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Bimetallic Nanoparticles with Specific Insight into Nanoremediation

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Abstract

Nowadays, nanotechnology and all its products are earning importance in various fields because of their invaluable properties. Nanomaterials are those types of engineered agents that have at least one dimension in 1-100 nm. Nanoparticles (NPs) are a type of nanomaterials which many other products have been generated based on their extraordinary effects. Bimetallic NPs are a class of NPs that are composed of two distinct metals. Depending on the applied metals, size and atomic arrangements, bimetallic NPs offer synergistic or novel features in comparison to their corresponding monometallic NPs. There are three main types of bimetallic configurations (Intermetallic, Hetero-structure and Core-shell) which are influenced by miscibility, preparation conditions, and the kinetics of change of metal precursors. Versatile characterization techniques have tried to disclose internal and external physic-chemical properties of the bimetallic NPs such as different electron microscopy, spectroscopy and diffraction instruments. Achieving precise information about the chemical and structural of these NPs is so significant for finding proper use in industrial sections. However, these multifunctional chemicals have extended their applications because of the outstanding and excellent properties such as optical, magnetic, catalytic, biological features. Since the emergence of nanotechnology, nanomaterials especially monometallic NPs have carried out significant tasks in the eradication of organic and inorganic pollutants in air, soil and aqueous media, but bimetallic NPs overtook the properties of monometallic NPs in the case of heavy metals removal, breaking dyes, pesticides and antibiotics. Thus, the highlighted catalytic properties of the bimetallic NPs in the degradation of pollutants made them as a promising recyclable agent in nano-remediation.

Introduction

In recent years, nanotechnology has introduced itself as a main edge innovation that is expanding its boundaries in both environmental and health applications. This particular part of science is concerned with the manipulation of the materials at the atomic or molecular stage to produce the materials with extraordinary properties and structures. These materials have been exploited in numerous fields such as drug delivery, solar cells, water purification, cancer therapy, food packaging and so forth [1]. The outcome of the nanotechnology; nanomaterials turned the worldwide consideration toward themselves due to their customizable physical, chemical, and biological features offering improved properties in comparison to their corresponding bulk materials. These substances are confided to 1-100 nm dimension internally or externally [2]. Nanomaterials based on their dimensions are categorized into four groups including 0D, 1D, 2D and, 3D [3]. 0D or zero-dimensional nanomaterials do not have any dimension larger than 100 nm like Nanoparticles (NPs), quantum dots, etc. 1D nanomaterials consist of one dimension larger than 100 nm, for example, nanofibers and nanowires can fit in this group. 2D nanomaterials include nanofilms, nanoplates and, monolayers which have two dimensions larger than 100 nm. 3D nanomaterials are nanophase materials which are constituted from the other types of nano-objects like a bundle of nanofibers or dendrimers [4].

NPs are divided into two main groups: organic and inorganic NPs. Micelles and liposomes belong to the first group, while fullerenes, quantum dots, silica, and all metallic NPs like gold NPs belong to the second group [5].

Based on the numbers of the metals applied in the structure of the NPs, two sorts of NPs are generated: monometallic and bimetallic NPs. Monometallic NPs are comprised of only one distinct metal in their composition. Their structure can be stabilized by using various functional groups. They have earned much of interest recently due to their exceptional physical, chemical, and biological properties that are open their ways to electronics, microbiology, optics and catalysis [6]. Gold, silver and copper NPs uncover a remarkable plasmon resonance in which a clear absorbance peak appears in the visible region suggesting these materials as a promising sensing agent. Also, the metallic NPs can be exploited in catalytic processes for example, Ag NP is applied in hydration of nitriles and Pd NP roles as a catalyst in Suzuk-Miyaura coupling in water [7]. To overcome the restricted properties of monometallic NPs, bimetallic NPs were synthesized with the combination of two distinct metals in their structure. These types of NPs disclose intriguing properties such as increased optical, electronic, magnetic and, catalytic properties in contrast with their monometallic partners, a fact that is brought about by synergistic highlights of two metals [8]. Simultaneously, two distinct properties can be added to a multifunctional bimetallic NP by blending two metals in with various properties like Au-Fe bimetallic NP [9]. Engineering of the features and the activity of a bimetallic NP is completely pertinent to the choice of suitable metallic combination and the optimization of the metallic arrangement [8] which are attributed to the electronic coupling between two different metals and geometric impacts created by discrete lattice constants [10]. On the other hand, by blending two metals, you can master over the manipulation of the size and morphology of the bimetallic NPs that determine their functionality [11].

Classification of Bimetallic NPs

Up to now, numerous classification patterns have been proposed to suggest a framework to cover all possible configurations, but the best way is to categorize them according to their atomic ordering (**Figure 1**) which gives rise to three models as follows:

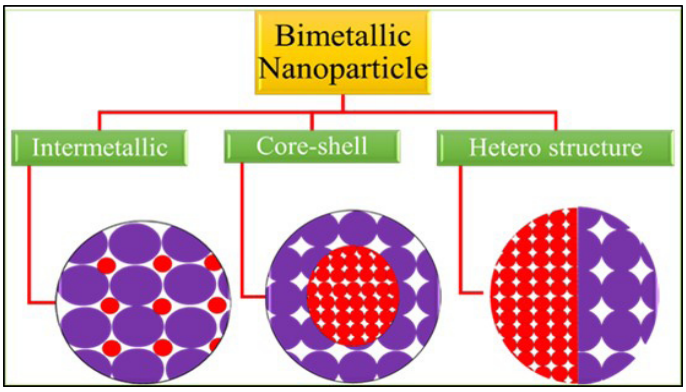

Figure 1: The schematic view of bimetallic NPs on atomic ordering.

A) Intermetallic NPs: Two atoms (A and B) with similar or different atomic radius and lattice structure join together and according to the proportion of differences, an alloy or a solid solution scheme appear. When these factors are relatively equal in both metals, once metal A incorporates in the lattice structure of the second metal B largely, creates alloy pattern in which the atoms find long-range atomic ordering, leading to a homogenous and mixed-phase composite like $Pd_{0.5}Cu_{0.5}$. On the other hand, if the mentioned determining factors are unlike each other, metal A finds its way among the atoms of metal B lattice structure and delivers a structure called solid solution [12].

B) Core-shell nanoparticles: The structure of these types of NPs is shaped of one metal that roles as the core metal and the second metal which covers the core metal. Depending on the number of shells and cores incorporated in the structure of these NPs, versatile configurations appear. When only one atomic layer covers the individual metallic core, one layer core-shell nanoparticle is produced, but it is even possible to enhance the number of atomic layers on the core material, leading to the generation of multi-atomic layer core-shell NPs. If the core part of the NPs is removed by calcination or dissolution, the shell remains that exhibits a different class of NPs like nanocages, nanoframes, nanoboxes and, moveable core shells [13]. When one metal engulfs several core metals, a multi-core shell NP forms. Sometimes deformed cores are trapped within an irregular shell that results in the fabrication of an irregular core-shell NP.

C) Heterostructure NPs: This type of NP belongs to a group of bimetallic NPs that two different metals share an interface at two, three, or more points. There are two versions of these NPs: dendrimer NPs and sub-cluster NPs. The shared interface in dendrimer NPs like highly branched, multi-pod, star, pentacle and sea urchin like flower is smaller than in the case of sub cluster NPs. The dimer and dumbbell NPs are comprised of two metals with a single shared interface. Janus NPs are relatively significant among the other bimetallic configurations because they offer unique asymmetry. Two types of Janus NPs are fabricated. One type has an individual diagonal interface between two metals while the second metal only covers the surface of the core particle partially in the other type. The route for compartmentalization of two metals determines which one of two possible configurations of Janus NPs can be shaped [14]. In other forms of sub-cluster group, the common metallic interfaces increase to more than one, leading to the production of regular and irregular mosaic shapes (**Figure 2**).

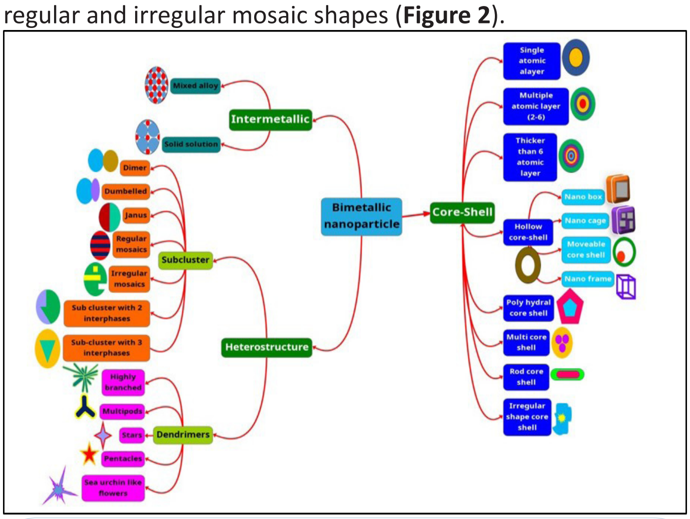

Figure 2: The classification of bimetallic nanoparticles.

Synthesis of Bimetallic NPs

The general layout for the synthesis of NPs is categorized as Top-Down and Bottom-Up approaches. In the Top-Down approach, the bulk material is trimmed into fine particles with nanometer dimensions whereas, in the Bottom-Up approach, every single metallic atom of the precursors links together that produce metal clusters and make a particle in nanometer scale. On the other hand, there are chemical, physical, and biological methods to fabricate NPs with different shapes, structures and, morphologies [15]. The conventional disciplines for the synthesis of monometallic NPs can be partially assigned to the production of bimetallic NPs. Scientists believe that the final configuration and atomic ordering of two metals are tightly dependent on the preparation conditions, miscibility and, the kinetics of change of metal precursors [16].

Ferrando & et al (2008) suggested five influential factors indicating the degree of segregation/atomic orders in bimetallic NPs:

1) The strength of A-A, B-B and, A-B bonds. If A-B is stronger than A-A or B-B, the production of a mixed alloy is preferred, but if the A-A or B-B are stronger, so a homogenous core made up of one metal will form, resembling a core-shell NP.

2) The metals with similar surface energies tend to incorporate into each other equally while when the factor differs drastically, the one with lower surface energy tends to migrate to the surface and a core-shell configuration appears.

3) Small atoms tend to gather in the core portion of a bimetallic NP while if the atomic radius of the metals is equal, alloy or solid solution form.

4) Electron flow from an electropositive metal to an electronegative metal supports the fabrication of an alloy structure.

When two metals have similar lattice parameters like crystal structure and lattice constant), they effort to mix thoroughly [17] (**Table 1**).

Table 1: Physiochemical properties of some metals [18].

Metal	Crystal lattice	Lattic constant (Å)	Surface free energy (Jm^{-2})	Atomic radius (pm)	Electronegativity
Fe	bcc	2.87	0.98, 1.27, 1.80	126	1.83
Co	hcp	a = 2.51, c = 4.07	2.78, 3.04, 3.79	200	1.88
Ni	fcc	3.52	2.01, 2.43, 2.37	163	1.91
Cu	fcc	3.61	1.95, 2.17, 2.24	128	1.95
Ru	hcp	a = 2.71, c = 4.28	3.93, 4.24, 4.86	205	2.2
Rh	fcc	3.80	2.47, 2.80, 2.90	200	2.28
Pd	fcc	3.89	1.92, 2.33, 2.23	163	2.2
Ag	fcc	4.09	1.17, 1.20, 1.24	172	1.93
Ir	fcc	3.84	2.97, 3.72, 3.60	200	2.2
Pt	fcc	3.92	2.30, 2.73, 2.82	175	2.28
Au	fcc	4.08	1.28, 1.63, 1.70	166	2.54

It is well-known that the size and shape of nano-scale materials indicate their properties, thus it is vital to introduce the synthetic routes which can control the condition for the production of NPs with desired features. These factors also give us the idea to separate the nucleation step from the growth process and to control the growth process to reach the fine nanostructures. As previously mentioned, NPs can be produced through chemical, physical and biological methods which can be applied also for the fabrication of bimetallic NPs with some modifications.

Chemical synthesis

The change of two corresponding metal precursors in a solution with a protecting agent to control the NP's growth and sizing is the most frequent and convenient applied method for the synthesis of bimetal NPs. The protecting agent roles in determining the size of bimetallic NPs. The other additional factor is the kinetics of nucleation and growth of the bimetallic NPs. As we all know, the physical and chemical features of the NPs are determined by their size distribution and in the case of the bimetallic NPs, the homogeneity of the composition also matters a lot. This issue can be met by the separation of nucleation from the growth process. The kinetics of this pathway can be controlled by manipulating the experimental conditions such as temperature, pressure, solvent nature, the composition of metallic precursors, reducing and, capping agents [19]. A variety of chemical synthetic routes have been applied to produce bimetallic NPs and even in some cases, elaborated processes have been used.

Co-reduction

Co-reduction is the most prevalent method for the synthesis of alloyed and intermetallic NPs. This process includes the concurrent reduction of two metal precursors to zero-valent atoms which nucleate and generate A-B nanocrystals. Generally, co-reduction can make different bimetallic configurations in which the resulting nanocrystal can be tailored additionally by parameters like reduction potential of the metal ions involved, the strength of reducing agent, the stabilizer and the temperature of the process [18]. For example, $PtCu_3$ alloy NPs were produced in water/oil micro-emulsions with water/cetyltrimethylammonium bromide (CTAB)/isooctane/n-butanol at room temperature. According to the HR-TEM results, the particle size was 1.6 nm and the lattice space of this nanocrystal was 1.87 Å [20].

Thermal decomposition

The process is conducted under high temperature in the presence of two metallic precursors. The precursors decompose into the corresponding metallic ions. Subsequently in the second media with the presence of capping agent and at a lower temperature, the polynuclear cluster begin to generate and lately the growth of these cores leads to the growth of the clusters. The outcome of this process is a narrow particle size distribution (19). The production of Pd-Ir bimetallic NP was carried out by thermal decomposition. According to the analysis, the Ir was located in the core and Pd covered the core as a shell. The size distribution of the corresponding NPs extended from 10 to 50 nm [21].

Seed-mediated growth

In this synthetic pathway, once the core is formed by thermal decomposition, co-reduction, or any other synthetic route, the shell metal covers the whole surface of the core which contributes to the production of a core-shell NP [22]. Han & et al (2020) reported the assembly of AuPt core-shell NPs through seed-mediated pathway. At first, the Au core was prepared by thermal decomposition and subsequently the shell part incorporated over the core by injecting K_2PtC_{l4} into the Au NPs colloid [23].

Galvanic replacement

Galvanic replacement provides a synthetic pathway for the production of hollow bimetallic nanostructures that are mostly unachievable by other conventional pathways. Galvanic replacement is an electrochemical process in which one metal oxides (template) by the atoms of the other metal with a positive reduction potential. Once this phenomenon occurred, the metal atoms detach the electrons from the template, become reduced and subsequently cover the exterior of the template while its interior dissolves into the solution [18]. In a study, Ag nanocubes were applied as a template to react with Pt ions in the presence of HCl. Finally, Pt/Ag hollow nanocubes, dimers, multimers or popcorn shaped nanostructures remained which contained one, two or more hollow chambers [24].

Physical synthesis

Physical Vapour Deposition (PVD) is a thin-coating film process that generates thin layers of monometallic, bimetallic and, ceramic materials with a thickness in the range of 1-100 nm. This process is used for research studies and industrial scales. The fundamentals of this synthetic procedure are similar to the chemical process, but the difference is that the thin layers of NPs form on a surface rather than the bulk solution in chemical routes. Further, the NPs generated by this process is without any stabilizing agent, offering this point that these types of NPs are almost equal to the stimulated and modeled NPs. Along with all suggested advantages, PVD can generate a broad spectrum of bimetallic NPs. Another physical pathways are co-deposition which creates disordered alloy composition and subsequent deposition synthesizes core-shell nanostructures [19,25].

Biosynthesis

Biological pathways sound so fascinating and interesting for the researchers because the processes are environmentally friendly, fast-paced and, economic. During the process, natural sources like plants and microbes can be exploited as a pool of capping and producing agents which can act efficiently [15]. Here are some examples of biosynthesized bimetallic NPs. AL-Haddad & et al (2020) produced Ag-Cu bimetallic NP from the leaves of a date palm tree (*Phoenix dactylifera*). The catalytic activity of this NP was evaluated for degradation of methylene blue dye in an aqueous solution [26]. In another study, Gallic acid rolled as a reducing and stabilizing agent for the production of Se/Ru bimetallic NPs. This NP could halt the proliferation of HeLa cells by triggering the apoptosis at a concentration which is safe for normal human cells [27].

Characterization of bimetallic nanoparticles

Mass spectrometry

It is an analytical technique for studying the mass abundance of the clusters in the structure of bimetallic NPs. The peaks of this analysis which are called “magic numbers” can be associated with the most stable and frequent clusters in the sample regarding thermodynamic or kinetic stability [25].

Diffraction

As you know, XRD is an essential analysis in nanotechnology and material science to determine the structure, crystallinity, lattice spacing, crystal size and, chemical composition of the NPs. It is a tool for the diagnosis of bimetallic structures and can distinguish their differences. The intermetallic NPs share a similar crystal structure and space group of their corresponding bulk metals, but a shift appears in XRD peaks relative to the size of the substituted atom. A core-shell NP reveals completely different XRD patterns with additional peaks which can be because of superlattice structure [12].

Electron microscopy

The first objective of TEM analysis is to give information about the size, morphology and, aggregation state. It is the aim of many other analytical tools to give information about the homogeneity of the produced NPs because it dramatically affects the physical and chemical properties of the NPs. However, TEM is an indispensable instrument for the analysis of metallic NPs. When heavy metals like gold and silver are mounted on the grid of TEM and covered by a thin layer of gold, a high level of resolution and contrast are generated. By equipping the previous instruments with a high voltage electron beam technique, the resolution even increased more to the angstrom range. High-Resolution TEM (HRTEM) not only provides information about the size and morphology of the NPs, but also it gives us crystallographic information about the NPs. One of the best techniques provided by HRTEM is the marginal measurement which unveils information about the area composed of a crystalline metallic NP. In addition, in-situ TEM observation can be taken to analyze the particle growth directly. If Energy Dispersive X-ray Microanalysis (EDX) is incorporated into the HRTEM, elemental analysis can be carried out from all parts of the sample [28]. Scanning Transmission Electron Microscope (STEM) is an instrument in which the electron beam sweeps across the sample. This method can be aligned with HAADF or Z-contrast (two imaging modes) to receive chemical and structural information from the internal structure of the sample. This instrument is so useful for studying the bimetallic NPs with the metals with similar lattice spacing, so the metallic territories can be distinguished easily [29].

When primary electron beams bombard the surface of the sample which is covered by a thin layer of gold coating, secondary electrons emit from the surface of the sample and the detector absorbs all the emitted electrons and presents a 3D picture of the surface with more accuracy [17]. The information retrieved from this analysis can help us with understanding about the size of a nanoparticle, morphology, and the distribution of the NPs. Contrary to the micrographs of TEM, it is too hard to recognize the margins of a core inside a core-shell structure [30], but recently Field Emission Scanning Electron Microscopy (FE-SEM) gives more details about the core-shell NPs due to its high magnification, for example, it determines whether the shell surface is smooth or rough [13].

Scanning probe Microscopy

These groups of microscopes are so versatile regarding their applications. Two major instruments of this category are Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM). These microscopes provide precise and detailed records from the surface of a sample. Analyzing the strength of the interaction between the tip of the microscope with the sample surface extract some information about the topology, electronic-magnetic structure and chemical composition of the surface [25,31].

X-ray Spectroscopy

X-ray radiation is specifically so helpful for the analysis of metallic NPs because it assists the researchers to distinguish metals close to each other in the periodic table. X-ray Absorption Spectroscopy (XAS) is employed for investigating the interior parts of the metallic NPs and any functional groups mounted on them. Since each atoms' X-ray absorption pattern is different so that it can be utilized to pinpoint the presence of each type of element promptly. Also, local atomic atmosphere, geometry, electron density, oxidation state, electronic configuration, coordination number and interatomic distances can be measured. Extended X-ray Absorption Fine Structure (EXAFS) is another newborn equipment which can be implemented to discover atomic number, atomic distance and coordination number [32]. The most significant invented instrument based on X-ray radiation is X-ray Photoelectron Spectroscopy (XPS) that is completely based on photoelectric energy. The energy of the incident X-ray energy is enough to overtake the binding energy of the valence and core electrons. The energy of the core electron is like a fingerprint for each element. At the same time, the peak area can be applied to determine the composition. The pattern of peak and the binding energy are sensitive to the oxidation and chemical state of the emitting atom, thus it can give us information about the chemical bonds [33].

UV-Visible spectroscopy

It has been proved that optical properties are influenced extremely by the surface modifications of a nanoparticle, so it can present precise information about the coating materials covering the core metals in the case of a core-shell NP. Further, the UV-Visible band faces shifts with different chemical compositions and the atomic ordering in bimetallic NPs. Any shift in this spectrum can be due to the change of precursors into the bimetallic NPs and their aggregation state, so this technique is applied for early diagnosis of NP's production. The NPs with energy adsorption capacity in the UV-Visible region can reveal an absorbance band in this region. In the case of a core-shell NP, the spectrum of the corresponding monometallic NPs should be compared with that of the bimetallic NP [13,25].

Energy-Disperse X-ray Microanalysis (EDX, EDS)

In this analysis, a beam of electrons attack the surface of one type of conducting material, subsequently X-ray beam gets emitted. The scanning electron beam moves across the sample and an elemental map generates. EDX is a high-resolution microscopy instrument that presents significant information about the chemical composition of the NPs [18].

Infrared (IR) Spectroscopy

This technique is widely applied to detect the vibrational spectra of small molecules attached to the surface of the NPs. These molecules usually are generated from the compounds which work as stabilizing or reducing agents in the reaction solution [35].

Properties of Bimetallic Nanoparticles

As previously described, incorporation of two different metals gives rise to brilliant electronic, magnetic, chemical, biological, mechanical, and thermal effects which are not achievable by monometallic NPs. The choice of the metals determines the final properties of a bimetallic NPs whether they are synergistic or a new feature will be revealed [1].

Catalysis

Catalysis is the most significant application of the metallic NPs. The catalytic performance (activity, selectivity and, durability), the catalytic nature, the composition, size, shape, and the structure of the NPs have been investigated for a long time. Among all metals, transition metals like Ag, Au and, Cu atoms exhibit high catalytic potentials for numerous inorganic reactions. Also, based on different studies, the size and facet of a nanocrystal play a brilliant role in the activity of a nanocatalyst. When a second metal is added to a nanocatalyst with a highlighted function, the catalytic performance enhances. Many of these NPs have been studied as an immobilized agent on a surface to serve as a multi-functional catalyst [28]. Generally, these supported bimetallic NPs, have confirmed their potential in catalytic oxidation of dyes, glucose, CO, benzyl alcohol, crotyl alcohol, methanol and, etc [16]. For example, Pd-Ni bimetallic NP encapsulated in MIL-100 (Fe) (Pd-Ni@MIL-100 (Fe) was produced to work as a remarkable catalyst for the reversible dehydrogenation/hydrogenation of N-Heterocycles in water under mild atmosphere [35]. In another work carried out by Zhu & et al (2012), the catalytic performance of PdPt and PdAu alloy nanowires were evaluated for electro-oxidation of methanol. They examined various compositions of these NPs and reported $Pd_{45}Pt_{55}$ is the best catalyst for methanol oxidation [36].

Optical properties

Noble metallic NPs have attracted attention toward themselves due to their deep colors. The fascinating optical properties of these NPs originate from an intense reaction between the valence electrons in the NP and the incident light. This optical behavior is coined as Localized Surface Plasmon Resonance (LSPR) and this peak is located in the visible part of the electromagnetic spectrum for Cu, Ag and Au while for the Ultra Violet part is marked for the spectrum of Ru, Rh, Pd and Pt. A vast and versatile functions have been introduced based on this theory like photo-catalysis, artificial photosynthesis, solar cells, biomedicine, and photo-thermal therapy and sensing. Studies have displayed that the position of LSPR and the LSPR profile of a nanoparticle is tightly dependent on the size, shape, composition, electron density on the surface of that NP and the dielectric constant of the ambiance. The combination of a plasmonic NP like Ag NP with a magnetic NP leads to the introduction of a phenomenon which is called ferroplasmon that can be used for data storing systems and optical materials. A group of scientists presented that plasmonic behavior intensifies in the vicinity of the ferromagnetic part of the Ag/Co dimer NP. They discovered this unique event can lead to many advantageous applications [37,38].

Photo-catalytic properties

The rise for hybridizing plasmonic nanocrystals (e.g, Ag. Au or Cu) with catalytic nanocrytals (e.g., Pt or Pd) is remarkable. In these nanohybrids, the rate of catalytic reaction is enhanced by the incidence of light. Scientists have found that the electron flow needed for a catalytic reaction can be provided readily by a plasmonic metal like Ag [18]. For example, Pt-Cu alloy is readily activated by photons and functions as a promising catalyst in the conversion of aerobic oxidation of alcohols at room temperature [39]. Additionally, TiO_2 which is nowadays a hot topic and related to the semiconductors and photocatalysis can be doped or alloyed with plasmonic metals to improve its optical properties in the visible region of the light. Cu/Ag-TiO_2 revealed the highest efficacy for oxidizing 2-propanol under UV-Visible light in comparison to the corresponding monometallic NPs [40].

Magnetic properties

Highlighted ranges of applications have been reported from bimetallic magnetic NPs including biomedicine and Ultra high-density information storage. Monometallic systems like Co, Ni and Fe are the ferromagnetic agents. Their intermetallic and alloy configurations such as CoNi, FePt and $CoPt_3$ beside core-shell structures such as $MnFe_2O_4$@$CoFe_2O_4$ [41] suggest them as excellent data storing systems. Based on the literature, a magnetic nanocrystal can function as a single magnetic domain when its domain decreases to a critical size. This limit is strictly dependent on the crystal size and composition. When a ferromagnetic nanocrystal's size is reduced more, it finally reaches a limit assigned as the superparamagnetic domain [18]. Takahashi & et al (2015) worked on the production of Ag/Fe-Co/Ag core doubled-shell magnetic-plasmonic NPs which can be used as a magnetic agent for filtering out and separating the subcellular components [42].

Biological properties of bimetallic nanoparticles

Numerous scientific works have been conducted to study the biological properties of a nanoparticle. Silver NP has presented excellent cytotoxic effects toward a bacterial cell which has introduced it as a suitable agent for antimicrobial coatings and sheets. Other NPs have exhibited a lower level of cytotoxicity which being hybridized with the silver NP can tune the cytotoxic effect of these Ag-based bimetallic NPs. Because of outstanding antibacterial activities, these types of NPs are applied in biomedical applications. However, the underlying mechanism of the antibacterial effect caused by silver NP is still unclear. If a bimetallic NP is going to be applied in biomedical application, its physical and chemical properties such as size average, particle size distribution, surface properties like charge and surface functionalization should be elucidated. Further, the elemental composition and distribution of the NP should be examined along with other significant factors affecting the biological properties [11,43]. Besides to the application in biomedicine, these NPs can be exploited in cell imaging like Ag-Cu NP that exhibits applications in imaging because of the incorporation of two plasmon metals [44]. Another example of these vast applications is sensing and working as a biomarker for early diagnosis of the diseases. Yin & et al developed a colorimetric sensor based on Au@Ag for precise detection of disease biomarkers [45].

Nano-remediation

As previously mentioned, the advancement in nanotechnology has contributed to significant progress in subjects like environment, medicine, agriculture, industry and etc. The role of nanotechnology in environmental science can be put into three domains as following: Source reduction or pollution prevention, remediation or, degradation of the pollutants and sense of the pollutants [46]. The application of nanomaterials especially NPs for the elimination of the pollutants is a hot topic nowadays, which contributes to the introduction of a new science called: Nano-remediation. This field of science attempts to remove the pollutants from water, air, soil, sewage [47]. Unfortunately, the traditional routes of remediation do not meet our needs in this case, for example, the discharge of pollutants into landfills is expensive and time-consuming to reach our set expectations. Meanwhile, they are associated with the generation of toxic by-products like the production of dichloroethylenes and vinyl chloride as intermediates during in-situ remediation by trichloroethylene. Nanotechnology can pinpoint all these drawbacks and reward us with the most accurate and promising procedures. NPs; these fine agents can penetrate into the groundwater easily and remediate the water directly. Because of large surface area, they can exhibit high catalytic activities and degrade the pollutants to a large extent. Those types of NPs which are mounted on to a solid matrix can be applied for the treatment of water or gaseous material like air [46,48]. Scientists have shown that NPs can be applied in degradation and removal of organic and inorganic compounds that in this study we are going to review some of them.

Organic pollutants

Persistent Organic Pollutants (POP) are synthetic chemicals (aldrin, chlordane, hexachlorocyclohexane, dichlorodiphenyltrichloroethane (DDT), etc.) which cannot break down through biological, photolytic and chemical processes in the environment for many years. These chemicals are discharged into the environment by human activities and are exposed to human body and lead to severe health problems because they accumulate in the organs of human and animal tissues easily which contributes to the diseases like cancer, gastric disorders, dysfunctional immune system, birth abnormalities and so forth [49].

Ulucan-Altuntas and Debik (2020) reported Fe/Pd bimetallic NP could degrade DDT which is widely applied as an organic pollutant pesticide. The functionality of this NP was compared to zero valent Iron NP (nZVI). The analysis showed that within 40 minutes, the Fe/Pd bimetallic NP could degrade DDT largely and its efficacy overtook that of Fe/Pd NP [50]. A group of researchers fabricated Cu-Ag, Cu-Ni and Ni-Ag NPs loaded on ginger powder as nanocomposites and analyzed the catalytic rate of the bimetallic NPs for degradation of 2-nitrophenol, 4-nitrophenol, methyl orange, congo red, rhodamine B. It was discovered that the Cu-Ag and Cu-Ni bimetallic NPs have more potential in degradation of all organic compounds. The produced bimetallic NPs presented a high level of reusability and stability too [51] which is of a great importance for environmental and catalytic applications. A bimetallic nanostructure with Cu doped on the surface of iron NP was decorated on the surface of the granular activated carbon which could be applied to remove γ-HCH. Cu worked as a catalytic enhancer in dechlorination of Fe NP. The efficiency of this reaction was more than 99% [52]. Barakat

& et al (2013) produced Ag-Pt bimetallic NP which was immobilized on photocatalytic titania. This assembled NP could degrade 2-chlorophenol (2-CP) through a photocatalytic reaction only within 120 minutes [53]. These examples are just a small portion of the use of bimetallic NPs on degradation of organic pollutants.

Inorganic pollutants

Pollution of the environment by the inorganic pollutants is too dreadful for all living creatures. The source of this type of pollution is inorganic chemical industry, the exhaust of automobile and the wastes of petroleum companies. Similar to the organic pollutants, they can accumulate in the organs and tissues, lead to an abnormal growth and stick tightly to the genetic material and bring about disastrous consequences like cancer [54]. Countless researchers have found that arsenic, fluoride and heavy metals are present in the groundwater and soil [55], thus they have developed and proposed many procedures like nano-remediation. For instance, Fe-Cu bimetallic NPs are effective for removing arsenic from aqueous media. In acidic pH, this NP presented the highest activity and desorption of the arsenic happened in basic pH [56]. Harikumar and TK (2019) compared the efficiency of Cu NP and Cu-Ni bimetallic NP for removing Cd^{+2}, Pb^{+2} and Zn^{+2} ions from the aqueous media. The results indicated that Cu-Ni NP performed better than Cu NP. The highest removal was observed in higher pH values and the efficiency order follows the order: $Zn^{+2} > Pb^{+2} > Cd^{+2}$ [57]. The analysis suggested Cu and Ni had synergistic effects in this remediation effort. The scientists warned us about the side effects of fluoride which is added to our health care staff such as water, toothpaste and creams in minor concentrations. The high amount of fluoride intake contributes to fluorosis. This incident have made World Health Organization (WHO) to set a concentration limit less than 1.5 mg/L. Some strategies have been proposed to separate it such as reverse osmosis, nanofilteration and electrodialysis but adsorption seems the best possible way with a high efficacy, simple mechanism and cost-effective nature [58]. Chen & et al (2012) produced Fe-Ti oxide bimetallic nano-adsorbent fabricated by co-precipitation could adsorb high amount of fluoride from drinking water. They discovered that both Fe and Ti worked synergistically and Ti-O-Fe on the surface of the NP and hydroxyl groups provided a cave for the adsorbing process [59].

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