discovering new and favorable applications for both the manufacturing sector and academia, which has found nanoscience as a growing and exciting field. The applications referred to are diverse, and range from environmental development to consumer products, and even therapeutic usage (Fig. 1).

Nanoparticles can take many shapes, including powder, crystal, and cluster formulae. Nano powder is used to describe mixtures of fine powder, whereas ultrafine particle mixtures are described as nanocrystals. Clusters can be further classified as nanoclusters if they have a narrow size distribution in the range of 1-10 nm and a minimum of one dimension. Metal nanoparticles are believed to be probable candidates for catalysis due to their relatively large surface area per volume or weight unit as compared with bulk metal, meaning heterogeneous metal nanoparticles catalysts typically function on metal surfaces. A variety of techniques is used to develop and supports for industrial metal catalysts, which

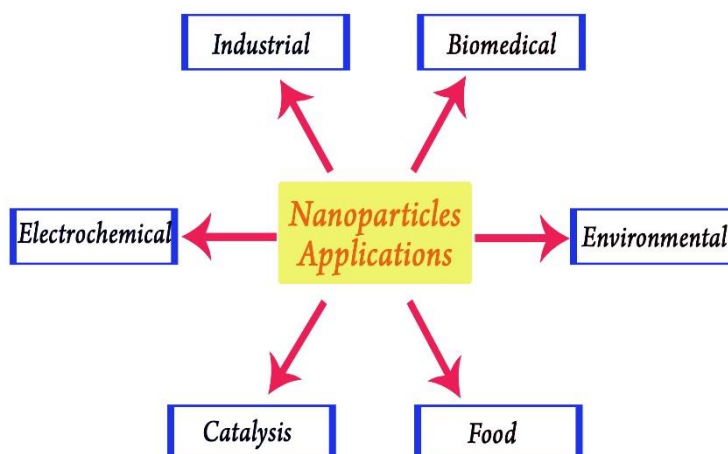


Fig. 1. General applications of nanoparticles in various fields.

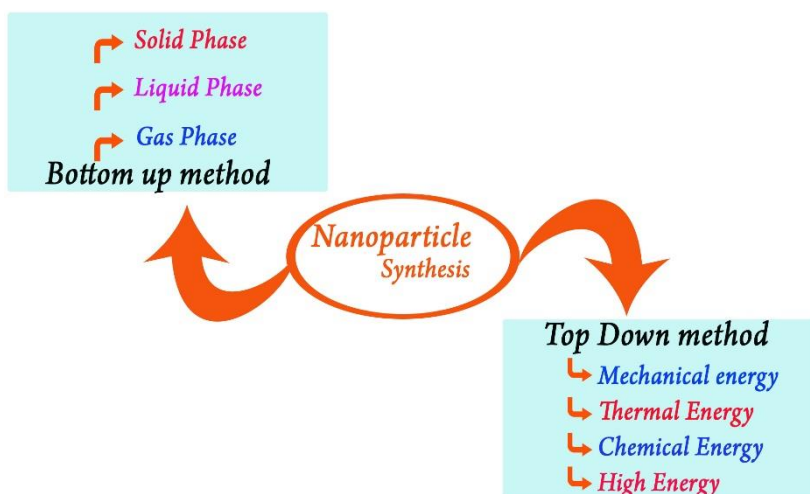


Fig. 2. Some important synthetic approaches for fabricating metal nanoparticles.

are frequently inorganic and characterized by highly dispersed metals and voluminous surface area. Metal nano particles are having a tendency to collaborate, consisting of more than one particle in a range of forms and dimensions. Polyhedral particles are formed from the interaction of metal nanoparticles with the inorganic supports. Silica gel, activated charcoal, and alumina, among others, are examples of transition metals that are formed from metal particles distributed onto inorganic supports. These are superior to metal powders for numerous reasons such as stable thermal capacity, reduced cost, larger surface area, and effective use of metal nanoparticles in the form of wide dispersion [15].

SYNTHESIS AND CHARACTERIZATION

SYNTHETIC METHODS

Metal nanoparticle synthesis typically takes place in one of two ways: top-down or bottom-up approach, as shown in Fig. 2. The top-down approach uses an external force to pressure bulk materials, eventually causing these materials to break down into smaller components by means of mechanical, chemical, or some other energy sources. A bottom-up approach takes place in a reverse approach, growing precursor particle size by using chemical reactions to combine atomic or molecular species. It should be noted that the top-down approach is considered to be a physical method while the bottom-up approach is chemical.

Table 1. Summary of some selected characterization techniques of metal nanoparticles.

SI No	Characterization techniques	Information received	Reference
1	Scanning electron microscopy (SEM)	Size and Morphology of MNPs	[16]
2	Transmission electron microscopy (TEM)	Size and Morphology of MNPs	[16]
3	X-ray photoelectron spectroscopy (XPS)	Surface composition of supported MNPs	[17]
4	UV-Vis spectrum	Formation of colloidal MNPs (Plasmon band)	[18]
5	X-ray diffraction (XRD)	Crystal structure and size, chemical composition	[19]
6	Dynamic light scattering (DLS)	Size and size distribution of MNPs in solution	[20]
7	Fourier transformed infrared spectroscopy (FTIR)	Different functional groups and metal-metal and/or metal-oxygen bond identification	[21]
8	Energy Dispersive X-ray (EDX)	Element and distribution of MNPs	[22]
9	Scanning tunneling microscope Raman Spectroscopy	Size and structure of MNPs Chemical structure, phase and morphology	[22-26]

Both approaches can be applied in a range of states, including liquid, solid, gas, supercritical fluids, or vacuum. The final desired outcome and manufacturer must play into the choice between the two methods. Because size and shape of the metal particles is the most vital aspect to be altered for improved application performance, it is a dynamic aspect to take into account for catalysis as an example. This section will address some selected methods for fabricating metal nanoparticles, including physical and chemical methods.

CHARACTERIZATION METHODS

Nanoscale materials have a special set of properties, making them appropriate for a variety of applications and resulting in them being a focal point for a range of researches. Deep understanding of the properties of metal particles at nanoscale level is essential to understand the nature of active sites, which in turn can help to find and tune the key performance signs. Numerous techniques exist that are designed to characterize nanoparticles, although none of these are able to supply full information regarding investigated materials. For this reason, several techniques must be used to categorize each sample in order to understand the size, structure, and catalytic properties. Table 1 describes the various methods of analyses are used for the characterization of metal nanoparticles.

In common method of characterizing MNPs include transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [16]. Other techniques include X-ray photoelectron

spectroscopy (XPS) [17], UV visible spectroscopy [18], atomic force microscopy, powder X-ray diffractometry (XRD) [19], and dynamic light scattering (DLS) [20]. UV spectroscopy and Fourier transformed infrared spectroscopy (FTIR) [21] methods would be combined to examine gold and palladium nanoparticles, as described elsewhere. Conversely, silver nanoparticles would be examined using TEM, high-resolution TEM, and selected area diffraction pattern (SAED). Finally, X-ray diffraction, SEM, and FTIR would be combined to examine magnetite, Ag, zinc, and Au nanoparticles [22–26].

CATALYTIC APPLICATIONS OF METAL NANOPARTICLES

Nano catalysis is newly growing field and is essential component of “sustainable technology and organic transformations” applicable to almost all types’ catalytic organic transformations [27]. In chemical technology the use of catalysts is of great importance. Limited amount of catalyst with high activities is particularly desirable for economic and environmental considerations. Among all nano catalysts, several forms such as magnetic nano catalysts [7], nano mixed metal oxides, core-shell nano catalysts, nano-supported catalysts, graphene-based nano catalysts have been employed in catalytic applications (Table 2) [28]. Magnetic nano catalysts stand apart in this group of reusable nano catalysts due to their low preparation cost, excellent activity, great selectivity, high stability, efficient recovery and good recyclability.

Further, various metal nanoparticles are used in organic synthesis in different reaction

Table 2. Different types of nanomaterials and their size, shape, and catalytic applications.

Sl. No.	Nanomaterials	Size	Shape	Applications	Reference
01	Zinc oxide (ZnO)	100nm	Nanorods, wires and particles	Shape dependent oxidative decomposition of Butane. It could completely oxidize butane into carbon oxides (CO _x). Better carbon balance and CO _x selectivity were obtained with the ZnO Nano wires and Nanorods than with the nanoparticles.	[29]
02	Graphene oxide (GO) and Carbon	--	Multi-wall Carbon nano tubes	In the presence of graphene oxide the catalytic activity of cyt c increases up to 78-fold & up to 2.5-fold in the presence of other functionalized carbon based nanomaterials.	[30]
03	Strontium (II)-added ZnAl ₂ O ₄ nanomaterials	2-5 μ m	Spinel structure	Addition of strontium improves the performance of zinc aluminate for selective oxidation of alcohols and decreases the grain size.	[31]
04	Au-Pt nanomaterials	5-10nm	Cage bell structures	Catalytic activity in the direction of oxygen reduction in proton exchange membrane fuel cells because of higher surface areas than their solid counterparts. Nano-channels on the Pt shell permit the access of the inner surface areas. Electronic coupling effect occurs between the inner-placed Au core and the Pt shell. Mixed catalysts also demonstrated improved oxygen reduction reaction activities. CCNTs had an uncommon feature by which can construct a multi-dimensional network to facilitate the mass transportation and electrons/protons transfer.	[32]
05	Carbon Nano tubes (CNTs)	--	Coiled in shape	Catalytic activity toward oxygen evolution of the nanomaterials was investigated. CuO nanowire had lowest over potential for water oxidation and CuO microsphere material had the best catalytic current densities from 1.10- 1.40 V.	[33]
06	CuO Nanomaterials	200-500 nm	Microspheres, nano sheets, nano wires	For heating water for a variety of potential thermal, thermo chemical and mechanical applications.	[34]
07	Graphite Oxide	50-500 nm	Flakes	Activation of COF-102 and COF-103 for gas adsorption measurements. Low Pressure (0-760mTorr) Argon Adsorption Measurements for COF-102.	[35]
08	Covalent Organic Frameworks (COF)	1 μ m	--	Studied photo catalytic degradation and antimicrobial activities.	[36]
09	ZnO nanoparticles	10nm	Sheet, particle & spindle	Studied photo catalytic degradation and antimicrobial activities.	[2]
10	BiVO ₄ nanoparticles	--	nanoparticles	Studied photo catalytic degradation and antimicrobial activities.	[4]

conditions. The synthesis of quinoxalines was carried out by oxidative coupling of 1, 2-diamines, and 1, 2-dicarbonyl compounds, by using gold nanoparticles supported on nano particulated ceria (Au/CeO) or hydrotalcite (Au/HT) as catalysts and air as an oxidant. The use of nanoparticles led to the gentle reaction conditions such as base-free reactions, using mild temperature and air as an oxidant [37]. Khan and coworkers synthesized 1-(4, 5-dihydropyrazol-1-yl) isoquinolines, from chalcones and 1-hydrazinyl isoquinoline and using iron-oxide nanoparticles and this method of synthesis eliminates the autooxidation of the desired pyrazolines to the corresponding pyrazoles [38]. Furthermore, ZnO- nanoparticles were synthesized using the microwave assisted sol-gel technique with an average particle size of 24 nm and well characterized. After the synthesis photocatalytic degradation of food dye Tartrazine (Acid Yellow 23) was tested and obtained a

promising results [22, 23].

Structure and shape-dependent properties of any materials at its nanoscale size can likewise impact the reactant mobility of a material. Further, the calibration of nano catalyst in specific shape and size for synthesis has achieved more noteworthy selectivity [39-41]. By better understanding of these applications, a researcher can design and develop nano catalysts which are extremely dynamic, deeply specific, and extremely tough. Every one of these points of interest will empower modern synthetic responses to turn out to be more asset proficient, consume less energy, and produce less waste which help to counter the ecological effect brought about by our dependence on synthesis process. Nanoparticles are perceived as the most significant modern catalyst and have more extensive application extending from chemical manufacturing to energy transformation and storage applications [42-44].

FUTURE PROSPECTS AND CHALLENGES

With the advancements in nanomaterial science' synthetic techniques and expansion of their diverse application scopes, the production of nanomaterials in industrial scale have a great impact on the traditional chemical industry and its allied production industries. Metallic nanomaterials, a new and emerging type of nanomaterial, have provocative prospects in the fields of microelectronics, optoelectronics, and sensors, especially in catalytic areas, due to the excellent electrical, optical, magnetic and thermal properties. Further, preparation of metallic nanomaterials is a quite difficult to attain the large-scale industrial production. Therefore, there is still a long way to realize the industrial production and allied applications. In additional, there are many challenges to be addressed, among a few is mentioned here the first challenge is, in the industrialization is how to achieve the mass production of metallic nanomaterials. Secondly, as catalytic materials, it is very vital to construct novel structures and compositions on the nanometer scale, so as to design and synthesize appropriate catalysts used in various reactions so on.

Investigation of the bio-inspired efforts in the synthesis of the nanomaterials and its catalytic application in the recoverability, biodegradability and bioremediation are the forthcoming fields of the nanocatalysts. The various catalytic applications of nano materials could be bettered near future. Further, it is also becoming very significant to explore the applications of metallic nanomaterials actively in other fields and broaden the breadth and sophistication of their applications in materials science, chemistry, biology, physics and some allied disciplines.

CONCLUSIONS

This review is the effort to assemble the literature on the topic of nanomaterials application in organic synthesis and other catalytic properties. It should be well-known that a correct and update citation and literature survey is very significant for researchers to find relevant information, pioneer ideas, and progress of any topic. On the other hand, published data using nanomaterials indicate a wide synthetic potential of the described catalysts and a great interest of researchers in this field. The use of green nanocatalyst for the synthesis of a variety of heterocycles has advantages such as short reaction time, high yield, inexpensive chemicals usage, easy

work-up procedure, and very specific reactions. In most of the reactions the spent catalyst can be easily separated from the reaction mixture, also it can be reused without noticeable change in its catalytic activity. Further, nanotechnology can be used to design pharmaceuticals that can target specific organs or cells in the body such as cancer cells, and enhance the effectiveness of therapy. Nanomaterials can also be added to cement, cloth and other materials to make them stronger and yet lighter. Their size makes them extremely useful in electronics, and they can also be used in environmental remediation or clean-up to bind with and neutralize toxins.

ACKNOWLEDGEMENTS

All the authors are gratefully acknowledging the NIE Management and JSS Mahavidyapeeta, for their encouragement and constant support to carry out the research work.

CONFLICT OF INTEREST

Authors have no conflict of interest.

REFERENCES

- [1] Ojima I., Clos N., Bastos C., (1989), Recent advances in catalytic asymmetric reactions promoted by transition metal complexes. *Tetrahedron*. 45: 6901-6939.
- [2] Mallikarjunaswamy C., Lakshmi Ranganatha V., Ramu R., Udayabhanu U., Nagaraju G., (2020), Facile microwave-assisted green synthesis of ZnO nanoparticles: Application to photodegradation, antibacterial and antioxidant. *J. Mater. Sci. Mater. Electron*.31: 12-18.
- [3] Ranganatha V. L., Nithin K. S., Khanum S. A., Nagaraju G., (2019), Zinc oxide nanoparticles: A significant review on synthetic strategies, characterization and applications, AIP Conference Proceedings 2162, 020089.
- [4] Pramila S., Nagaraju G., Mallikarjunaswamy C., Latha K. C., Chandan S., Ramu R., Rashmi V., Lakshmi Ranganatha V., (2020), Green Synthesis of BiVO₄ nanoparticles by microwave method using Aegle marmelos juice as a fuel: Photocatalytic and antimicrobial study. *Anal. Chem. Lett*. 10: 298-306.
- [5] Basina G., Polychronopoulou K., Zedan A. F., Dimos K., Katsiotis M. S., Fotopoulos A. P., Ismail I., Tzitzios V., (2020), Ultrasmall metal-doped CeO₂ nanoparticles for low-temperature CO Oxidation. *ACS Appl. Nano Mater*. 3: 10805-10813.
- [6] Choudhury B., Choudhury A., (2012), Ce³⁺ and oxygen vacancy mediated tuning of structural and optical properties of CeO₂ nanoparticles. *Mater. Chem. Phys*. 131: 666-671.
- [7] Ranganatha V. L., Pramila S., Nagaraju G., Surendra B. S., Mallikarjunaswamy C., (2020), Cost-effective and green approach for the synthesis of zinc ferrite nanoparticles using Aegle Marmelos extract as a fuel: Catalytic, electrochemical, and microbial applications. *J. Mater. Sci. Mater. Electron*. 20: 1-18.

- [8] Shanmugam S., Hari A., Pandey A., Mathimani T., Felix L., Pugazhendhi A., (2020), Comprehensive review on the application of inorganic and organic nanoparticles for enhancing biohydrogen production. *Fuel*. 270: 117453-117459.
- [9] Jiang L., Liu K., Hung S.-F., Zhou L., Qin R., Zhang Q., Liu P., Gu L., Chen H. M., Fu G., (2020), Facet engineering accelerates spillover hydrogenation on highly diluted metal nanocatalysts. *Nat. Nanotechnol.* 15: 848-853.
- [10] Tegenaw A., Sorial G. A., Sahle-Demessie E., Han C., (2020), Role of water chemistry on stability, aggregation, and dissolution of uncoated and carbon-coated copper nanoparticles. *Environ. Res.* 187: 109700-109708.
- [11] Zablotsky D., Kuzovkov V., Kotomin E., (2020), Role of intrinsic dipoles in the evaporation-driven assembly of perovskite nanocubes into energy-harvesting composites. *Phys. Status Solidi*. 217: 1900533-1900539.
- [12] Moudgil D., Khullar V., (2020), Direct photo-thermal energy storage using nanoparticles laden phase change materials. *Solar Energy*. 235-246.
- [13] García-Rodríguez A., Moreno-Olivas F., Marcos R., Tako E., Marques C. N. H., Mahler G. J., (2020), The role of metal oxide nanoparticles, *Escherichia coli*, and *Lactobacillus rhamnosus* on small intestinal enzyme activity. *Env. Sci. Nano*. 12: 25 Pages.
- [14] Liu H., Guan J., Mu X., Xu G., Wang X., Chen X., (2016), Nanocatal Encycl. *Phys. Org. Chem.* 1-75.
- [15] Alshammari A. S., Chi L., Chen X., Bagabas A., Kramer D., Alromaeh A., Jiang Z., (2015), Visible-light photocatalysis on C-doped ZnO derived from polymer-assisted pyrolysis. *RSC Adv*. 5: 27690-27698.
- [16] Altenhoff M., Aßmann S., Teige C., Huber F. J. T., Will S., (2020), An optimized evaluation strategy for a comprehensive morphological soot nanoparticle aggregate characterization by electron microscopy. *J. Aerosol Sci.* 139: 105470.
- [17] Baer D. R., (2020), Guide to making XPS measurements on nanoparticles. *J. Vac. Sci. Technol. A Vacuum, Surf. Film*. 38: 31201-31207.
- [18] Kumar B., Smita K., Debut A., Cumbal L., (2020), Synthesis and characterization of SnO₂ nanoparticles using cochineal dye. *Appl. Phys. A*. 126: 1-9.
- [19] Sundaram P. S., Sangeetha T., Rajakarthisan S., Vijayalakshmi R., Elangovan A., Arivazhagan G., (2020), XRD structural studies on cobalt doped zinc oxide nanoparticles synthesized by coprecipitation method: Williamson-Hall and size-strain plot approaches. *Phys. B Condens. Matter*. 595: 412342-412348.
- [20] Ahmad T., Nazim A., Farooq U., Khan H., Jain S. K., Ubaidullah M., Ahmed J., (2020), Biosynthesis, characterization and photo-catalytic degradation of methylene blue using silver nanoparticles. *Mater. Today Proc.* 29: 1039-1043.
- [21] Sinha N., Joshi A. S., Thakur A. K., (2020), Analytical validation of an ATR-FTIR based method for quantifying the amount of polysorbate 80 adsorbed on PLGA nanoparticles. *Anal. Methods*. 44: 7 page(s).
- [22] Srivastava S. K., Yamada R., Ogino C., Kondo A., (2013), Biogenic synthesis and characterization of gold nanoparticles by *Escherichia coli* K12 and its heterogeneous catalysis in degradation of 4-nitrophenol. *Nanoscale Res. Lett.* 8: 70-77.
- [23] Parida U. K., Bindhani B. K., Nayak P., (2011), Green synthesis and characterization of gold nanoparticles using onion (*Allium cepa*) extract. *World J. Nano Sci. Eng.* 1: 93-98.
- [24] Petla R. K., Vivekanandhan S., Misra M., Mohanty A. K., Satyanarayana N., (2012), Soybean (*Glycine max*) leaf extract based green synthesis of palladium nanoparticles. *J. Biomater. Nanobiotech.* 3: 14-19.
- [25] Lee J. H., Ahn K., Kim S. M., Jeon K. S., Lee J. S., Yu I. J., (2012), Continuous 3-day exposure assessment of workplace manufacturing silver nanoparticles. *J. Nanopart. Res.* 14: 1134-1139.
- [26] Yang H., Wang Y., Huang H., Gell L., Lehtovaara L., Malola S., Häkkinen H., Zheng N., (2013), All-thiol-stabilized Ag 44 and Au 12 Ag 32 nanoparticles with single-crystal structures. *Nat. Commun.* 4: 2422-2427.
- [27] Gawande M. B., (2014), Sustainable nanocatalysts for organic synthetic transformations. *Org. Chem. Curr. Res.* 3: 1000e137.
- [28] Gawande M. B., Shelke S. N., Zboril R., Varma R. S., (2014), Microwave-assisted chemistry: synthetic applications for rapid assembly of nanomaterials and organics. *Acc. Chem. Res.* 47: 1338-1348.
- [29] Sanjeeva Gandhi M., Mok Y. S., (2014), Shape-dependent plasma-catalytic activity of ZnO nanomaterials coated on porous ceramic membrane for oxidation of butane. *Chemosphere*. 117: 440-446.
- [30] Patila M., Pavlidis I. V., Diamanti E. K., Katapodis P., Gournis D., Stamatis H., (2013), Enhancement of cytochrome c catalytic behaviour by affecting the heme environment using functionalized carbon-based nanomaterials. *Process Biochem.* 48: 1010-1017.
- [31] Kumar T. R., Selvam C. S. N., Ragupathi C., Kennedy J. L., Vijaya J. J., (2014), Synthesis, characterization and performance of porous Sr(II)-added ZnAl₂O₄ nanomaterials for optical and catalytic applications. *Powder Technol.* 224: 147-154.
- [32] Qu J., Liu H., Ye F., Hu W., Yang J., (2012), Cage-bell structured Au-Pt nanomaterials with enhanced electrocatalytic activity toward oxygen reduction. *Int. J. Hydrogen Energy*. 37: 13191-13199.
- [33] Zhang J., Tang S., Liao L., Yu W., Li J., Seland F., Haarberg G. M., (2014), Improved catalytic activity of mixed platinum catalysts supported on various carbon nanomaterials. *J. Power Sources*. 267: 706-713.
- [34] Liu X., Cui S., Sun Z., Du P., (2015), Copper oxide nanomaterials synthesized from simple copper salts as active catalysts for electrocatalytic water oxidation. *Electrochim. Acta*. 160: 202-208.
- [35] Abdelsayed V., Moussa S., Hassan H. M., Aluri H. S., Collinson M. M., El-Shall M. S., (2010), Photothermal deoxygenation of graphite oxide with laser excitation in solution and graphene-aided increase in water temperature. *J. Phys. Chem. Lett.* 1: 2804-2809.
- [36] Rabbani M. G., El-Kaderi H. M., (2011), Template-free synthesis of a highly porous benzimidazole-linked polymer for CO₂ capture and H₂ storage. *Chem. Mater.* 23: 1650-1653.
- [37] Climent M. J., Corma A., Hernández J. C., Hungria A. B., Iborra S., Martínez-Silvestre S., (2012), Biomass into chemicals: one-pot two- and three-step synthesis of quinoxalines from biomass-derived glycols and 1, 2-dinitrobenzene derivatives using supported gold nanoparticles as catalysts. *J. Catal.* 292: 118-129.
- [38] Khan F. N., Manivel P., Prabakaran K., Jin J. S., Jeong

- E. D., Kim H. G., Maiyalagan T., (2012), Iron-oxide nanoparticles mediated cyclization of 3-(4-chlorophenyl)-1-hydrazinylisoquinoline to 1-(4, 5-dihydropyrazol-1-yl) isoquinolines. *Res. Chem. Intermed.* 38: 571-582.
- [39] Sadjadi S., Majid M. H., Malmir M., (2018), Pd (0) Nanoparticle immobilized on cyclodextrin nanosponge-decorated $\text{Fe}_2\text{O}_3@/\text{SiO}_2$ core-shell hollow sphere: an efficient catalyst for CC coupling reactions. *J. Taiwan Inst. Chem. Eng.* 86: 240-251.
- [40] Candelaria S. L., Shao Y., Zhou W., Li X., Xiao J., Zhang J.-G., Wang Y., Liu J., Li J., Cao G., (2012), Nanostructured carbon for energy storage and conversion. *Nano Energy*. 1: 195-220.
- [41] Yan K., Chen A., (2013), Efficient hydrogenation of biomass-derived furfural and levulinic acid on the facilely synthesized noble-metal-free Cu–Cr catalyst. *Energy*. 58: 357-363.
- [42] Cuenya B. R., (2010), Synthesis and catalytic properties of metal nanoparticles: Size, shape, support, composition, and oxidation state effects. *Thin Solid Films*. 518: 3127-3150.
- [43] Sun C. Q., S(2007), Size dependence of nanostructures: Impact of bond order deficiency. *Prog. Solid State Chem.* 35: 1-159.
- [44] Saurabh Somwanshi B., Prashant B., Kharat B., (2020), Nanocatalyst: A brief review on synthesis to applications. *J. Phys: Conf. Series* 1644: 012046-012052.