Review

Metal Nanoparticles as Green Catalysts

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Abstract: Nanoparticles play a significant role in various fields ranging from electronics to composite materials development. Among them, metal nanoparticles have attracted much attention in recent decades due to their high surface area, selectivity, tunable morphologies, and remarkable catalytic activity. In this review, we discuss various possibilities for the synthesis of different metal nanoparticles; specifically, we address some of the green synthesis approaches. In the second part of the paper, we review the catalytic performance of the most commonly used metal nanoparticles and we explore a few roadblocks to the commercialization of the developed metal nanoparticles as efficient catalysts.

Keywords: nanocatalysts; reuse; catalysis; biocatalyst; sustainability

1. Introduction

With accelerating pollution and environmental problems, finding an appropriate solution to impede the harming of the earth has become a critical issue [1–4]. Specifically, cost-effective and environmentally friendly approaches have become significantly important. However, the revolution of materials science and nanotechnology has steeply evolved in developing multifunctional materials for future technologies on a nanoscale. Among different fields of study, the studies on the synthesis of nano-sized particles using a green chemistry approach offer an excellent platform for developing green, economical, recyclable, and sustainable materials for future applications [5–7].

In a typical experiment, catalysts work by lowering the activation energy, leading towards a reaction that can run to completion without the input of external energy, which is a commodity that has recently become especially crucial. Specifically, to be more efficient, the reactions should occur under conditions where lower temperatures and pressures are prevalent. This not only increases efficiency but also effectively decreases costs on a large scale. Among a wide range of catalysts, the nanocatalysts derived from nanoparticles appear as excellent alternatives to conventional nanocatalysts due to their outstanding surface area, robustness, and stability [8–11]. Nano-sized catalysts have more open active surfaces than bulk catalysts and thereby provide efficient contact between the reactant and the catalysts. It was reported that the catalytic rate increases directly with the number of catalytic sites exposed to the reaction: a catalytic site with a larger area for reactions to occur yields a faster rate of reaction and, thus, higher catalytic activity. Also, with a larger surface area comes a more significant number of reactive sites, which helps the reaction to run to completion with higher efficiency.

The other advantage is the insolubility of the catalysts in the reaction mixture, which helps easy separation and re-use of the nanocatalysts. However, despite these benefits, this area has been relatively studied due to the complexities involved in the separation of the catalysts from the final product [12,13]. The presence of these exciting features has prompted the use of catalysts in various areas of science and technology. Recently, metal-based nanoparticles have been considered very useful for different catalysis applications. In general, metal nanoparticles serve many uses, such as increasing the thermal stability of nanofluids and deriving materials with magnetic capabilities [14–19].
2. Metal Nanoparticles

Metal nanoparticles are created from nanoscale matter (1–100 nm) containing both organic and inorganic materials combined with various metals [20–23]. These include transition metals, semiconductors, alkali metals, etc. The metal part of the nanoparticles plays a great role in the use of metal nanoparticles as green catalysts due to their large surface area-to-volume ratio compared to the bulk material. This enables efficient bonding, thereby allowing reactants to bind together at metal sites, and hence, reactions occur more efficiently. Also, layered transition metal dichalcogenides (TMDs) were found to serve as rare metals in combination with nanoparticles [24]. Some examples include molybdenum disulfide (MoS$_2$), tungsten disulfide (WS$_2$), molybdenum diselenide (MoSe$_2$), molybdenum telluride (MoTe$_2$), etc. TMDs are of particular interest specifically because of their unique properties such as their excellent optical and electrical properties and large energy density [25,26]. Figure 1 shows the importance of metal nanoparticles and green catalysts, as seen through the increase in the volume of publications in different fields of study.

Figure 1. Statistics of publications between 2000 and 2018. (a) Approximate number of publications on green catalysts, (b) Approximate number of publications on metal nanoparticles, (c) Approximate number of publications on nanocatalysts, (d) Approximate percentage of publications on green catalysts. Source: Web of Science.

Similarly, metal nanoparticles have gained substantial interest due to their interesting properties and enhanced catalytic activity. More importantly, research in this field has attracted widespread attention and is thought-provoking for the development of advanced catalysts for both fundamental studies and industrial applications. The versatility and cost-effective synthesis of metal nanoparticles have transformed these materials into the fundamental building blocks that will become more prevalent in future technologies. The primary reasons of the rapid expansion of metal nanoparticles include their easy scalability and promising catalytic activity. The presence of such exciting features, such as high surface areas and fine-tunable porosities, is considered advantageous for catalytic support [27–30].

Additionally, the electronic charges promote synergetic interactions and thus help to improve the catalytic properties significantly. The presence of these unique attributes has expanded the usage of metal nanoparticles for various applications in the optical, medicinal, technological, and biomedical
areas [31–37]. However, surface contamination, the removal of capping agents, and particle aggregation are some of the commonly encountered problems. The most significant advantages due to the metals present in metal nanoparticles derive from their thermal and mechanical stability, electrical conductivity, strong optical and magnetic properties, and high melting and boiling points. Thermal stability plays a significant role in the use of metal nanoparticles. For example, Gould et al. reported that silver nanoparticles embedded in amorphous silicon (a-Si) exhibit higher thermal stability, thereby allowing for a more extensive range of applications [38].

3. Synthesis of Metal Nanoparticles

Studies on the synthesis of different nanocatalysts and their toxicities are critically important. It was reported that the toxicity and biological activity of metal nanoparticles depend on various factors such as shape, size, and surface properties [39]. Similarly, other factors, such as solubility and chemical composition, play a substantial role in the recycling process. Usually, metal nanoparticles are synthesized using different approaches depending on the desired outcome and applications. However, the synthesis procedure can be broadly classified into physical and chemical-based processes. The physical approach include flame spray pyrolysis (FSP), spray pyrolysis, electrospray process, and unconventional machining processes [40]. For example, the FSP process is particularly useful when synthesizing metal nanoparticles on a large scale [41]. In this technique, an aqueous solution consisting of metal salts is sprayed as a mist through a thin tube into a flame. Droplets form, and the metal salts turn into metal oxides. After agglomeration of the oxides, the nanoparticles begin to form and are finally collected. In spray pyrolysis, the process begins when droplets of a solution are placed in high-temperature environments. Once evaporation occurs, the droplets and the precipitated solvent are dried, precipitate annealing takes place, and the metal nanoparticles are formed.

Aside from physical processes, various chemical processes were attempted to create metal nanoparticles. One popular method is using enzymatic biomaterials. For instance, Ahmad et al. reported a method of synthesizing cadmium sulfide (CdS) metal nanoparticles from the fungus *Fusarium oxysporum* [42]. Biomineralization, another biological process, can also occur when elements extracted from the local environment are turned into functional materials, and metal nanoparticles can thus be created [43]. The hot-injection technique has been more popularly studied recently and is considered critical due to its efficiency. Although used mainly for the growth of nanocrystals, the hot-injection synthesis procedure demonstrates the ability to generate more uniform nanocrystals, thereby suggesting ways to synthesize metal nanoparticles uniformly [44].

The Turkevich method, discovered by J. Turkevich, is one of the well-known chemical processes for the synthesis of monodispersed spherical gold nanoparticles. In general, the mechanism involves the reduction of citrate at 100 °C, followed by mixing with a gold hydrochlorate solution. Different concentrations of a citrate solution were used to achieve different particle sizes with tunable properties. The key feature of this approach is the quick nucleation process, which practically exhausts the supply of gold ions. Also, the temperature plays a critical role in controlling the particle size (i.e., at a low temperature, the nucleation process is moderate, leading to a broad size distribution) [45]. In another approach, Uppal et al. observed a gradual decrease of the diameter of gold nanoparticles due to an increase in the intensity of surface plasmon resonance [46]. The evolution followed an inverse Ostwald growth by which the size of gold nanoparticles decreases due to digestive ripening, and more mono-dispersed gold particles are formed. This technique allows for greater control over the properties of the synthesized metal nanoparticles. Besides, other techniques were reported, substituting the citrate solutions with citrate buffers to control the variability of the particle size; also, ethylenediaminetetraacetic acid was introduced to control the uniformity of the shape of the nanoparticles [47].

Apart from the above-mentioned metal nanoparticle synthesis techniques, several other green approaches have been proposed to synthesize metal nanoparticles. For instance, palladium-based nanoparticles of different morphologies were prepared at room temperature using Vitamin B1 as a
source. Somorjai et al. reported the synthesis of platinum (Pt)-metalcore coated silica nanocatalyst [48]. The developed nanocatalyst was used in high-temperature catalytic reactions such as ethylene hydrogenation and CO oxidation. Among others, gold, copper, and iron-based metal nanoparticles have been rigorously studied due to their reduced toxicity and biodegradability. For a better understanding, we have tabulated various modern catalysts and their applications in Table 1.

Table 1. Various metal nanoparticles synthesized and their catalytic properties.

| Metal Nanoparticles at Mesoporous N-doped Carbons and Carbon Nitrides | Metal Nanoparticles | Catalysis | Reference |
|---|---|---|---|
| Molybdenum–Bismuth Bimetallic Chalcogenide Nanoparticles | CO₂ to Methanol | [49] |
| Platinum–Antimony Tin Oxide Nanoparticles | Cathode catalysis for direct methanol fuel cells via an oxygen reduction reaction (ORR) | [50] |
| Cobalt Oxide Nanocrystals | Cobalt Oxide Nanocrystals with CoO nanocrystals coupled with carbon nanotubes as catalysts for chlor-alkali electrolysis systems | [51] |
| Iron Oxide Magnetic Nanoparticles | Catalytic oxidation of phenolic and aniline chemical compounds (Fe₃O₄) | [52] |
| Zirconia Nanoparticles | Catalysts for sol–gel synthesis, aqeous precipitation, thermal decomposition, and hydrothermal synthesis | [53] |
| Tin Oxide Nanoparticles | Catalysts for the reduction and photodegradation of organic compounds | [54] |
| Silver Nanoflakes | Silver nanoflakes on molybdenum sulfide (MoS₂) films for the catalytic oxidation of tryptophan | [55] |
| Tungsten Oxide Nanoparticles | Hetero-nanostructured photoelectrodes synthesized via the atomic layer decomposition of tungsten oxide (WO₃) combined with an oxygen evolving catalyst | [56] |
| Cuprous Oxide Nanoparticles | Cuprous oxide nanoparticles on reduced graphene oxide (RGO) for usage as an efficient electrocatalyst in ORR | [57] |
| Titanium Dioxide Nanoparticles | Carbon modified titanium dioxide (TiO₂) can be used in daylight photocatalysis | [58] |
| Iridium Oxide Nanoparticles | Ligand-free iridium oxide nanoparticles for high electrocatalytic activity | [59] |
| Palladium Nanoparticles | Catalytic formic acid oxidation can take place through the oleylamine-mediated synthesis of palladium nanoparticles | [60] |
| Gold Nanoparticles | Gold nanoparticles help to create an active catalyst for the reduction of nitroarenes in an aqueous medium when placed on top of nanocrystalline magnesium oxide | [61] |
| Elemental Sulfur Nanoparticles | Catalysis occurred when elemental sulfur nanoparticles were placed on chromium (VI) with a sulfide reaction | [62] |
| Silica Titanium Oxide Nanoparticles | Exhibit catalytic properties that can be tested for the oxidation of saturated and unsaturated hydrocarbons | [63] |
| Silica Vanadium Oxide Nanoparticles | Exhibit catalytic properties that can be tested for the oxidation of saturated and unsaturated hydrocarbons | [64] |
| Dendrimer-Encapsulated Metal Nanoparticles | Dendrimers can be used to control the placement and other properties of metal nanoparticles for their usage as catalysts | [65] |
| Imidazolium Metal Nanoparticles | Metal nanoparticles immersed in imidazolium ionic liquids exhibit unique catalytic properties | [66] |
| Zinc Oxide Nanoparticles | Semiconducting zinc oxide nanowires made from nanoparticles can be tested for photoluminescence properties through catalytic growth | [67] |
| Silver Nanoparticles | Silver nanoparticles can be used as chemically stable nanoparticles with no environmentally harmful effects on microbes under anaerobic conditions | [68] |
| Magnesium Oxide Nanoparticles | EXAFS spectroscopy shows that magnesium oxide is a precursor of a type of mononuclear complex of gold that can catalyze ethene hydrogenation | [69] |
| Calcium Oxide Nanoparticles | Calcium oxide nanoparticles can be catalyzed with pyridine in an aqueous ethanol medium | [70] |
| Strontium-Doped Zinc Oxide Nanoparticles | Can be created with the sol–gel method, and tests showed successful photocatalytic activity of these nanoparticles when removing methylene blue (MB) | [71] |
| Titanium Carbide Nanoparticles | Such nanoparticles can support platinum catalysts for methanol electrooxidation in acidic mediums | [72] |
| Cerium Oxide Nanoparticles | These nanoparticles with their catalytic properties can be used for a variety of biomedical applications | [73] |
| Antimony–Vandium Oxide Catalysts | Catalysts prepared are selective for acrylonitrile formation | [74] |
| Metal Nanoparticles | Metal nanoparticles at mesoporous N-doped carbons and carbon nitrides held in Mott–Schottky heterojunctins can function as efficient catalysts | [75] |
| Metal Nanoparticles | Catalytic properties of metal nanoparticles can be used in the synthesis of single-walled carbon nanotubes | [76] |
4. Catalysts

The development of robust, recyclable, green catalysts is considered a significant challenge in chemistry and materials science. This area has been steadily expanding, and understanding its efficiency when using metal nanoparticles is becoming essential. More importantly, the development of green catalysts that are eco-friendly and re-usable help minimize waste disposal, and these catalytic materials are considered indispensable [78–81]. In a broader context, the catalysts have been classified as homogenous catalysts, heterogeneous catalysts, and biocatalysts. A reaction is considered homogenous when both the reactant and the catalyst are present in the same phase or physical state. These homogenous catalysts are popularly used in several industrial processes where the reactants and products are in the same (either gaseous or liquid) phase. On the other hand, heterogenous catalyst are catalysts that are in a different phase with respect to the reactants. A typical example is a solid catalyst with either liquid or gases as reactants.

The heterogeneous catalysts are considered to be more active, efficient, and selective compared to the homogeneous catalysts. This is primarily due to the even dispersion of the metal nanoparticle catalysts in the reactants, which can provide more active sites for the reactions to occur at a faster rate. Nevertheless, the homogenous dispersibility of the catalysts makes it more challenging to separate the catalysts after completion of the reactions. Most commonly in heterogeneous catalysts, transition metals and their compounds are coated onto the surface of the catalysts to form highly active sites that lower the energy through the adsorption of reactant molecules on their surface. Heterogeneous catalysts have played a substantial role in the chemical industry for decades and they are considered essential for energy and chemical transformations [82].

5. Metal Nanoparticles in Catalysis Application

Metal nanoparticles play a notable role in catalysis applications. Specifically, metal nanoparticles with high surface area and more active sites promote faster reactions and increase product yield. These particles can be broadly divided into two main groups: noble-metal (Au, Pt, Ag, etc.)-supported metal nanoparticles and non-noble-metal (Fe, Cu, Ni, Co, etc.)-based nanoparticles.

In the last two decades, developments in materials science and nanotechnology have helped to achieve spectacular control over the synthesis of metallic nanoparticles with various shapes, sizes, and composition [83–89]. More importantly, the capability to fine-tune the structure and morphology using colloidal chemistry allows for more exceptional techniques to derive catalysts with higher active sites. These advancements act as a bridge between materials and their studies as heterogeneous catalysts. Such revolutions started when Haruta and Hutchings opened a new area of scientific debate by studying the catalytic behavior of carbon monoxide (CO) in the presence of gold nanoparticles deposited on a metal oxide [86–88]. They observed that sub-nanometer clusters and nanoparticles of ~1–3 nm were found to be essential for the catalysis of CO oxidation reactions and had a significant impact on the overall catalytic performance. Haruta’s group explored different procedures to optimize the particle size by controlling the calcination temperature and found that 3 nm Au nanoparticles were more efficient for the oxidation of CO. This interesting observation stimulated more studies on the synthesis of numerous metallic Au-supported nanoparticles; these nanoparticles were then widely used as catalysts for many catalytic applications [90–92].

Apart from gold, platinum-supported nanoparticles have been widely employed in various areas, including electrocatalytic oxidations for fuel cells, due to their high dispersibility and catalytic activity. Metallic Pt (Platinum) has been supported on different nanoparticles, including magnetic nanoparticles such as iron oxides, to form a stable and active catalyst for the oxidation of alcohols, CO, vitamin precursors, etc. [93–95]. Another exciting material which has been popularly studied is Palladium (Pd), to produce Pd-supported nanoparticles. Metallic Pd was supported on different substrates such as porous carbons, nanoparticles, polymers, etc. to derive active catalysts for several catalytic applications [96–99]. Overall, metal nanoparticles containing Pt, Pd, Au displayed excellent activity and selectivity towards the selective oxidation of alcohols under mild conditions. Recent studies also suggest
that single-atom catalysts such as Pd-supported mesoporous alumina are efficient in the selective oxidation of allylic alcohols. In comparison, single-atom Pd supported on mesoporous alumina displayed a higher turnover frequency (TOF) than Au nanoparticles, despite its poor selectivity. However, the high cost and toxicity of noble-metal-supported catalysts emphasizes the need for alternatives for the development of readily available, non-toxic, and less expensive catalytic materials.

Among many different options, non-noble-metal supported nanoparticles (based on Fe, Cu, Ni, etc.) have been widely studied due to their remarkable catalytic properties and large availability. Also, due to their tremendous catalytic activity, excellent stability, and environmental sustainability, Fe, Cu, and Ni have been considered as active players for heterogenous catalysis applications [100–104]. A single-atom doping of Co, Fe, Cu, Ni with nitrogen-doped carbon (N–C) was found to catalyze the oxidative esterification of alcohols effectively. It was reported that Cu-doped N–C displayed better performance; however, it showed reduced activity towards the oxidation of aliphatic alcohols. In another work, atomically dispersed Co was encapsulated into a metal–organic framework (Co–MOF) and tested for selective hydrogenation of nitroarenes. Co–Ni-based metal catalysts have also been studied for electrocatalytic water-splitting applications for the production of H\textsubscript{2}. Apart from Co-, Ni-, Cu-, and iron (Fe)-based nanoparticles have received much attention in recent days. It was reported that sub-nanometric Fe clusters performed much efficiently than Fe nanoparticles and catalyzed the hydrogenation of alkenes under mild conditions. Some other examples include the incorporation of magnetic Fe nanoparticles into graphene, Carbon Nanotubes (CNTs), activated carbons, and two-dimensional (2D) materials, which was found to influence their catalytic properties significantly. It has also been reported that iron oxide (FeO)-supported Au clusters are active in CO oxidation. However, there is still debate on the reactivity of different types of Au species. In a broader context, the synthesis of atomic thin metal clusters has a significant influence on the catalytic behaviors. Synthesized metal-supported nanoparticles have been widely employed in various industrial processes and for different applications such as water splitting and environmental remediation [105,106]. Considering this scenario, the controllable synthesis of atom-thick metal nanoclusters is still considered as a roadblock. Therefore, developing robust methodologies will be more critical for understanding and improving the performance of catalysis.

6. Summary and Outlook

Overall, a wide range of metal-supported nanoparticles has been synthesized in the recent past for a comprehensive study of catalytic applications. Collectively, the synthesis of green catalysts appears to be easily achievable, seems likely to overcome most of the environmental problems linked to the existing chemical processes, and may even be able to help manufacture products at high yields. However, the question of the sustainable preparation of metal nanoparticles arises (i.e., the use of environmentally friendly precursors, solvents, etc.). Interestingly, there are a few reports which suggest the use of bio-derived materials such as starch and a range of plant-derived materials for the preparation of eco-friendly metal nanoparticles containing Au, Cu, Ag, etc. These metal nanoparticles are set upon different substrates, including CNTs and proteins such as soybeans, poly-L-lysine, etc., to develop bio-inspired hybrid materials [107–110].

Another possibility is the encapsulation of metal nanoparticles on biopolymers, such as chitosan, cellulose, etc., which are sometimes used for the removal of chlorine in the water. Similarly, these nanoparticle-supported substrates can be utilized in many applications, including hydrogen sorption, environmental remediation, and fuel cell usage. Despite the possibility of the production of highly active and selective catalysts through sustainable routes, we still are far from the implementation of the existing techniques. The other primary concern is toxicity, which is yet to be revealed, associated with the synthesized nanoparticles. Metal nanoparticles, such as those based on Pd, Pt, and Rh, are poisonous, and their toxicity levels are reported to depend on various other factors, including particle size, coordinated ligands, etc. Although Fe-, Cu-, and Ni-based catalysts are found to be less toxic than Pd-, Pt-, and Rh-based catalysts, a systematic study still needs to be carried out to meticulously
evaluate the cytotoxicity and biocompatibility of these nanoparticles before their bulk development and industrialization [111–113].

7. Conclusions

In this review, we discussed the various synthesis methods and designs of a wide range of metal catalysts and also addressed some of their catalytic applications. Despite the significant achievements in this area, there are still several roadblocks to be resolved, such as: (1) Establishing easy methods to synthesize bulk quantities of less toxic, uniform, robust nanoparticles with high surface areas and selectivity properties, (2) Maintaining the catalytic properties of the nanoparticles under harsh conditions, (3) Understanding the mechanisms of the catalytic process to engineer robust catalytic systems, (4) Studying the biocompatibility of the nanoparticles, taking into consideration different factors such as particle size, coordination ligands, etc., (5) Designing various strategies for bulk production. All these obstacles need to be urgently evaluated for present and future industrial applications. Though many challenges exist and various processes have not yet been methodically evaluated, these problems are expected to be addressed in the near future, leading towards the development and commercialization of efficient catalysts for many practical applications.

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References

1. Radhi, H. Evaluating the Potential Impact of Global Warming on the UAE Residential Buildings—A Contribution to Reduce the CO₂ Emissions. Build. Environ. 2009, 44, 2451–2462. [CrossRef]
2. Solomon, S.; Plattner, G.K.; Knutti, R.; Friedlingstein, P. Irreversible Climate Change Due to Carbon Dioxide Emissions. Proc. Natl. Acad. Sci. USA 2009, 106, 1704–1709. [CrossRef]
3. Hughes, T.P.; Kerry, J.T.; Álvarez-Noriega, M.; Álvarez-Romero, J.G.; Anderson, K.D.; Baird, A.H.; Babcock, R.C.; Beger, M.; Bellwood, D.R.; Berkelmans, R.; et al. Global Warming and Recurrent Mass Bleaching of Corals. Nature 2017, 543, 373–377. [CrossRef]
4. Cherubini, F.; Peters, G.P.; Berntsen, T.; Strømman, A.H.; Hertwich, E. CO₂ Emissions from Biomass Combustion for Bioenergy: Atmospheric Decay and Contribution to Global Warming. GCB Bioenergy 2011, 3, 413–426. [CrossRef]
5. Egorova, K.S.; Ananikov, V.P. Which Metals Are Green for Catalysis? Comparison of the Toxicities of Ni, Cu, Fe, Pd, Pt, Rh, and Au Salts. Angew. Chem. Int. Ed. 2016, 55, 12150–12162. [CrossRef] [PubMed]
6. Issaabadi, Z.; Nasrollahzadeh, M.; Sajadi, S.M. Green Synthesis of the Copper Nanoparticles Supported on Bentonite and Investigation of Its Catalytic Activity. J. Clean. Prod. 2017, 142, 3584–3591. [CrossRef]
7. Edison, T.N.J.I.; Lee, Y.R.; Sethuraman, M.G. Green Synthesis of Silver Nanoparticles Using Terminalia Cuneata and Its Catalytic Action in Reduction of Direct Yellow-12 Dye. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2016, 161, 122–129. [CrossRef] [PubMed]
8. Hu, H.; Xin, J.H.; Hu, H.; Wang, X.; Miao, D.; Liu, Y. Synthesis and Stabilization of Metal Nanocatalysts for Reduction Reactions—A Review. J. Mater. Chem. A 2015, 3, 11157–11182. [CrossRef]
9. Yang, Q.; Xu, Q.; Jiang, H.L. Metal-Organic Frameworks Meet Metal Nanoparticles: Synergistic Effect for Enhanced Catalysis. Chem. Soc. Rev. 2017, 46, 4774–4808. [CrossRef]
10. Saxena, V.; Kumar, N.; Saxena, V.K. A Comprehensive Review on Combustion and Stability Aspects of Metal Nanoparticles and Its Additive Effect on Diesel and Biodiesel Fuelled C.I. Engine. Renew. Sustain. Energy Rev. 2017, 70, 563–588. [CrossRef]
11. Hunt, S.T.; Milina, M.; Alba-Rubio, A.C.; Hendon, C.H.; Dumesic, J.A.; Román-Leshkov, Y. Self-Assembly of Noble Metal Monolayers on Transition Metal Carbide Nanoparticle Catalysts. Science 2016, 352, 974–978. [CrossRef] [PubMed]
12. Shylesh, S.; Schünemann, V.; Thiel, W.R. Magnetically Separable Nanocatalysts: Bridges between Homogeneous and Heterogeneous Catalysis. Angew. Chem. Int. Ed. 2010, 49, 3428–3459. [CrossRef] [PubMed]
13. Majedi, S.M.; Lee, H.K. Recent Advances in the Separation and Quantification of Metallic Nanoparticles and Ions in the Environment. *TrAC Trends Anal. Chem.* 2016, 75, 183–196. [CrossRef]

14. Ramprasad, R.; Zurcher, P.; Petras, M.; Miller, M.; Renaud, P. Magnetic Properties of Metallic Ferromagnetic Nanoparticle Composites. *J. Appl. Phys.* 2004, 96, 519. [CrossRef]

15. Xuan, Y.; Li, Q. Heat Transfer Enhancement of Nanofluids. *Int. J. Heat Fluid Flow* 2000, 21, 58–64. [CrossRef]

16. Yamamoto, Y.; Miura, T.; Nakae, Y.; Teranishi, T.; Miyake, M.; Hori, H. Magnetic Properties of the Noble Metal Nanoparticles Protected by Polymer. *Phys. B Condens. Matter* 2003, 329, 1183–1184. [CrossRef]

17. Ali, N.; Teixeira, J.A.; Addali, A. A Review on Nanofluids: Fabrication, Stability, and Thermophysical Properties. *J. Nanomater.* 2018, 2018, 1–33. [CrossRef]

18. Yu, F.; Chen, Y.; Liang, X.; Xu, J.; Lee, C.; Liang, Q.; Tao, P.; Deng, T. Dispersion Stability of Thermal Nanofluids. *Prog. Nat. Sci. Mater. Int.* 2017, 27, 531–542. [CrossRef]

19. Rudakov, G.A.; Tsiberkin, K.B.; Ponomarev, R.S.; Henner, V.K.; Ziolkowska, D.A.; Jasinski, J.B.; Sumanasekera, G. Magnetic Properties of Transition Metal Nanoparticles Encased in Carbon Nanocages. *J. Magn. Magn. Mater.* 2019, 472, 34–39. [CrossRef]

20. Crooks, R.M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, I.K. dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Applications to Catalysis. *Acc. Chem. Res.* 2001, 34, 181–190. [CrossRef]

21. Sun, Y.; Xia, Y. Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Science* 2002, 298, 2176–2179. [CrossRef] [PubMed]

22. Iravani, S. Green Synthesis of Metal Nanoparticles Using Plants. *Green Chem.* 2011, 13, 2638. [CrossRef]

23. Murphy, C.J.; Sau, T.K.; Gole, A.M.; Orendorff, C.J.; Gao, J.; Gou, J.; Hunyadi, S.E.; Li, T. Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications. *J. Phys. Chem. B* 2005, 109, 13873–13870. [CrossRef] [PubMed]

24. Hong, X.; Liu, J.; Zheng, B.; Huang, X.; Zhang, X.; Tan, C.; Chen, J.; Fan, Z.; Zhang, H. A Universal Method for Preparation of Noble Metal Nanoparticle-Decorated Transition Metal Dichalcogenide Nanobelts. *Adv. Mater.* 2014, 26, 6250–6254. [CrossRef] [PubMed]

25. Orofeo, C.M.; Suzuki, S.; Sekine, Y.; Hibino, H. Scalable Synthesis of Layer-Controlled WSe2 and MoS2 Sheets by Sulphurization of Thin Metal Films. *Appl. Phys. Lett.* 2014, 105, 83112. [CrossRef] [PubMed]

26. Eichfeld, S.M.; Hossain, L.; Lin, Y.C.; Piasecki, A.F.; Kupp, B.; Birdwell, A.G.; Burke, R.A.; Lu, N.; Peng, X.; Li, J.; et al. Highly Scalable, Atomically Thin WSe2 Grown via Metal-Organic Chemical Vapor Deposition. *ACS Nano* 2015, 9, 2080–2087. [CrossRef] [PubMed]

27. Cuena, B.R. Synthesis and Catalytic Properties of Metal Nanoparticles: Size, Shape, Support, Composition, and Oxidation State Effects. *Thin Solid Films* 2010, 518, 3127–3150. [CrossRef]

28. Moreno-Áñez, M.; Pleixats, R. Formation of Carbon-Carbon Bonds under Catalysis by Transition-Metal Nanoparticles. *Acc. Chem. Res.* 2003, 36, 638–643. [CrossRef] [PubMed]

29. Dhakshinamoorthy, A.; Garcia, H. Catalysis by Metal Nanoparticles Embedded on Metal-Organic Frameworks. *Chem. Soc. Rev.* 2012, 41, 5262. [CrossRef]

30. Narayanan, R.; El-Sayed, M.A. Catalysis with Transition Metal Nanoparticles in Colloidal Solution: Nanoparticle Shape Dependence and Stability. *J. Phys. Chem. B* 2005, 109, 12663–12676. [CrossRef]

31. Singh, M.; Manikandan, S.; Kumaraguru, A.K. Nanoparticles: A New Technology with Wide Applications. *Res. J. Nanosci. Nanotechnol.* 2011, 1, 1–11. [CrossRef]

32. Conde, J.; Doria, G.; Baptista, P. Noble Metal Nanoparticles Applications in Cancer. *J. Drug Deliv.* 2012, 2012, 751075. [CrossRef] [PubMed]

33. Mohanpuria, P.; Rana, N.K.; Yadav, S.K. Biosynthesis of Nanoparticles: Technological Concepts and Future Applications. *J. Natn. Res.* 2008, 10, 507–517. [CrossRef]

34. Zijlstra, P.; Orrit, M. Single Metal Nanoparticles: Optical Detection, Spectroscopy and Applications. *Rep. Prog. Phys.* 2011, 74, 106401. [CrossRef]

35. Liao, H.; Nehl, C.L.; Hafner, J.H. Biomedical Applications of Plasmon Resonant Metal Nanoparticles. *Nanomedicine* 2006, 1, 201–208. [CrossRef]

36. Jain, P.K.; Huang, X.; El-Sayed, I.H.; El-Sayed, M.A. Noble Metals on the Nanoscale: Optical and Photothermal Properties and Some Applications in Imaging, Sensing, Biology, and Medicine. *Acc. Chem. Res.* 2008, 41, 1578–1586. [CrossRef]
37. Biju, V.; Itoh, T.; Anas, A.; Sujith, A.; Ishikawa, M. Semiconductor Quantum Dots and Metal Nanoparticles: Syntheses, Optical Properties, and Biological Applications. *Anal. Bioanal. Chem.* 2008, 391, 2469–2495. [CrossRef]

38. Gould, A.L.; Kadkhodazadeh, S.; Wagner, J.B.; Catlow, C.R.A.; Logsdail, A.J.; Di Vece, M. Understanding the Thermal Stability of Silver Nanoparticles Embedded in A-Si. *J. Phys. Chem. C* 2015, 119, 23767–23773. [CrossRef]

39. Sukanova, A.; Bozrova, S.; Sokolov, P.; Berestovoy, M.; Karaulov, A.; Nabiev, I. Dependence of Nanoparticle Toxicity on Their Physical and Chemical Properties. *Nanoscale Res. Lett.* 2018, 13, 44. [CrossRef]

40. Singh, P.K.; Kumar, P.; Das, A.K. Unconventional Physical Methods for Synthesis of Metal and Non-Metal Nanoparticles: A Review. *Proc. Natl. Acad. Sci. India Sec. A Phys. Sci.* 2019, 89, 199–221. [CrossRef]

41. Gröhn, A.J.; Pratsinis, S.E.; Sánchez-Ferrer, A.; Mezzenga, R.; Wegner, K. Scale-up of Nanoparticle Synthesis by Flame Spray Pyrolysis: The High-Temperature Particle Residence Time. *Ind. Eng. Chem. Res.* 2014, 53, 10734–10742. [CrossRef]

42. Ahmad, A.; Mukherjee, P.; Mandal, D.; Senapati, S.; Khan, M.I.; Kumar, R.; Sastry, M. Enzyme Mediated Extracellular Synthesis of CdS Nanoparticles by the Fungus, Fusarium Oxysporum. *J. Am. Chem. Soc.* 2002, 124, 12108–12109. [CrossRef] [PubMed]

43. Chen, C.L.; Zhang, P.; Rosi, N.L. A New Peptide-Based Method for the Design and Synthesis of Nanoparticle Superstructures: Construction of Highly Ordered Gold Nanoparticle Double Helices. *J. Am. Chem. Soc.* 2008, 130, 13555–13557. [CrossRef] [PubMed]

44. Kimling, J.; Maier, M.; Okenve, B.; Kotaidis, V.; Parkin, I.P. The Extended Time Evolution Size Decrease of Gold Nanoparticles Formed by the Turkевич Method. *New J. Chem.* 2010, 34, 1401. [CrossRef]

45. Schulz, F.; Homolka, T.; Bastús, N.G.; Puntes, V.; Weller, H.; Vossmeyster, T. Little Adjustments Significantly Improve the Turkевич Synthesis of Gold Nanoparticles. *Langmuir* 2014, 30, 10779–10784. [CrossRef]

46. Joo, S.H.; Park, J.Y.; Tsung, C.K.; Yamada, Y.; Yang, P.; Somorjai, G.A. Thermally Stable Pt/Mesoporous Silica Core-Shell Nanocatalysts for High-Temperature Reactions. *Nat. Mater.* 2009, 8, 126. [CrossRef]

47. Sun, X.; Zhu, Q.; Kang, X.; Liu, H.; Qian, Q.; Zhang, Z.; Han, B. Molybdenum-Bismuth Bimetallic Chalcogenide Nanosheets for Highly Efficient Electrocatalytic Reduction of Carbon Dioxide to Methanol. *Angew. Chem. Int. Ed.* 2016, 55, 6771–6775. [CrossRef]

48. You, D.J.; Kwon, K.; Pak, C.; Chang, H. Platinum-Antimony Tin Oxide Nanoparticle as Cathode Catalyst for Direct Methanol Fuel Cell. *Catal. Today* 2009, 146, 15–19. [CrossRef]

49. Liang, Y.; Wang, H.; Diao, P.; Chang, W.; Hong, G.; Li, Y.; Gong, M.; Xie, L.; Zhou, J.; Wang, J.; et al. Oxygen Reduction Electrocatalyst Based on Strongly Coupled Cobalt Oxide Nanocrystals and Carbon Nanotubes. *J. Am. Chem. Soc.* 2012, 134, 15849–15857. [CrossRef] [PubMed]

50. Zhang, S.; Zhao, X.; Niu, H.; Shi, Y.; Cai, Y.; Jiang, G. Superparamagnetic Fe3O4 Nanoparticles as Catalysts for the Catalytic Oxidation of Phenolic and Aniline Compounds. *J. Hazard. Mater.* 2009, 167, 560–566. [CrossRef] [PubMed]

51. Bansal, V.; Rautaray, D.; Ahmad, A.; Sastry, M. Biosynthesis of Zirconia Nanoparticles Using the Fungus Fusarium Oxysporum. *J. Mater. Chem.* 2004, 14, 3303. [CrossRef]

52. Seabra, A.B.; Durán, N. Nanotoxicology of Metal Oxide Nanoparticles. *Metals* 2015, 5, 934–975. [CrossRef]

53. Xia, X.; Zheng, Z.; Zhang, Y.; Zhao, X.; Wang, C. Synthesis of Ag-MoS2/Chitosan Nanocomposite and Its Application for Catalytic Oxidation of Tryptophan. *Sens. Actuators B Chem.* 2014, 192, 42–50. [CrossRef]

54. Liu, R.; Lin, Y.; Chou, L.Y.; Sheehan, S.W.; He, W.; Zhang, F.; Hou, H.J.M.; Wang, D. Water Splitting by Tungsten Oxide Prepared by Atomic Layer Deposition and Decorated with an Oxygen-Evolving Catalyst. *Angew. Chem. Int. Ed.* 2011, 50, 499–502. [CrossRef]

55. Yan, X.Y.; Tong, X.L.; Zhang, Y.F.; Han, X.D.; Wang, Y.Y.; Jin, G.Q.; Qin, Y.; Guo, X.Y. Cuprous Oxide Nanoparticles Dispersed on Reduced Graphene Oxide as an Efficient Electrocatalyst for Oxygen Reduction Reaction. *Chem. Commun.* 2012, 48, 1892–1894. [CrossRef]

56. Sakthivel, S.; Kisch, H. Daylight Photocatalysis by Carbon-Modified Titanium Dioxide. *Angew. Chem. Int. Ed.* 2003, 42, 4908–4911. [CrossRef]
78. Campelo, J.M.; Luna, D.; Luque, R.; Marinas, J.M.; Romero, A.A. Sustainable Preparation of Supported Metal Nanoparticles Using a Sacrificial Acid and Its Photocatalytic Performance under Medium Pressure Mercury UV Lamp. *Chem. Eng. J.* 2009, 155, 660–665. [CrossRef]

79. Raveendran, P.; Fu, J.; Wallen, S.L. Completely “Green” Synthesis and Stabilization of Metal Nanoparticles. *ChemSusChem* 2015, 8, 402–406. [CrossRef]

80. Zhao, Y.; Hernandez-Pagan, E.A.; Vargas-Barbosa, N.M.; Dysart, J.L.; Mallouk, T.E. A High Yield Synthesis of Ligand-Free Iridium Oxide Nanoparticles with High Electrocatalytic Activity. *J. Phys. Chem. Lett.* 2011, 2, 402–406. [CrossRef]

81. Dupont, J.; Fonseca, G.S.; Umpierre, A.P.; Fichtner, P.F.P.; Teixeira, S.R. Transition-Metal Nanoparticles in Imidazolium Ionic Liquids: Recyclable Catalysts for Biphasic Hydrogenation Reactions. *J. Am. Chem. Soc.* 2002, 124, 4228–4229. [CrossRef] [PubMed]

82. Mazumder, V.; Sun, S. Oleylamine-Mediated Synthesis of Pd Nanoparticles for Catalytic Formic Acid Oxidation. *J. Am. Chem. Soc.* 2009, 131, 4588–4589. [CrossRef] [PubMed]

83. Layek, K.; Kantam, M.L.; Shirai, M.; Nishio-Hamane, D.; Sasaki, T.; Maheswaran, H. Gold Nanoparticles Stabilized on Nanocrystalline Magnesium Oxide as an Active Catalyst for Reduction of Nitroarenes in Aqueous Medium at Room Temperature. *Green Chem.* 2012, 14, 3164–3174. [CrossRef]

84. Lopez, N.; Nørskov, J.K. Catalytic CO Oxidation by a Gold Nanoparticle: A Density Functional Study. *J. Am. Chem. Soc.* 2002, 124, 11262–11263. [CrossRef] [PubMed]

85. Lan, Y.; Deng, B.; Kim, C.; Thornton, E.C.; Xu, H. Catalysis of Elemental Sulfur Nanoparticles on Chromium(VI) Reduction by Sulfide under Anaerobic Conditions. *Environ. Sci. Technol.* 2005, 39, 2087–2094. [CrossRef]

86. Martinez-Méndez, S.; Henríquez, Y.; Domínguez, O.; D’Ornellas, L.; Krentzien, H. Catalytic Properties of Silica Supported Titanium, Vanadium and Niobium Oxide Nanoparticles towards the Oxidation of Saturated and Unsaturated Hydrocarbons. *J. Mol. Catal. A: Chem.* 2006, 252, 226–234. [CrossRef]

87. Migowski, P.; Dupont, J. Catalytic Applications of Metal Nanoparticles in Imidazolium Ionic Liquids. *Chem. Eur. J.* 2007, 13, 32–39. [CrossRef]

88. Wang, Y.W.; Zhang, L.D.; Wang, G.Z.; Peng, X.S.; Chu, Z.Q.; Liang, C.H. Catalytic Growth of Semiconducting Zinc Oxide Nanowires and Their Photoluminescence Properties. *J. Cryst. Growth* 2002, 234, 171–175. [CrossRef]

89. Yang, Y.; Zhang, C.; Hu, Z. Impact of Metallic and Metal Oxide Nanoparticles on Wastewater Treatment and Anaerobic Digestion. *Environ. Sci. Process. Impacts* 2013, 15, 39–48. [CrossRef]

90. Guzman, J.; Gates, B.C. Structure and Reactivity of a Mononuclear Gold-Complex Catalyst Supported on Magnesium Oxide. *Angew. Chem. Int. Ed.* 2003, 42, 690–693. [CrossRef]

91. Safaei-Ghomi, J.; Ghasemzadeh, M.A.; Mehrabi, M. Calcium Oxide Nanoparticles Catalyzed One-Step Multicomponent Synthesis of Highly Substituted Pyridines in Aqueous Ethanol Media. *Sci. Iran.* 2013, 20, 549–554. [CrossRef]

92. Yousefi, R.; Jamali-Sheihi, F.; Cheraghizadeh, M.; Khoosravi-Gandomani, S.; Sáaeedi, A.; Huang, N.M.; Basirun, W.J.; Azarang, M. Enhanced Visible-Light Photocatalytic Activity of Strontium-Doped Zinc Oxide Nanoparticles. *Mater. Sci. Semicond. Process.* 2015, 32, 152–159. [CrossRef]

93. Ou, Y.; Cui, X.; Zhang, X.; Jiang, Z. Titanium Carbide Nanoparticles Supported Pt Catalysts for Methanol Electrooxidation in Acidic Media. *J. Power Sources* 2010, 195, 1365–1369. [CrossRef]

94. Walkey, C.; Das, S.; Seal, S.; Erlichman, J.; Heckman, K.; Ghibelli, L.; Traversa, E.; McGinnis, J.F.; Self, W.T. Catalytic Properties and Biomedical Applications of Cerium Oxide Nanoparticles. *Environ. Sci. Nano* 2015, 2, 33–53. [CrossRef]

95. Nilsson, R.; Lindblad, T.; Andersson, A. Ammonoxidation of Propene over Antimony-Vanadium-Oxide Catalysts. *Catal. Lett.* 1994, 29, 409–420. [CrossRef]

96. Li, X.H.; Antonietti, M. Metal Nanoparticles at Mesoporous N-Doped Carbons and Carbon Nitrides: Functional Mott–Schottky Heterojunctions for Catalysis. *Chem. Soc. Rev.* 2013, 42, 6593. [CrossRef]

97. Moisala, A.; Nasibulin, A.G.; Kauppinen, E.I. The Role of Metal Nanoparticles in the Catalytic Production of Single-Walled Carbon Nanotubes—A Review. *J. Phys. Condens. Matter* 2003, 15, S3011–S3035. [CrossRef]

98. Campelo, J.M.; Luna, D.; Luque, R.; Marinas, J.M.; Romero, A.A. Sustainable Preparation of Supported Metal Nanoparticles and Their Applications in Catalysis. *ChemSusChem* 2009, 2, 18–45. [CrossRef]

99. Raveendran, P.; Fu, J.; Wallen, S.L. Completely “Green” Synthesis and Stabilization of Metal Nanoparticles. *J. Am. Chem. Soc.* 2003, 125, 13940–13941. [CrossRef]

100. Virkutyte, J.; Varma, R.S. Green Synthesis of Metal Nanoparticles: Biodegradable Polymers and Enzymes in Stabilization and Surface Functionalization. *Chem. Sci.* 2011, 2, 837–846. [CrossRef]
81. Atsushi, F.; Dhepe, P.L. Sustainable Green Catalysis by Supported Metal Nanoparticles. *Chem. Rec.* 2009, 9, 224–235. [CrossRef]

82. Fadhel, A.Z.; Pollet, P.; Liotta, C.L.; Eckert, C.A. Combining the Benefits of Homogeneous and Heterogeneous Catalysis with Tunable Solvents and Nearcritical Water. *Molecules* 2010, 15, 8400–8424. [CrossRef] [PubMed]

83. Saboktakin, M.; Ye, X.; Oh, S.J.; Hong, S.H.; Fafarman, A.T.; Chettiar, U.K.; Engheta, N.; Murray, C.B.; Kagan, C.R. Metal-Enhanced Upconversion Luminescence Tunable through Metal Nanoparticle-Nanophosphor Separation. *ACS Nano* 2012, 6, 8758–8766. [CrossRef] [PubMed]

84. Neto, A.O.; Dias, R.R.; Tusi, M.M.; Linardi, M.; Spinac... [CrossRef] [PubMed]

85. Jensen, T.R.; Malinsky, M.D.; Haynes, C.L.; Van Duyne, R.P. Nanosphere Lithography: Tunable Localized Surface Plasmon Resonance Spectra of Silver Nanoparticles. *J. Phys. Chem. B* 2000, 104, 10549–10556. [CrossRef]

86. Zhang, L.; Blom, D.A.; Wang, H. Au-Cu$_2$O Core-Shell Nanoparticles: A Hybrid Metal-Semiconductor Heteronanostructure with Geometrically Tunable Optical Properties. *Chem. Mater.* 2011, 23, 4587–4598. [CrossRef]

87. Wang, H.H.; Liu, C.Y.; Wu, S.B.; Liu, N.W.; Peng, C.Y.; Chan, T.H.; Hsu, C.F.; Wang, J.K.; Wang, Y.L. Highly Raman-Enhancing Substrates Based on Silver Nanoparticle Arrays with Tunable Sub-10 Nm Gaps. *Adv. Mater.* 2006, 18, 491–495. [CrossRef]

88. Diez, I.; Pusa, M.; Kulmala, S.; Jiang, H.; Wahlber, A.; Goldmann, A.S.; Müller, A.H.E.; Ikka, O.; Ras, R.H.A. Color Tunability and Electrochemiluminescence of Silver Nanoclusters. *Angew. Chem. Int. Ed.* 2009, 48, 2122–2125. [CrossRef]

89. Kelly, K.L.; Coronado, E.; Zhao, L.L.; Schatz, G.C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *J. Phys. Chem. B* 2003, 107, 668–677. [CrossRef]

90. Herzing, A.A.; Kiely, C.J.; Carley, A.F.; Landon, P.; Hutchings, G.J. Identification of Active Gold Nanoclusters on Iron Oxide Supports for CO Oxidation. *Science* 2008, 321, 1331–1335. [CrossRef]

91. Haruta, M. Catalysis of Gold Nanoparticles Deposited on Metal Oxides. *CATTECH* 2002, 6, 102–115. [CrossRef]

92. Hutchings, G.J.; Haruta, M. A Golden Age of Catalysis: A Perspective. *Appl. Catal. A Gen.* 2005, 291, 2–5. [CrossRef]

93. Hrapovic, S.; Liu, Y.; Male, K.B.; Luong, J.H.T. Electrochemical Biosensing Platforms Using Platinum Nanoparticles and Carbon Nanotubes. *Anal. Chem.* 2004, 76, 1083–1088. [CrossRef] [PubMed]

94. Neto, A.O.; Dias, R.R.; Tusi, M.M.; Linardi, M.; Spinacé, E.V. Electro-Oxidation of Methanol and Ethanol Using PtRu/C, PtSn/C and PtSnRu/C Electrocatalysts Prepared by an Alcohol-Reduction Process. *J. Power Sources* 2007, 166, 87–91. [CrossRef]

95. Hong, Y.; Yan, X.; Liao, X.; Li, R.; Xu, S.; Xiao, L.; Fan, J. Platinum Nanoparticles Supported on Ca(Mg)-Zeolites for Efficient Room-Temperature Alcohol Oxidation under Aqueous Conditions. *Chem. Commun.* 2014, 50, 9679–9682. [CrossRef]

96. Narayanan, R.; El-Sayed, M.A. Effect of Catalysis on the Stability of Metallic Nanoparticles: Suzuki Reaction Catalyzed by PVP-Palladium Nanoparticles. *J. Am. Chem. Soc.* 2003, 125, 8340–8347. [CrossRef]

97. Scheuermann, G.M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Müllhaupt, R. Palladium Nanoparticles on Graphite Oxide and Its Functionalized Graphene Derivatives as Highly Active Catalysts for the Suzuki-Miyaura Coupling Reaction. *J. Am. Chem. Soc.* 2009, 131, 8262–8270. [CrossRef]

98. Mei, Y.; Lu, Y.; Polzer, F.; Ballauff, M.; Drexler, M. Catalytic Activity of Palladium Nanoparticles Encapsulated in Spherical Poly Electrolyte Brushes and Core-Shell Microgels. *Chem. Mater.* 2007, 19, 1062–1069. [CrossRef]

99. Cheong, S.; Watt, J.D.; Tilley, R.D. Shape Control of Platinum and Palladium Nanoparticles for Catalysis. *Nanoscale* 2010, 2, 2045. [CrossRef]

100. Mahmoudi, M.; Simchi, A.; Milani, A.S.; Stroeve, P. Cell Toxicity of Superparamagnetic Iron Oxide Nanoparticles. *J. Colloid Interface Sci.* 2009, 336, 510–518. [CrossRef]

101. Gupta, A.K.; Gupta, M. Synthesis and Surface Engineering of Iron Oxide Nanoparticles for Biomedical Applications. *Biomaterials* 2005, 26, 3995–4021. [CrossRef] [PubMed]
102. Rispoli, F.; Angelov, A.; Badia, D.; Kumar, A.; Seal, S.; Shah, V. Understanding the Toxicity of Aggregated Zero Valent Copper Nanoparticles against Escherichia Coli. *J. Hazard. Mater.* **2010**, *180*, 212–216. [CrossRef] [PubMed]

103. Ponce, A.A.; Klabunde, K.J. Chemical and Catalytic Activity of Copper Nanoparticles Prepared via Metal Vapor Synthesis. *J. Mol. Catal. A Chem.* **2005**, *225*, 1–6. [CrossRef]

104. Tu, C.H.; Wang, A.Q.; Zheng, M.Y.; Wang, X.D.; Zhang, T. Factors Influencing the Catalytic Activity of SBA-15-Supported Copper Nanoparticles in CO Oxidation. *Appl. Catal. A Gen.* **2006**, *297*, 40–47. [CrossRef]

105. Wang, F.; Shifa, T.A.; Zhan, X.; Huang, Y.; Liu, K.; Cheng, Z.; Jiang, C.; He, J. Recent Advances in Transition-Metal Dichalcogenide Based Nanomaterials for Water Splitting. *Nanoscale* **2015**, *7*, 19764–19788. [CrossRef]

106. Zhang, G.; Wang, G.; Liu, Y.; Liu, H.; Qu, J.; Li, J. Highly Active and Stable Catalysts of Phytic Acid-Derivative Transition Metal Phosphides for Full Water Splitting. *J. Am. Chem. Soc.* **2016**, *138*, 14686–14693. [CrossRef]

107. Sharma, V.K.; Yngard, R.A.; Lin, Y. Silver Nanoparticles: Green Synthesis and Their Antimicrobial Activities. *Adv. Colloid Interface Sci.* **2009**, *145*, 83–96. [CrossRef]

108. Bar, H.; Bhui, D.K.; Sahoo, G.P.; Sarkar, P.; Pyne, S.; Misra, A. Green Synthesis of Silver Nanoparticles Using Seed Extract of Jatropha Curcas. *Colloids Surfaces A Physicochem. Eng. Asp.* **2009**, *348*, 212–216. [CrossRef]

109. Thema, F.T.; Manikandan, E.; Dhlamini, M.S.; Maaza, M. Green Synthesis of ZnO Nanoparticles via Agathosma Betulina Natural Extract. *Mater. Lett.* **2015**, *161*, 124–127. [CrossRef]

110. Kulkarni, N.; Muddapur, U. Biosynthesis of Metal Nanoparticles: A Review. *J. Nanotechnol.* **2014**, *2014*, 510246. [CrossRef]

111. Bystrzejewska-Piotrowska, G.; Golimowski, J.; Urban, P.L. Nanoparticles: Their Potential Toxicity, Waste and Environmental Management. *Waste Manag.* **2009**, *29*, 2587–2595. [CrossRef] [PubMed]

112. Asharani, P.V.; Lianwu, Y.; Gong, Z.; Valiyaveettil, S. Comparison of the Toxicity of Silver, Gold and Platinum Nanoparticles in Developing Zebrafish Embryos. *Nanotoxicology* **2011**, *5*, 43–54. [CrossRef] [PubMed]

113. Jacinto, M.J.; Santos, O.H.C.F.; Landers, R.; Kiyohara, P.K.; Rossi, L.M. On the Catalytic Hydrogenation of Polycyclic Aromatic Hydrocarbons into Less Toxic Compounds by a Facile Recoverable Catalyst. *Appl. Catal. B Environ.* **2009**, *90*, 688–692. [CrossRef]