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METAL NANOPARTICLES IN CATALYSIS MECHANISM AND APPLICATIONS

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ABSTRACT

Metal nanoparticles (MNPs) have emerged as powerful catalysts due to their high surface-area-to-volume ratio and unique electronic properties, enabling exceptional catalytic activity, selectivity, and stability. This review explores the mechanisms underlying catalysis by metal nanoparticles, highlighting their role in facilitating diverse chemical transformations. Key processes such as adsorption, activation of reactants, and intermediate formation are discussed to elucidate how MNPs enhance reaction kinetics. The applications of metal nanoparticles in catalytic processes are examined across various domains, including organic synthesis, environmental remediation, and industrial-scale production. Furthermore, challenges like nanoparticle aggregation, recyclability, and sustainability are addressed, alongside advancements in synthesis strategies and functionalization to improve catalytic performance. This comprehensive review aims to provide insights into the evolving field of metal nanoparticle-based catalysis, emphasizing their potential in addressing global scientific and industrial challenges.

Keywords: *Metal nanoparticles, catalysis, reaction mechanisms, catalytic activity, applications*

INTRODUCTION

The term “catalysis” was coined in 1835 by the Swedish chemist Berzelius. Still, a suitable definition was introduced only many years later by Ostwald, who wrote in 1894: “Catalysis is the acceleration of a slow chemical process by the presence of a foreign material [1]. Today, more than 100 years later, every student learns that a catalyst accelerates a reaction by lowering its activation energy, and he knows that the catalyst achieves this by attaching itself to the reactant molecule, thereby interacting with it. Although the catalyst participates in the reaction it is not used up and can transform many molecules. However, for porous materials, there is often a debate whether the catalytic activity is restricted to the outer surface or whether and to which extent the surface inside the pores contributes. This is of course also a question of transport limitation in the pores. Furthermore, the preference for nanometer over micrometer-size catalytic particles is not only a question of the economy of better using expensive materials like platinum metal. Small particles have a larger fraction of their atoms on the surface. Still, on top of this, an atom on the surface of a small metal particle has electronic properties that are significantly different from those on top of a large particle [2].

Nanoparticles, in particular gold nanoparticles, have been used for millennia in China and Egypt by women for both curative and aesthetic purposes and by artists for the making and decoration of glasses and ceramics such as the illustrious Lycurgus cup (fifth century AD). Catalytic nanoparticle families are not restricted to mono- and bimetallic nanoparticles, but they extend to binary and ternary particles with main group elements. Complex nanoparticle support ensembles are often called nanocomposites. The complexification of the nanocatalyst design is sometimes reminiscent of the complexity organized by Mother Nature. For instance, supported sub nanoparticles of MoS_2 type containing only a few atoms resemble MoS-based nanoclusters serving as cofactors of the nitrogenase enzymes that catalyze N_2 fixation. These biomimetic aspects are useful for instance for the design of processes involving nanocatalytic H_2O, N_2, and CO_2 reduction. In this context, the role of light is essential in particular toward the activation of small molecules, hydrogen production, and water splitting [3].

Metal catalysis on a single crystal surface and on nanoparticles:

The intact FA molecule chemisorbs weakly on Pd or Pt metal surfaces. However, there is a general agreement that HCOOH dissociates readily into surface-bound HCO_2 • and H•. HCO_2 • adsorbs preferentially on large flat terrace sites in a bridge-bonded (bidentate) mode, Chemical Society The CO_2 product desorbs since it is only weakly chemisorbed. Alternatively, on unsaturated surface sites at small particles (adatoms, corner atoms, steps and kinks) which provide a higher binding energy it can bind in a linear fashion (monodentate, Figure 1b). They lead preferentially to CO formation with strong bonding to most transition metals, and thus to catalyst poisoning[4]. CO-free H2 production was found for a catalyst consisting of Au nanoparticles supported on SiO2. This is very attractive for applications to operate hydrogen fuel cells. The kinetics of HCOOH decay was of zero-order, i.e. the rate did not depend on the formic acid concentration. This means that under the conditions of investigation the catalyst operates at its full capacity because the substrate concentration is sufficiently high so that all available sites are active (compare production line work). The first step of FA decay, the dissociative adsorption to the state shown in Figure 1b, is fast and does not influence the kinetics. The rate limiting step is thought to be the dissociation of the C–H bond, but the mechanism of this is not known in detail. While the surface-bound H atoms are mobile and can recombine to undergo activated desorption it is conceivable that a significant coverage of HCO_2 • fragments builds up on the metal surface. If two of these fragments come into close proximity as e.g. in the configuration suggested in Figure 1c, the two H atoms may recombine to H_2, leaving two CO_2 molecules which will readily desorb. Aiming at a detailed understanding of the reaction mechanism, a large number of theoretical calculations has been carried out which model the reaction on various metal and metal oxide surfaces, and for various sites. A recent overview gives an impression of the complexity of this effort [5]. Chemical Society Reviews With a TOF reaching 1.38×106 s −1 and an apparent activation energy of 22(1) kJ mol^{-1}, monodisperse 2.2 nm AgPd nanoparticles with 42% Ag and 58% Pd show the best catalytic performance ever reported for the FA dehydrogenation reaction among all heterogeneous catalysts tested in aqueous solution [6].Note the dramatic reduction of the activation energy which is partly compensated by a low pre-exponential factor (see Section 4). It is instructive to look at more details about hydrogen adsorption. We will do it for the examples of a Pt(111) surface and a zeolite-supported Pt13 cluster. H_2 chemisorbs dissociatively on a Pt surface. In order to do this spontaneously, the binding energy of the two H atoms to Pt must exceed the H−H binding energy of 436 kJ mol^{-1}. The desorption energy of H2 from Pt(111) which amounts to 0.8 eV (77 kJ mol−1) represents this excess energy. Thus, the binding energy of each of the H atoms is ½ (436+77) kJ mol^{-1}, or 256 kJ mol−1 , which is a respectable chemical bond. For the Pt13 clusters in KL zeolite this is even more impressive [7] from the 2.1 eV desorption energy we obtain a Pt−H bond energy of 319 kJ mol^{-1}. The example demonstrates the necessary strength of interactions if bonds are to be dissociated, but we emphasise that full initial dissociation is not necessary for catalysis to occur when the new bonds can begin to form before the old bond is broken. On another point: strongly adsorbed species, even the seemingly innocent chemisorbed hydrogen in the above Pt13 cluster, can successfully block the surface so that catalysis is inhibited, as for example in the reaction with O_2 [8].It is commonly expected that the efficiency of a nanoparticle catalyst increases with decreasing particle size because the binding energy to the smaller particles is higher [9].In the case of the Au/SiO_2 catalyst no such dependence was found.19.However, as expected, the turnover frequency (TOF, the number of molecules reacted per active centre and per unit time, a common measure of the efficiency) increases with temperature, and the activation energy determined for H_2 production amounted to 58.5 kJ $mol^{-1.}$ 20

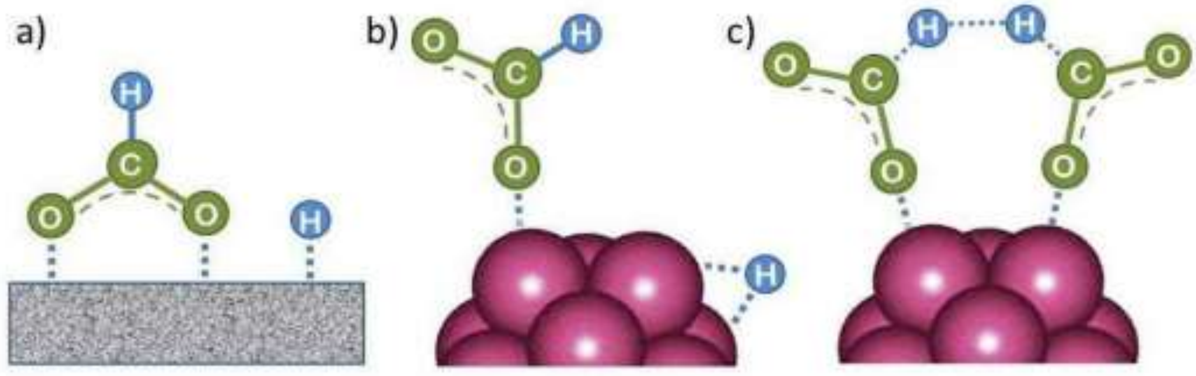
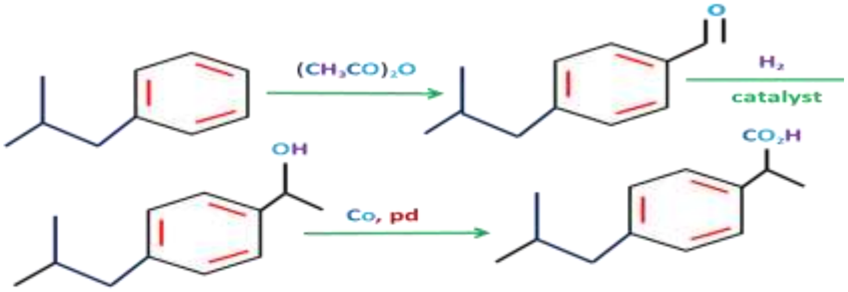


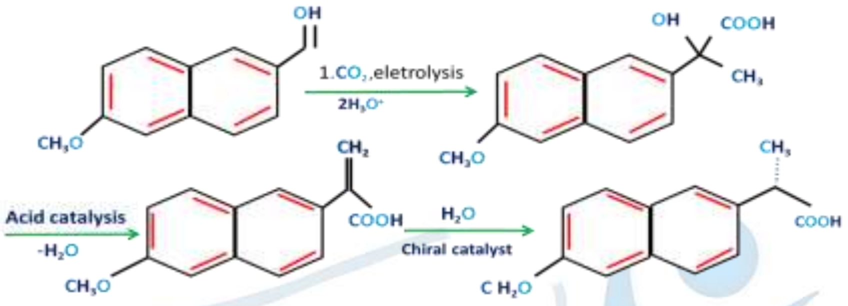
Figure 1: a) First reaction intermediate of formic acid dehydrogenation on the surface of a single crystal (bidentate, bridged-bond), b) on a nanocluster (monodentate, linear bond) metal catalyst. c) While surface-bound H can recombine to form H_2, hydrogen formation from the HCO_2 •. fragment is suggested here to occur via a cyclic transition state, but other mechanisms have been considered as well [10].

Catalyst applications:

The application of catalysts is ubiquitous in the chemical industry in areas ranging from pharmaceuticals to polymers to petroleum processing. More than 90% of all industrial processes are based on catalysis [11]. The widespread utilization by industry of catalytic processes reflects the economic and environmental benefits achieved through catalysis. Ibuprofen is one of the most commonly used over-the-counter pain relievers. The traditional synthesis requires six steps that use large volumes of solvent, corrosive reagents, and stoichiometric quantities of materials. This protocol also exhibits poor atom economy, only 40% of the atoms in the starting materials are incorporated into the product. In contrast, the BHC synthesis[12] of ibuprofen is accomplished in only three steps (Scheme 2). Catalytic amounts of reagents are used, and more than 99% of the HF catalyst is recycled and reused. Atom economy doubles to 80%, significantly reducing the amount of waste generated. While there is concern that this improved synthesis of ibuprofen relies on anhydrous hydrogen fluoride, it, however, does serve as both catalyst and solvent to minimize aqueous and organic waste streams and maximize reaction efficiency. Another anti-inflammatory drug, Naproxen, can be synthesized in high yield via a catalytic route (Scheme 3) [13]. The final step in the synthetic sequence employs a chiral transition metal catalyst. containing BINAP [2,2 -bis(diarylphospheno)-1,1 - binaphthyl] to produce the desired enantiomer in 97% yield. The high selectivity of the transition metal catalyst is attributed to steric factors that restrict rotation. Improved selectivity through catalysis minimizes or eliminates the need for product separation, reducing the use of solvents and separation agents.



Scheme 2 BHC synthesis of ibuprofen



Scheme 3. synthesis of naproxen.

In recent years, the catalytic use of metal nanoparticles (MNPs) has experienced a growing interest. This fact is mainly due to the special features of MNPs as catalysts, which combine the advantages of homogeneous and heterogeneous catalysis. MNPs display the characteristic high stability and recyclability/reusability of heterogeneous catalysts but with a higher activity due to their small size and large number of surface active sites. These specific properties make MNPs perfect catalysts for many catalytic processes. In this context, the incorporation of new reactions, novel catalysts, and recent advances in this research area is of great interest to the scientific community [14]. The study lacks in-depth insights into the long-term stability and recyclability of metal nanoparticles in real-world catalytic applications. Additionally, the environmental and economic implications of large-scale nanoparticle production and usage remain underexplored.

This review explores the catalytic mechanisms and applications of metal nanoparticles, focusing on their synthesis, structure, and surface chemistry. It highlights their role in industrial processes, energy conversion, and environmental remediation. Challenges like stability and scalability are addressed, with suggestions for future research. The review aims to inspire interdisciplinary advancements in nanotechnology and catalysis.

Mechanism:

Metal nanoparticles hold great promise in heterogeneous catalysis because of their high surface-to-volume ratio, rich active surface atoms, and unique electronic structures as compared with their bulk counterparts [15]. For example, Au, a metal with the least reactivity toward molecules, [16] showed surprisingly high activity toward CO oxidation when its size is smaller than 5 nm.6−8 Cu-based nanoparticles proved to be an efficient catalyst for the production of methanol from the syngas (CO + H_2) [17].Plasmonic nanoparticles such as Ag and Au can be used as catalysts for solar-driven photocatalytic water splitting, CO_2 reduction, and degradation of organic pollutants [18]. Pt-, Ir-, and Ru-based nanoparticles manifest low overpotential for electrocatalytic hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and oxygen evolution reaction (OER), which are important half-reactions for the conversion and storage of renewable energy. Because of their high surface energy, metal nanoparticles are thermodynamically unstable and prone to migration and coalescence during catalysis, especially at high reaction temperatures. These structural changes are usually accompanied by a dramatic decrease in catalytic activity and selectivity[19].

Heterogeneous catalysis is vital to produce fuels, fertilizers, and fne chemicals. Heterogeneous catalysts ofer many advantages over homogeneous catalysts such as easy catalyst separation and reusability [16]. Various methods such as sol–gel process, chemical vapour deposition, chemical reduction method, solution-based synthesis, solvothermal, reverse micelle and co-precipitation methods have been used for the synthesis of metal nanoparticles. Among these methods, the chemical reduction-based polyol and colloidal synthesis methods are more efficient for preparing metal nanoparticles with precise structure. When the size of nanoparticles is decreased to the nanometre scale, the surface to volume ratio increased and hence impart enhanced catalytic activity [20]. The electronic and geometric structures of single atoms, nanoclusters, and nanoparticles different significantly and hence import different catalytic properties [21].

Catalytic Processes:

In particular, a desorption step may not be equilibrated in a catalytic cycle, as postulated in the classical Langmuir–Hinshelwood mechanism, where both adsorption and desorption are assumed to be equilibrated, while a surface reaction step is rate-determining. Let us explore how a desorption step can operate more than equilibrium, when $vd > va$ Clearly, one way to increase vd at constant d product pressure and constant temperature is to improve the concentration or fugacity of the adsorbed species above its equilibrium value. This can be done through a kinetically coupled preceding adsorption step in the catalytic cycle. With the fugacity of the adsorbed species higher than that corresponding to equilibrium with the desorbed species, the latter is not an inhibitor of the desorption step if $vd >> va$ The lack of d inhibition of the rate of a catalytic cycle by a desorption product is, therefore, an indication that adsorption-assisted desorption has taken place. Kinetic coupling between steps in a catalytic cycle works in both ways through the Le Chatelier principle. A thermodynamically unfavorable step is helped either by the removal of a product through a subsequent step faster than the rate at which the product can return to reactant; or by the accumulation of a reactant through a preceding step. The latter case is that of AAD in a catalytic cycle. Soon after Yamashita et al. [22] published their work on AAD, they found that a similar phenomenon was observed in the decomposition of methanol on $Cr_2 O_3$. In that case, 2 3 adsorbed formate ions formed by adsorption of methanol decompose to reaction products much faster under ambient pressure of methanol than in its absence. This is the first reported case of AAD in a catalytic cycle, although other examples were reported previously, but not recognized as cases of AAD. Let us describe briefly four such cases as well as a carefully documented case of AAD in the sense of the Tamaru school [23].

Types of nanoparticles in catalysis:

Gold nanoparticles as catalysts:

The initial discovery of the catalytic efficiency of gold [24] was surrounded by some confusion. It was observed by Bond and co-workers [25] that very small particles of Au were active on the hydrogenation reaction. However, many reports stated that the catalytic activity observed may just be due to impurities [43]. In the last three decades, there have been a number of discoveries which demonstrate that catalysis by Au nanoparticles (Au-NPs) offers a myriad of possibilities to activate and reacting molecules [26]. Those discoveries, given the long-believed chemical inertia of Au, have entirely changed the researcher's perception of that metal. AuNPs were therefore used in many catalytic systems including low-temperature CO oxidation [48], acetylene hydro chlorination, selective hydrogenation of nitro compounds [27], and selective oxidation of alcohols along with many other important reactions [28] The performance of Au-based Nano catalysts on the liquid-phase oxidation of benzyl alcohol to benzaldehyde was investigated [28]. A good activity, as well as selectivity toward benzaldehyde, was obtained from the Au-based catalysts compared to the other catalysts. Nowadays, Au-NPs are not just good catalysts, but they are the best [29].

Palladium nanoparticles as catalysts:

Palladium was used earlier in catalysis for organic transformations. The use of palladium as a catalyst in organic chemistry was mostly stimulated by the discovery of palladium-catalyzed oxidation of ethylene to acetaldehyde by air [30] The Nobel Prize in Chemistry 2010 was awarded to R.F. Heck, E. Negishi, and A.

Suzuki for the palladium-catalyzed cross-coupling reactions, families of organic synthesis that use palladium complexes as catalysts. Monfared et al. have recently highlighted the advance in applying palladium nanoparticles (Pd-NPs) for Hiyama cross-coupling reactions [31]. The investigation showed that Pd-NPs were catalytically highly effective in fluoride-free Hiyama coupling reactions. The importance of the choice of the carrier was also mentioned, with carbon carrier being the most suitable. Pd-NPs have been effective catalysts for synthesizing various compounds [32]. The activity of the Pd-NPs is size and shape-dependent. It was revealed that very sharp-shaped Pd-NPs show strong catalytic activity for organic reactions such as Heck, Suzuki, and Stille couplings. In a study conducted in our group [33], Pd-NPs supported on SBA-15 typical silica material were revealed to be an efficient catalyst for Suzuki coupling. High performance in terms of turnover frequencies was obtained even under an aqueous system and fairly low temperatures.

Silver nanoparticles as catalysts:

Silver metal has been used in numerous technologies and incorporated into a wide range of consumer products that take advantage of their distinct physical, chemical and biological properties [34]. The catalysis of silver nanoparticles (Ag-NPs) has been widely exploited, and it is of great interest in organic synthesis because of their specific reactivity, selectivity and stability in many catalytic systems. Dong and co-workers highlighted some modern advancement of Ag-NP-catalyzed organic reactions [34]. Supported Ag-NPs have been found to be effective catalysts in many reduction processes of functional molecules, including reduction of carbonyl and nitroaromatic compounds. Various heterogeneous silver nanocatalysts have been recognized as powerful catalysts for oxidation of alcohols, silanes and olefins, and related oxidative transformations [35]. In a study conducted in our group, Ag-NPs encapsulated within silica nanospheres showed auspicious results in the oxidation of benzyl alcohol. Furthermore, Ag-NPs catalyzed the chemiluminescence from luminol–hydrogen peroxide system with better activity than colloidal Pt and Au [36].

Types of reactions:

Oxidation: Catalytic oxidation of hydrocarbons is the largest category of catalytic organic reactions in the petrochemical industry. If oxidation is considered in the formal way i.e., an increase in the formal oxidation number of the carbon atom, then reactions such as dehydrogenation should also be classified as oxidation reactions. Oxidation reactions may be classified into: vapor-phase reactions which are mainly heterogeneously catalyzed, and liquid-phase reactions which are commonly homogeneously catalyzed. For some reactions, the two categories exist and have both been used industrially with varying importance over time e.g. oxidation of ethylene to acetaldehyde. However, for our discussion in this text oxidation reactions will be classified according to the type of organic reactant. We shall therefore be talking about the oxidation of saturated hydrocarbons, olefins, aromatic compounds, alcohols, and compounds with other functional groups

ETHYLENE OXIDATION

(a) Ethylene Oxide

Ethylene oxide is used relatively little by itself, but it is an important intermediate, especially in the manufacture of ethylene glycol, which accounts for about two-thirds of the consumption of ethylene oxide. The worldwide 1980 production of ethylene oxide was more than six million metric tons. Production today is almost entirely by direct oxidation of ethylene with air or oxygen over a supported silver catalyst according to the equation [37].

Reduction:

Oxidation reduction reaction can take place via two pathways. The first, commonly referred to as partial reduction, involves a two electron pathway resulting in the production of adsorbed hydrogen peroxide. Full reduction follows a more efficient four electron pathway which does not involve the production of H_2O_2 [38]. Due to the improved efficiency of full reduction as well as the relatively high reactivity of hydrogen peroxide compared to the stability of water, full reduction is the pathway that is sought after when choosing a catalyst for the ORR [39]. For partial reduction to take place, O_2 is first adsorbed on to the catalyst surface. Then, two hydrogen additions take place resulting in an adsorbed H_2O_2 molecule. The hydrogen peroxide product can then undergo further reduction to produce two water molecules, or it can simply dissociate resulting in a free H_2O_2 molecule [40]. Full reduction is a dissociative adsorption process which begins with the adsorption of O_2 on the catalyst surface. Following O_2 adsorption, the first electron transfer in the form of hydrogen addition takes place resulting in *OOH. This is followed by the second electron transfer, again in the form of hydrogen addition. Depending on whether this second hydrogen addition takes place at the oxygen molecule adsorbed to the catalyst or if it takes place at the oxygen already bound to the hydrogen determines how the reaction moves forward. If the second hydrogen addition takes place at the oxygen adsorbed to the catalyst (mechanism 1), it results in two adsorbed OH groups. Subsequent electron transfers in the form of hydrogen addition take place at each *OH group resulting in the production of two water molecules. If the second hydrogen addition takes place at the oxygen already bound to the first hydrogen (mechanism 2), this results in desorption of a water molecule and an adsorbed O atom. Two electron transfers in the form of hydrogen addition to the *O follow resulting in desorption of a second water molecule. DFT simulations of the two pathways show that mechanism 1 is thermodynamically favored, and it is therefore the more realistic method [41].

Mechanism 1:

$$O_2 \longrightarrow {*O_2} \quad {*O_2} + e^- H^+ \longrightarrow {*OOH} \quad {*OOH} + e^- + H^+ \longrightarrow {*OH} + {*OH}$$

$$2{*OH} + 2e^- + 2H^+ \longrightarrow 2H_2O$$

Mechanism 2:

$$O_2 \longrightarrow {*O_2} \quad {*O_2} + e^- H^+ \longrightarrow {*OOH} \quad {*OOH} + e^- + H^+ \longrightarrow {*O} + H_2O \quad {*O} + e^- + H^+ \longrightarrow$$

$$
{*OH} \quad {*OH} + e^- + H^+ \longrightarrow H_2O$$

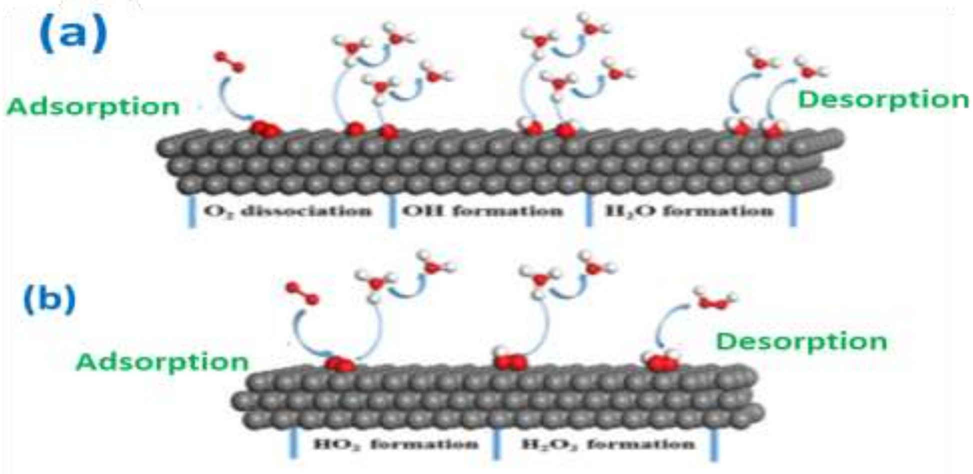


Figure 2: Mechanism schematics based on the work of Zhang et al. [42]of (a) full reduction and (b) partial reduction of oxygen.

Photo catalysis and electrocatalysis:

Generally, photocatalysis, as one of the common catalysis, is the utilization of semiconductor photocatalysts to accelerate photochemical reactions, where the photogenerated separated electron-hole pairs participate in the following oxidation-reduction reactions [43]. Electro catalysis is a specific form of catalysis that accelerates charge transfer between the electrodes and the electrolyte interfaces, where most commonly electro catalysts are a kind of catalysts attached to the surface of electrodes or as the electrode surface that are largely beneficial for electron transfer between reactants and electrodes [44]. So far, photo catalysis and electro catalysis are often essential parts of chemical processes for water splitting and pollution treatment, which are important reactions for harvesting ubiquitous forms of ambient energy. To enhance the photocatalytic and electro catalytic performance, growing attention has been attached to the development of 2D nanomaterials with good electrical conductivity and large surface area. In contrast to conventional 3D bulk nanomaterials, these atomically thin 2D nanomaterials have attracted attention in environmental and energy-related research sectors as a result of their extraordinary stability and activity, often on account of their high specific surface area, robust mechanical structure, and excellent electrical conductivity. In addition, 2D nanomaterials have been pursued as economical alternatives to more expensive precious metals, such as platinum and rhodium. Recent progress in multiple atomically thin 2D nanomaterials has broken new ground; there have been rapid developments in the synthesis of 2D nanomaterials, and their resulting properties, surface chemistry, and catalytic applications [45].

Table 1: characteristics and types of catalyst

		Photocatalysis	**Electro catalysis**
Characteristics of catalysts	Type	2D nanomaterial powders or composite thin films	2D nanomaterial thin films or powders loaded on an electrode surface
	Hydrophobicity recyclability	hydrophilic Recyclability Complex for powders, feasible for thin films	Hydrophobic or hydrophilic
Conditions of reaction systems	Energy input configuration	Solar energy one reaction chamber	Externally applied electric bias in one reaction chamber or two chambers separated by bias
Benefits	Charge transfer pathway, and cost efficiency	Low	High including expensive electrode and electric energy Relative high

Bimetallic Nanoparticles

The degree of complexity for the geometric structures of bimetallic nanoparticles further increases in comparison with bimetallic nanoclusters. The bimetallic nanoclusters usually show disordered and flexible geometric structures because of the lack of enough metal−metal bonding. In the case of bimetallic nanoparticles, ordered geometric structures with crystalline features are formed, which leads to the higher stability of bimetallic nanoparticles than the nanoclusters. Of course, there are also some reports on bimetallic nanoparticles with an amorphous structure, in which the spatial arrangements of the metal atoms are not as ordered as the crystalline structure. It can be expected that the structural stability of the amorphous bimetallic nanoparticles will lie between the crystalline nano-particles and the nanoclusters. As illustrated in Figure 3, the presence of more atoms in bimetallic nanoparticles also leads to the complexity in terms of to simplify the situation, one may focus on the surface or subsurface structural features of the bimetallic nanoparticles because these regions are more relevant in catalysis. In practical catalysts, the surface of a bimetallic nanoparticle is usually rough, with multiple types of surface structures such as terrace, corners, flat facts, and defective sites. The coordination number of the surface atoms has been proposed as a key factor that determines the activity because the adsorption of reactant and intermediation the surface atoms is influenced by the neighboring atoms [46]. It has been revealed in the literature that, a specific catalytic reaction, may follow different reaction pathways when the reactant is adsorbed on different surface sites [47].The site-specific catalytic behavior has already been established in some monometallic systems, and it can be expected that such behavior/phenomenon will be more complicated when dealing with the bimetallic system. Nevertheless, the combination of bimetallic nanoparticles with a solid carrier will further increase the complexity of the geometric structural features of bimetallic nanoparticles due to the formation of a metal−support interface. The chemical bonding between the bimetallic nanoparticles and the supports related to the chemical properties of the two components. For instance, Metal−O bonding can be present in oxide-supported bimetallic nanoparticles. When the support is changed to carbon-based materials, the Metal−C/N/S bonding may serve as the linkage at the metal−support interface. Besides, due to the difference in metal−support affinity of the two metal elements, local segregation may appear at the interface between bimetallic nanoparticles and the support. Because of the above reasons, the theoretical modeling of bimetallic nanoparticle is not an easy task. There are already some studies on modeling of the morphology and possible segregation of the bimetallic nanoparticles under various conditions [48]. For instance, a genetic algorithm is employed to predict the composition of thermodynamically stable bimetallic nanoparticles comprising tens of thousands of atoms. Because it is very difficult to measure the three-dimensional atomic structures of bimetallic nanoparticles, a fast modeling approaches helpful to give an estimation of the plausible geometric structure and composition ordering[49]. (see Figure 3).50

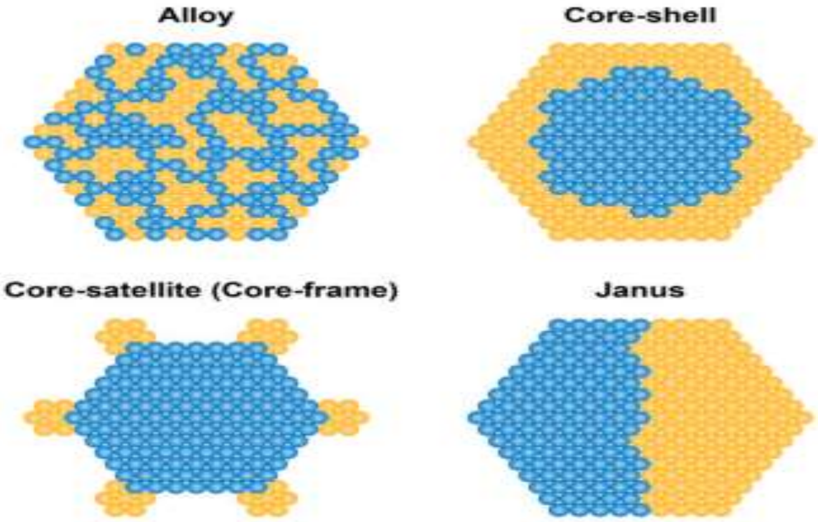


Figure 3. Schematic illustration of several types of bimetallic nanoparticles with different spatial distributions of the two metal elements within the individual bimetallic nanoparticles. Reproduced with permission from ref [50]. Copyright 2021 Wiley-VCH.

Figure 4. Results of the combined simulations of molecular dynamics (MD) and Monte Carlo (MC) for 0.5(A):0.5(B) composition for [51] combinations of bimetallic nanoparticles. For different combinations of two metals, the thermodynamically stable configurations give different spatial distributions of the metal elements, spanning from alloy structure to core−shell structure. Reproduced with permission from ref [52]. Copyright 2021 American Chemical Society.

Electrochemical method

The electrochemical method for producing ceramic flms was developed by Switzer. This method has been used to develop nano metal oxides (MOs) such as SiO2, TnO2, etc. The contact between a metal-containing electrolyte solution and an electrically conductive metal substrate is where electrochemical deposition takes place. An electrolyte containing 0.01 mM AgNO3 was used to electrochemically create silver nanoparticles. The working electrode and counter electrode were used with the electrode made of glassy carbon and silver metal as shown in Fig. 1a. Ag NPs exhibited dendritic growth, and it was discovered that a high concentration of the silver ion encourages the formation of aggregations and dendrites. In general, silver ions can be reduced cathodically in the following way at room temperature [51]. Metal or MOs are formed at zero oxidation state as a result of reduction when the heavy metal is oxidized at the anode and the metal cations go to the cathode. The ammonium stabilizer prevents agglomeration and the production of unwanted metal powder. Platinum and Ti metal sheets that are 1 ×1 cm each were utilized as cathode and anode respectively, in the initial experiment. The distance between the two electrodes was 1 cm. The supporting electrolyte used was tetra propyl ammonium bromide (TPAB-0.01 M) in acetonitrile (4:1). More than 90% of the TiO2 groups were stabilized by TPAB after applying current density. The process of electrolysis was done in a nitrogen atmosphere. The color of TiO2 NPs was discovered to be white. Due to the material's intractable nature in the used solvent mixture, the workup was ultimately reduced to simple decantation. The decanted solid product was then washed with dry tetrahydrofuran 3 to 4 times to remove any excess TPAB before being dried under vacuum desiccators. To preserve this dried sample, it was calcined at 550 °C and placed in sealed glass vials at room temperature [53].

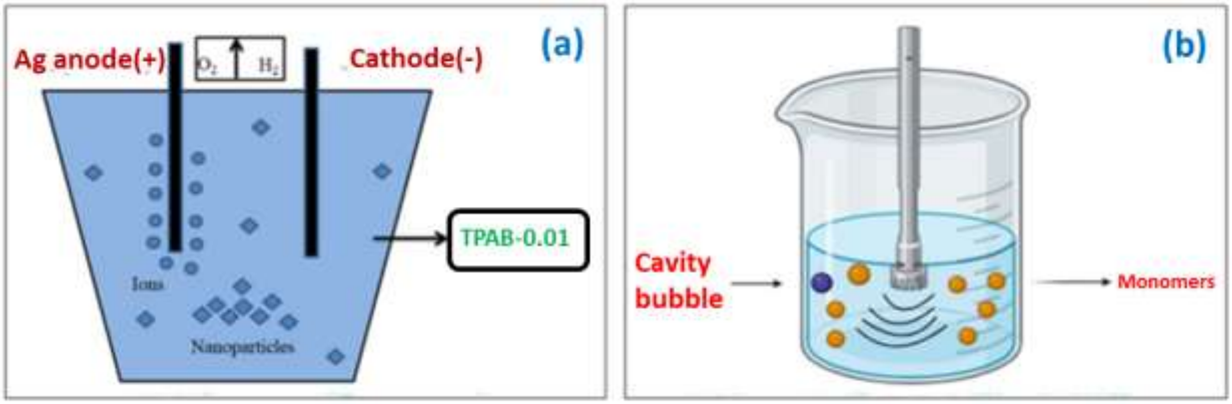


Figure 5(a): Electrochemical synthesis of silver nanoparticles b sonochemical method of synthesis of nanoparticle using probe sonication

Sol–gel

Low temperatures (often less than 100 °C) and the liquid condition are used to execute the sol–gel process. The ultimate product is solid, of course, and these solids are produced by the polymerization process, which entails creating metal-hydroxyl-metal or metal-oxide-metal between the metal atoms in the raw materials. Using the sol–gel method, there are two processes involved in the synthesis of aerogels [54]. The first stage entails the production of distinct, colloidal solid particles of nanoscale size. A gel is formed in the second stage as a result of colloidal particles in the solvent combining with them as shown in Figure 6. Due to its simplicity and speed, the sol–gel method is frequently employed to design nanoparticles. This strategy is well-liked because it guarantees accurate control over nanoparticle size. The procedure was changed to produce nanoparticles with sizes ranging from 10 to 40 nm. Jayaprakash et al. employed a sol–gel approach to produce copper oxide (CuO) NPs with sizes of 25 nm. The physical characteristics of CuO NPs are modified using the sol–gel technique and the calcination times.Furthermore, when creating functional nanoparticles via the sol–gel technique, physical limits are essential since the size of nanoparticles in this procedure correlates with temperature. As an illustration, Jayaprakash et al. created uncapped and capped CuO NPs using the sol–gel method and ethylene diamine tetraacetic acid (EDTA). To measure the size of CuO NPs, a blocking agent was applied. CuO NP can be synthesized in the presence of copper acetate and urea. Researchers believe that this approach could allow for precise control of the morphology and shape of nanoparticles [55].

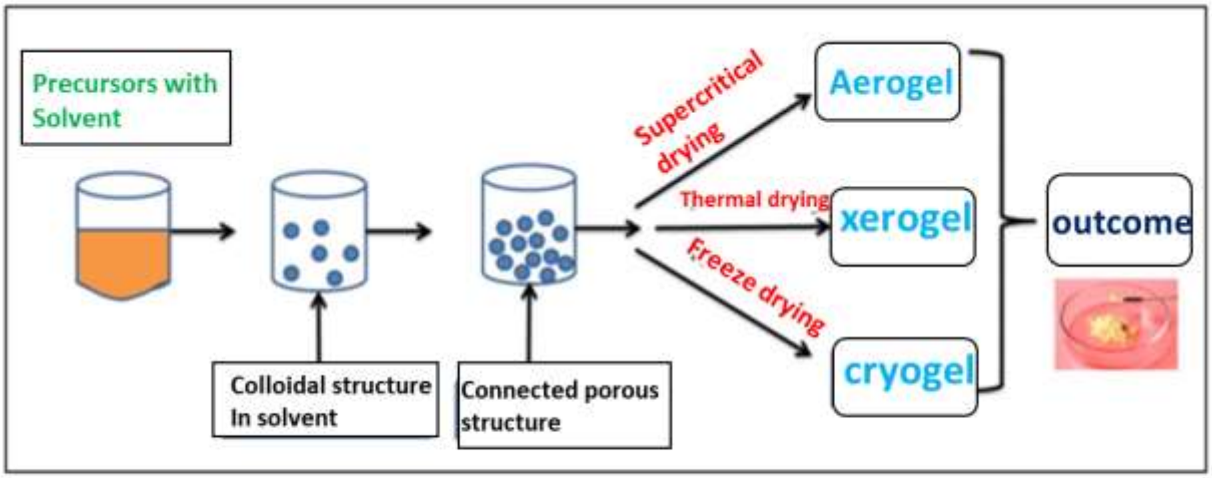


Figure 6: Method of synthesis of nanoparticles using the Sol–gel method [56].

Factors Affecting NPs Synthesis

Adjustment of shape and size of metal NPs further enhances their functionality for various applications. The morphological parameters of NPs can be manipulated by changing various experimental parameters such as reaction time, reactant concentration, pH, temperature, aeration, salt concentration, etc. [57]. Precise control of these parameters can play a critical role during the optimization of metal NPs synthesis via the biological route. The size and shape of NPs can be controlled by varying the pH of the medium, while the acid pH leads to the formation of large-sized NPs [58]. During synthesis of Au NPs using oat (Avena sativa) biomass, Armendariz et al. observed smaller sized gold NPs at pH 3.0 and 4.0 in comparison to the synthesized NPs at pH 2.0. This is due to the better accessibility of functional groups present in the extract for nucleation at higher pH compared to the presence of fewer groups at a lower pH range. In addition to pH, the concentration of biomolecules in the extract also affects the size and shape of synthesized NPs. Increase in the concentrations of Aloe vera leaf extract resulted in the synthesis of higher amount of spherical gold NPs instead of triangular which is due to the presence of carbonyl compounds in the extract. In addition, the size of the NPs was modulated in the range of 50 to 350 nm by varying the extract concentration in the solution. The duration of reaction also plays a crucial role in the reduction of NPs and their size, which is primarily Catalysts 2021, 11, 902 10 of 35 confirmed by rapid change in color of the reaction mixture. This duration can range from few minutes to few days. A change in particle size of silver NPs was observed in the range of 10–35 nm by increasing the reaction time from 30 min to 4 h using Azadirachta indica leaf extract. Furthermore, the reaction temperature is one of the important parameters in the biological synthesis of NPs which also determines the shape, size, and yield of NPs. The average size of silver NPs decreased from 35 to 10 nm with the increase in reaction temperature from 25 to 60 ◦C using Citrus sinensis (sweet orange) peel extract [59].

Applications:

Carbon Nanoparticles in Electrochemistry:

Carbon in its various modifications plays an important role in almost any kind of electrochemical storage device [60].The good electrical and thermal conductivity, low density, sufficient corrosion resistance, and the relative low activity for electrochemical oxidation or reduction makes carbon an interesting material for passive as well as electroactive components in electrochemical devices. In addition, carbon materials can be produced in a variety of modifications such as powders, fibers, and solid or porous sheets [61].Moreover, the cost and availability of carbon is highly advantageous. Consequently, carbon is used in batteries, low-temperature fuel cells, electrochemical capacitors as well as in electrochemical synthesis and electro analysis. Carbon is used as the support for noble metals and other electro catalysts in electrodes for batteries and fuel cells. The diffusion layer in gas-consuming electrodes for metal–air batteries or fuel cells is made from carbon in the form of powder, cloth, or paper Microstructure bipolar plates were also made from glassy carbon to investigate catalyst utilization in fuel cells. Carbon, typically in the form of graphite powders or graphite fibers, is often used as conductive additive in electrodes for electrochemical devices, such as Leclanch-type cells, to improve MnO_2 cathode performance. The extensive surface area available with carbon electrodes, and the double-layer capacitance of such electrodes, are utilized in commercial electrochemical capacitors. For the above-mentioned applications carbon powders are utilized with particle sizes typically in the micrometer regime. Carbon nanoparticles or nanotubes, however, have not yet found their way into industrial electrochemical energy storage and conversion devices in a major way. On the research level, however, the potential use of carbon nanoparticles or carbon nanotubes in electrochemical devices is being investigated with increasing effort. In particular, the template technique has gained increasing attention in recent years for the preparation of well-defined nanomaterials for electrochemistry [62].

Nanotechnology in dairy industry

Nanotechnology is also making its presence felt in the dairy industry with Industrial Nanotech launching their company's Nansulate protective coating to provide thermal insulation and corrosion protection of dairy processing equipment's. The company uses an insulating oxide material which they claim to be the world's worst conducting material of thermal energy. Thermal conduction through the material is hindered by the tiny area of contact between the tiny particles making up the conduction path that are linked in a three-dimensional network. Thermal energy transfers through the solid occurs through a very complicated maze and is not very effective. Air and gas in the material can inherently also transport thermal energy, but the gas molecules within the matrix experience what is known as the Knudsen effect (increase in the collision between gas molecules and the pore wall when the pore size is reduced) and the exchange of energy is virtually eliminated. Thermal conduction is limited because the conducting paths are comparable to the mean-free path for molecular collisions and molecules collide with the solid network as frequently as they collide with each other. Radiative conduction is also low due to small mass fractions and large surface areas [63].

Particles as chemically inert additives:

Small, chemically inert particles have been prominently used in pigments, polymer fillers and surface finishing next to bulk applications such as ceramics. None of them were traditionally called ‘‘nano’’, and most scientist are little aware of the rather broad, established use of small particles. Historically most interesting is the use of various carbon soot pigments in cave and pottery paintings and carefully reduced iron oxide colloids as red and yellow pigments.

2D particles as polymer fillers

Apart from the modification of the mechanical, electrical, surface or optical properties, polymer fillers are also broadly used for altering the permeability of polymer films. This is usually achieved by dispersing plate-like fillers in a polymer matrix; ideally the platelets are aligned with the plane of the polymer film. The crystalline and thus impermeable 2D particles allow reducing the permeability of a film by orders of magnitude compared to the polymer alone. Often applied flakes include nanoclays, graphite, mica or vermiculite [64].

Effect pigments, dyes and UV protection.

More recent advances in aerosol synthesis permitted the low cost manufacturing of Nano particulate titania and zinc oxide. In pigments, the high-refractive index titania permits strong optical effects and high color depth. After recognizing the estrogen-like activity of numerous organic sunscreen additives, inorganic UV absorbing pigments based on titania and zinc oxide were introduced at large scale to the cosmetics industry, in polymers, consumer goods and surface treatments. There, nanoparticles were advantageous since below about 50 nm, visible light scattering becomes negligible, and corresponding UV protection can be realized with a visually (human eye) nearly transparent additive (Figure 7)

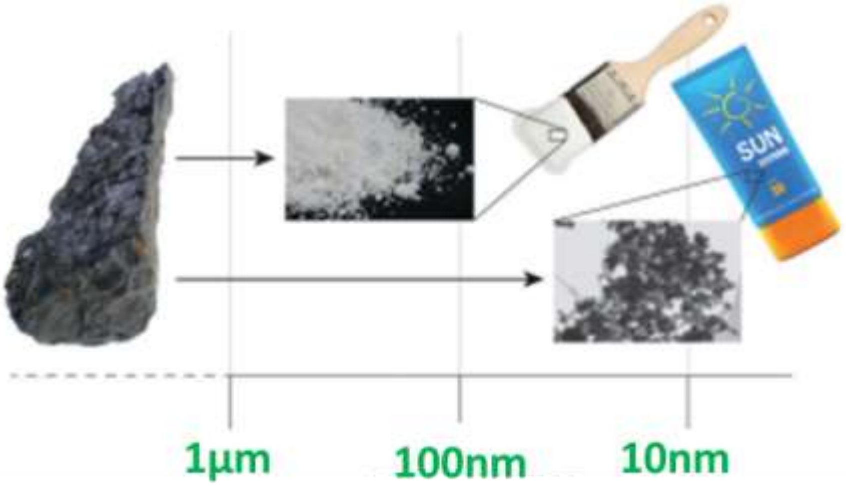


Figure 7: Classical submicron sized TiO2 pigments (B0.2 mm) as e.g. used in paints and as opacifiers in various applications are prepared from illmenite (a titania ore) using chemical processes (dry or wet). Further reducing the particle size to nano-sized particles (o50 nm) recently allowed increasing light absorbance in the

UV region whilst reducing (undesired) skin whitening in high-quality sunscreen. Chem Soc Rev Tutorial Review Published on 11 February 2015. Downloaded by FORDHAM UNIVERSITY on 17/02/2015 17:19:39 [65].

Wastewater Treatment Process

The increase in population growth rate, industrialization, and excessive use of chemicals has contaminated the aquatic environment by releasing wastewater to the environment. The water from natural resources is not suitable for consumption due to the presence of organic (dyes, pesticides, surfactants, etc.), inorganic (fluoride, arsenic, copper, mercury, etc.), biological (algae, bacteria, viruses, etc.), and radiological contaminants (cesium, plutonium, uranium, etc.) [66]. Figure 8 depicts some of the common contaminants found in water. Several techniques such as physical, chemical, and biological have been adopted for the treatment of wastewater. However, search for new efficient technologies to improve water purification at low-cost is the current research focus. Currently, nanotechnology provides a new strategy for the removal of contaminants from wastewater with high efficiency. Several approaches have been developed in combination with various NPs for the successful removal of contaminants from wastewater.

The adsorption process is defined as the attachment of gaseous or liquid molecules over the surface of the solid and forms a layer or film of molecules. This process is mainly limited to the surface of the adsorbent where the adsorbate accumulates. The adsorption process could be physisorption or chemisorption depending upon the nature of bonding between the adsorbate and adsorbent i.e., van der Waals forces, covalent bonding, or electrostatic attraction. Adsorption is the most commonly used technique for the removal of contaminants from water due to its low-cost, easy operation, and absence of secondary pollutants formation. Due to the development of nanotechnology and its wide applications in the past few decades, several nanostructured materials have been explored as adsorbent for their potential application in the treatment of industrial effluents, surface water, groundwater, and drinking water [67]. Nanoadsorbents exhibit higher efficiency and faster adsorption rate compared to the conventional adsorbent due to their small size, high porosity, and large active surface area. Additionally, these nanoadsorbents show high reactivity and catalytic efficiency. Nanomaterials such as carbon nanotubes (CNTs), ferric oxide (Fe_3O_4), graphene, titanium oxide (TiO_2), manganese oxide (MnO_2), zinc oxide (ZnO), and magnesium oxide (MgO) are successfully used as adsorbent for the removal of contaminants such as heavy metals, azo dyes, etc. from the water [68]. Several nanosized metal oxide adsorbents including ferric oxide, aluminum oxides, manganese oxides, titanium oxides, magnesium oxides, and cerium oxides are proved to be promising for the removal of pollutants from water. Furthermore, different metal oxide NPs are superparamagnetic which allows the easy separation of these adsorbents from the reaction mixture with the application of an external magnetic field. Das et al.[69] reported the removal of methylene blue dye, Cu(II), and Catalysts 2021, 11, 902 18 of 35 Co(II) from aqueous solution using green synthesized magnetite NPs from crude latex of Jatropha curcas and leaf extract of Cinnamomum tamala. The removal of Cd(II) from contaminated solution was studied by using silver NPs prepared using leaf extract of Ficus tree (Ficus Benjamina) [70]. In a similar type of study, the removal of cadmium ions from contaminated solution was carried out using iron oxide NPs prepared by co-precipitation method with tangerine peel extract. Maximum removal efficiency 90% achieved at pH 4.0 and adsorbent dose of 0.4 g/100 mL. Zinc oxide NPs synthesized from Aloe vera and Cassava starch used as copper ion adsorbent and higher removal efficiency was observed for Aloe vera synthesized NPs with the increase in adsorbate concentration. These Nano adsorbents demonstrate remarkable efficiency in the removal of pollutants from wastewater; however, the toxicity of residual NPs in the wastewater and reduced potential activity due to the use of a huge number of NPs in the treatment process to minimize the process duration are the major shortcomings of this process [71].

Filtration of contaminated water or wastewater through membranes is another way to remove the pollutants from the water. Nanofiltration is efficient and effective for the removal of different types of contaminants (organic, heavy metals, pathogens, etc.) from wastewater, and the removal efficiency is mainly dependent upon the pore size and charge characteristics of the membrane. Numerous studies have focused on the development and use of a composite membrane, prepared by the introduction of NPs into the polymeric or inorganic membranes for the treatment of water. The incorporation of metal oxide NPs like silica, alumina, zeolite, and TiO_2 [72] into polymeric membrane improved the membrane hydrophobicity and permeability. In addition to this, the incorporation of antimicrobial NPs like silver NPs into membrane matrix hinders bacterial attachment and biofilm formation. Metal NPs are extensively used as nano-catalysts in water treatment due to their high surface-to-volume ratio and surface catalytic activity. These nano-catalysts improve the quality of water by degrading various contaminants, viz. dyes, pesticides, herbicides, polychlorinated biphenyls, nitro aromatics, etc. Various kinds of nano-catalysts such as electrocatalysts, photocatalysts, and Fenton-based catalysts are employed in the waste water treatment process. The mechanism behind photocatalysis is the photoexcitation of electron present in the catalysts. The light irradiation causes the generation of holes (H^+) and exited electrons (e^-). Further, the generated holes (H^+) are trapped by water molecules (H_2O) in aqueous media that subsequently form the hydroxyl radicals (•OH). These hydroxyl radicals are highly reactive and powerful oxidizing agents which oxidize the organic pollutants leading to the formation of water and gaseous degradation products. Numerous studies reported photocatalytic activity of green synthesized Ag, Au, Pt, and Pd NPs in degradation of different dyes [73]. Additionally, various metal oxide NPs such as ZnO, CuO, FeO, SnO2, TiO_2, NiO, CeO_2, etc. exhibited excellent photocatalytic activity for the degradation of different organic pollutants [74].

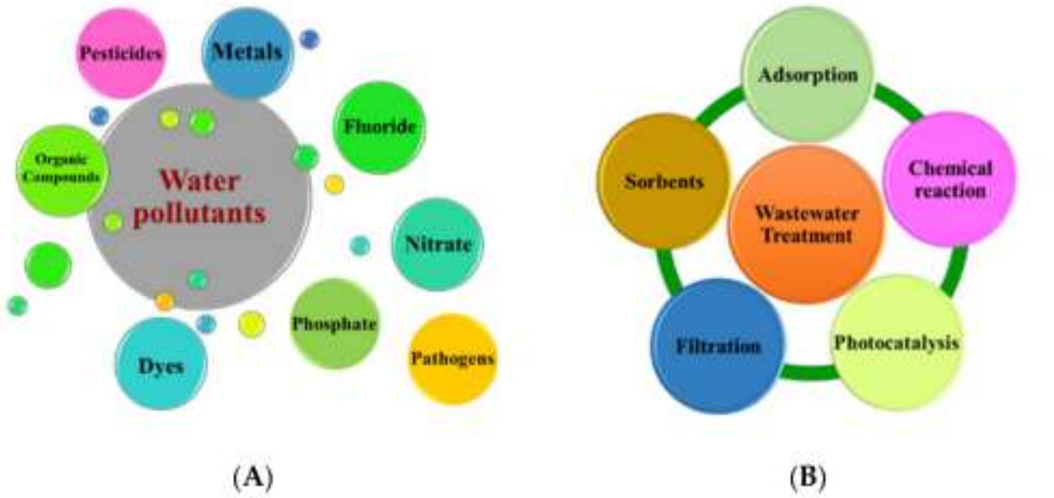


Figure 8: Common pollutants found in water and the treatment processes. (A) Common pollutants present in water. (B) Treatment approaches used for wastewater using nanoparticles[75].

Conclusion:

Metal nanoparticles have revolutionized the field of catalysis, offering unparalleled efficiency and versatility in facilitating chemical reactions. Their unique properties, such as a high surface-area-to-volume ratio, quantum size effects, and tunable surface chemistry, make them ideal candidates for a wide range of catalytic applications. This review highlights the underlying mechanisms of their catalytic activity and demonstrates their broad applicability in areas like organic synthesis, environmental remediation, and industrial processes. Despite their remarkable potential, challenges such as nanoparticle stability, aggregation, and recyclability remain significant barriers to their widespread adoption. Advancements in synthesis techniques, surface modification, and integration into hybrid systems provide promising solutions to overcome these limitations, ensuring enhanced performance and sustainability. Moving forward, a multidisciplinary approach combining nanotechnology, material science, and green chemistry will be crucial for unlocking the full potential of metal nanoparticles in catalysis. By addressing current challenges, metal nanoparticles can contribute significantly to developing sustainable and efficient catalytic processes, thereby advancing both scientific innovation and industrial applications.

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