NANOCATALYST IN CHEMISTRY FROM SYNTHESIS TO INDUSTRIAL APPLICATIONS

Farwa Saleem[1], Muhammad Umair Khan*[2], Mehmood Hassan[3], Muniba Fatima[4], Waqas Mahmood[5], Awais Ur Rehman[6], Muhammad Shahzaib[7], Nayab Ahmad[8]

[1]*Department of Chemistry, Government College University Faisalabad, Pakistan*
[*2]*Department of Chemistry, Abdul Wali Khan University Mardan, Pakistan*
[3,4]*Department of Chemistry, Riphah International University Campus, Faisalabad, Pakistan*
[5]*Department of Pharmaceutical Chemistry, The Islamia University of Bahawalpur, Pakistan*
[6]*Department of Physics, Hazara University Mansehra, Pakistan*
[7]*Department of Chemistry, Ghazi University, Dera Ghazi Khan, Pakistan*
[8]*Institute of Biotechnology and Genetic Engineering, The University of Agriculture Peshawar, Pakistan*

[1]saleemfarwa16@gmail.com, [*2]umairxaib1@yahoo.com, [3]mehmmodhassan435@gmail.com, [4]fmuniba089@gmail.com, [5]Drwaqasmta@gmail.com, [6]awaisurrehmanphysicist@gmail.com, [7]shahzaibahmdani1@gmail.com, [8]NayabAhmadkhan8314@gmail.com

DOI: https://doi.org/10.5281/zenodo.14974316

Keywords
Nanocatalysts, synthesis, green chemistry, industrial applications, sustainability, energy production

Article History
Received on 25 January 2025
Accepted on 25 February 2025
Published on 04 March 2025

Corresponding Author: *

Abstract

Nanocatalysis has emerged as a transformative field in chemistry, offering enhanced efficiency, selectivity, and sustainability in a wide range of chemical processes. This review focuses on nanocatalysts, examining their synthesis, mechanisms, and industrial applications. The ability to tailor the size, shape, and surface properties of nanocatalysts provides unique advantages over traditional catalysts, enabling faster reaction rates and higher selectivity for specific reactions. The synthesis of Nanocatalysts can be achieved through top-down and bottom-up methods, with approaches such as chemical vapor deposition, sol-gel processes, and green synthesis gaining significant attention for their eco-friendly nature. Characterization techniques like TEM, XPS, and BET analysis allow for the detailed study of Nanocatalyst morphology, surface area, and catalytic activity. The review explores how Nano catalysts function, particularly focusing on their surface effects, interaction with reactants, and the influence of their nanostructure on catalytic performance. Nanocatalysts have found widespread applications in diverse industrial sectors, including energy production, environmental remediation, and the pharmaceutical industry. They play a crucial role in green chemistry, such as in CO2 reduction, wastewater treatment, and biofuel production. Additionally, nanocatalysts are integral to the synthesis of fine chemicals, enhancing the efficiency of reactions used in pharmaceuticals, polymers, and agrochemicals. Despite their promising applications, challenges remain regarding scalability, cost, recyclability, and environmental impact. However, advancements in nanocatalyst design and emerging technologies are paving the way for more sustainable and effective industrial processes. This review highlights the critical role of nanocatalysts in shaping the future of chemical industries.

INTRODUCTION

Catalysis is one of the pioneer utilizations of nanoparticles. Different components and materials like aluminum, iron, titanium dioxide, and silica all have been utilized as catalysts in nanoscale form in the past decades[1],[2]. In any case, suitable clarification of its gigantic synergist conduct appearing by NPs despite everything has not been completely comprehended. The enormous surface area of nanoparticles has a straightforward beneficial outcome on reaction rate and may likewise be a sensible clarification of its reactant movement. The structure and shape-dependent properties of any material at its nanoscale size can likewise impact the reactant movement of a material. The calibrating of nanocatalysts, as far as synthesis, shape, and size has achieved more noteworthy selectivity. In this way, the inquest here is how the physical properties of nanoparticles influence their reactant properties, and how manufacture boundaries can thus influence those physical properties[3],[4]. By better comprehension of these, a researcher can design and develop nanocatalysts that are exceptionally dynamic, profoundly particular, and exceptionally 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 helps to counter the ecological effect brought about by our dependence on the synthesis process. Nanoparticles are perceived as the most significant modern catalyst and have more extensive applications extending from chemical manufacturing to energy transformation and storage applications.

Homogeneous catalysis and heterogeneous catalysis each have their advantages and disadvantages. For example, homogeneous catalysis exhibits a high reactivity, a good selectivity, and excellent reaction yield; however, it is easier to manage heterogeneous catalytic reactions and to remove the catalysts from the reaction mixtures after these reactions. Nonetheless, there is considerable difficulty in product/catalyst separation in homogeneous catalysis and decreased overall catalytic efficiency in heterogeneous catalysis [5],[6]. Therefore, new catalyst systems are highly desirable.

Because of their high surface area, nanomaterials have emerged to bridge the gap between homogeneous and heterogeneous catalysis approaches. Common nanocatalysts include carbon-based nanomaterials (fullerenes [7] graphene and carbon nanotubes, metals (iron, silver, gold, and cobalt, oxides (zinc oxide, titanium dioxide, and silicon dioxide, and other nanomaterials (such as quantum dots [8]. Compared to regular catalysts, nanocatalysts possess certain unique advantages, such as an enhanced mixing with reactants and easy separation from the reaction mixture due to their insolubility in various solvents. Moreover, it is easier to regulate the catalytic activity and selectivity of nanocatalysts by tailoring the chemical and physical properties of the catalysts. Indeed, the use of nanocatalysts may lead to improved energy efficiency and economy. For instance, a hydrotalcite nanocatalyst was found to be stable, inexpensive, highly active, and selective for the hydrolysis of cellulose to glucose. Much less chemical waste and optimized feedstock utilization have also been achieved using nanocatalysts. Given the numerous potential benefits (Figure 1), nanocatalysts have been applied in various areas, including refineries [9], petrochemical plants, the pharmaceutical industry , the chemical industry , food processing , and environmental applications [10]. According to Global Industry Analysts, the global nanocatalyst market is projected to reach 6 billion US dollars by 2015. When the size of a material is reduced to the nanoscale, the material often exhibits unusual physicochemical properties. In addition to improved catalytic activity, conductivity, reactivity, and optical sensitivity, nanosized materials also exhibit increased uptake in and interactions with biological tissues and can affect biological functions. Indeed, recent studies on potential nanotoxicity to human health and the eco-environment have drawn attention from both government agencies and the general public [11].

Nanocatalysts are transforming sustainable chemical processes by offering enhanced performance, efficiency, and selectivity. Their unique properties and capabilities align well with the principles of green chemistry, making them invaluable in developing more sustainable chemical processes. Nanocatalysts have a high surface area-to-volume ratio, which provides more active sites for catalytic reactions compared to bulk catalysts. This increased surface area results in higher catalytic activity and efficiency, allowing for faster reaction rates and lower catalyst concentrations. By improving the efficiency of catalytic reactions, nanocatalysts help reduce the amount of catalyst required and minimize waste generation, aligning with the principle of prevention in green chemistry [12]. Nanocatalysts can be engineered to exhibit high selectivity for specific reactions, leading to the formation of desired products with fewer by-products. This high selectivity reduces the need for extensive purification steps, decreasing the amount of waste generated during the chemical process. For example, nanocatalysts with tailored surface properties can selectively catalyze certain reactions, enhancing product yield and purity while minimizing the formation of unwanted by-products. Many nanocatalysts enable chemical reactions to proceed under milder conditions, such as lower temperatures and pressures. This ability to operate efficiently under less extreme conditions reduces the energy requirements of chemical processes, leading to lower energy consumption and decreased environmental impact. The use of milder reaction conditions is consistent with the green chemistry principle of energy efficiency and helps in minimizing the overall carbon footprint of chemical processes [13]. Nanocatalysts often exhibit excellent stability and can be reused multiple times without significant loss of activity. This reusability reduces the need for fresh catalyst material and minimizes waste production. Techniques such as magnetic separation or recovery through filtration make it easier to retrieve and recycle nanocatalysts, further supporting the sustainability of chemical processes. Recyclable nanocatalysts contribute to the principles of less hazardous chemical synthesis and recycling, promoting more sustainable practices in industrial applications[14]. Nanocatalysts are increasingly being used to catalyze reactions involving renewable feedstocks, such as biomass-derived materials. By facilitating the conversion of renewable resources into valuable chemicals, nanocatalysts help reduce reliance on non-renewable raw materials and support the principle of using renewable feedstocks. This approach not only contributes to sustainability but also supports the development of green chemistry solutions for producing bio-based chemicals and materials Nanocatalysts offer several significant advantages over traditional catalysts, primarily due to their unique size-dependent properties and enhanced performance characteristics. One of the most notable benefits is their extremely high surface area-to-volume ratio, which provides more active sites for catalytic reactions compared to bulk catalysts. This increased surface area leads to higher catalytic activity and efficiency, resulting in faster reaction rates and improved overall performance. Likewise, the high surface area allows nanocatalysts to achieve high activity in smaller quantities, reducing material consumption and waste. The nanoscale size and unique electronic properties of nanocatalysts further enhance their catalytic activity, enabling more reactant molecules to interact with the catalyst and accelerating the reaction process. Moreover, the ability to engineer the size and shape of nanocatalysts for specific reactions often results in significantly higher reaction rates compared to traditional bulk catalysts. Nanocatalysts also offer improved selectivity, stability, and versatility, which are crucial for advancing chemical processes and achieving sustainability goals. By tailoring the size, shape, and surface properties of nanocatalysts, precise control over their catalytic behavior can be achieved, enhancing selectivity for specific reactions and minimizing unwanted by-products. This high selectivity improves product yields and reduces the need for extensive downstream purification processes, making chemical processes more efficient and sustainable. Furthermore, nanocatalysts can facilitate reactions under milder conditions, such as lower temperatures and pressures, reducing energy requirements and minimizing environmental impact. Their enhanced stability and longevity, along with excellent recyclability and reusability, support sustainability by reducing the need for frequent catalyst replacement and minimizing waste. The versatility of nanocatalysts, which can be designed with specific properties for a wide range of applications, makes them suitable for diverse chemical processes, from industrial synthesis to environmental remediation and emerging technologies like nanomedicine and energy technologies [15].

The objectives of this review are to explore various synthesis methods of nanocatalysts, analyze their physicochemical properties, and examine their fundamental catalytic mechanisms. It also aims to review their industrial applications and assess challenges such as scalability, stability, and environmental impact. The research gap includes limited large-scale production, lack of long-term stability studies, and an incomplete understanding of catalytic mechanisms. Additionally, concerns about environmental toxicity and the need for optimization in industrial applications remain unresolved. This review will address these gaps and propose future directions for sustainable nanocatalyst development.

3: Fabrication Techniques for Nanocatalyst

Bottom-Up Methods:

Nanostructures, nanomaterials, and nanocomposites can be fabricated using two different techniques, top-down and bottom-up [16]. The top-down approach involves lateral patterning of bulk materials by either subtractive or additive methods to realize nano-sized structures. Several methods are used to fabricate nanostructures using the top-down approach such as photolithography, scanning lithography, laser machining, soft lithography, nanocontact printing, nanosphere lithography, colloidal lithography, scanning probe lithography, ion implantation, diffusion, deposition [17]. Although the top-down approach has been playing a vital role in the fabrication of nanostructures, it has several limitations such as the development of imperfections in processed materials, high cost (lithographic processes), requirement of high surface finished materials, longer etching times [18]. In the bottom-up approach, nanostructures are fabricated by building upon single atoms or molecules. In this method, controlled segregation of atoms or molecules occurs as they are assembled into desired nanostructures (2–10 nm size range). In general, there are two basic methods utilizing the bottom-up approach, i.e., gas-phase synthesis and liquid-phase formation. Some of the methods used in the bottom-up approach include plasma arcing, chemical vapor deposition process, metal-organic decomposition, laser pyrolysis, molecular beam epitaxy, sol-gel method, wet synthesis, and self-assembly processes.

3.1 Chemical Vapor Deposition (CVD)

The chemical vapor deposition process is mostly used in the semiconductor industry for depositing thin films of various materials. The process involves exposure of the substrate to one or more volatile precursors. These precursors decompose the substrate and react with it to produce the desired deposit. In the process, vaporized precursors are first adsorbed onto a substrate at a high temperature, which then react with one another or decompose and produce crystals. There are three main steps involved in the process: (i) Reactants are transported onto the growth surface by a boundary layer, (ii) chemical reactions take place on the growth surface, and (iii) by-products formed by the gas-phase reaction are removed from the growth surface. Homogeneous nucleation takes place in gas phase, whereas heterogeneous nucleation takes place in the substrate.

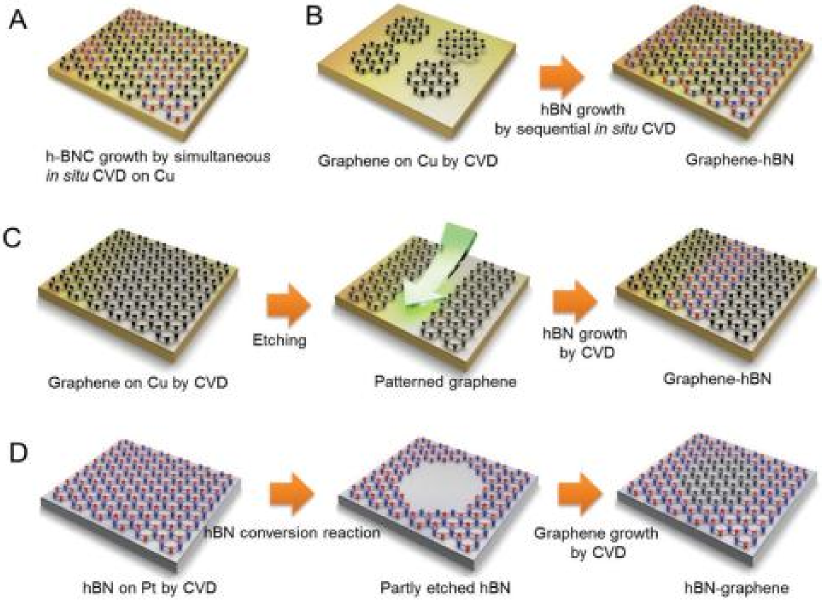

Figure 1: A schematic diagram of the growth of in-plane graphene and hBN heterostructures *via* various techniques: (A) simultaneous *in situ* CVD growth, (B) sequential *in situ* CVD growth, (C) lithography-assisted growth, and (D) conversion growth. Reprinted with permission from Copyright: ©2016, Elsevier B.V. All rights reserved.

3.1.1 Solgel Synthesis

In the sol-gel process, dispersed solid nanoparticles (sols with a diameter of 1–100 nm) are mixed in a homogeneous liquid medium and agglomerated to form a continuous three-dimensional network (gel) with pore diameter in the sub-micrometer domain in the liquid phase [19]. A sol is a liquid in which solid colloidal particles are dispersed, e.g., black inkjet ink (carbon black is dispersed in water), while a gel is a wet solid-like rigid network of interconnected nanostructures in a continuous liquid phase. Generally, three approaches have been employed to fabricate sol-gel film: (i) gelation of a solution of solid colloidal particles, (ii) hydrolysis and polycondensation of alkoxides followed by hypercritical drying of gels, and (iii) hydrolysis and polycondensation of alkoxide followed by aging and drying under ambient conditions. Several steps are involved in the process mixing (formation of suspended colloidal solution by mixing of nanoparticles in water), casting of a sol, gelation (formation of three-dimensional network), aging (for increasing the life of cast objects immersed in liquid), drying (removal of liquid from the interconnected continuous pore network), dehydration or chemical stabilization (to improve stability), and densification (heating the sol-gel at higher temperatures to eliminate pores and enhance the density, e.g., densification of alkoxide gels carried out at a temperature of 1000 °C). The properties of sol-gels depend on important parameters such as pH, type of solvent, temperature, time, catalysts, and agitation mechanisms.

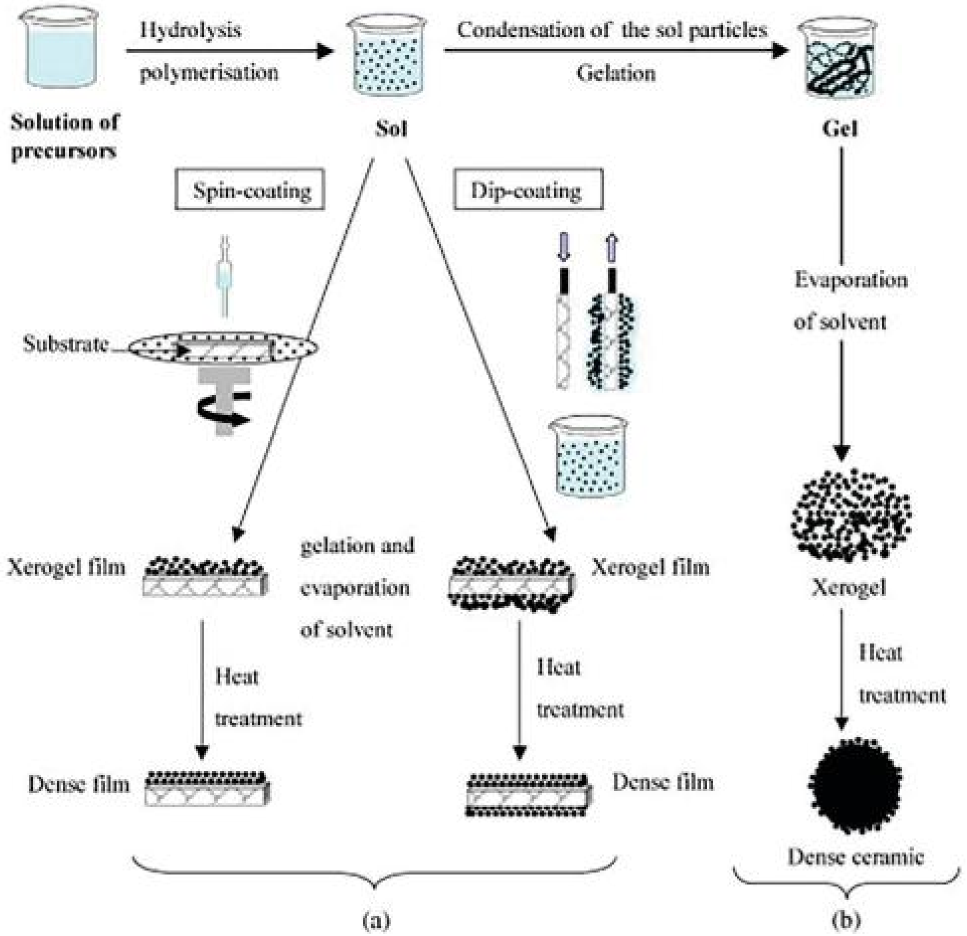

Figure 2: An overview showing two sol-gel method synthesis examples: (a) films from a colloidal sol and (b) powder from a colloidal sol transformed into a gel. Reprinted with permission from Copyright: ©2010, Elsevier B.V. All rights reserved.

4 Top-down approaches:

Mechanical milling. Mechanical milling is a cost-effective method for producing materials at the nanoscale level from bulk materials. Mechanical milling is an effective method for producing blends of different phases, and it is helpful in the production of nanocomposites. The principle of the ball milling method is shown in Fig. 3 Mechanical milling is used to produce oxide- and carbide-strengthened aluminum alloys, wear-resistant spray coatings, aluminum/nickel/magnesium/copper-based nanoalloys, and many other nanocomposite materials[20]. Ball-milled carbon nanomaterials are considered a novel class of nanomaterial, providing the opportunity to satisfy environmental remediation, energy storage, and energy conversion demands[21].

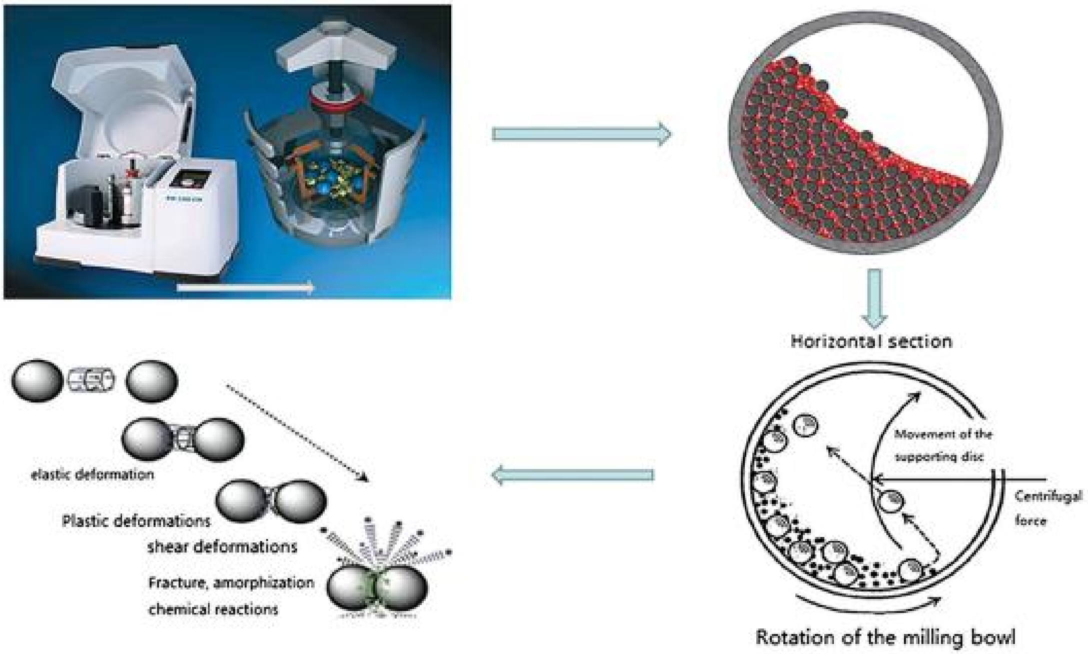

Figure 3: The principle of the ball milling method. Reprinted with permission from Copyright: ©2016, John Wiley & Sons, Ltd.

Electrospinning. Electrospinning is one of the simplest top-down methods for the development of nanostructured materials. It is generally used to produce nanofibers from a wide variety of materials, typically polymers[22]. One of the important breakthroughs in electrospinning was coaxial electrospinning. In coaxial electrospinning, the spinneret comprises two coaxial capillaries. In these capillaries, two viscous liquids, or a viscous liquid as the shell and a non-viscous liquid as the core, can be used to form core–shell nanoarchitectures in an electric field. Coaxial electrospinning is an effective and simple top-down approach for achieving core–shell ultrathin fibers on a large scale. The lengths of these ultrathin nanomaterials can be extended to several centimeters. This method has been used for the development of core–shell and hollow polymer, inorganic, organic, and hybrid materials[23]. A schematic diagram of the coaxial electrospinning approach can be seen in Fig. 3.30

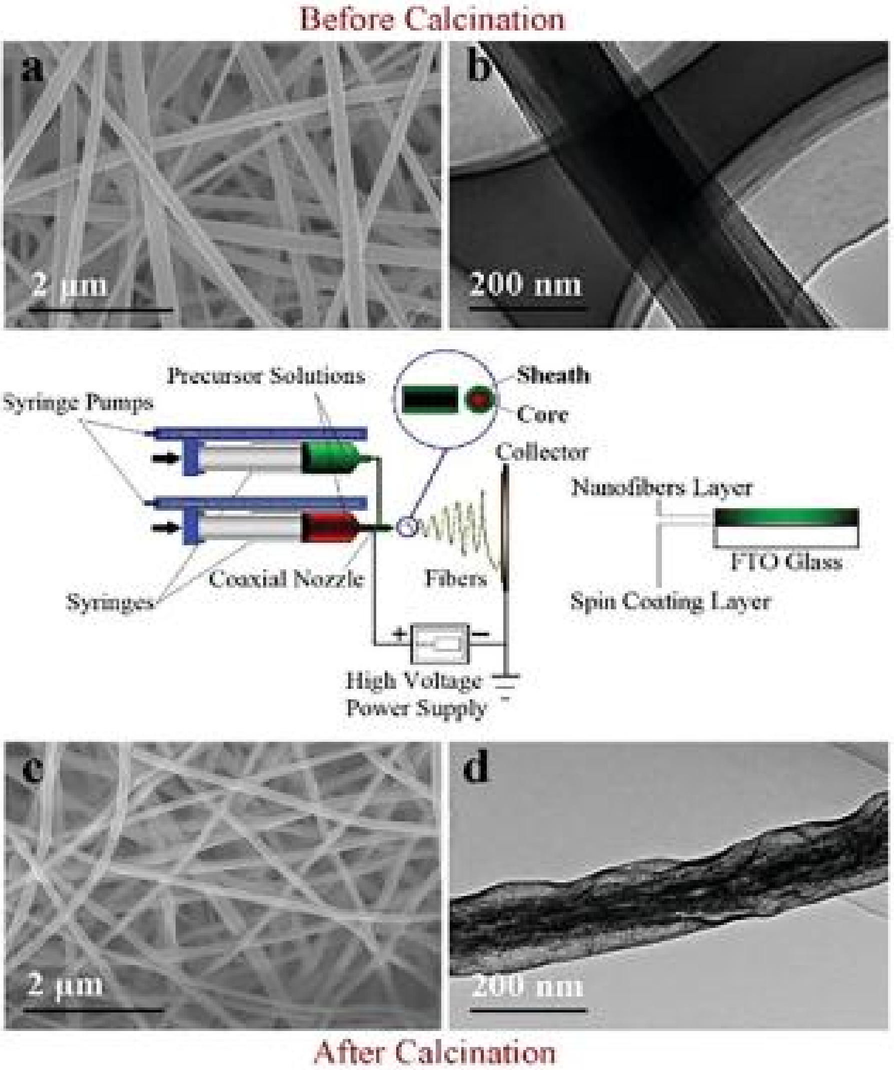

Figure 4: A schematic diagram of the coaxial electrospinning technique (center), FESEM (a and c), and TEM (b and d) images of fibers before and after calcination. Reprinted with permission from. Copyright: ©2012, Elsevier Ltd. All rights reserved.

4.1 Lithography.

Lithography is a useful tool for developing nanoarchitectures using a focused beam of light or electrons. Lithography can be divided into two main types: masked lithography and maskless lithography. In masked nanolithography, nanopatterns are transferred over a large surface area using a specific mask or template. Masked lithography includes photolithography, nanoimprint lithography,[21]. and soft lithography.Maskless lithography includes scanning probe lithography, focused ion beam lithography, and electron beam lithography. In maskless lithography, arbitrary nanopattern writing is carried out without the involvement of a mask. 3D freeform micro-nano-fabrication can be achieved via ion implantation with a focused ion beam in combination with wet chemical etching, as shown in Fig. 5

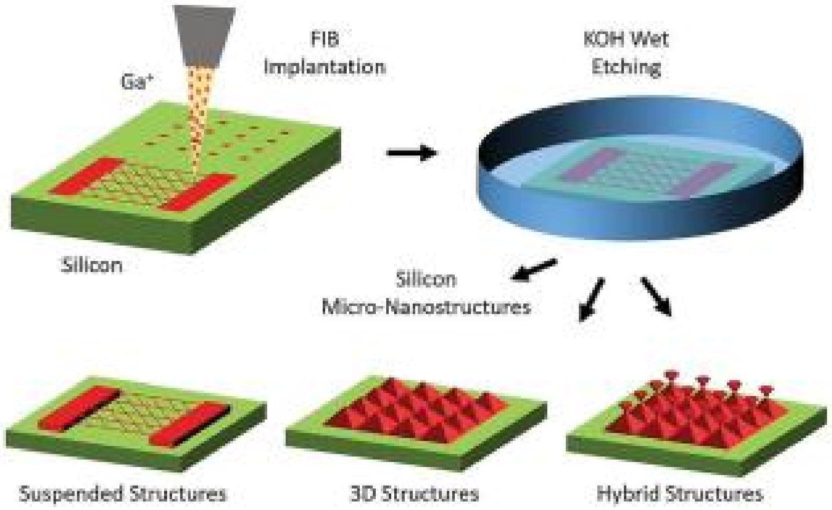

Figure 5: A schematic diagram of the fabrication of 3D micro-Nano-structures with an ion beam through bulk Si structuring. This involves the implantation in Si through Ga FIB lithography and mask-writing at nanometer resolution, subsequent anisotropic wet etching in KOH solution, and the fabrication of Si micro-nanostructures via the selective removal of the unimplanted region. Reprinted with permission from [24]. Copyright: r2020, Elsevier B.V. All rights reserved.

4.2 Sputtering:

Sputtering is a process used to produce nanomaterials via bombarding solid surfaces with high-energy particles such as plasma or gas. Sputtering is considered to be an effective method for producing thin films of nanomaterials. In the sputtering deposition process, energetic gaseous ions bombard the target surface, causing the physical ejection of small atom clusters depending upon the incident gaseous-ion energy (Fig. 6).The sputtering process can be performed in different ways, such as utilizing magnetron, radio-frequency diode, and DC diode sputtering. In general, sputtering is performed in an evacuated chamber, to which the sputtering gas is introduced. A high voltage is applied to the cathode target and free electrons collide with the gas to produce gas ions. The positively charged ions strongly accelerate in the electric field towards the cathode target, which these ions continuously hit, resulting in the ejection of atoms from the surface of the target [25]. Magnetron sputtering is used to produce WSe2-layered nanofilms on SiO2 and carbon paper substrates [26].The sputtering technique is interesting because the sputtered nanomaterial composition remains the same as the target material with fewer impurities, and it is cost-effective compared with electron-beam lithography[27].

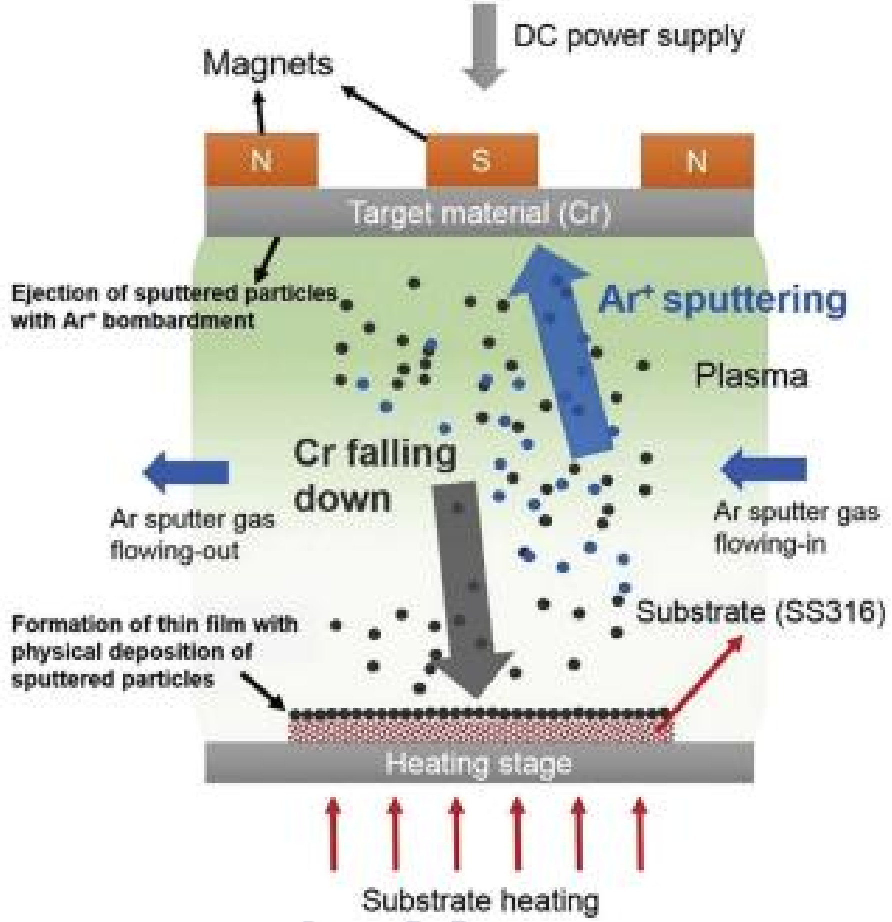

Figure 6: A schematic diagram of the DC magnetron sputtering process. Reprinted with permission from [28]. Copyright: ©2017, Elsevier Ltd. All rights reserved.

5 Characterization techniques:

Characterization is also important to ensure that the prepared particles are at a nanoscale. In material science, the term "characterization" refers to the general and broad processes through which the properties and structure of the material are explored. This fundamental process is a must for scientific understanding of the material. Characterization involves techniques required to explore material properties and microscopic structures, that is, any process that deals with material analysis such as mechanical testing, thermal analysis, and density calculation. Newer and more advanced techniques are constantly emerging, joining characterization techniques that have been practiced for centuries. Characterization helps to determine the composition and structure of materials and also allows us to assess whether the method was successful or not. Some techniques are qualitative, whereas some are quantitative. The primary objective of this chapter is to provide a theoretical and practical description of the methods used to characterize a broad range of materials. Our team will focus on the suitability of the method, sample preparation, and anticipated results. In this manner, you will be informed regarding the best method to use for a particular material. Scanning electron microscope (SEM) analysis, energy dispersive X-ray analysis (EDX), transmission electron microscope (TEM) analysis, scanning tunneling microscopy (STM), atomic force microscopy (AFM), Raman spectroscopy, ultraviolet-visible spectrometry (UV-vis), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), X-ray diffraction (XRD), and zeta potential analysis offer more advantages to observe submicron-sized materials.

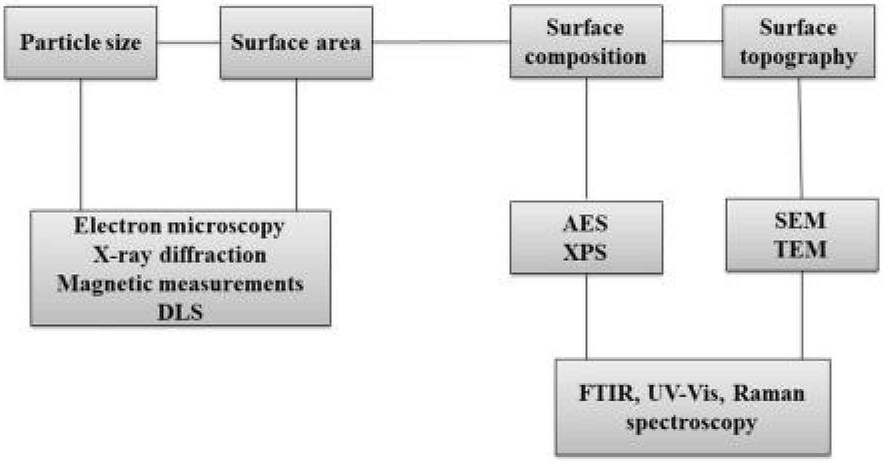

Figure 7: Common characterization methods for nanoparticles[29].

5.1 Transmission Electron Microscopy (TEM):

Transmission electron microscopy (TEM) is a microscopy technique that exploits the interaction between a uniform current density electron beam (i.e. the energies are usually within a range of 60 to 150 keV) and a thin sample. When the electron beam reaches the sample, part of the electrons are transmitted, while the rest are elastically or inelastically scattered [30]. The magnitude of the interaction depends on several factors, such as size, sample density and elemental composition. The final image is built with the information acquired from the transmitted electrons. As it is clear from the previous sections, size and morphology define the unique set of physical properties, such as optical, magnetic, electronic and catalytic,[31]of NPs, as well as their interaction with biological systems[32]. TEM is the most common technique to analyse nanoparticle size and shape, since it provides not only direct images of the sample but also the most accurate estimation of the nanoparticle homogeneity. Nevertheless, some limitations have to be considered when using this technique, such as the difficulty in quantifying a large number of particles or misleading images due to orientation effects. When characterizing very homogeneous samples, other techniques that analyse larger amounts of NPs can provide more reliable results, such as SAXS for larger and spherical NPs,[33] or XRD by exploiting the bordering of the XRD reflections and the Scherrer formula[34].However, a previous analysis has to be performed to ensure sample homogeneity.

Nanoparticle properties not only depend on their size and morphology but also other factors, like interparticle distance. For instance, when two metal NPs are brought nearby, their plasmons couple, red-shifting their plasmon band and changing their color. Therefore, TEM has been used to characterize nanoparticle aggregation for different biomedical applications, including (1) sensing and diagnostics, where the aggregation depends on the presence of a biomarker or analyte;[35] (2) therapy, where the aggregation causes an increase of the nanoparticle therapeutic effect and (3) imaging, where the aggregation improves the response signal.To obtain reliable results, extra care should be taken for sample preparation, since an inadequate protocol can result in sample alteration or artifact creation. e.g. aggregation during the drying of the colloid suspension. Thus, TEM is usually combined with other techniques that can measure larger numbers of particles, and require less sample preparation, such as UV-Vis and DLS. In recent years strong control over the nanoparticle assembly has been achieved, and a controlled NP self-assembly can lead to well-defined NP superlattices. The systematic assembly of different nanocrystals yields new multifunctional structures that combine the features of the individual building blocks, as well as the rise of new and exciting properties[36].

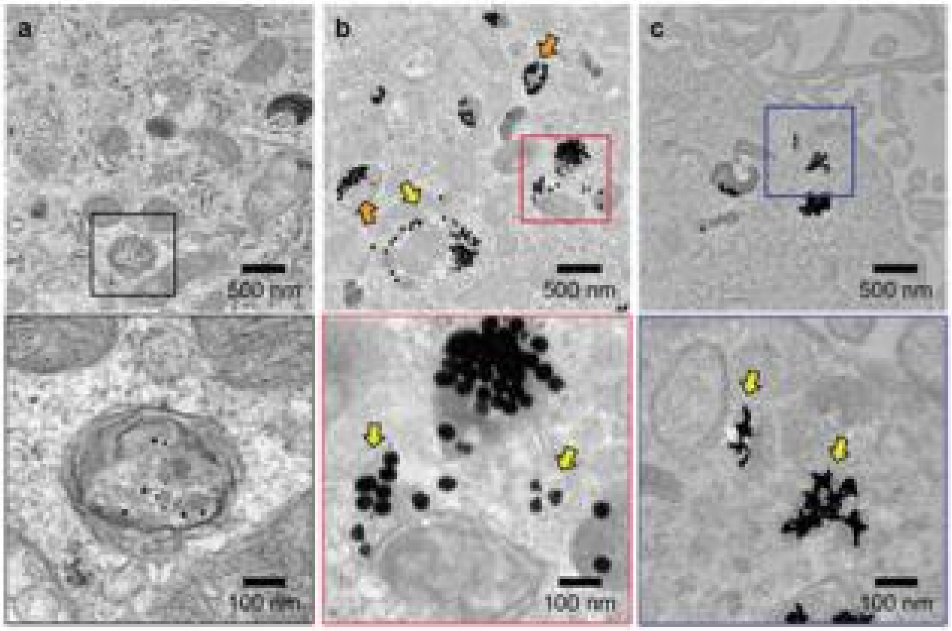

Figure 8: Representative TEM images of U87 cells after treatment with NP-siRNA constructs indicate that larger constructs can distribute in the cytoplasm. U87 cells were treated with 0.5 nM of (a) 13 nm spheres, (b) 50 nm spheres, and (c) 40 nm stars for 24 h. The images in the boxes (lower panel) indicate zoomed-in views. The yellow arrows indicate NPs distributed outside vesicles; the orange arrows indicate locally disrupted vesicle membranes. Reprinted with permission from[37].Copyright 2017 American Chemical Society.

5.2 Scanning Electron Microscopy (SEM)

SEM can be operated in the transmission mode, i.e. through the technique called 'transmission in scanning electron microscope' (T-SEM) (see Fig. 9). In the transmission mode, advanced NP analysis can be carried out by gaining in-depth information as well as analysis of ensembles of NPs. In a paper by Rades et al., the combination of complementary techniques as SEM, T-SEM, EDX and scanning Auger microscopy (SAM) was proven to be a powerful strategy for comprehensive morphological and chemical evaluation of the properties of individual silica and titania NPs. On the other hand, methods such as SAXS, DLS, XPS, XRD and BET would be suitable to characterize only the ensembles of the NPs, and not single particles. T-SEM allows a quick examination of the NP shape, though its lateral resolution is limited to NP sizes down to 5–10 nm. TEM provides images with better quality, but T-SEM can be easily combined with EDX for a fast check of the NP size and elemental composition[38]. Hodoroaba et al. proved that T-SEM imaging provides a size distribution that is slightly broader than that obtained by TEM. For small SiO2 NPs, the precise delimitation of the particles in the T-SEM mode is definitely constrained by the lower spatial resolution achieved compared to that of conventional TEM. In addition, with the T-SEM, the surface layer of the particles might not be always easily detected.507 The same author noted in another paper that the conventional SEM imaging mode could not detect the NPs on the back side of the support film that was required for the observations. Therefore, an explicit knowledge of the T-SEM operator is needed for the measurements. The authors observed that the obtained SiO2 NP size distributions by SEM and TSEM in their work and for various conditions agreed well with each other, within the associated measurement uncertainties[39]. In another report, 3D reconstruction by focused ion beam (FIB) cutting and SEM imaging were combined to comprehend the evolution of pore volume, pore shape and other parameters during the two-step sintering of ZnO NPs. In this way, the sintering process at the nanoscale for such particles can be better understood [40]. Ni- and Cu-co-doped zinc oxide NPs prepared by the co-precipitation method were investigated by Ashokkumar and Muthukumaran by microstructure, optical and FTIR measurements. The depicted shape by SEM was in good agreement with the mathematical determinations from XRD, whereas FTIR provided important information on chemical bonding [41].

Figure 9: Scheme of a SEM/EDS system operating in the transmission mode with the Zeiss single-unit transmission setup (PE: primary electrons; SE1: secondary electrons emitted at the point of impact of the PE on the sample; TE: transmitted electrons; BF: bright field; DF: dark field; E–T: Everhart–Thornley detector). Reprinted with permission from [42].

6 Mechanisms of Nanocatalyst:

6.1 Structural Effects

Important structural changes in the size and morphology occur during the preparation of nanocatalysts and when applied under certain conditions (e.g., during a chemical reaction). The structural changes are illustrated schematically in Figure 10. Materials have a higher specific surface when their particle size is reduced. To give an example, for a spherical dot of 1 mm across the volume, the surface-to-volume ratio is only 1%, but for a dot of 10 nm size it is 25%. The surface-to-volume ratio reaches 100% when the solid is ca. 1 nm (sections of three atomic shells or less). An enrichment often assists the particle size reduction in the surface defects (crystal edges, corners and faces). The effect on the catalyst performance also depends on how the accessible active sites are fitted into the porous structure and onto the surface of the support. Tuning the porosity characteristics of the support is an essential task in the design of functional catalysts. Porosity analysis not only provides data on the specific surface area (m2 g1), pore sizes (nm) and volumes (cm3 g1), but also on the pore morphology, topology and tortuosity (interconnection between the pores). Porous materials can be classified into macro, meso and microporous materials, described by established porosity analysis methods, although in some cases these are not applied or interpreted correctly. Analytical challenges still exist in the characterization of more advanced materials, such as hierarchical porous and nanoporous materials, owing to the effects of physical confinement (phase changes, condensation, etc.) Researchers not only pursue catalysts with a high activity and selectivity, but also catalysts with a high stability, depending on the temperature, pH, solvent, and so forth. Catalysts can be deactivated in many ways due to surface aggregation (alloying), sintering, phase changes, leaching, and so forth. A wide range of analytical techniques are used to study these effects both on the surface layers, such as in bulk nanomaterials, including inductively coupled plasma optical emission spectroscopy (ICP-OES), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, powder X-rays diffraction (XRD) spectroscopy, X-ray photoelectron (XPS) spectroscopy, X-ray absorption spectroscopy (XAS), electron paramagnetic resonance (EPR), scanning electron microscopy (SEM), (high resolution-) transmission electron microscopy ((HR-)TEM), scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), energy-dispersive X-ray spectroscopy (EDX), high-angle annular dark-field (HAADF) imaging, electron energy loss spectroscopy (EELS), extended X-ray absorption fine structure analysis (EXAFS), thermogravimetric analysis (TGA), and temperature-programmed desorption (TPD), reduction (TPR) and oxidation (TPO). To study the stability of a catalyst, these techniques should ideally be employed operando, or at least in situ, but many of them require conditions that are different from the reaction conditions (e.g. vacuum) and are not always sufficiently timeresolved to allow studying of fast catalytic cycles and structural changes.In some cases spatial-time resolved techniques have been developed[43].

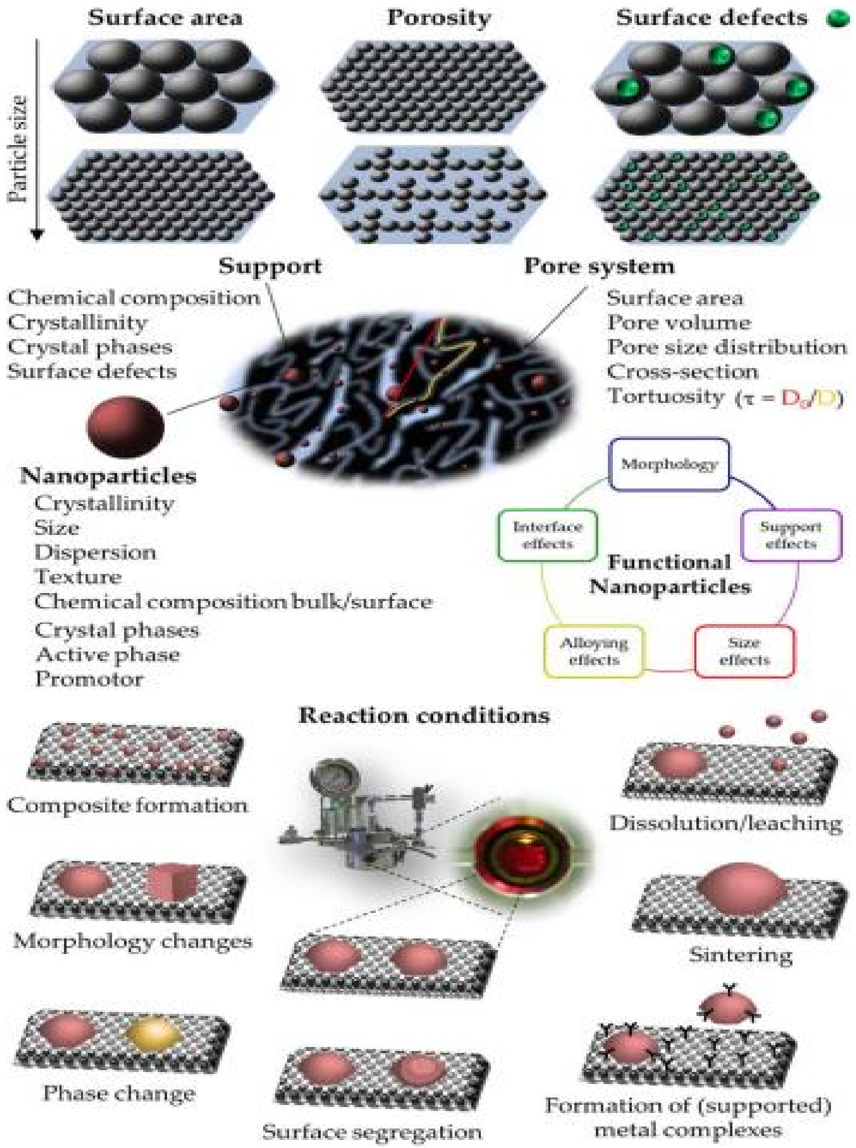

Figure 10: Structural changes upon size reduction of the porous support and metal NPs and possible deactivation mechanisms of the supported metal NPs. with permission from John Wiley and Sons, r 2017 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA.

7 Quantum Size Effects in Nanoparticles

Quantum effects only occur in very small dimensions. These effects are caused by changes in the electronic configurations of atoms in nanomaterials, which are significantly different from those of their bulk counterparts. When the size of a nanocrystal (i.e. a single crystal nanoparticle) is smaller than the Broglie wavelength, discrete electronic energy levels arise, as electrons and holes are spatially confined giving rise to the formation of electric dipoles. The separation between the adjacent energy levels increases with decreasing particle size, resulting in changes in the spatial electron energy density configurations of the nanocrystals, which eventually change the electronic and optical properties. This is schematically illustrated in Figure 11 a–d for bulk, quantum wells, quantum wires (or rods), and quantum dots (QDs) in semiconductor materials. These quantum materials are spatially confined in one, two, and three dimensions, respectively. To describe the confinement effects mathematically, at least in semiconductor nanocrystals, the Bloch wave functions of the bulk materials are multiplied with an envelope function to correct for the spatial confinement of the charge carriers (electrons and holes) and the exciton. The band gap of the QDs is the sum of the fundamental bulk band gap (Eg) and the confinement energy (Econf) of both the electrons and holes. Quantum confinement effects lead to larger band gaps with decreasing size and to the formation of discrete energy levels with different quantum numbers at the band edges of both the conduction and valence bands (Figure 11 e).

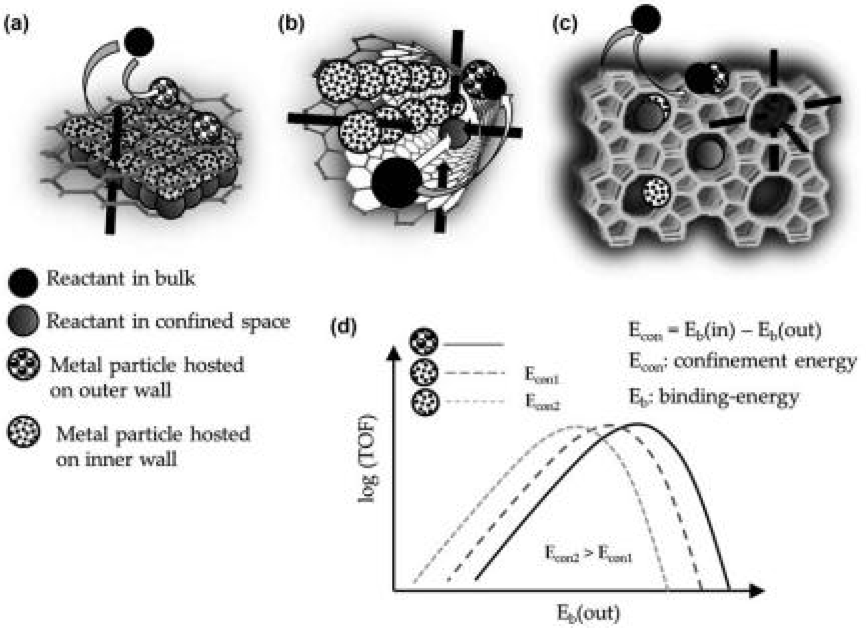

Figure 11: Schematic illustration of catalytic confinement effects in (a) onedimension (1D); (b) 2D (CNTs); and (c) 3D (zeolites). (d) The shift of the catalytic volcano curves induced by 2D confinement effects

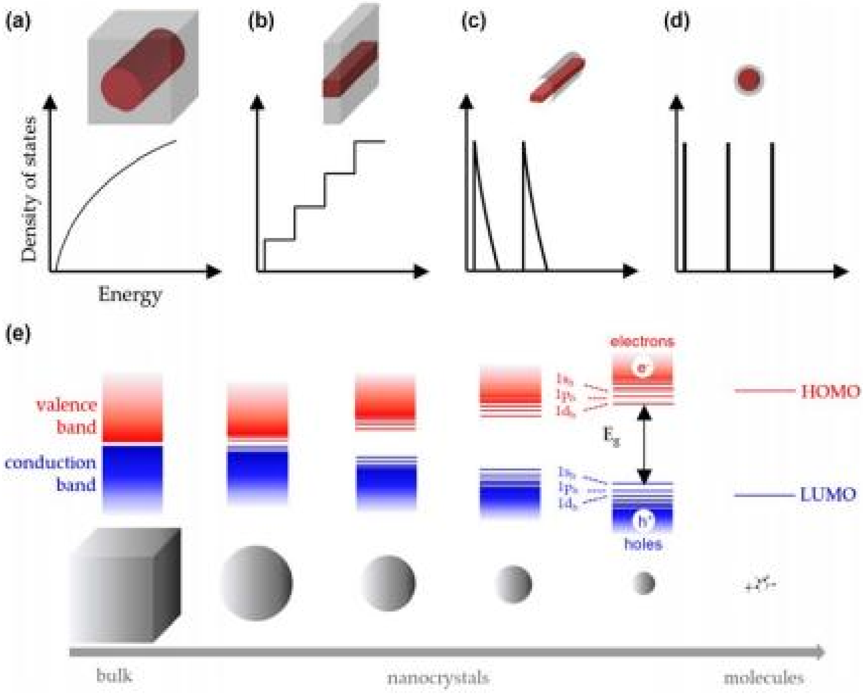

Figure 12: Schematic illustration of the quantum size effect in semiconductor materials including (a) bulk material; (b) quantum well; (c) quantum wires (or nanorods); and (d) quantum dots. Size effects in quantum dots on the electronic energy levels are shown in (e)[44]. with permission from Springer Nature, Copyright 2014.

8 stability mechanism of Nanocatalyst

Metal and metal oxide-based materials are widely exploited in their macroscale form due to their catalytic, electric, optical, magnetic, mechanical, and thermal properties. As their dimensions decrease to the nanoscale, the wavelength of light becomes large concerning size, the total surface area to volume ratio increases, surface energy elevates, and the number of low coordination surface atoms (relative to interior atoms) increases. All of these size-dependent characteristics impact the electronic and crystal structure of these materials and as a result, their chemical and physical properties as a function of composition size, and/or shape. To maintain these properties for further application, understanding these transformations or by definition, stability, is relevant. As such and as summarized in Table 1, stability in terms of aggregation, metal/metal oxide composition, shape, size, and surface chemistry are discussed in this section.

Table 1: Nanoparticles stability and quantitative characterization

Nanoparticle Stability	**Definition**	**Quantitative Characterization**		**References**
		Non-Plasmonic	**Plasmonic**	
Aggregation	Preservation of primary nanoparticles upon collisions	DLS	LSPR, SERS	
Metal/Metal Oxide Composition	Unchanged chemical identity and crystallinity of the core during the course of an experiment or relevant time period	EDX, XRD		
Shape	Preservation of local structure	AFM, HR-TEM,		[45]

	and radius of curvature at the atomic and nanoscales	SEM, XRD		
Size	Preservation of nanoparticle dimension during the course of storage and/or experiment	AFM, DLS, SEM, SAXS, TEM		[45]
Surface Chemistry	Original surface potential, chemical identity, structure, and functionality of surface chemistry	Low energy ion scattering, XPS, ζ potential		[46]

Stability in Terms of Nanoparticle Size.

Stability in terms of nanoparticle size is defined as the preservation of nanoparticle dimensionality during storage and/or an experiment. Because the physicochemical properties of nanoscale metal/metal oxides are size dependent, instability refers to an increase or decrease in nanoparticle dimensionality that causes a significant variation in catalytic, optical, magnetic, mechanical, and thermal properties of materials. Magnetic nanoparticles, for example, can exhibit superparamagnetism where the average magnetic moment of small particles is zero in the absence of an external magnetic field but increases rapidly upon application of an external field. This property is only observed for feature sizes that support single-domain behavior. Likewise, nanoparticles can become efficient thermal conductors with decreasing size. This is because diffusion coefficients are indirectly proportional to size; therefore, heat transfer is facilitated as nanoparticle diffusion coefficients increase and as size decreases. Thus, retention of nanostructure dimensions is required for reproducible chemical and physical properties of nanoscale metals and metal oxides. Nanoparticle dimensions can be imaged directly or inferred through movement in a solution. TEM and scanning electron spectroscopy (SEM) routinely provide spatial resolution down to 0.2–0.5 nm119 and 0.4–1.6 nm,120 respectively. Imaging materials using these techniques typically require that a sample is deposited and dried on a support thus only provide accurate nanoparticle dimensions if the material is not influenced by solvation and/or mobile surface chemistries/ions. Chemical transformation is common when the medium changes (i.e., oxidation). High-resolution images can also be measured using AFM34, 121 as vertical and lateral resolutions of 0.1 and 0.2 nm,122 respectively, can be achieved. As with any scanning probe microscopy, sampling is limited by scan rate, sample size, and probe properties. Other techniques including small-angle X-ray scattering technique (SAXS)123 and DLS121 can also be used to analyze nanostructure size in solution. Both SAXS and DLS rely on the Stokes-Einstein equation124 to quantify nanoparticle size. DLS, for instance, facilitates the estimation of hydrated particle dimensions from translational diffusion coefficient (D) estimations from light scattering measurements.

Nanoparticle dimensions can be quantified directly from images, 122, or indirectly121 from mobility and spectroscopy measurements. The complex dimensionality of core-nanostructures composed of Ag, Au, and SiO2 is shown in Figure 4A.46 Dimensions of the various components are observed due to differences in how electrons interact with the various materials. Additional information can be assessed using SAXS as size, shape, and surface details can be determined. The nucleation and growth of gold nanoparticles, for instance, was evaluated using SAXS. Details related to size125 and shape (i.e., nanocubes,126 nanorods,127 or nanotriangles128) were successfully determined. The dimensionality of plasmonic nanostructures can also be determined from LSPR spectroscopy,which are in excellent agreement with theory[47]. thus adding an alternative and fast method for monitoring and quantifying changes in nanoparticle dimensionality.

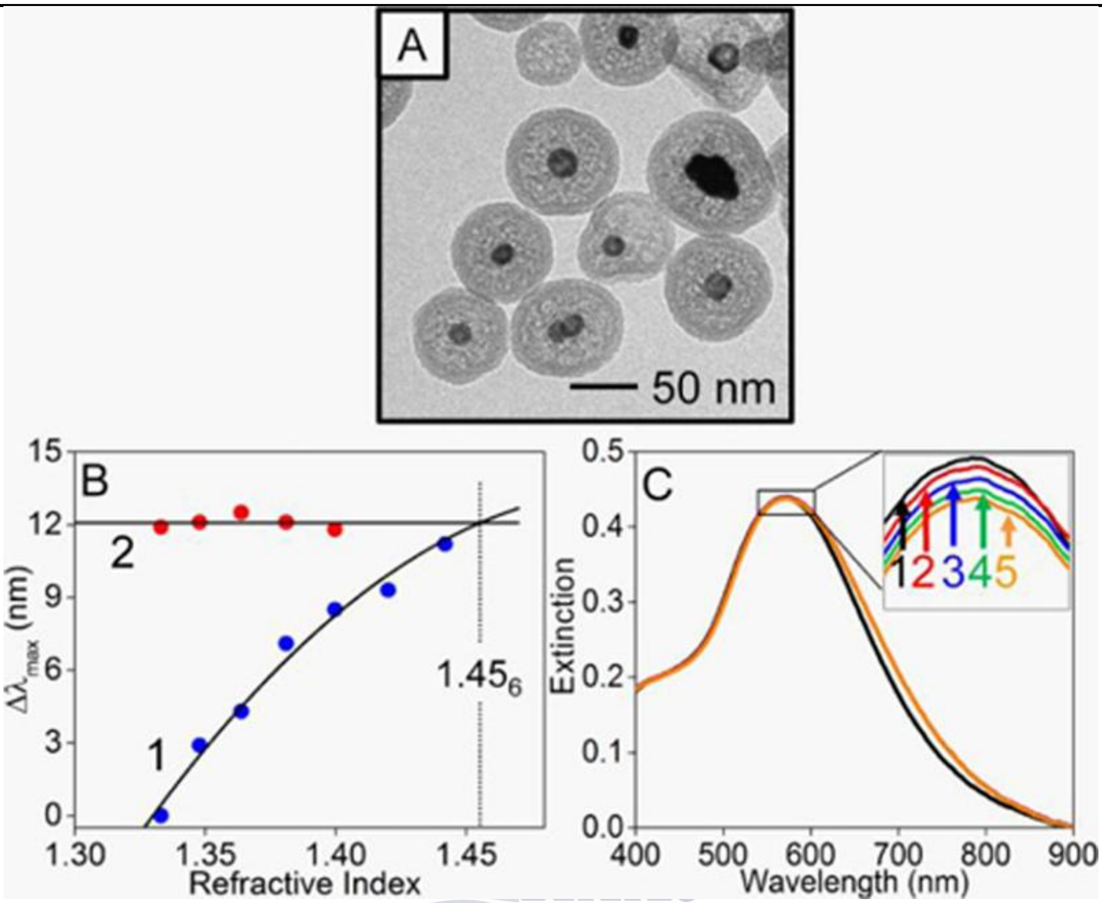

Figure 13: (A) TEM image of internally etched Ag@Au@SiO2 nanoparticles. (B) Changes in extinction maximum wavelength from LSPR spectra (1) without and (2) with silica membranes as a function of bulk refractive index. (C) LSPR spectra of the same materials (1) before and after incubation with 4-mercaptobenzoic acid in pH 4.5 buffer for (2) 1, (3) 10, (4) 30, and (5). minutes. Reprinted with permission from ref 46. Copyright 2018 American Chemical Society.

9 Structural Transformation of nanocatalysts:

The structural transformation of nanocatalysts can be controlled and exploited to expand the reach of nanocatalyst design that may not be attainable through conventional nanomaterial synthesis. However, achieving such transformation toward intrinsically active surfaces in a controlled manner requires guiding principles. Multiple parameters need to be considered including. the surface energy of the nanocatalyst that determines its propensity for structural rearrangement before the reaction, the surrounding environment it is subject to during CO_2 electrocatalysis, and the nanocatalyst–support interactions. These parameters are convoluted and thus require comprehensive consideration from which various strategies can be devised to guide the evolution of nanocatalysts (Figure 14). The surface energy is highly dependent on the composition and exposed facets of the nanocatalyst, as well as the molecular species that interact with its surface. This generally involves reaction species adsorbed to surface atoms (i.e., reaction intermediates such as *CO), species in the electrolyte (e.g., electrolyte ions, hydroxide ions), and at times, the organic passivating agents used in the synthesis of the nanocatalyst. The presence of ligands is an excellent example of how to control the surface properties of a nanocatalyst while mediating interactions with other species. Several works have shown how the presence or absence thereof significantly influence the structural transformation of nanocatalysts during CO_2 electrolysis. In general, the ligand–metal surface binding strength, which is determined by the ligand headgroup and nanocatalyst exposed facets, dictates the resilience of the surface structure to the structural transformation. For instance, with strongly bound ligands, the structural transformation under bias can be deterred, and thus, the nanocatalysts tend to retain their initial structure and catalytic performance. Another strategy to preserve the initial morphology of nanocatalysts is to employ a conductive protective layer such as graphene oxide.Wrapping Cu nanowire catalysts with graphene oxide was demonstrated to improve the structural stability while maintaining the electrocatalyst activity.

However, these approaches may hamper the access of CO_2 molecules to active sites and also the formation of potentially more active reaction sites due to a restricted structural transformation. Recently, Chen et al. reported a systematic study of how the removal of surface ligands from Au nanoclusters influences the overall activity of CO_2-to-CO electroconversion.In this work, different thermal and electrochemical treatments prior to CO_2 electrolysis were conducted to compare their effectiveness in removing the organic ligands, exposing the undercoordinated Au cluster reaction sites, and enhancing catalytic activity. It was also found that harsh treatment conditions can result in excessive nanocluster coalescence and thus a reduction in surface area and the number of undercoordinated sites. Furthermore, an S-doped graphene support used in this work allowed for the stabilization of the nanoclusters during CO_2RR by anchoring the catalysts through the sulfur–Au cluster interactions. This work highlights the duality between preserving a surface and degrading the accessibility to greater catalytic activity, but it also exemplifies how the nanocatalyst–support interactions can be used as another knob to control the structural transformation during CO_2 electrolysis.

Therefore, we identify as a primary goal the creation of more active and selective nanocatalysts that may exist in a metastable state as a result of the dynamic structural evolution under CO_2-reducing conditions. In this approach, the as-synthesized nanocatalyst can be thought of as a precursor to make a better-performing catalyst. One example of this concept is our group’s in-depth study on the electrochemical evolution of Cu nanoparticles to undercoordination-rich Cu nanocatalysts, which exhibited a remarkable enhancement in intrinsic activity. This approach has attracted growing attention in the CO_2RR research field. For instance, the Sinton group recently demonstrated that low-coordination Cu clusters can be created from controlled in situ reduction of molecular catalysts (i.e., Cu(II) phthalocyanine) via carbon nanoparticle confined agglomeration. By driving low-coordination formation, the authors achieved a catalytic selectivity enhancement otherwise unattainable from the original catalyst. We envision that this type of strategy that generates nanocatalysts with improved catalytic performance via structural evolution during CO_2 electrolysis will open up new avenues for catalyst innovations.

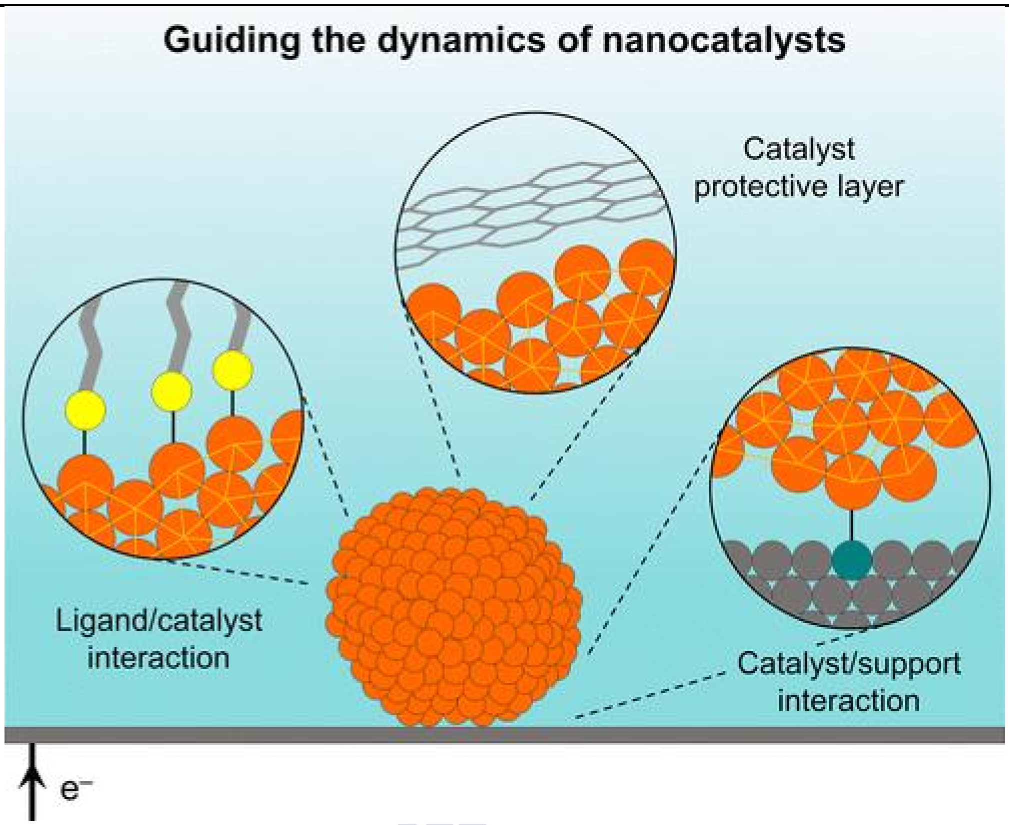

Figure 14: Schematic illustration of various approaches to guiding the structural evolution of nanocatalysts under CO2-reducing conditions. To control and ultimately harness the dynamic transformation of nanocatalysts for enhanced catalytic performance, various strategies can be devised, utilizing ligand/catalyst interaction, catalyst/support interaction, and a catalyst-protecting layer [48].

10 Application of Nanocatalyst

10.1 Nano-adsorbents for heavy metal remediation from water

Water scarcity, as projected due to the rapidly growing population graph has turned the attention of people towards reusing wastewater after remediation and making it potable and also as a model of recycling of water thereby reducing wastage. The reuse of wastewater gives sufficient time for the rejuvenation of the underground soil water table of the particular area also termed as ground water recharge phenomenon. Every nation has its criteria and standards for the reuse of wastewater. Some nations have allowed treated or cleaned wastewater to be used for only non-potable purposes. In contrast, with the use of advanced separation technologies, the developed nations have allowed treated wastewater to be in the drinking water category. However, before considering applying any ultimate decision on wastewater reuse, the heavy metal contents, electrical conductivity and dissolved organic matter concentrations should be thoroughly determined. Nanomaterials and nanotechnology have opened up several areas of solutions for the treatment of wastewater such as surface coatings in filtration, membranes, adsorbent materials, nanocatalysts, and functionalized surfaces of nanoparticles along with reagents. Among them, nano-sorbents carry the most demand as they are available in various variants and are easy to apply. The high surface area of nanosorbents allows higher adsorption capacity that attracts the contaminants to bind to the particles via chemisorption or physisorption, depending upon the functional modification of the nanosorbents. The term heavy metals refers to those elements whose atomic weights fall between 63.5 and 200.6. These heavy metals are part of different biological functions in living organisms in a defined concentration which is very low, but their presence above a certain concentration threshold in an aqueous environment is considered toxic. Electroplating wastewater, municipal wastewater, mining waste, leaching, and urban runoff water comprises of Mercury (Hg), Thallium (Tl), cadmium (Cd), lead (Pb), nickel (Ni), copper (Cu), chromium (Cr) and arsenic (As) as heavy element contaminant. Typically, those water bodies where these heavy metals are found at concentration levels of >5 g cm— 3 are designated as polluted or unfit. The nature of an adsorbent plays a primary role in the whole process where its capacity determines the economics, versatility, and efficiency of the method. Traditionally, activated charcoal granules, clay minerals, zeolites, and chelating materials have been used as adsorbents for water purification. Most of the traditional nanosorbents suffer from inefficiency of low adsorption capacities. Nano particles in the range of 1 nm to 100 nm have been developed to counter the deficiency of the traditional sorbent approaches. The shape and size of the nanoparticles in the nanosorbents determine overall efficacy of the product. Therefore, various morphological designs are crafted keeping in mind to create a balance between the energy from the surface area and polar charge coupled with elastic deformation. The morphological formations of nanosorbents built dictate its behavior towards toxic materials. The approach for preparation of nanosorbents is categorized into top-down process and bottoms up process. The top-down process is the traditional way of preparation where the material is subsequently reduced in shape and size to particle nature by mechanical milling, reactive milling or advance ball milling. In the bottoms up approach, which is the most modern way of manufacturing nanosorbents, the particles are synthesized by adding molecule by molecule using processes like sol gel method, chemical or physical vapour deposition. Inherent advantages and disadvantages plague each approach, the nanoparticles fabricated using top-down approach are marred by loss in crystallinity and surface demography, whereas in bottoms up method production is less and high amount of chemical purification is needed. The ideals of a good nanosorbent must be that it should be non-toxic, should be able to remove toxic materials present in very low concentrations and be easily reactivated.

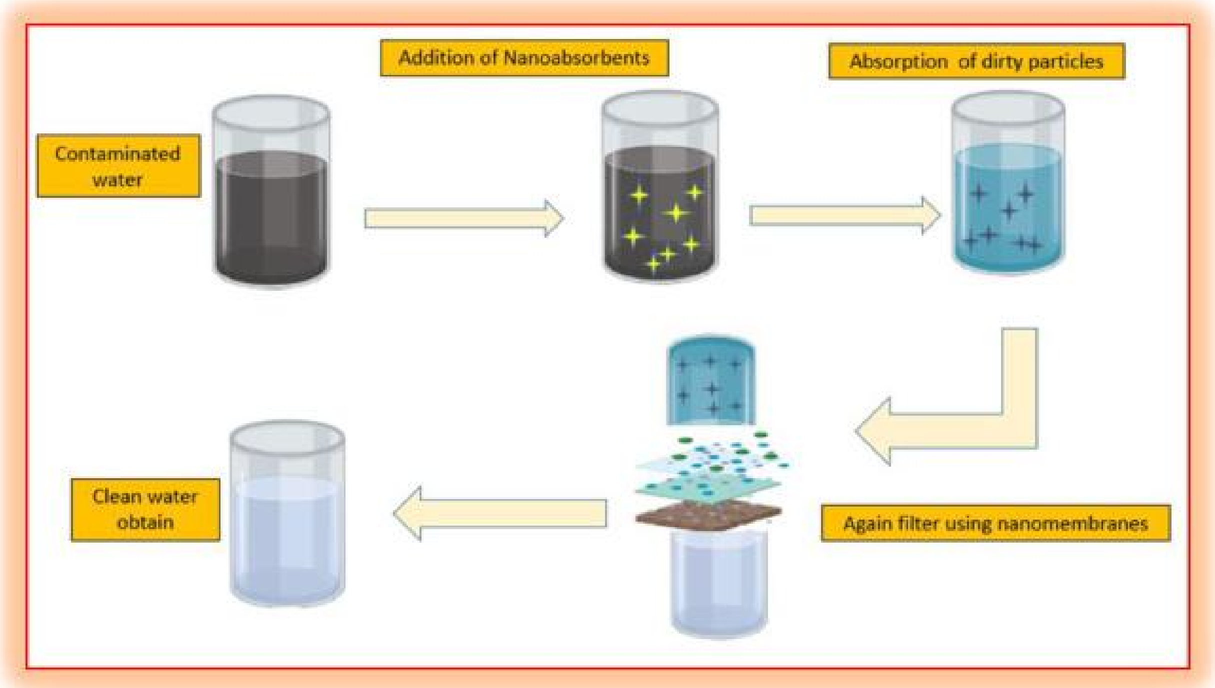

Figure 15: the process involves the removal of metal ions [49].

ROS including $\cdot O_2$–, $\cdot OH$, $RO\cdot$, $ROO\cdot$, H_2O_2 and 1 O_2 play an important role in redox balance maintenance, and any aberrance of redox balance in cells may lead to a pathological process, such as oxidative stress-induced apoptosis, which is used to kill cancer cells and bacteria. Typically, photocatalysis is widely utilized to degrade organic contaminants under solar energy in industry and to oxidize organelles by photocatalytically generated ROS under irradiation of visible/NIR light (such as PDT) in medicine. To efficiently utilize solar energy, enhance tissue penetration and lower phototoxicity, the development of nanocatalysts with high NIR-catalytic activity is pursued but challenging at present. On the other way, the upconversional, scintillating and Cerenkov strategies have been used to locally convert NIR light and X-ray into UV lights for UV-sensitive photocatalysts by integration of UCNP (upconversion nanoparticle), SCNP (scintillating nanoparticle) and radionuclide with UV-sensitive photocatalysts (TiO_2, ZnO or TCPP). In addition, local synthesis of RNS from ROS and NO can further amplify the efficiency of cancer therapy because RNS had higher oxidation. In addition to NIR, other excitation sources with stronger tissue penetration such as US, MW, and magnetic field have also been applied for catalytically controlled ROS generation. Many photosensitizers such as TiO_2 and Mnporphyrin were developed as sonosensitizers for sonodynamic therapy (SDT) based on US-medicated sonocatalysis similar to photocatalysis . Interestingly, Meng et al. recognized Mn-doped zirconium metal-organic framework (Mn-ZrMOF) nanocubes as a microwave sensitizer enabling microwave dynamic therapy (MDT)39, and also co-loaded ionic liquid (IL) as an MW-heating sensitizer and Ga3In liquid metal (LM) super nanoparticles as a microwave sensitizer into mesoporous ZrO2 NPs for a combination of microwave thermal therapy (MTT) with MDT. Recently, Shi et al. developed US/ magnetostriction-mediated piezoelectric nanocatalysis based on $BaTiO_3$ and $CoFe2O_4$–$BiFeO_3$ NPs to catalytically generate ROS for cancer therapy, presenting a new strategy of US/magnet-controlled nanocatalytic medicine (Fig. 16) 41,42. Fenton/Fenton-like catalysis that has been successfully applied in municipal wastewater treatment can be introduced in catalytic medicine, owing to the high oxidizability of catalytically generated ·OH. Instead of direct use of free metal ions in industry, metal-based NPs favor the tumor-targeted delivery of metal to induce the ferroptosis, cuproptosis and zincosis of cancer cells by Fenton/Fenton-like catalysis. By utilization of acidic microenvironment in solid tumor, Shi et al. developed acid-responsive amorphous iron nanoparticles and Fe-incorporated mesoporous silica nanoparticles (MSN) as Fenton catalyst precursors for chemodynamic therapy (CDT) of cancer1,44. Similarly, Fenton-like nanocatalysts such as MnO_2, Fe_3O_4 NPs and CoMoO4 nanosheets can be delivered into tumors for CDT by Fentonlike reaction. Such a local Fenton catalysis strategy based on nanocatalysts provides a candidate for highly specific cancer therapy. Generally, the therapeutic strategy of catalytic ROS generation draws inspiration from the well-established practices of industrial catalysis, becoming a new-generation therapeutic method. Some endogenous gasotransmitters including NO, CO, H_2S, O_2 and H_2 are vital in many physiological and pathological processes, exhibiting wide-spectrum anti-inflammation and anti-cancer effects49. These gas molecules are generally generated under catalysis of enzymes such as iNOS, HO1, and CBS50. The delivery of their substrates is expected to enhance catalytic generation of them in the body, but commonly lack focus-targeting capability. Therefore, the development of artificial nanocatalysts for site-specific stimuli-controlled catalytic generation of therapeutic gas molecules attracts increasing attention. Photo-/sono-/electro-/WM-catalysis are frequently used for wastewater treatment but rarely for the production of gases expect H_2 in the industry because of the low efficiency of catalytic gas production. Zhang et al. constructed the Z-scheme nanocatalysts based on Ag3PO4/carbon dots-decorated C3N4 (Ag3PO4/C/C3N4) to realize the photocatalytic reduction of endogenous CO_2 and NO3 - into CO and NO, respectively, under irradiation of 660 nm laser for cancer therapy (Fig. 16) 51,52. To enhance the tissue penetration capability, we recently developed a Z-scheme SnS1.68-WO2.41 nanocatalyst, a C/Kincorporated carbon nitride sheet (C3N4:C/K) and a hydrogen incorporated titania (TiO_2:H) nanorod to achieve NIR-photocatalytic generation of H2 for hydrogen therapy (Fig. 16) 53–56. Compared to photocatalysis, sono-/magneto-/WM-catalysis are more desired for catalytic gas generation because US, WM and magnetic fields have higher tissue penetration capability compared with light. Piezoelectric nanocatalysis has been developed to enhance the efficiency of chemical reactions recently57–59. In industry, pressure for piezoelectric nanocatalysis is generally offered by ball milling60. Inspired from the characteristics of pressure-initiated diseases such as pressure ulcer, we think that piezoelectric nanocatalyst can be used for local piezocatalytic generation of therapeutic gas molecules for their treatment. In addition to the localized pressure, the cavitation effect of US can also cause instantaneous but intense pressure to mediate piezocatalytic generation of gas with mesocrystalline ZnS nanoparticles, C3N4 nanosheets, SnS nanosheets and Pt-Bi2S3 heterostructure (Fig. 16) 61–65. High biosafety and high sonopiezocatalytic efficiency as two key factors have to be carefully considered for biomedical applications. Moreover, magnetostriction-mediated piezoelectric and thermoelectric nanocatalysis based on magnetostrictive-piezoelectric/ thermoelectric nanocatalysts should be greatly valuable but have not been reported for piezocatalytic generation of therapeutic gas molecules. Many transition metal ions have shown a potential for disease treatment by disturbing intracellular redox homeostasis. For instance, PtII, AsIII, CoIII and AuI ions are able to strongly bind with sulfur-/selenoamino acids and DNA, leading to significant inhibition of DNA/protein replication and transcription66–68. Typically, Fe2+ induces Fentoncatalytically oxidative damage to cells, causing the ferroptosis which is an emerging type of programmed cell dead different from apoptosis and necrosis69,70. Similarly, Cu+ , Co2+, Ba2+ and Mn2+ can also induce ferroptosis based on their Fenton-like characteristics (Fig. 3) 71. It could be learned that catalytic route can be used to amplify the cytotoxicity of metal ions. In addition, endogenous metal ions such as Na+ , K+ , Ca^{2+} and Mg^{2+} are critical to cell functions, including transport of amino acids, maintenance of intracellular pH, and control of cell volume. Local imbalance of their concentration will cause cellular disorder and even death, which provides an innovative strategy for targeted therapy. The off-target effect of drug delivery commonly occurs, even as for targeted nanomedicines developed at present, leading to severe toxic side effects of therapeutics and limited therapy efficacy. In recent years, the strategy for the local catalytic synthesis of active drugs from low-toxicity precursors becomes an emerging and promising solution to address the issue. This strategy has been used in the industrial production of drugs, where neither the toxicity of precursors nor the biocompatibility of reaction conditions needs to be considered. But the catalytic strategy and approaches are still worthy to be learned for catalytic medicine even if catalytic efficiency might be sacrificed to a certain extent in the physiological/pathological conditions. Site-specific/targeted trigger of catalytic reaction is vitally important, and its specificity depends on the precision of external stimuli and the selectivity of internal stimuli. A wide range of industrially used metalbased nanocatalysts, such as Pd, Au, Cu and Ru nanoparticles, and enzymes (GOx), horseradish peroxidase, β-galactosidase) have been used to biorthogonally synthesize a variety of drugs for local disease treatment (Figure 16). It has to be noted that the off-target effect of nanocatalysts is unavoidable according to present technological level. In order to avoid the undesired toxicity of nanocatalyst and target-off drug, Gu et al. constructed a bioorthogonal catalytic patch comprising a microneedle array patch integrated with Pd nanoparticles conjugated TiO_2 nanosheets, which can locally activate a systemically administered prodrug, N-allyloxycarbonyl-caged doxorubicin (alloc-DOX), into DOX for melanoma treatment (Fig. 16) 80. Importantly, this device was robust and removable, and thus completely avoided the in vivo residual of nanocatalysts and consequent toxicity risk. It can be envisioned that a bioorthogonal catalytic patch could be a promising tool for high-efficacy and low-toxicity treatment of superficial diseases.

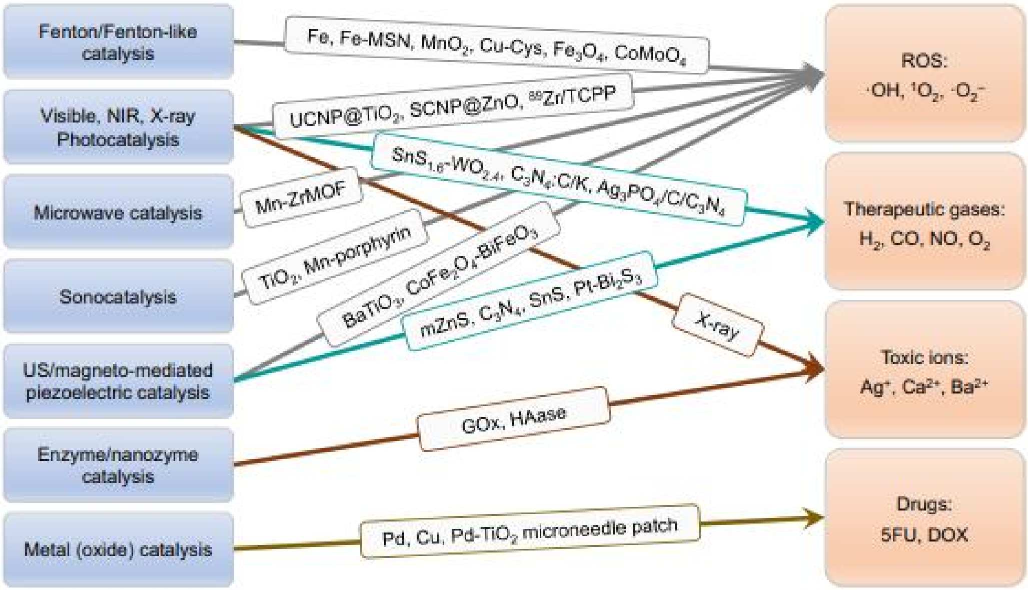

Figure 16: The developed catalytic reactions and catalysts for catalytic generation of therapeutic products[50].

Plant diseases and insect pests are effectively managed in agriculture by the application of pesticides. However, the high concentrations of chemical components applied per hectare has given rise to several issues, including environmental deterioration, pest resistance, bioaccumulation, and health risks. Due to microbial activity, air drift, soil leaching, degradation processes including photolysis and hydrolysis, amongst other factors, more than 90% of the pesticides that are applied are lost. It is only a small amount of the remaining 10% that eventually reaches the target site. This necessitates repeated application which eventually results in high costs and environmental pollution. Moreover, certain pesticides have been shown to have adverse effects on human health such as cancer, birth defects, reproductive defect, neurological and developmental impairment, immunotoxicity, and disruption of the endocrine system, when ingested through the consumption of pesticidecontaminated food. Although some environment-specific nanopesticides are on the market, nano-formulations with effective delivery mechanisms which result in application of modest amounts of nanopesticides are required. Nanopesticides provide innovative strategies for delivering the active ingredient of pesticides to the target site. Slow-releasing qualities, enhanced stability, permeability, solubility, and specificity are all features of nano-encapsulated pesticide formulations. They are specifically created to make the active ingredient (AI) more soluble and release it at the target site in a controlled manner. Due to this, only a small amount of the AI needs to be applied for it to be effective for an extended period of time. Nanopesticides are classified into two types. Type 1 nanopesticides are metal-based, whereas Type 2 materials contain AIs that are enclosed by nanocarriers, such as polymers, clays, and zein nanoparticles. The most prevalent analytes for Type 1 nanopesticides are Ag-, Ti-, and Cu-based nanomaterials (NMs). These nanopesticides can suppress a variety of plant pathogens, including fungal (such as Candida and Fusarium), as well as bacterial (such as Escherichia coli and Staphylococcus). If properly applied, nanopesticides could increase crop output, food safety, and nutritional value. For several plants treated with Type 1 nanopesticides (such as Ag-, Ti-, Cu-, and Zn-based NMs), improvements in the concentration of sugar, fatty acids, chlorophyll, carotenes, and important elements (such as P, K, Ca, Mg, S, Fe, Si, Mn, and Zn) have been documented. Suppression of pathogenic activity is one of the factors contributing to these enhancements. The abundance, structure, and network functioning of the plant-associated microbiome, which includes archaea, bacteria, and fungi, can be changed by adding metal-based nanopesticides to soil and plant.

This in turn may change the bioavailability and recycling of macronutrients (such as C, N, P, and S). More importantly, in order to fully utilize nanopesticides, it is necessary to comprehend how they interact with nutrients, soil, plant-associated microbiota, and other factors. Nanopesticides have obvious pesticidal activity and as such can exhibit toxicity toward non-target organisms. Studies show that, in comparison to their non-nanoscale equivalents, nanopesticides are 43.1% less toxic .This is primarily due to their AI delivery system, which is targetspecific, and thereby minimizes the exposure to non-target organisms. Cu(OH)2 nanopesticides applied to target soil agroecosystems for 365 days, had only minor negative effects on non-target wetland systems and the bacterial and fungal communities that live there. However, a few studies have shown negative impacts related to nanopesticide exposure. showed that long-term exposure to high concentrations of atrazine-containing nanopesticides (NPATZs) dramatically reduced the metabolic capability of bacterial communities in the rhizosphere and changed the makeup of those communities in comparison to conventional ATZ. An investigation into the long-term (117 days) effects of Ag nanopesticides (100 mg/kg) on the microbiome of the maize rhizosphere revealed negative effects on microbial diversity, the nitrogen cycle, and crop output. Low concentrations (0.5, 1.0, and 2.0 mg/g) of zinc oxide (ZnO) applied directly to soil enhanced the relative abundance of the essential bacterial group Bacillus in comparison to the control, but the higher concentrations had harmful effects on the bacterial population (You et al., 2018). A study by Zhao et al. (2017), discovered that exposure of spinach to Cu(OH)2 nanopesticide resulted in a significant reduction in antioxidant or defence-associated metabolites such as ascorbic acid, α-tocopherol, threonic acid, β sitosterol, 4-hydroxybutyric acid, ferulic acid, and total phenolics. Another study showed that captan@ZnO35- 45 nm and captan@SiO2 20–30nm nanofungicides influenced soil microorganisms by altering numerous microbial characteristics. Overall, literature suggests that nanopesticides may be more effective, resilient, and sustainable than their traditional analogues, with fewer negative environmental effects. However, future research is required to comprehend the effects of realistic nanopesticide doses on the rhizosphere microbiota, crop yield, and agroecosystem health in field settings. [51].

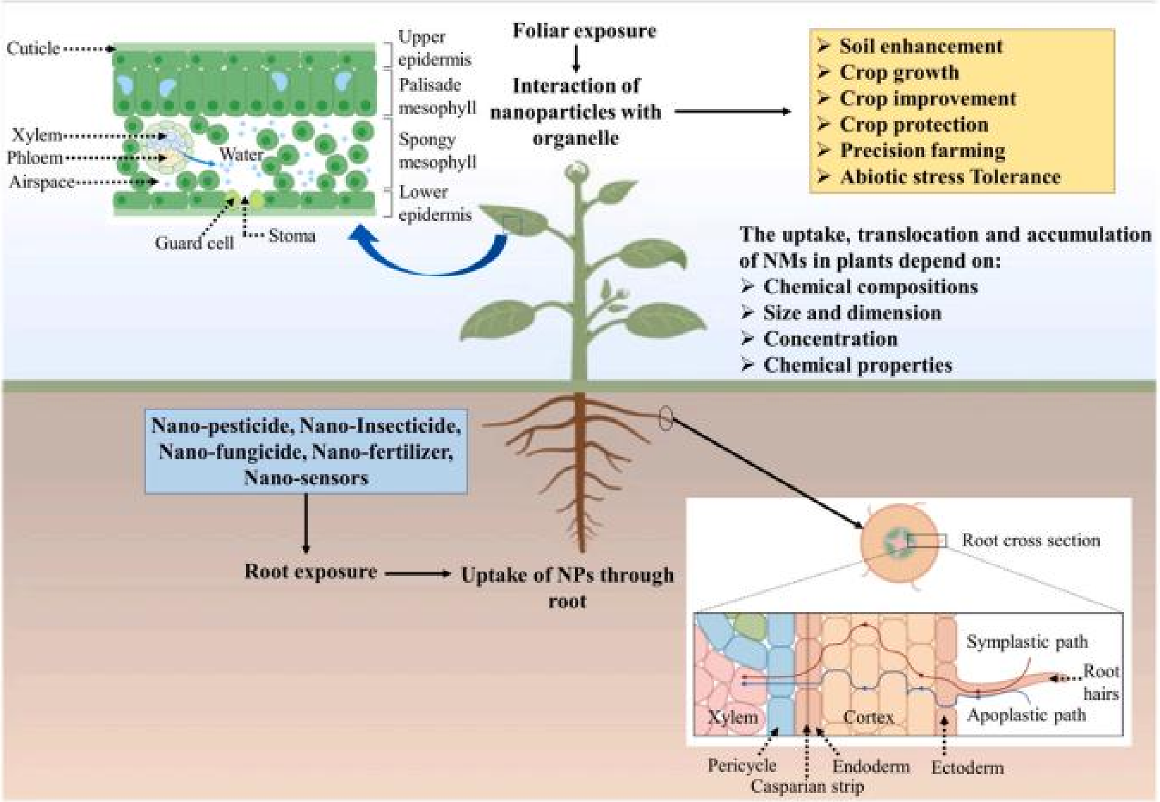

Figure 17: Nanoparticles can be applied to the root and foliar systems. Demonstrates the schematization of NPs translocation and delivery techniques in plants. Figure created with BioRender.com (https://app.biorender.com/biorender-templates).

11 Challenges and limitation of Nanocatalysts in Chemistry: From Synthesis to Industrial Applications

Nanocatalysts have gained significant attention in chemistry due to their enhanced surface area, unique reactivity, and potential applications in various catalytic processes. However, their synthesis and industrial implementation come with several challenges and limitations. One of the primary concerns is the complexity and cost associated with their synthesis. Many nanocatalysts require sophisticated techniques such as chemical vapor deposition (CVD) and hydrothermal methods, which are not only expensive but also difficult to scale up for industrial production. Furthermore, achieving precise control over the size, shape, and uniformity of nanoparticles remains a significant challenge, as even slight variations in morphology can impact catalytic efficiency. Stability issues, including aggregation due to high surface energy, further complicate their synthesis and storage. Additionally, traditional synthesis methods often involve toxic chemicals, raising environmental and safety concerns, thereby necessitating the development of greener and more sustainable approaches. Characterization and optimization of nanocatalysts present another major hurdle. Advanced techniques such as Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), and X-ray Diffraction (XRD) are required to analyze their structure and surface properties. However, these methods are expensive and not always accessible to researchers or industries. Moreover, functionalizing nanocatalysts to improve selectivity and stability requires precise surface modifications, which can be difficult to achieve uniformly. In practical applications, nanocatalysts often suffer from performance limitations such as low stability under extreme conditions, susceptibility to poisoning from reaction impurities, and the risk of leaching into reaction media. These factors can lead to decreased catalytic activity over time, making their reuse and regeneration a challenging task.

On an industrial scale, the application of nanocatalysts faces multiple barriers. High production costs remain a significant limitation, as the requirement for expensive raw materials and precise synthesis techniques increases the overall economic burden. Additionally, integrating nanocatalysts into existing industrial processes requires modifications to reactors, separation systems, and safety protocols, making large-scale adoption challenging. Regulatory concerns also play a crucial role in limiting the widespread use of nanocatalysts. The potential toxicity and environmental impact of nanoparticles, including their disposal and bioaccumulation, are still under investigation, leading to strict regulations and safety guidelines that industries must adhere to.Despite these challenges, various strategies are being explored to overcome these limitations and improve the feasibility of nanocatalysts in industrial applications. The development of green synthesis methods using biological sources such as plant extracts and bacteria can reduce environmental concerns while lowering production costs. Additionally, enhancing catalyst stability through protective coatings or embedding nanoparticles in support materials can improve their durability and reusability. Efficient recycling and recovery methods, such as magnetic separation and surface modifications, can also help improve economic feasibility. Collaboration between researchers and industries is crucial to tailoring nanocatalysts for specific applications, ensuring smoother integration into industrial processes. While nanocatalysts hold immense potential in revolutionizing chemical industries, addressing their synthesis, stability, scalability, and regulatory challenges is essential for their successful implementation on a larger scale.

12 Conclusion and future perspective:

Due to their exceptional surface properties and reactivity, nanocatalysts have emerged as a promising advancement in catalysis. However, their widespread application faces several challenges, ranging from complex and costly synthesis methods to stability, scalability, and industrial integration issues. The limitations associated with aggregation, leaching, and poisoning hinder their long-term efficiency and reusability, while environmental and regulatory concerns further restrict their commercial adoption. Despite these challenges, ongoing research and technological advancements continue exploring ways to enhance nanocatalysts' synthesis, stability, and sustainability.In the future, the focus should be on developing green and cost-effective synthesis approaches to minimize environmental risks and production expenses. Functionalization strategies, such as surface modification and the incorporation of nanocatalysts into robust support materials, can improve their stability and durability. Additionally, the integration of nanocatalysts into existing industrial processes requires innovations in reactor design and separation technologies to ensure seamless implementation. Addressing safety and regulatory concerns through in-depth toxicological studies and standardized guidelines will also play a crucial role in facilitating their large-scale application. With interdisciplinary collaboration between scientists, engineers, and industries, nanocatalysts have the potential to revolutionize chemical processes, making them more efficient, sustainable, and economically viable in the years to come.

REFERENCES:

[1]“S.L. Candelaria, Y. Shao, W. Zhou, X. Li, J. Xiao, J.-G. Zhang, Y. Wang, J. Liu, J. Li, G. Cao, Nanostructured carbon for energy storage and conversion, Nano energy, 1 (2012) 195-220.”.

[2]“K. Yan, A. Chen, Efficient hydrogenation of biomass-derived furfural and levulinic acid on the facilely synthesized noble-metal-free Cu–Cr catalyst, Energy, 58 (2013) 357-363.”.

[3]“B.R. Cuenya, Synthesis and catalytic properties of metal nanoparticles: Size, shape, support, composition, and oxidation state effects, Thin Solid Films, 518 (2010) 3127-3150.”.

[4]“C.Q. Sun, Size dependence of nanostructures: Impact of bond order deficiency, Progress in solid state chemistry, 35 (2007) 1-159.”.

[5]“Polshettiwar, V.; Varma, R.S. Green chemistry by nano-catalysis. Green Chem. 2010, 12, 743–754.”.

[6]“Somorjai, G.A.; Chaudret, B.; Serp, P.; Philippot, K. Nanomaterials in Catalysis, 1st ed.; Wiley-VCH: Weinheim, Germany, 2012.”.

[7]“Li, Y.; Zhou, Z.; Yu, G.; Chen, W.; Chen, Z. CO

catalytic oxidation on iron-embedded graphene: Computational quest for low-cost nanocatalysts. J. Phys. Chem. C 2010, 114, 6250–6254.”.

[8]“Arshadi, M.; Ghiaci, M.; Ensafi, A.; Karimi-Maleh, H.; Suib, S.L. Oxidation of ethylbenzene using some recyclable cobalt nanocatalysts: The role of linker and electrochemical study. J. Mol. Catal. A Chem. 2011, 338, 71–83.”.

[9]“Zarkesh, J.; Hashemi, R.; Ghaedian, M.; Khakdaman, H.R.; Ahmadpanah, S.J.; Khadzhiev, S.; Kadiev, H. HRH: Nano Catalytic Process to Upgrade Extra Heavy Crude/residual Oils. Presented at 19th World Petroleum Congress, Madrid, Spain, 29 June–3 July 2008.”.

[10]“Chen, X.; Zheng, Z.; Ke, X.; Jaatinen, E.; Xie, T.; Wang, D.; Guo, C.; Zhao, J.; Zhu, H. Supported silver nanoparticles as photocatalysts under ultraviolet and visible light irradiation. Green Chem. 2010, 12, 414–419.”.

[11]“Centi, G., Perathoner, S., 2003. Catalysis and sustainable (green) chemistry. Catal. Today 77, 287–”.

[12]“Dzwigol, H., Kwilinski, A., Lyulyov, O., Pimonenko,T., 2023. The Role of Environmental Regulations,Renewable Energy, and Energy EfficiencyinFinding the Path to Green EconomicGrowth.Energies 16, 3090.”.

[13]“Hill, C.L., Prosser-McCartha, C.M., 1995. Homogeneous catalysis by transition metal oxygen anion clusters. Coord. Chem. Rev. 143, 407–455. https://doi.org/https://doi.org/10.1016/0010- 8545(95)01141-B”.

[14]“Jurina, T., Cvetnić, T.S., Šalić, A., Benković, M., Valinger, D., Kljusurić, J.G., Zelić, B., Jurinjak Tušek, A., 2023. Application of Spectroscopy Techniques for Monitoring (Bio) Catalytic Processes in Continuously Operated Microreactor Systems. Catalyst”.

[15]“Kilic , A., Alhafeez , A., Aytar, E., Söylemez, R., n.d.The Sustainable Catalytic Conversion of CO2intoValue-Added Chemicals by Using Cobaloxime-Based Double Complex Salts as Efficient andSolvent-Free Catalysts. Available SSRN4360204.”.

[16]“Bellah MM, Christensen SM, Iqbal SM (2012) Nanostructures for medical diagnostics. J Nanomater 2012:2”.

[17]“Chi L (2010) Nanotechnology: volume 8: nanostructured surfaces, vol 7. Wiley, Weinheim”.

[18]“Mijatovic D, Eijkel J, Den Van, Berg A (2005) Technologies for nanofluidic systems: top-down versus bottom-up—a review. Lab Chip 5(5):492–500”.

[19]“Hench LL, West JK (1990) The sol-gel process. Chem Rev 90(1):33–72”.

[20]“T. Prasad Yadav, R. Manohar Yadav and D. Pratap Singh, Nanosci. Nanotechnol., 2012, 2, 22–48.”.

[21]“C.-W. Kuo, J.-Y. Shiu, Y.-H. Cho and P. Chen, Adv. Mater., 2003, 15, 1065–1068.”.

[22]“R. Ostermann, J. Cravillon, C. Weidmann, M. Wiebcke and B. M. Smarsly, Chem. Commun., 2011, 47, 442–444.”.

[23]“P. S. Kumar, J. Sundaramurthy, S. Sundarrajan, V. J. Babu, G. Singh, S. I. Allakhverdiev and S. Ramakrishna, Energy Environ. Sci., 2014, 7, 3192–3222.”.

[24]“V. Garg, R. G. Mote and J. Fu, Appl. Surf. Sci., 2020, 526, 146644.”.

[25]“J. Mun˜oz-Garcı´a, L. Va´zquez, R. Cuerno, J. A. Sa´nchez-Garcı´a, M. Castro and R. Gago, Toward Functional Nanomaterials, Springer US, New York, NY, 2009, pp. 323–398.”.

[26]“J. H. Nam, M. J. Jang, H. Y. Jang, W. Park, X. Wang, S. M. Choi and B. Cho, J. Energy Chem., 2020, 47, 107–111.”.

[27]“M. Nie, K. Sun and D. D. Meng, J. Appl. Phys., 2009, 106, 054314.”.

[28]“H. H. Son, G. H. Seo, U. Jeong, D. Y. Shin and S. J. Kim, Int. J. Heat Mass Transfer, 2017, 113, 115–128.”.

[29]“Nanoparticle characterization techniques”.

[30]“0 L. Reimer, H. Kohl, in: ‘Transmission Electron Microscopy Physics of Image

Formation', Springer: New York, 2009, vol. 51 pp. 1-15.".

[31]"D. Astruc, F. Lu and J. R. Aranzaes, Angew. Chem. Int. Ed., 2005, 44, 7852.".

[32]"Y. W. Jun, J. W. Seo and J. Cheon, Acc. Chem. Res., 2008, 41, 179.".

[33]"L. E. Alexander and H. P. Klug, J. Appl. Phys., 1950, 21, 137.".

[34]"M. R. Axet, K. Philippot, B. Chaudret, M. Cabié, S. Giorgio and C. R. Henry, Small, 2011, 7, 235.".

[35]"N. T. K. Thanh and Z. Rosenzweig, Anal. Chem., 2002, 74, 1624.".

[36]"A. Courty, A. Mermet, P. A. Albouy, E. Duval, M. P. Pileni, Nat. Mater., 2005, 4, 395.".

[37]"J. Yue, T. J. Feliciano, W. Li, A. Lee and T. W. Odom, Bioconjug. Chem., 2017, 28, 1791.".

[38]"S. Rades, V.-D. Hodoroaba, T. Salge, T. Wirth, M. P. Lobera, R. H. Labrador, K. Natte, T. Behnke, T. Gross and W. E. S. Unger, RSC Adv., 2014, 4, 49577.".

[39]"V.-D. Hodoroaba, C. Motzkus, T. Mace and S. VaslinReimann, Microsc. Microanal., 2014, 20, 602".

[40]"B. Chen, Z. Xia and K. Lu, J. Eur. Ceram. Soc., 2013, 33, 2499.".

[41]"M. Ashokkumar and S. Muthukumaran, Opt. Mater., 2014, 37, 671.".

[42]"A. Vilalta-Clemente, G. Naresh-Kumar, M. Nouf-Allehiani, P. Gamarra, M. A. di Forte-Poisson, C. Trager-Cowand and A. J. Wilkinson, Acta Mater., 2017, 125, 125.".

[43]"Zellner A., Suntz R., Deutschmann O. , Angew. Chem., Int. Ed., 2015, vol. 54 pg. 2653".

[44]"R. Koole, E. Groeneveld, D. Vanmaekelbergh, A. Meijerink and C. de Mello-Donegá, Size effects on semiconductor nanoparticles, in Nanoparticles, ed. C. de Mello Donegá, 2014, Springer, Berlin, Heidelberg, p. 13".

[45]") Baturina, O. A.; Lu, Q.; Padilla, M. A.; Xin, L.; Li, W.; Serov, A.; Artyushkova, K.; Atanassov, P.; Xu, F.; Epshteyn, A.; Brintlinger, T.; Schuette, M.; Collins, G. E. CO2 Electroreduction to Hydrocarbons on Carbon-Supported Cu Nanoparticles. ACS Catal".

[46]"Morales-Guio, C. G.; Cave, E. R.; Nitopi, S. A.; Feaster, J. T.; Wang, L.; Kuhl, K. P.; Jackson, A.; Johnson, N. C.; Abram, D. N.; Hatsukade, T.; Hahn, C.; Jaramillo, T. F. Improved CO2 reduction activity towards C2+ alcohols on a tandem gold on copper el".

[47]"Kim, D.; Yu, S.; Zheng, F.; Roh, I.; Li, Y.; Louisia, S.; Qi, Z.; Somorjai, G. A.; Frei, H.; Wang, L.-W.; Yang, P. Selective CO2 electrocatalysis at the pseudocapacitive nanoparticle/ordered-ligand interlayer. Nat. Energy 2020, 5 (12), 1032−1042".

[48]"The Interactive Dynamics of Nanocatalyst Structure and Microenvironment during Electrochemical CO2 Conversion".

[49]"Nanocatalyst in remediating environmental pollutants".

[50]"Critical learning from industrial catalysis for nano catalytic medicine".

[51]"Nanoparticle applications in agriculture: overview and response of plant-associated microorganism".