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EDITED BY
Abhishek Kumar,
Washington University in St. Louis, United States

REVIEWED BY
Meghana Ramani,
Wayne State University, United States
Rohit Kumar Singh,
Ben-Gurion University of the Negev, Israel

*CORRESPONDENCE
Dirk Linke,
dirk.linke@ibv.uio.no

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Synthesis methods and applications of palladium nanoparticles: A review

Nadeem Joudeh[1], Athanasios Saragliadis[1], Gerbrand Koster[2], Pavlo Mikheenko[3] and Dirk Linke[1]*

[1]Department of Biosciences, University of Oslo, Oslo, Norway, [2]Inven2 AS, Oslo, Norway, [3]Department of Physics, University of Oslo, Oslo, Norway

Palladium (Pd) is a key component of many catalysts. Nanoparticles (NPs) offer a larger surface area than bulk materials, and with Pd cost increasing 5-fold in the last 10 years, Pd NPs are in increasing demand. Due to novel or enhanced physicochemical properties that Pd NPs exhibit at the nanoscale, Pd NPs have a wide range of applications not only in chemical catalysis, but also for example in hydrogen sensing and storage, and in medicine in photothermal, antibacterial, and anticancer therapies. Pd NPs, on the industrial scale, are currently synthesized using various chemical and physical methods. The physical methods require energy-intensive processes that include maintaining high temperatures and/or pressure. The chemical methods usually involve harmful solvents, hazardous reducing or stabilizing agents, or produce toxic pollutants and by-products. Lately, more environmentally friendly approaches for the synthesis of Pd NPs have emerged. These new approaches are based on the use of the reducing ability of phytochemicals and other biomolecules to chemically reduce Pd ions and form NPs. In this review, we describe the common physical and chemical methods used for the synthesis of Pd NPs and compare them to the plant- and bacteria-mediated biogenic synthesis methods. As size and shape determine many of the unique properties of Pd NPs on the nanoscale, special emphasis is given to the control of these parameters, clarifying how they impact current and future applications of this exciting nanomaterial.

KEYWORDS

biogenic nanoparticles, palladium, catalyst, antimicrobial, anticancer

Introduction

Palladium and its applications

Palladium, Pd, is a chemical element with atomic number 46. It is a silvery-white lustrous rare metal that was discovered in 1803 by the English chemist William Hyde Wollaston. Pd was named after the asteroid Pallas that had previously been discovered, in 1802. Pd, together with platinum (Pt), rhodium (Rh), ruthenium (Ru), iridium (Ir), and osmium (Os) form a group of metals that are referred to as Platinum Group Metals

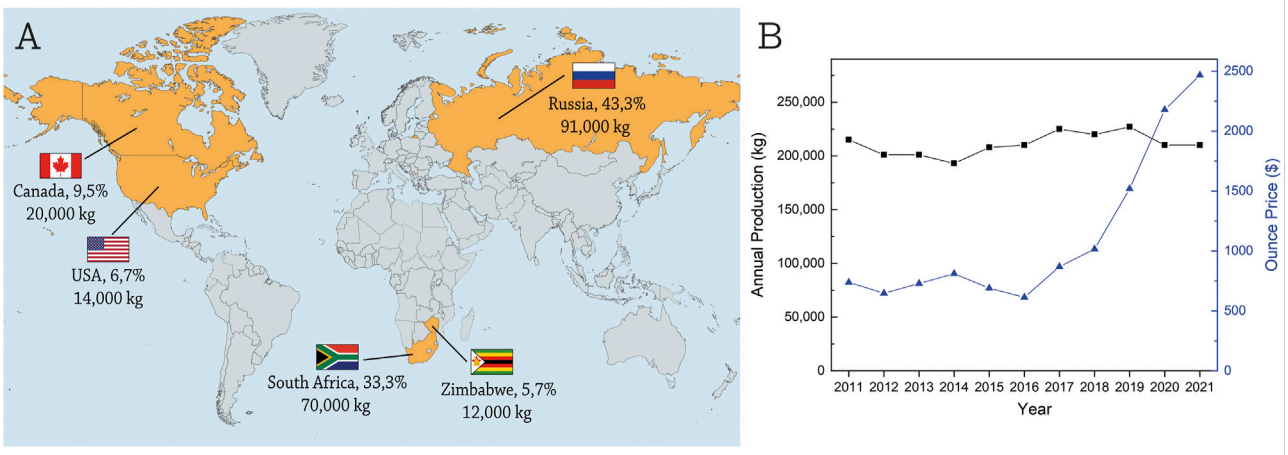

FIGURE 1
Pd mine production and price. **(A)** the major producers of Pd, where the countries shown produced 98.5% of world's Pd in 2020. **(B)** the annual mine production of Pd is not growing over time (black line), while the price of one ounce of Pd has increased 5-fold in the last 10 years (blue line).

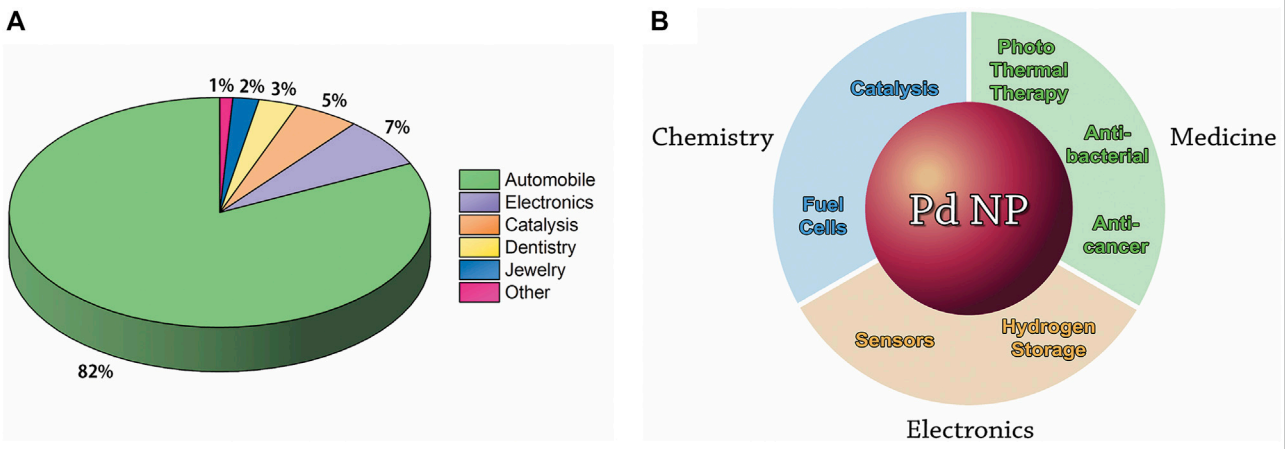

FIGURE 2
Applications of Pd in different industries (Palladium consumption worldwide in 2020, 2022). **(A)** the industrial consumption of bulk Pd by industry in 2020. **(B)** the major applications of Pd NPs in chemistry, medicine, and electronics.

(PGMs). These elements have similar chemical properties overall, but Pd is the least dense and has the lowest melting temperature amongst them.

Pd is mostly extracted from ore deposits in a few countries. In 2020, the overall mine production of Pd reached 210,000 kg; major producers are illustrated in Figure 1A (Geological Survey, 2020). Recycling Pd forms an additional source of supply. In 2020, 96,000 kg of Pd was recycled, mainly from automotive catalytic converters, jewelry, and electronic scrap (Key trends in the Palladium, 2022). The production of Pd is limited and cannot keep up with the increased use. Consequently, the price for Pd has dramatically increased over the last years (Figure 1B) (Geological Survey, 2020; Palladium Prices, 2022).

The largest application of Pd today is in automobile catalytic converts. Nobel metals are used in catalytic converters to reduce carbon monoxide, hydrocarbons, and nitrous oxide in automotive emissions by converting them to carbon dioxide and nitrogen. 90% of these pollutants are eliminated from emissions with the use of autocatalysts (Zereini and Alt, 2006). In 1993, the catalytic converter industry began producing Pd-based catalytic converts as an alternative to the traditional Pt-Rh catalyst used. Formerly, Pd had not been considered for use in automobile catalysts by the industry for two reasons: it is not as stable as Pt, and it is more prone to contamination by impurities contained in automobile emissions.

However, due to technical improvements and economic influences, Pd has been increasingly used instead of Pt (Zereini and Alt, 2006).

In 2020, 302 tons of Pd were industrially consumed, and 82% of this consumption was in the automobile industry, followed by 7% in electronics, 5% in chemical catalysis, 3% in dental alloys, 2% in jewelry, and 1% in other industries (summarized in Figure 2A) (Palladium consumption worldwide in 2020, 2022). The current Pd price remains above acceptable levels for several large-scale commercial applications; Pd-based nanomaterials, and especially NPs, thus have the potential to provide more efficient and cost-effective solutions to meet the requirements of present and evolving applications (Chen and Ostrom, 2015).

Pd NPs and Pd-based alloy clusters have been extensively investigated in the last decades. Pd NPs form a versatile catalyst that has a wide range of applications in organic reactions such as in hydrogenation (Favier et al., 2019), carbon–carbon bond forming [Heck reaction (Heck and Nolley, 1972) and Suzuki coupling (Miyaura et al., 1979)], as well as in petroleum cracking (Cagran and Pottlacher, 2006). In fact, the Nobel Prize in Chemistry in 2010 was awarded to Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki for the discovery of Pd-catalyzed cross-coupling reactions in organic synthesis (The Nobel Prize in Chemistry, 2010). In addition to the catalysis of organic reactions, applications of Pd NPs include fuel cells (Antolini, 2009) and hydrogen sensing and storage (Adams and Chen, 2011). Potential electronics applications also include sensors (Silva et al., 2011). Moreover, several applications in biomedical therapies including photothermal, antibacterial, and anticancer therapies have been developed or discussed (Phan et al., 2020). The applications of Pd NPs are summarized in Figure 2B and are described in more detail in Section 5. In this review, we describe and compare the existing physical, chemical, and biological methods for Pd NP production.

Physical methods for Pd NP synthesis

Pd NPs, on the industrial scale, are currently synthesized by physical or chemical methods. The commonly used physical methods are physical vapor deposition, magnetron sputtering, and laser ablation. In most cases, the physical methods of synthesis require expensive equipment and energy-intensive processes that include maintaining high temperatures and/or pressure (Qazi et al., 2016; Vishnukumar et al., 2017).

Physical vapor deposition

Physical vapor deposition involves different techniques that provide the conversion of the material from a condensed phase (solid or liquid) to a vapor phase and then back to a condensed phase (all carried out in vacuum) (Faraji et al., 2018; Prabakaran and Rajan, 2021). In thermal evaporation deposition technique, the material to be deposited is heated to evaporation temperature using resistive heating (the production of heat by passing an electric current through a conductor). The evaporated particles travel directly to the deposition target (substrate) where they condense and form a thin film of NPs (Rajput, 2015) (Figure 3A). Another technique is based on arc deposition, in which the surface of a cathode is struck with a high-current, low-voltage arc that vaporizes the material of the cathode producing vapor that travels to the substrate where it condenses and forms NPs (Rajput, 2015) (Figure 3B). In physical vapor deposition techniques, the particle size and film thickness can be controlled by varying the deposition parameters (Mehl et al., 2015).

Magnetron sputtering

Sputtering is a physical process in which atoms or molecules are ejected out of a material to a substrate by the bombardment of high-energy particles. Before the 1970s, this method used high electric fields (also known as diode sputtering). However, an enhanced variant of the method emerged later in which an additional strong magnetic field is used (known as magnetron sputtering) (Dinca and Suchea, 2019). In this process, a high electric field is applied in a vacuum chamber containing an inert gas such as argon, where the cathode is attached to the metal source and the anode is attached to the substrate. Due to the collisions of electrons (released from the cathode) with the available gas molecule, positively charged (ionized) argon atoms are formed. Once formed, they are strongly attracted to the cathode resulting in high-energy collisions with the metal leading to the ejection of one or more atoms of the material. The ejected metal atoms are accelerated toward the anode bombarding its surface. As a result, small particles of that metal are formed on the substrate. The magnetic field used in this method helps in confining and trapping the electrons released from the cathode around the source (Pal et al., 2001; Musil et al., 2006) (Figure 3C). In this method, Ar pressure influences the particle size in an inverse manner, i.e., the particle size of Pd decreases with increasing Ar pressure (Slavcheva et al., 2014). The effect of using a mix of inert gases (Ar and He) on the particle size was studied by Alexeeva et al., 2015 (Alexeeva and Fateev, 2016). The researchers found that Pd particle size decreases with increasing helium flow rate due to the more frequent occurrence of three-body collisions. In addition, the He stream is extracted out of the vacuum chamber more effectively than for Ar, and nucleation time decreases in this case.

Laser ablation

This technique is based on the irradiation of a material with a laser beam resulting in the removal of small particles from that material. The laser flux, laser wavelength, and the duration of

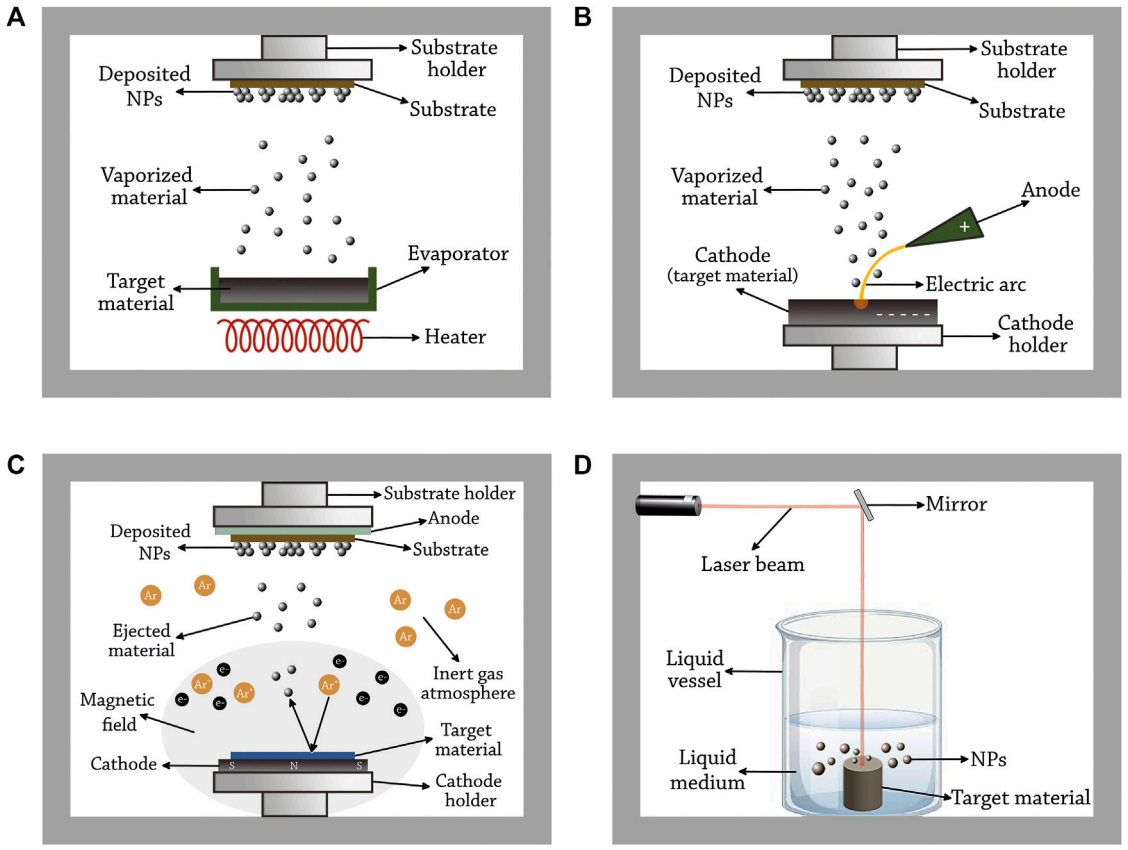

FIGURE 3
Principles of the common physical methods used for Pd NP synthesis. **(A)** thermal evaporation deposition, **(B)** arc deposition, **(C)** magnetron sputtering, and **(D)** pulsed laser ablation in liquid.

irradiation are some of the parameters that are used to precisely control the size of released particles of the material (Chichkov et al., 1996). This technique has different variants based on the atmosphere in the chamber. A common variant of this method, known as pulsed laser ablation in liquid, is based on the immersion of the source material in a solvent. The atomized material released from the target interacts with the solvent and nucleates to form NPs (Cristoforetti et al., 2011) (Figure 3D).

The effect of different salts on the size of Pd NPs produced by pulsed laser ablation in liquid was evaluated by Marzun et al. (2015). The ablation of Pd in deionized water results in bimodal size distribution where large NPs lead to colloidal instability. It was found that the use of salts with low ionic strength (0.005 mM phosphate, 0.01 mM carbonate, 0.03 hydroxide) significantly inhibits the formation of large NPs (>30 nm). Moreover, Mendivil et al. (2015) studied the effect of variation of ablation fluence on the size of Pd NPs formed in different liquids. It was found that in distilled water the average size of NPs increased with the decrease in ablation fluence, while the opposite effect was found in sodium dodecyl sulfate (SDS) solutions.

Chemical methods for Pd NP synthesis

The chemical methods for NPs synthesis rely on the chemical reduction of metal ions to zerovalent metal atoms and their nucleation to form NPs. These methods include electrochemical deposition, sonochemical preparation, supercritical fluid nucleation, and wet chemical methods such as the sol-gel method or the reduction by alcohols or other reductants. In most cases, these chemical methods of synthesis involve hazardous solvents, reducing or stabilization agents, or produce toxic by-products (Singh et al., 2018; Manjare et al., 2021).

Electrochemical deposition

In this method, the metal cations are reduced and deposited on the electrode of an electrolytic cell by a direct electric current. The electrolytic cell is filled with a salt solution of the metal to be deposited, in which the positive metal cations are attracted to the

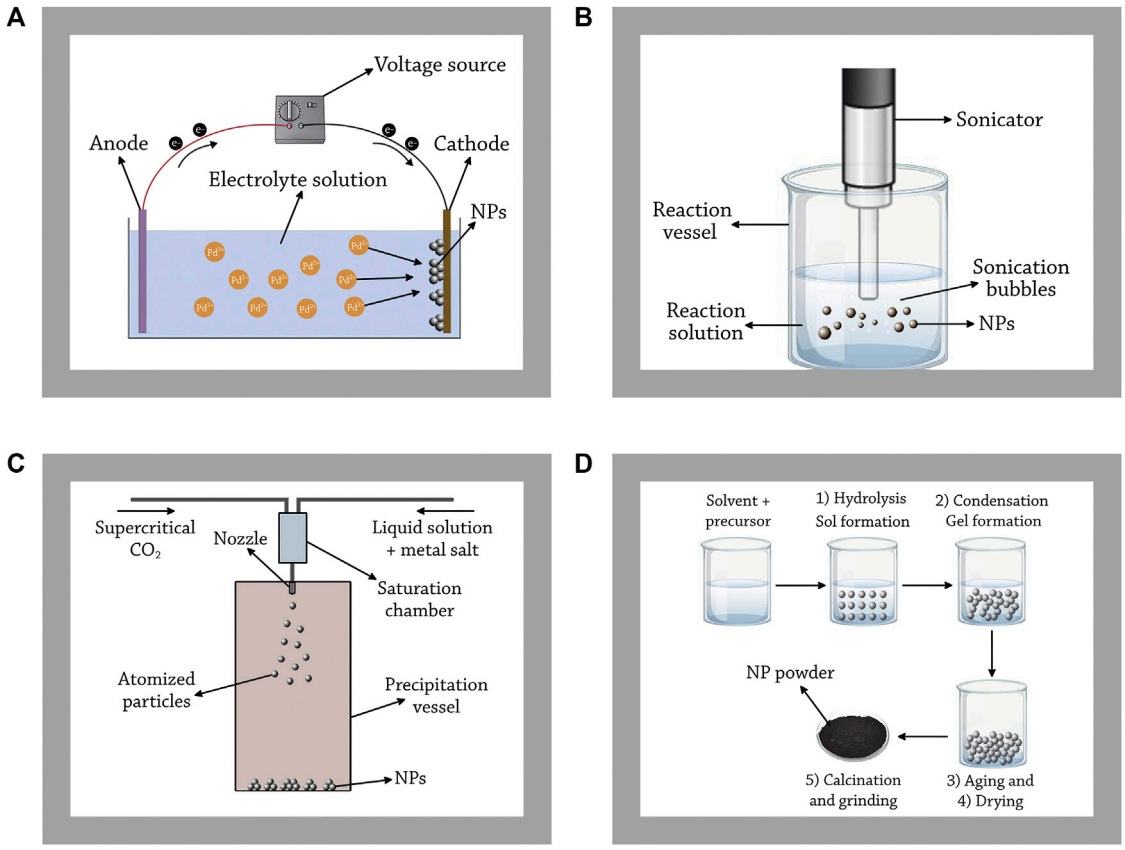

FIGURE 4
Principles of the common chemical methods used for Pd NP synthesis. **(A)** electrochemical deposition, **(B)** sonochemical preparation, **(C)** supercritical fluid nucleation, and **(D)** sol-gel method.

cathode of the cell and reduced on its surface to zerovalent metal by gaining the required electrons (Diculescu et al., 2007; Shendage et al., 2013). In some cases, the opposite reaction may occur on the surface of the anode (oxidation of the metal to form cations), thus, the anode should be made of a material that is resistant to electrochemical oxidation, such as carbon or lead (Dufour, 2006). Figure 4A graphically illustrates this method.

For the synthesis of size-controlled Pd NPs using this method, a chemical stabilizing agent should be added into the solution. The stabilizing agents, such as poly (N-vinylpyrrolidone) (PVP), promote the formation process of Pd NPs, inhibit the electrodeposition process of Pd onto the cathode, and stabilize the formed NPs (Pan et al., 2008). The size of the NPs can by controlled by adjusting the applied current and the concentration of the stabilizing agent. For instance, for the synthesis of Pd NPs using tetrachloropalladate as the precursor, the concentration of PVP was found to be inversely proportional with the mean diameter of the NPs formed. Changing the concentration of PVP from 15 to 30 g dm^{-3} resulted in lowering the mean diameter of the NPs formed from 22.2 to 10.1 nm. For controlling the size of NPs by adjusting the applied current, the researchers found that the higher the current density, the higher the overpotential, and thus the smaller the size of the NPs formed (Pan et al., 2008).

Sonochemical preparation

This process is based on the application of powerful ultrasound frequencies (20 kHz–10 MHz) on a solution containing the ions of the metal in question in order to generate NPs (Gedanken, 2004). In this range of frequency, the ultrasonic waves have wavelengths ranging from 10 cm to 100 μm, much larger than the molecular size. Consequently, the effects on the chemistry of molecules do not arise from the direct interaction between sound waves and chemical species, but rather from a physical phenomenon called acoustic cavitation, which is defined as the formation, growth, and the implosive collapse of bubbles (Xu et al., 2013). When sound waves propagate through a liquid, alternating expansive and compressive waves produce dynamic tensile stress changing

the density of the liquid, which creates bubbles from pre-existing impurities. At a critical size, these bubbles collapse adiabatically, producing the characteristic extreme and transient conditions of sonochemistry: temperatures above 5000 K and pressures exceeding 1000 bar (Xu et al., 2013). Under these extreme conditions in so called hot spots, high-energy chemical reactions occur such as the dissociation of chemical bonds. At the same time, nonvolatile precursors may undergo chemical reactions with radicals or other high-energy products of sonolysis inside the collapsing bubbles, providing electrons for the reduction of metal cations. When these atoms are injected into the liquid phase, they nucleate and form NPs (Xu et al., 2013). In some cases, chemical reducing and stabilizing agents such as ethylene glycol and poly (vinylpyrrolidone), respectively, are added to the liquid phase in order to control the size and the shape of Pd NPs produced (Nemamcha et al., 2006). Figure 4B graphically illustrates this method.

Similar to electrochemical deposition, a chemical stabilizing agent should be added into the solution in order to synthesize size-controlled Pd NPs sonochemically. The size and shape of the NPs formed can be controlled by varying the concentration of the stabilizing agent, the current density, the ultrasonic intensity, and the interval between two continuous ultrasonic pulses (Qiu et al., 2003). Sonochemical preparation method is also used to synthesize substrate-supported Pd NPs, such as alumina-supported Pd NPs. For that, an alcohol additive is typically added to the solution in order to accelerate the reduction of Pd(II) ions. The size of supported-NPs can be controlled by varying the alcohol additive, the concentration of alcohol additive, and the concentration of the support particles (Okitsu et al., 1999; Okitsu et al., 2000).

Supercritical fluid nucleation

This method is based on the saturation of a supercritical fluid with a solid substrate, and the depressurization of the solution through a nozzle into a low-pressure chamber. This process results in the nucleation of the material of the substrate, generating NPs that are collected from the gaseous stream (Byrappa et al., 2008). There are different variants for this method, however, rapid expansion of supercritical solution (RESS) is the common variant used for Pd NPs synthesis, in which supercritical carbon dioxide is usually used as the supercritical fluid (Kameo et al., 2003). Figure 4C graphically illustrates this method.

Supercritical fluid nucleation is used to synthesize substrate-supported and functionalized Pd NPs (Cansell and Aymonier, 2009; Tang and Shim, 2015). For the synthesis of substrate-supported Pd NPs, the substate is mixed together with Pd precursor in a pressure reactor. The size of the NPs can be easily controlled by adjusting the concentration of the Pd precursor, for instance, adjusting the concentration of palladium (II) hexafluoroacetylacetonate in the process of synthesizing RGO (reduced graphene oxide)-supported Pd NPs (Tang and Shim, 2015). In addition, supercritical fluid nucleation has been used to synthesize Pd NPs functionalized with fluorinated and non-fluorinated alkyl moieties, Pd NPs capped with thiols, and Pd-impregnated Nafion membranes (Jiang et al., 2005; Moisan et al., 2008; Cansell and Aymonier, 2009). The synthesis of functionalized NPs using this approach is comparatively simple, as it limits the number of steps in the preparation of functional NPs. The size of the NPs formed can also be controlled by varying the solvent, and the operating parameters such as the temperature (Cansell and Aymonier, 2009).

Sol-gel method

This technique is based on the conversion of a colloidal solution (sol) into a gel composed of discrete metal NPs. This method involves five different stages: hydrolysis, condensation, ageing, drying, and calcination. Firstly, the NP precursor (a metal alkoxide) is dissolved in water or organic solvents to produce a homogenous solution. Then, an acid or base is added to the solution to achieve the hydrolysis/alcoholysis of the precursor, forming a colloidal solution. In a next step, the solvent is removed to achieve the condensation of adjacent molecules through metal linkages. Condensation occurs *via* two processes; the formation of a (-OH-) bridge between two metal centers (called olation), or the formation of (-O-) bridge between two metal centers (called oxolation). Both types of condensation increase the viscosity of the solution forming a porous structure called gel. Next, an aging step is done where the condensation of the solution continues slowly, decreasing the porosity and increasing the distance between colloidal particles. Then, the gel is thermally dried to evaporate the remaining solvent. Lastly, the dried gel is calcinated and grinded to form NP powders (Kumari et al., 2019). Figure 4D graphically illustrates this method.

The sol-gel method is used to synthesize Pd composites such as Pd@SiO_2 core-shell NPs (Hu et al., 2013; Li et al., 2014). The nanosized Pd cores are formed by reducing tetrachloropalladate with sodium borohydride reducing agent and tetradecyl trimethyl ammonium bromide (TTAB) as a stabilizing agent, then the silica shells were formed by using tetraethyl orthosilicate (TEOS). The size of NPs and the thickness of the shells can be controlled by varying the concentration of the chemicals, the molar ratios, and the pH value of the solutions (Hu et al., 2013).

Biological methods for Pd NP synthesis

There are several disadvantages for the physical and chemical methods used for Pd NPs synthesis. The physical methods

require energy-intensive instrumentation that include maintaining high temperature or pressure. The chemical methods may involve harmful solvents, hazardous chemical reducing or stabilization agents such as sodium borohydride and hydrazine, or produce toxic pollutants and by-products. In addition, the chemical synthesis of Pd NPs may result in adsorbing the chemical surfactants or toxic molecules on the surface of the NPs, which would compromise the use of these NPs in biomedical and pharmaceutical applications (Qazi et al., 2016; Vishnukumar et al., 2017; Fahmy et al., 2020; Manjare et al., 2021).

Recently, the biogenic synthesis of NPs has attracted attention from the scientific community as it could in principle provide simple, rapid, cost-effective, and potentially more environmentally friendly alternative processes for the synthesis of NPs. These processes are based on the use of naturally occurring biomolecules or metabolites from different organisms as reducing and stabilizing agents. In addition, these biogenic processes have been shown to offer very high levels of control over the properties of NPs, such as the size and shape (Qazi et al., 2016; Vishnukumar et al., 2017; Fahmy et al., 2020; Manjare et al., 2021).

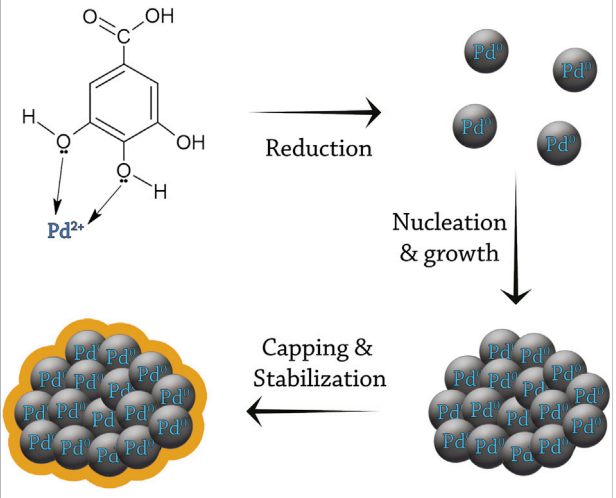

FIGURE 5
The mechanism of biogenic synthesis of Pd NPs. The chemical compound presented in this figure (gallic acid) is an example (Jia et al., 2009).

Mechanism of biogenic synthesis of Pd NPs

Biogenic synthesis of NPs can be achieved through plant-mediated, bacteria-mediated, algae-mediated, or fungi-mediated processes. For the synthesis of Pd NPs, a Pd precursor (Pd salt solution) is mixed with either a plant extract or with bacterial/algal/fungal biomass, usually at room temperature. The synthesis process immediately starts and frequently lasts no more than 2 hours, which is indicated by the color of the reaction medium (the color typically changes to dark brown or black) (Fahmy et al., 2020).

The exact mechanism of the biogenic synthesis of Pd NPs is not fully understood and requires more research, however, three major steps have been suggested. Firstly, Pd^{2+} ions need to be reduced to zerovalent Pd by acquiring electrons from a donor biomolecule or metabolite. Then, the reduced ions nucleate and start to grow and agglomerate together forming thermodynamically stable Pd NPs. Lastly, the synthesized NPs are capped by a variety of functional groups such as aldehydes, ketones, alcohols, amines, or carboxylic acids, which help in the stabilization of the NPs. The synthesized NPs can be of different sizes or form different shapes depending on the reaction conditions (Qazi et al., 2016; Vishnukumar et al., 2017; Fahmy et al., 2020; Manjare et al., 2021). Figure 5 graphically illustrates the three major steps of the biogenic synthesis of Pd NPs.

Plant-mediated synthesis of Pd NPs

Plants possess natural mechanisms for the detoxification of metal ions in the soil. These processes can be exploited for the purification of ground water and for coping with soil salinity (Manjare et al., 2021). The term phytoremediation has been coined for plant-based approaches for the extraction, removal, or for lowering the availability of soil pollutants (Yan et al., 2020). Phytoremediation includes several mechanisms depending on the plant in question and on the pollutant, such as phytoaccumulation, phytofiltration, phytostabilization, and phytodegradation (Ali et al., 2013). These mechanisms are the basis for the development of plant-mediated synthesis methods of NPs.

Plant-mediated synthesis of NPs is based on the bioactive compounds in plant extracts, which include polyphenols, alkaloids, terpenoids, flavonoids. These compounds are believed to be responsible for the reduction of metal ions into metal NPs (Vishnukumar et al., 2017). Extracts of various plant parts, *e.g.,* leaves, seeds, fruits, and roots, have been successfully employed to biologically synthesize Pd NPs with different sizes and shapes (Table 1). The size and morphology of plant-mediated Pd NPs are affected by Pd precursor concentration, the concentration of the plant extract, and the duration, temperature, and pH of the reaction (Qazi et al., 2016; Vishnukumar et al., 2017; Fahmy et al., 2020; Manjare et al., 2021).

Examples: leaf extract of *Anacardium occidentale* was used for the synthesis of 2.5–4.5 nm spherical Pd NPs. Fourier-transform infrared spectroscopy (FTIR) analysis showed the involvement of soluble polyols in the reduction of Pd ions, and of negatively charged carboxylate ions together with protein molecules in the stabilization of Pd NPs (Sheny et al., 2012). Several other plant extracts were also successfully used to produce small spherical Pd NPs with a narrow size distribution.

TABLE 1 Plant-mediated Pd NPs.

Plant	Plant part	NP size	NP shape	Pd precursor	Ref.
Allium cepa L.	Bulb extract	19 nm	Spherical	$PdCl_2$	Liu and Wu (2017)
Anacardium occidentale	Leaf extract	2.5–4.5 nm	Spherical	$PdCl_2$	Sheny et al. (2012)
Ananas comosus	Leaf extract	1–16 nm	Spherical	$PdCl_2$	Olajire and Mohammed. (2019)
Annona squamosa L.	Peel extract	80 nm	Spherical	$Pd(OAc)_2$	Roopan et al. (2012)
Anogeissus latifolia	Plant gum	2–8 nm	Spherical	$PdCl_2$	Kora and Rastogi (2018)
Antigonon leptopus	Plant extract	5–70 nm	Spherical	$PdCl_2$	Ganaie et al. (2016)
Artemisia abrotanum	Leaf extract	-	Spherical	Na_2PdCl_4	Salehi et al. (2019)
Artemisia annua	Leaf extract	20–30 nm	Spherical	$PdCl_2$	Edayadulla et al. (2015)
Artocarpus lakoocha Roxb	Hearth wood	10–30 nm	Spherical	$PdCl_2$	Baruah et al. (2015)
Aspalathus linearis	Leaf extract	4–22 nm	Several shapes	$PdCl_2$	Ismail et al. (2017)
Asparagus racemosus L.	Root extract	1–6 nm	Spherical	$PdCl_2$	W Raut et al. (2013)
Astraglmanna	Plant extract	5–25 nm	Spherical	$PdCl_2$	Farhadi et al. (2013)
Barleria prionitis	Leaf extract	5–7 nm	Spherical	$PdCl_2$	Rokade et al. (2017)
Bauhinia variegata	Bark extract	1–9 nm	Cylindrical	$PdCl_2$	Vaghela et al. (2018)
Beta vulgaris	Juice	5 nm	Spherical	-	Kou and Varma (2012)
Berberis vulgaris	Fruit extract	18 nm	Spherical	$PdCl_2$	Nasrollahzadeh et al. (2016)
Boswellia serrata	Gum	2–9 nm	Spherical	$PdCl_2$	Kora and Rastogi (2016)
Cacumen platyclade	Leaf extract	6–8 nm	Spherical	$Pd(NO_3)_2$	Lu et al. (2014)
Camellia sinensis	Leaf extract	5–8 nm	Spherical	$PdCl_2$	Lebaschi et al. (2017)
Catharanthus roseus	Leaf extract	38 nm	Spherical	$Pd(OAc)_2$	Kalaiselvi et al. (2015)
Cinnamomum camphora L.	Leaf extract	3–6 nm	Quasi-spherical	$PdCl_2$	Yang et al. (2010)
Cinnamomum zeylanicum	Bark extract	15–20 nm	Spherical	$PdCl_2$	Sathishkumar et al. (2009a)
Cissus quadrangularis	Stem extract	12–26 nm	Spherical	$PdCl_2$	Anjana et al. (2019)
Citrullus lanatus	Rind extract	96 nm	Spherical	$PdCl_2$	Lakshmipathy et al. (2015)
Cochlospermum gossypium	Gum	1–12 nm	Spherical	$PdCl_2$	Rastogi et al. (2017)
Cocos nucifera	Coir extract	62 nm	Spherical	$Pd(OAc)_2$	Elango et al. (2017)
Coleus amboinicus	Leaf extract	16–23 nm	Spherical	$PdCl_2$	Bathula et al. (2020)
Colocasia esculenta L.	Leaf extract	-	Irregular	$PdCl_2$	KumaráBorah et al. (2015)
Couroupita guianensis Aubl	Fruit extract	5–15 nm	Spherical	$PdCl_2$	Gnanasekar et al. (2018)
Curcuma longa	Tuber extract	15–20 nm	Spherical	$PdCl_2$	Sathishkumar et al. (2009b)
Delonix regia	Leaf extract	2–4 nm	Not given	$PdCl_2$	Dauthal and Mukhopadhyay (2013)
Dioscorea bulbifera	Tuber extract	10–20 nm	Spherical	$PdCl_2$	Ghosh et al. (2015)
Diospyros kaki	Leaf extract	50–120 nm	Spherical	$PdCl_2$	Attar and Altikatoglu Yapaoz (2018)
Eclipta prostrata	Leaf extract	27 nm	Spherical	$Pd(OAc)_2$	Rajakumar et al. (2015)
Eryngium caeruleum	Plant extract	5–25 nm	Spherical	$PdCl_2$	Saleh et al. (2021)
Eucommia ulmoides	Bark extract	10–20 nm	Spherical	$PdCl_2$	Duan et al. (2015)
Euphorbia granulate	Leaf extract	25–30 nm	Irregular	$PdCl_2$	Nasrollahzadeh and Sajadi (2016c)
Euphorbia thymifolia L.	Leaf extract	20–30	Spherical	$PdCl_2$	Nasrollahzadeh et al. (2015c)
Evolvulus alsinoides	Leaf extract	5 nm	Spherical	$PdCl_2$	Gurunathan et al. (2015)
Filicium decipiens	Leaf extract	2–22 nm	Spherical	$PdCl_2$	Sharmila et al. (2017b)
Gardenia jasminoides Ellis	Fruit extract	3–5 nm	Spherical	$PdCl_2$	Jia et al. (2009)
Gloriosa superba	Tuber extract	5–8 nm	Spherical	$PdCl_2$	Rokade et al. (2018)
Glycine max	Leaf extract	15 nm	Spherical	$PdCl_2$	Kumar Petla et al. (2012)
Camellia sinensis	Leaf extract	1–25 nm	Spherical	Pd/C	Palliyarayil et al. (2018)
Hibiscus sabdariffa L.	Flower extract	5–8 nm	Spherical	$PdCl_2$	Hekmati et al. (2017)
Hippophae rhamnoides L.	Leaf extract	2.5–14 nm	Spherical	$PdCl_2$	Nasrollahzadeh et al. (2015d)
Lagenaria Siceraria	Peel extract	16–73 nm	Spherical	$Pd(OAc)_2$	Kalpana and Rajeswari (2018)
Lithodora hispidula (Sm.) Griseb	Leaf extract	22 nm	Rod-shaped	K_2PdCl_4	Turunc et al. (2017)

(Continued on following page)

TABLE 1 (*Continued*) Plant-mediated Pd NPs.

Plant	Plant part	NP size	NP shape	Pd precursor	Ref.
Melia azedarach	Leaf extract	10–20 nm	Spherical	$PdCl_2$	Bhakyaraj et al. (2017)
Moringa oleifera	Flower extract	2–18 nm	Spherical	$Pd(OAc)_2$	Anand et al. (2016)
Moringa oleifera	Peel extract	27 nm	Spherical	$Pd(OAc)_2$	Surendra et al. (2016)
Musa paradisiaca	Peel extract	50 nm	Irregular	$PdCl_2$	Bankar et al. (2010)
Origanum vulgare L.	Plant extract	2.2 nm	Spherical	$PdCl_2$	Shaik et al. (2017)
Parthenium hysterophorus	Leaf extract	2–6 nm	Spherical	$PdCl_2$	Naqvi et al. (2021)
Peganum harmala L.	Seed extract	16–32 nm	Spherical	$Pd(OAc)_2$	Fahmy et al. (2021)
Pelargonium graveolens	Leaf extract	50–140 nm	Spherical	$PdCl_2$	Li et al. (2017)
Phoenix dactylifera	Leaf extract	2–25 nm	Spherical	$PdCl_2$	Tahir et al. (2016b)
Phyllanthus emblica	Seed extract	28 nm	Spherical	$Pd(OAc)_2$	Dinesh et al. (2017)
Pinus spp.	Needle extract	1–21 nm	Spherical	Na_2PdCl_4	Liu et al. (2017)
Piper betle	Leaf extract	4 nm	Spherical	$PdCl_2$	Mallikarjuna et al. (2013)
Piper longum	Fruit extract	5–40 nm	Spherical	$PdCl_2$	Nasrollahzadeh et al. (2015e)
Piper nigrum	Seed extract	2–7 nm	Spherical	$Pd(OAc)_2$	Kandathil et al. (2018)
Pistacia atlantica	Fruit extract	60 nm	Spherical	$PdCl_2$	Molaie et al. (2012)
Prunus × *yedoensis*	Leaf extract	50–150 nm	Spherical	$PdCl_2$	Manikandan et al. (2016)
Pulicaria glutinosa	Plant extract	20–25 nm	Spherical	$PdCl_2$	Khan et al. (2014)
Punica granatum	Peel extract	20–24 nm	Spherical	$PdCl_2$	Ün et al. (2021)
Quercus	Fruit gum	5–7 nm	Spherical	$PdCl_2$	Veisi et al. (2016a)
Vitis vinifera	Pomace extract	5–10 nm	Spherical	Na_2PdCl_4	Baruwati and Varma (2009)
Rosa canina	Fruit extract	7–10 nm	Spherical	$PdCl_2$	Veisi et al. (2016b)
Rosmarinus officinalis	Leaf extract	15–90 nm	Several shapes	$Pd(OAc)_2$	Rabiee et al. (2020)
Rubus glaucus Benth	Leaf extract	55–60 nm	Decahedral	K_2PdCl_6	Kumar et al. (2015)
Salvadora persica L.	Root extract	2.2–15 nm	Spherical	$PdCl_2$	Khan et al. (2017)
Salvia hispanica	Leaf extract	9–20 nm	Semi-Spherical	$PdCl_2$	Kiani et al. (2020)
Santalum album	Leaf extract	10–40 nm	Spherical	$PdCl_2$	Sharmila et al. (2017a)
Sapium sebiferum	Leaf extract	5 nm	Spherical	$PdCl_2$	Tahir et al. (2016a)
Saururus chinensis	Leaf extract	2–10 nm	Spherical	$PdCl_2$	Basavegowda et al. (2016)
Silybum marianum	Seed extract	10–25 nm	Spherical	$PdCl_2$	Gopalakrishnan et al. (2017)
Solanum nigurum	Leaf extract	3–35 nm	Spherical	$PdCl_2$	Vijilvani et al. (2020)
Solanum trilobatum	Leaf extract	60–100 nm	Spherical	$PdCl_2$	Kanchana et al. (2010)
Prunus cerasus	Gum	2.5–15 nm	Spherical	$PdCl_2$	Nasrollahzadeh (2014)
Syzygium aromaticum	Bud extract	20–25 nm	Spherical	$PdCl_2$	Shanthi et al. (2017)
Camellia sinensis & *Coffea arabica*	Leaf and dried seed	20–60 nm	Spherical	$PdCl_2$	Nadagouda and Varma (2008)
Terminalia chebula	Fruit extract	80–100 nm	Cubic	$PdCl_2$	Kumar et al. (2013)
Trigonella foenum	Seed extract	113 nm	Irregular	$PdCl_2$	Nazeruddin et al. (2014)
Urtica	Leaf extract	3–12 nm	Irregular	$PdCl_2$	Gulbagca et al. (2021)

A fruit extract of *Gardenia jasminoides* Ellis yielded 3–5 nm spherical Pd NPs. In this case, FTIR analysis showed that the antioxidants present in the crude water extract of the fruit (such as geniposide, chlorogenic acid, crocins and crocetin), were involved in the production of Pd NPs, and that the properties of the Pd NPs are temperature-dependent. At different temperatures ranging from 40 to 90°C, the synthesis reaction produced Pd NPs where the size, shape, and dispersity change systematically (Jia et al., 2009). Other examples include the tuber extract of *Gloriosa superba* (Rokade et al., 2018), the leaf extract of *Parthenium hysterophorus* (Ahsan et al., 2020), and the seed extract of *Piper nigrum* (Kandathil et al., 2018) that also produced small spherical NPs with narrow size distributions between 5 and 8 nm, 2 and 6 nm, and 2 and 7 nm, respectively.

Other plant extracts can yield larger spherical Pd NPs or NPs populations with wide size distributions. The Pd NPs produced by the fruit peel extract of *Annona squamosa* L. (Roopan et al., 2012) and rind extract of *Citrullus lanatus* (Lakshmipathy et al., 2015) were 80 nm and 96 nm, respectively. For *Annona squamosa* L., the exact reducing molecule was not identified,

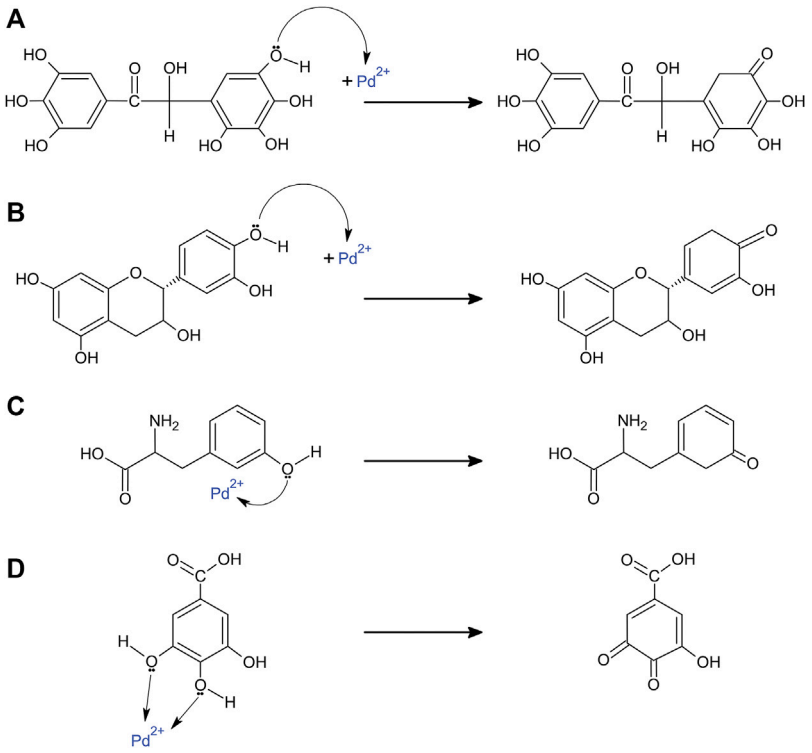

FIGURE 6
Suggested plant compounds responsible for the reduction of Pd^{2+} ions. **(A)** 6-O-galloyl-D-glucose (*Sapium sebiferum,* produces 5 nm spherical Pd NPs), **(B)** catechin (*Phoenix dactylifera,* produces 2–25 nm spherical Pd NPs), **(C)** tyrosine (*Glycine max,* produces 15 nm spherical Pd NPs), and **(D)** gallic acid (*Delonix regia,* produces 2–4 nm Pd NPs).

however, aldehyde and hydroxyl functional groups were found to be involved as capping agent for the synthesized NPs. For *Citrullus lanatus*, the reduction and capping of Pd NPs was dependent on polyhydroxylated molecules. Regarding the large size distribution, leaf extracts of *Pelargonium graveolens* (Li et al., 2017) and *Prunus* × *yedoensis* (Manikandan et al., 2016) yielded 50–140 nm NPs and 50–150 nm NPs, respectively. The reason why some plant extracts produce Pd NPs with a narrow size distribution and others with a broad size distribution is unknown. However, we speculate that the large size distribution is due to the presence of several biomolecules that could act as reducing and capping agents in parallel, each resulting in a differently sized Pd NPs.

The shape of plant-mediated NPs is not limited to spherical particles. Several plant extracts were found to synthesize Pd NPs with distinct shapes. The bark extract of *Bauhinia variegata* produced 1–9 nm cylindrical Pd NPs (Vaghela et al., 2018), the leaf extract of *Lithodora hispidula* (Sm.) Griseb produced 22 nm rod-shaped Pd NPs (Turunc et al., 2017), the leaf extract of *Rubus glaucus* Benth. produced 55–60 nm decahedral Pd NPs (Kumar et al., 2015), and the fruit extract of *Terminalia chebula* produced 80–100 nm cubic Pd NPs (Kumar et al., 2013). The shape of the biogenically synthesized Pd NPs in these examples was attributed to the biomolecules acting as reducing and capping agents, or to the specific reaction conditions.

Only in some cases, the specific reducing agent/s responsible for reducing Pd^{2+} to Pd^{0} in the extract solutions were identified or at least investigated in some detail. For the leaf extract of *Sapium sebiferum*, the phenolic compound 6-O-galloyl-D-glucose was suggested as the reducing agent of Pd^{2+}. This compound donates one electron per molecule from one of its hydroxyl groups (Figure 6A). As a result, the leaf extract of this plant produces 5 nm spherical Pd NPs (Tahir et al., 2016a). Another phenolic compound was found in the leaf extract of *Phoenix dactylifera*; catechin also donates one electron per molecule from one of it hydroxyl groups (Figure 6B), producing 2–25 nm spherical Pd NPs (Tahir et al., 2016b). For the leaf extract of *Glycine max*, the amino acid tyrosine was suggested to be the main reducing agent of Pd^{2+} (Figure 6C). The leaf extract of this plant produces 15 nm spherical Pd NPs (Kumar Petla et al., 2012). For the leaf extract of *Delonix regia*, different phenolic compounds, namely gallic acid, protocatechuic acid, 3-hydroxybenzoic acid, and catechin, were suggested as electron donors for the reduction of Pd^{2+} ions. Unlike the aforementioned compounds, gallic acid donates two electrons per molecule from two of its hydroxyl groups, thus, only one molecule is needed for the complete reduction of one

TABLE 2 Biogenic bimetallic, trimetallic, and substrate-supported Pd NPs.

Organism	Type of NP	NP size	NP shape	NP precursors	Ref.
Bacillus benzeovorans	RuPd NPs	1–8 nm	Spherical	Na_2PdCl_4 and $RuCl_3$	Omajali et al. (2019)
Myrica gale tannin	AuPd NPs	5–40 nm	Spherical	$PdCl_2$ and $HAuCl_4$	Huang et al. (2011)
Berberis vulgaris	Pd/RGO NPs	18 nm	Spherical	$PdCl_2$ and GO	Nasrollahzadeh et al. (2016)
Cacumen platycladi	AgPd NPs	7–13 nm	Spherical	$Pd(NO_3)_2$ and $AgNO_3$	Lu et al. (2014)
Cacumen platycladi	AuPd NPs	5–9 nm	Spherical	$PdCl_2$ and $HAuCl_4$	Zhan et al. (2011)
Cacumen platycladi	AuPd/TiO_2 NPs	20–30 nm	Spherical	$Pd(NO_3)_2$, $HAuCl_4$, and TiO_2	Hong et al. (2014)
Cacumen platycladi	AuPd/MgO NPs	9.7 nm	Spherical	$PdCl_2$, $HAuCl_4$, and MgO	Zhan et al. (2012)
Coffea arabica	PtPd/RGO NPs	100 nm	Spherical	$PdCl_2$ and H_2PtCl_6	Feng et al. (2014)
Dioscorea bulbifera	PtPd NPs	20–25 nm	Irregular	$PdCl_2$ and H_2PtCl_6	Ghosh et al. (2015)
Escherichia coli MC4100	AuPd NPs	16 nm	Quasi-spherical	Na_2PdCl_4 and $HAuCl_4$	Deplanche et al. (2012)
Escherichia coli MC4100	PtPd NPs	50 nm	Spherical	Na_2PdCl_4 and K_2PtCl_6	Murray et al. (2018)
Euphorbia condylocarpa M.Bieb.	Pd/Fe_3O_4 NPs	39 nm	Irregular	$PdCl_2$ and $FeCl_3$	Nasrollahzadeh et al. (2015a)
Euphorbia condylocarpa M.Bieb.	AuPd NPs	80 nm	Irregular	$PdCl_2$ and $HAuCl_4$	Nasrollahzadeh et al. (2014)
Euphorbia stracheyi Boiss.	Pd/Fe_3O_4 NPs	10 nm	Spherical	$PdCl_2$ and $FeCl_3$	Nasrollahzadeh and Sajadi (2016a)
Fritillaria imperialis	Pd/Fe_3O_4 NPs	20–30 nm	Quasi-spherical	Na_2PdCl_4 and $FeCl_2$	Veisi et al. (2021)
Vitis vinifera	FePd NPs	2–20 nm	Quasi-spherical	$PdCl_2$ and $FeCl_2$	Luo et al. (2016)
Camellia sinensis	FePd NPs	20–30 nm	Spherical	K_2PdCl_4 and $FeCl_2$	Smuleac et al. (2011)
Lithodora hispidula (Sm.) Griseb	AgPd NPs	-	Rod	K_2PdCl_4 and $AgNO_3$	Turunc et al. (2017)
Myrtus communis L.	Pd/TiO_2 NPs	17–25 nm	Spherical	$PdCl_2$ and Degussa P-25 TiO_2	Nasrollahzadeh and Sajadi (2016b)
Peganum harmala L.	PtPd NPs	24–44 nm	Spherical	$Pd(OAc)_2$ and $PtCl_4$	Fahmy et al. (2021)
Piper longum	Pd/natrolite zeolite	6–26 nm	Spherical	$PdCl_2$ and natrolite zeolite	Hatamifard et al. (2015)
Shewanella oneidensis	AuPd NPs	1–20 nm	Spherical	Na_2PdCl_4 and $AuCl_3$	Kimber et al. (2021)
Shewanella oneidensis	AgPd NPs	1–60 nm	Spherical	Na_2PdCl_4 and $AgNO_3$	Kimber et al. (2021)
Syzygium aromaticum and *Aegle marmelos*	AgAuPd NPs	8–11 nm	Spherical	$PdCl_2$, $AgNO_3$, and $HAuCl_4$	Rao and Paria, (2015)
Theobroma cacao L.	Pd/CuO NPs	40 nm	Irregular	$PdCl_2$ and $CuCl_2$	Nasrollahzadeh et al. (2015b)
Withania coagulans	Pd/RGO/Fe_3O_4 NPs	7–13 nm	Spherical	$PdCl_2$, $FeCl_3$, and GO	Atarod et al. (2016)

Pd^{2+} ion (Figure 6D). The leaf extract of *Delonix regia* produces 2–4 nm Pd NPs (Dauthal and Mukhopadhyay, 2013).

In addition to monometallic Pd NPs, bimetallic, trimetallic, and substrate-supported Pd NPs can also be made using plant extracts (Table 2). For bimetallic Pd NPs, 5–40 nm spherical AuPd NPs were produced by *Myrica gale* tannin in a one-step reduction reaction. The synthesized NPs had an Au core and Pd shell structure. Interestingly, the researchers found that changing the molar ratio of Au^{3+}/Pd^{2+} and the concentration of *Myrica gale* tannin results in changes on the morphology of the Pd shell from spherical to cubic. Adding Au^{3+} and Pd^{2+} in a 1:1 M ratio with 0.4 g/L *Myrica gale* tannin resulted in the synthesis of AuPd NPs with a cubic Pd shell, in which some of these bimetallic NPs had multiple Au cores per Pd shell. By decreasing the concentration of *Myrica gale* tannin to 0.1 g/L, spherical Pd shells were generated. Modifying the molar ratio of Au^{3+}/Pd^{2+} from 1:1 to 2:1 also resulted in the synthesis of spherical Pd shells (Huang et al., 2011). Many other examples for the production of bimetallic Pd NPs using various plant extracts exist. The seed extract of *Peganum harmala* L. produced 24–44 nm spherical PtPd bimetallic NPs (Fahmy et al., 2021). *Camellia sinensis* and *Vitis vinifera* leaf extracts produced 20–30 nm and 2–20 nm FePd bimetallic NPs, respectively (Smuleac et al., 2011; Luo et al., 2016). The leaf extract of *Cacumen platyclade* produced 7–13 nm AgPd bimetallic NPs (Lu et al., 2014).

Plant extracts can also be used to produce monometallic or bimetallic Pd NPs supported on different oxide substrates. The root extract of *Euphorbia condylocarpa* M. Bieb. (Nasrollahzadeh et al., 2015a). and *Euphorbia stracheyi* Boiss. (Nasrollahzadeh and Sajadi, 2016a). and the flower extract of *Fritillaria imperialis* (Veisi et al., 2021) were used to produce monometallic Pd NPs supported on Fe_3O_4. The parameters of the biosynthesized NPs were different in each case, being 39 nm with irregular shapes, 10 nm spherical, and 20–30 nm quasi-spherical, respectively. The fruit extract of *Berberis vulgaris* produced 18 nm spherical Pd NPs supported on RGO (reduced graphene oxide) (Nasrollahzadeh et al., 2016), while the fruit extract of *Piper longum* produced 6–26 nm spherical Pd NPs supported on natrolite zeolite (Hatamifard et al., 2015). The seed extract of *Theobroma cacao* L. was used to produce 40 nm Pd NPs supported on CuO (Nasrollahzadeh et al., 2015b). The leaf extract of *Myrtus communis* L. yielded 17–25 nm spherical Pd

NPs supported on TiO_2 (Nasrollahzadeh and Sajadi, 2016b). Other plant extracts were successfully used to synthesize bimetallic Pd NPs supported on different oxide substrates. For instance, the leaf extract of *Cacumen platycladi* was used to produce 20–30 nm spherical AuPd NPs supported on TiO_2 (Hong et al., 2014), and 9.7 nm spherical AuPd NPs supported on MgO (Zhan et al., 2012). Even trimetallic Pd NPs can be synthesized using plant extracts. For this, the extract of two plants was used to provide the reducing and capping agents required for the biosynthesis of trimetallic-alloy NPs. The bud extract of *Syzygium aromaticum* together with the leaf extract of *Aegle marmelos* was used to produce 8–11 nm spherical AgAuPd NPs (Rao and Paria, 2015).

Bacteria-mediated synthesis of Pd NPs

Unlike in the case of plant extracts, bacteria-mediated synthesis of Pd NPs requires live bacteria for the reduction and formation of Pd NPs. The first report of bacteria able to produce Pd NPs was on the anaerobic sulfate-reducing bacterium *Desulfovibrio desulfuricans* (Lloyd et al., 1998). The bacterial biomass was mixed with a Pd precursor and with external, bioavailable electron donors (sodium pyruvate, formate, or H_2 gas) simultaneously. The color of the reaction medium changed to black within 10 min and the color intensified within up to 24 h. The controls (heat-killed bacterial biomass and live biomass lacking the electron donors) did not undergo any color change. The examination of bacteria under Transmission electron microscopy (TEM) revealed the deposition of 50 nm Pd NPs in the periplasmic space, whereas the controls did not show any NPs. This strongly suggested that the reduction of Pd^{2+} ions to elemental Pd is based on the action of enzymes. The researchers suspected the involvement of hydrogenase enzymes in this process. Therefore, they inhibited those enzymes by adding 0.5 mM Cu^{2+}. They found that Cu^{2+}-treated bacterial solution did not change in color and did not show any Pd NPs in TEM. This supported the direct involvement of hydrogenase enzymes in the reduction of Pd^{2+} ions (Lloyd et al., 1998).

A second bacterium able to synthesize Pd NPs is the dissimilatory metal-reducing species *Shewanella oneidensis MR-1* (De Windt et al., 2005). In that study, three main variables were tested: different electron donors, alternative electron acceptors, and the atmospheric conditions (aerobic or anaerobic). It was found that all tested electron donors resulted in the bioreduction of Pd^{2+} and formation of Pd NPs. However, formate and H_2 resulted in larger amounts of NPs than pyruvate, lactate, and ethanol. The addition of alternative electron acceptors such as nitrate and the exposure to oxygen did not affect the formation of Pd NPs. The synthesized Pd NPs were deposited on the outer membrane and in the periplasmic space of the bacteria. Pd NPs synthesized in the presence of H_2 as an electron donor were smaller than those formed in the presence of formate. In this paper, the researchers also suggested the involvement of hydrogenase enzymes in the process of Pd NPs synthesis.

Another sulfate-reducing bacterium, *Desulfovibrio fructosivorans*, was reported for its ability for synthesize Pd NPs (Mikheenko et al., 2008). In that study, the deposition of Pd NPs was tested for the wildtype and for mutants lacking the periplasmic NiFe hydrogenase gene, the periplasmic Fe hydrogenase gene, or both. It was found that the wildtype strain deposited small Pd NPs on both the cytoplasmic and outer membranes, while the mutant lacking both hydrogenase gene deposited large Pd NPs only on the cytoplasmic membrane. The researchers suggested that the role of periplasmic hydrogenases is to serve as a nucleation site assisting Pd NPs growth, where their gene knock-out experiments result in the absence of Pd NPs in the outer membrane.

Bacteria-mediated Pd NPs synthesis is not limited to sulfate- and metal-reducing bacteria. Two strains of cyanobacteria (*Calothrix pulvinate* and *Anabaena flos-aquae*) (Brayner et al., 2007), *Clostridium pasteurianum* (Chidambaram et al., 2010), and different gram-negative *alpha-*, *beta-* and *Gamma-proteobacteria* bacteria, including *Paracoccus denitrificans*, *Cupriavidus necator* H16, and *Pseudomonas putida* (Bunge et al., 2010), were reported to have the ability to synthesize Pd NPs. For the latter three species, 3–30 nm Pd NPs were synthesized in the periplasmic space when using formate as electron donor. In these cases, Pd NPs synthesis also proceeds in autoclaved cells where all proteins are inactivated, thus ruling out the direct involvement of hydrogenases in the synthesis of Pd NPs. For cyanobacteria, the nitrogenase enzyme complex was suggested to be responsible for the reduction of Pd^{2+} ions to metallic Pd.

Also the model bacterium *E. coli* can synthesize Pd NPs (Deplanche et al., 2010). In general, the biogenic synthesis process of Pd NPs is divided into two separate steps: the bacterial biosorption or uptake of Pd^{2+} ions from the reactions medium, and the reduction of Pd^{2+} ions to elemental Pd inside the bacteria (in the periplasm and/or the cytoplasm). In this study, the ability of *E. coli* wildtype and mutants lacking the genes encoding hydrogenase enzymes were assessed for their ability to take up and reduce Pd^{2+} ions. None of the mutants lost its ability to take up Pd^{2+} ions from the medium, suggesting that the three hydrogenases present in *E. coli* (Hyd-1, Hyd-2, and Hyd-3) are not involved in this step. For the reduction step, the mutants having only Hyd-1 or Hyd-2 did not show any significant difference compared to the wildtype. The mutant having only Hyd-3 was significantly slower in the reduction of Pd^{2+} ions. Hyd-1 and Hyd-2 hydrogenases are periplasmic hydrogenases (the catalytic subunit is exposed to the periplasmic side of the membrane), and apparently the presence of one of these hydrogenases is enough to reduce Pd^{2+} in the periplasm (where Pd^{2+} ions are expected to be). The catalytic subunit of

TABLE 3 Bacteria-mediated Pd NPs.

Bacterium	NP location	NP size	NP shape	Pd precursor	Ref.
Anabaena flos-aquae	Extra/Intracellular	3.2 nm	Spherical	$Pd(NO_3)_2$	Brayner et al. (2007)
Bacillus benzeovorans	Intracellular	1–8 nm	Icosahedral	Na_2PdCl_4	Omajali et al. (2015)
Bacillus megaterium Y-4	Extra/Intracellular	10–40 nm	Spherical	Na_2PdCl_4	Chen et al. (2019)
Bacillus Sphaericus	Periplasmic space	1–6 nm	Spherical	Na_2PdCl_4	Creamer et al. (2007)
Bacillus wiedmannii MSM	Periplasmic space	10–36 nm	Oval	Na_2PdCl_4	Chen et al. (2018)
Bacteroides vulgatus	—	—	—	Na_2PdCl_4	Hennebel et al. (2011)
Calothrix pulvinate	Extra/Intracellular	3.5 nm	Spherical	$Pd(NO_3)_2$	Brayner et al. (2007)
Citrobacter braakii	Extracellular	—	—	Na_2PdCl_4	Hennebel et al. (2011)
Citrobacter sp	Extracellular	17–26 nm	Irregular	$Pd(NH_3)_4Cl_2$	Matsena and Chirwa (2021)
Clostridium butyricum	Extracellular	—	—	Na_2PdCl_4	Hennebel et al. (2011)
Clostridium pasterianum	Extra/Intracellular	11.8 nm	Spherical	Na_2PdCl_4	Chidambaram et al. (2010)
Cupriavidus metallidurans CH34	Extra/Intracellular	2–40 nm	Dendrite	—	Tan et al. (2020)
Cupriavidus necator H16	Periplasmic space	1–25 nm	Spherical	Na_2PdCl_4	Søbjerg et al. (2011)
Desulfovibrio desulfuricans	Intracellular	1–2 nm	Icosahedral	Na_2PdCl_4	Omajali et al. (2015)
Desulfovibrio fructosivorans	Periplasmic space	—	Spherical	Na_2PdCl_4	Mikheenko et al. (2008)
Desulfovibrio vulgaris	Periplasmic space	—	—	Na_2PdCl_4	Zhang et al. (2006)
Enterococcus faecium	—	—	—	Na_2PdCl_4	Hennebel et al. (2011)
Escherichia coli MC4100	Extra/Intracellular	—	Spherical	Na_2PdCl_4	Deplanche et al. (2010)
Escherichia coli BL21	Intracellular	1–5 nm	Spherical	$PdCl_2$	Bachar et al. (2020)
Geobacter sulfurreducens	Extra/Intracellular	10–25 nm	Irregular	Na_2PdCl_4	Yates et al. (2013)
Klebsiella pneumoniae	—	—	—	Na_2PdCl_4	Hennebel et al. (2011)
Paracoccus denitrificans	Periplasmic space	3–30 nm	Spherical	Na_2PdCl_4	Bunge et al. (2010)
Plectonema boryanum UTEX 485	Extracellular	1–20 nm	Spherical	$PdCl_2$	Lengke et al. (2007)
Pseudomonas putida	Periplasmic space	3–30 nm	Spherical	Na_2PdCl_4	Bunge et al. (2010)
Rhodobacter sphaeroides	Periplasmic space	3–10 nm	Irregular	Na_2PdCl_4	Redwood et al. (2008)
Shewanella loihica PV-4	Extra/Intracellular	4–10 nm	Spherical	Na_2PdCl_4	Wang et al. (2018)
Shewanella oneidensis MR-1	Extracellular	2–12 nm	Spherical	Na_2PdCl_4	Zhang et al. (2022)
Staphylococcus sciuri	Extracellular	1–25 nm	Spherical	Na_2PdCl_4	Søbjerg et al. (2011)

Hyd-3 is facing the cytoplasm, and thus cannot fully reduce the Pd ions in the periplasm efficiently. The mutant lacking all the three hydrogenases was found to lose the ability to reduce Pd^{2+} into Pd NPs completely. Therefore, the hydrogenases are key enzymes for the reduction of Pd^{2+} ions in *E. coli*. Under TEM, the mutants having only Hyd-1, Hyd-2, or Hyd-3 hydrogenases showed somewhat different patterns of Pd NP deposition. For the mutant lacking these three hydrogenases, all the periplasmic and cytoplasmic small Pd NPs were not present. Instead, big clumps of Pd were deposited on the surface of the bacteria. These big clumps of Pd were suggested to be formed chemically rather than biologically at a slower rate compared to the biogenic process (Deplanche et al., 2010). After reports that Pd NPs can be synthesized under fermentative conditions in *Clostridium pasteurianum* (Chidambaram et al., 2010) and *E. coli* (Deplanche et al., 2010), Hennebel et al. (2011) tested five additional bacterial species (*Bacteroides vulgatus, Citrobacter braakii*, *Clostridium butyricum*, *Enterococcus faecium*, and *Klebsiella pneumoniae*) under fermentative conditions for their ability to produce biogenic Pd NPs. All species were able to reduce Pd^{2+} and to form crystalline Pd^0 NPs under fermentative conditions. The researchers suspected that the H_2 produced during the fermentation process was the reducing agent of Pd^{2+} ions. However, in a control experiment where the cells were centrifuged and resuspended in fresh medium to remove H_2 before the addition of Pd precursor, Pd NPs were also observed at the cell surfaces. Therefore, it was concluded that Pd^{2+} ions are reduced enzymatically, by H_2, or by a combination of the two processes. The selected bacterial species have different metabolic pathways and produce different amounts of H_2 gas per 1 molecule of glucose. However, no correlation between the reduction of Pd^{2+} and the amount of H_2 produced was found. The difference in Pd NP deposition patterns among the species was attributed to the differences in cell structure and composition, enzyme production, Pd toxicity resistance, and fermentation product type and its distribution.

New reports of bacterial strains and species able to synthesize Pd NPs (Table 3), along with methods to optimize the reaction

conditions and control the yield or the properties of Pd NPs are continuously published. Great efforts have been made in order to understand the influence of different abiotic factors on the biogenic synthesis of Pd NPs, and to characterize Pd NPs produced by different microorganisms (Omajali et al., 2015; Chen et al., 2018; Chen et al., 2019; Bachar et al., 2020; Tan et al., 2020). Other studies demonstrate the successful production of bimetallic Pd NPs such as Pd/Au, Pd/Ag, Pd/Pt, and Pd/Ru NPs using various bacterial strains (Murray et al., 2018; Omajali et al., 2019; Kimber et al., 2021). But despite these efforts, we are not much closer to understanding the underlying biological mechanisms for the formation of Pd NPs. No other enzymes or proteins except for the hydrogenases have been reported to be involved until recently.

In 2020, Matsumoto et al. (2020) performed a high-throughput experiment for the identification of genes responsible for the reduction of Pd ions in *E. coli*. The researchers screened the Keio collection, a single-gene knockout library of *E. coli* BW25113 (Baba et al., 2006). The difference in Pd-ion reduction ability for approximately 4000 mutants was measured through the change in the optical density (OD_{600}) between the mutants and the wildtype (relative reduction rate). The results showed that seven knock-out strains had a relative reduction rate increased more than 1.5-fold, suggesting that the genes missing in those knock-outs were repressing Pd reduction. At the same time, 261 knock-outs had a relative reduction rate decreased more than 0.5-fold (73 of which had a relative reduction rate lower than 0.3-fold), suggesting that the genes missing in those knock-outs are participating in Pd ion reduction. No single-gene knock-out had a relative reduction rate of zero, suggesting that the reduction process of Pd ions is complicated and is not carried out by only a single enzyme or protein.

The genes repressing Pd reduction were related to membrane transport, transcriptional regulation, and metabolism. The researchers believe that the deletion of transcriptional regulators has broad effects on metabolism and physiology, while the deletion of membrane transport or metabolic enzyme genes can directly affect Pd ion reduction. Therefore, these genes can be candidate genes for repressing Pd reduction. The list of the genes promoting Pd reduction included 3 genes from formate metabolism. The authors highlight that formate metabolism genes could be directly involved in Pd ion reduction since formate was used as an external electron donor for the synthesis of Pd NPs. Therefore, their knock-out directly affected the reduction of Pd ions (Matsumoto et al., 2020). However, these results provide just a list of candidate genes that might be involved in Pd reduction, therefore, more work is needed to find out the role of each of these genes.

Other examples of biologically-mediated synthesis of Pd NPs

In addition to plants and bacteria, other organisms such as algae, yeast, and fungi are also able to biologically synthesize Pd NPs with different sizes and shapes (Table 4). Several algal species have been successfully used to produce biogenic Pd NPs: *Botryococcus braunii* produces 2–7 nm Pd NPs (Anju et al., 2020), *Chlorella vulgaris* produces 5–20 nm spherical Pd NPs (Arsiya et al., 2017), *Dictyota indica* produces 19 nm spherical Pd NPs (Yazdani et al., 2018), *Padina boryana* produces 5–20 spherical Pd NPs (Sonbol et al., 2021), and *Sargassum bovinum* produces 5–10 nm octahedral Pd NPs (Momeni and Nabipour, 2015). Yeast and fungi can also biosynthesize Pd NPs. Dry granules of *Saccharomyces cerevisiae* yeast produced 32 nm hexagonal Pd NPs (Sriramulu and Sumathi, 2018), while the fruit extract of *Agaricus bisporus* mushroom produced 13–18 nm triangular Pd NPs (Mohana and Sumathi, 2020).

As an alternative to using the extract of various plant parts or the biomass of different microorganisms, specific bio-derived materials or substances for the synthesis of Pd NPs can be employed (see bottom of Table 4). For instance, a wide range of sugars and polysaccharides has been intensively utilized for this purpose. Using the products generated from acidic/alkaline treatment of glucose (Monopoli et al., 2010) and sucrose (Amornkitbamrung et al., 2014) as reducing agents for Pd^{2+} produced 15 nm and 4.3 nm spherical Pd NPs, respectively, while the use of a mix of glucose and starch produced 1–20 nm quasi-spherical and octahedral Pd NPs (Gioria et al., 2020). The acidic/alkaline treatment of glucose and sucrose generates chemical intermediates with aldehyde functionality, which act as reducing species for Pd ions. To produce Pd NPs with narrow size distribution and to prevent them from aggregation, a stabilizing agent should be used. For the production of Pd NPs using glucose, a chemical surfactant (tetrabutylammonium hydroxide) was used to stabilize the NPs (Monopoli et al., 2010). For the production of Pd NPs using sucrose, no additional stabilizing agent was needed as sucrose itself or its degradation products in the reaction act as a stabilizing agent preventing the NPs from aggregation (Amornkitbamrung et al., 2014). In a comparison of glucose and starch, glucose acted as a reducing agent while starch acts as a stabilizing agent (Gioria et al., 2020). The polysaccharides of different plant and bacterial gums have also been used for the biosynthesis of Pd NPs. For instance, guar gum produced 70–80 nm spherical Pd NPs (Anjum et al., 2020), gum acacia produced 9 nm spherical Pd NPs (Devi et al., 2011), and xanthan gum produced 10 nm spherical Pd NPs (Venkatesham et al., 2015). In addition, other sugars such as glucosamine (Ullah et al., 2018) and glucomannan (Chen et al., 2021) resulted in the synthesis of 3–9 nm and 6 nm spherical Pd NPs, respectively. Interestingly, gums, glucosamine, and glucomannan acted as both reducing and stabilization agents for the production of Pd NPs. These carbohydrate polymers act natural templates for the nucleation and growth of Pd NPs, acting as both reducing and stabilizing agents due to their functional and structural properties (Chen et al., 2021).

TABLE 4 Other sources for biogenic Pd NP synthesis.

	Organism/ compound	NP size	NP shape	Pd precursor	Ref.
Algae	*Botryococcus braunii*	2–7 nm	Irregular	$Pd(OAc)_2$	Anju et al. (2020)
	Chlorella vulgaris	5–20 nm	Spherical	$PdCl_2$	Arsiya et al. (2017)
	Dictyota indica	19 nm	Spherical	$PdCl_2$	Yazdani et al. (2018)
	Padina boryana	5–20 nm	Spherical	Na_2PdCl_4	Sonbol et al. (2021)
	Sargassum bovinum	5–10 nm	Octahedral	$PdCl_2$	Momeni and Nabipour (2015)
	Sargassum ilicifolium	60–80 nm	Spherical	$PdCl_2$	Naveen and Padmesh (2014)
	Spirulina platensis	10–20 nm	Spherical	$PdCl_2$	Sayadi et al. (2018)
Yeast	*Saccharomyces cerevisiae*	32 nm	Hexagonal	$Pd(OAc)_2$	Sriramulu and Sumathi (2018)
Fungi	*Agaricus bisporus*	13–18 nm	Triangular	$Pd(OAc)_2$	Mohana and Sumathi, (2020)
	Agaricus bisporus	1.7 nm	Spherical	$PdCl_2$	Mallikarjuns et al. (2011)
Bio-derived materials	Ascorbic acid	13–33 nm	Spherical	$Pd(OAc)_2$	Ameri et al. (2020)
	Ascorbic acid and chitosan	30 nm	Flower-shaped	$PdCl_2$	Phan et al. (2019)
	Glucomannan	6 nm	Spherical	$PdCl_2$	Chen et al. (2021)
	Glucosamine	3–9 nm	Spherical	$PdCl_2$	Ullah et al. (2018)
	Glucose	15 nm	Spherical	$Pd(OAc)_2$	Monopoli et al. (2010)
	Glucose and starch	1–20 nm	Quasi-spherical and octahedral	Na_2PdCl_4	Gioria et al. (2020)
	Guar gum	70–80 nm	Spherical	$PdCl_2$	Anjum et al. (2020)
	Gum acacia	9 nm	Spherical	$PdCl_2$	Devi et al. (2011)
	Honey	5–40 nm	Irregular	$PdCl_2$	Reddy et al. (2012)
	Hyaluronic acid	1.5–5 nm	Spherical	Na_2PdCl_4	Yin et al. (2021)
	Lentinan	2–5 nm	Spherical	Na_2PdCl_4	Han et al. (2019)
	Lignin	16–20 nm	Spherical	$PdCl_2$	Coccia et al. (2012)
	Oxytocin	15–20 nm	Polygonal	$PdCl_2$	Bendre et al. (2020)
	Propolis	3 nm	Irregular	$PdCl_2$	Al-Fakeh et al. (2021)
	Quercetin diphosphate	100–300 nm	Spherical	$PdCl_2$	Osonga et al. (2020)
	Sodium alginate	2 nm	Spherical	H_2PdCl_4	Xiong et al. (2020)
	Sucrose	4.3 nm	Spherical	Na_2PdCl_4	Amornkitbamrung et al. (2014)
	Tannic acid	11.3 nm	Spherical	$PdCl_2$	Kumari et al. (2013)
	Xanthan gum	10 nm	Spherical	$PdCl_2$	Venkatesham et al. (2015)

In addition to polysaccharides, other biological compounds such as vitamins and hormones were successfully used for the synthesis of Pd NPs previously. Ascorbic acid is a well-known reducing agent, and the use of ascorbic acid as a reducing agent together with sodium alginate as a stabilizing agent produced 13–33 nm spherical Pd NPs (Ameri et al., 2020). However, when chitosan was used as a stabilizing agent together with ascorbic acid, 30 nm flower-shaped Pd NPs were formed (Phan et al., 2019). The use of oxytocin hormone produced 15–20 nm polygonal Pd NPs; in this case, the amino acids present in oxytocin acted as both reducing and stabilizing agents (Bendre et al., 2020).

Many other bio-derived materials can act as both reducing and stabilizing agents and have been successfully used for the biosynthesis of Pd NPs, including compounds such as hyaluronic acid (Yin et al., 2021), lentinan (Han et al., 2019), lignin (Coccia et al., 2012), sodium alginate (Xiong et al., 2020), and tannic acid (Kumari et al., 2013). The synthesized Pd NPs were 1.5–5 nm, 2–5 nm, 16–20 nm, 2 nm, and 11.3 nm spherical Pd NPs, respectively.

Applications of Pd NPs

Applications in catalysis

Biogenic NPs, due to their unique physicochemical properties combined with properties of capping materials, display interesting catalytic reactivity, selectivity, and product yield in numerous organic reactions (Mughal et al., 2021; Palem et al., 2022). There are also extensive studies confirming their environmental advantage over physiochemically produced NPs (Palem et al., 2022). Specifically, Pd is a key catalyst in organic cross-coupling reactions such as Heck and Suzuki coupling reactions (Cui et al., 2017; Miller et al., 2017; Biffis et al., 2018). The unique electronic ground-state structure of Pd

($4d^{10}5s^0$) and the square-planar geometry of Pd(II) complexes with additional coordination sites at the axial positions, which can accommodate various ligands, give Pd unique properties in C-C bond formation and C-O bond cleavage (Jbara et al., 2017). Therefore, a wide range of biogenically produced Pd NPs is being tested for their catalytic performance.

Examples: Pd NPs produced by *Camellia sinensis* leaf extract showed potent catalytic activity for the synthesis of biaryls *via* Suzuki cross-coupling reaction and for the reduction of 4-nitrophenol. At the same time, the NPs displayed high reusability where the catalytic activity was not affected after the reuse of catalyst for nine cycles (Lebaschi et al., 2017). Pd NPs produced by *Citrullus lanatus* rind extract also showed potent catalytic activity for Suzuki cross-coupling reaction, in which the catalyst displayed high product yield for 12 different coupling reactions (Lakshmipathy et al., 2015). The biogenic Pd NPs produced by *Hibiscus sabdariffa* L. were tested for 23 different Suzuki cross-coupling reactions. The reaction time and yield were high except for three reactions. The reusability of the catalyst was also high, the yield was not significantly affected after 6 catalytic cycles (Hekmati et al., 2017). Interestingly, Pd NPs produced by *Colocasia esculenta* leaf extract exhibited superior catalytic activity for Suzuki cross-coupling reactions over conventional catalysts. Here, the reaction with the biogenic catalyst required a shorter time and less catalyst. However, the reusability of the biogenic catalyst was not high, the yield reduced 20% after five catalytic cycles (KumaráBorah et al., 2015).

For Heck cross-coupling reactions, the biogenic Pd NPs produced by *Rosmarinus officinalis* leaf extract were tested for 22 reactions between different combinations of aryl halides and olefins. The product yield was high for all aryl halides expect for aryl chlorides. However, in all Heck olefination reactions, the selectivity for the *trans*-product was 100%. At the same time, the researchers optimized the conditions for Heck cross-coupling reaction between iodobenzene and methyl acrylate using the biogenic catalyst and achieved >99% product yield. This yield was higher than the yield of four conventional catalysts used for comparison in the same study (Rabiee et al., 2020). Bacterial Pd NPs also exhibit potent catalytic performance in Heck cross-coupling reactions. The biogenic Pd NPs produced by *Desulfovibrio desulfuricans* were tested for Heck cross-coupling reaction between iodobenzene and ethyl acrylate in different reaction conditions. The researchers found that the reaction rate can reach values up to 95% with the biogenic catalyst compared to only 82% with the conventional one (Bennett et al., 2013). Aside from cross-coupling reactions, biogenic Pd NPs exhibited also potent catalytic performance in hydrogenation reactions (Jia et al., 2009; Dauthal and Mukhopadhyay, 2013), reduction reactions (Veisi et al., 2016a; Sharmila et al., 2017a; Gopalakrishnan et al., 2017; Veisi et al., 2021), and photocatalysis (Tahir et al., 2016a; Turunc et al., 2017).

Applications in medicine based on toxic effects of NPs

Metal NPs are widely known for their antibacterial activity. Several mechanisms of action for this activity were proposed, including the production of reactive oxygen species, DNA damage, cellular transport disruption, cellular membrane disruption, ATP depletion, and protein denaturation through the interaction with thiol groups (Rawashdeh and Haik, 2009; Rana and Kalaichelvan, 2011; Tahir et al., 2016a; Slavin et al., 2017), and probably a combination of these mechanisms makes the bacteria fail to establish a defense mechanism for adaptation and survival. Therefore, metal NPs are considered a promising agent for treating multi-drug resistant bacteria (Slavin et al., 2017). Due to the similarity of biomolecules between human and bacterial cells, metal NPs would be similarly cytotoxic to human cells. Interestingly, in a meta-analysis and statistical study of 71 published papers discussing the cytotoxicity of biogenic metal NPs on normal *versus* cancerous cells, it was found that biogenic metal NPs are 9 times more cytotoxic to human cancer cells than to normal cells (Barabadi et al., 2018). This huge difference was suggested to be a result of the high metabolic activity of cancer cells, which leads to the uptake of higher number of metal NPs compared to normal cells (Rai et al., 2016; Barabadi et al., 2018).

Examples: Biogenic Pd NPs display antimicrobial and anticancer activities. Some have a narrow range of activity, such as in the cases of Pd NPs produced by *Solanum nigrum* leaf extract (Vijilvani et al., 2020) and by *Cissus quadrangularis* stem extract (Anjana et al., 2019) exhibit antibacterial activity against *Escherichia coli*. Other biogenic Pd NPs were tested against a wider range of bacteria, and it was found that Pd NPs produced by *Filicium decipiens* leaf extract displayed antibacterial activity against both gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative (*Escherichia coli and Pseudomonas aeruginosa)* bacteria. The inhibition zone of gram-negative bacteria was larger than of gram-positive bacteria (twofold), which may suggest that Pd NPs can penetrate the thin outer membranes of gram-negative bacteria more easily than the thicker cell walls of gram-positive bacteria (Sharmila et al., 2017b). However, Pd NPs produced by *Sapium sebiferum* leaf extract demonstrated higher antibacterial activity against gram-positive than gram-negative bacteria (Tahir et al., 2016a). This suggests that different biogenic Pd NPs have different antibacterial mechanisms of action attributed to their different sizes, shapes, and their capping compounds.

The antimicrobial activities of Pd NPs are not limited to bacteria. For example, Pd NPs produced by *Piper betle* leaf extract exhibited antifungal activity against *Aspergillus niger* (Mallikarjuna et al., 2013), while Pd NPs produced by *Melia azedarach* leaf extract showed larvicidal activity against *Aedes aegypti* (Bhakyaraj et al., 2017). Moreover, Pd NPs produced by *Cocos nucifera* coir extract displayed anti-feedent and ovicidal

activity against *Callasobruchus maculates* agricultural pest (Elango et al., 2017). At the same time, other biogenic Pd NPs exhibited anticancer activity, as those produced by *Evolvulus alsinoides* leaf extract, which were efficient against A2780 ovarian cancer cells (Gurunathan et al., 2015), and the NPs produced by *Urtica*, which were efficient against MDA-MB-231 human breast cancer cells, HT-29 human colon cancer cells, and MIA PaCa-2 human pancreatic cancer cells (Gulbagca et al., 2021).

Some biogenic Pd NPs displayed a wide range of activities. For instance, Pd NPs produced by *Bauhinia variegate* bark extract exhibited antibacterial activity against *Bacillus subtilis* and *Stayphylococcus aureus*, antifungal activity against *Candida albicans*, and anticancer activity against MCF-7 breast cancer cells (Vaghela et al., 2018). Pd NPs produced by *Moringa oleifer* flower extract demonstrated antibacterial activity against *Enterococcus faecalis* (and not against *Bacillus cereus, Staphylococcus aureus, or E. coli*) and anticancer activity against A549 lung cancer cells (Anand et al., 2016). Interestingly, Pd NPs produced by *Rosmarinus officinalis* leaf extract exhibited a wider range of activities. They displayed antibacterial and antifungal activities against all tested species. Pd NPs produced by *Camellia sinensis* leaf extract exhibited antioxidant activity, antibacterial activity against *Escherichia coli* and *Staphylococcus epidermidis*, and anticancer activity against MOLT-4 T-lymphoblastic leukemia cells (Azizi et al., 2017). Additionally to that, Pd NPs produced by *Dioscorea bulbifera* tuber extract showed antioxidant activity and anticancer activity against HeLa cervical cancer cells (Ghosh et al., 2015). In the same study, the researchers produced bimetallic PtPd NPs using the same plant extract. Remarkably, the bimetallic NPs exhibited higher antioxidant and anticancer activities compared to the monometallic NPs (Ghosh et al., 2015). In the majority of these studies, a general mechanism of action was suggested for the biogenic Pd NPs. However, these studies lack a detailed evaluation of the role of the surface molecules capping the biogenic NPs on both the cellular uptake of these NPs and on their mechanism of promoting toxicity.

Applications in biomedical therapies

In addition to having a wide range of antimicrobial and anticancer properties, Pd NPs have also shown promising results in several biomedical therapy approaches. Due to the diversity in their size and shape, photothermal conversion efficiency, and photostability, Pd NPs are emerging as potentially efficient photothermal therapy agents (Phan et al., 2020). NP-mediated photothermal therapy (cancer cell death by heat generated in tumor tissue) has shown great potential for the treatment of cancer. However, the development of small-size biocompatible photothermal therapy agents with high photothermal conversion efficiency is a big challenge (Xiao et al., 2014). Porous 20 nm Pd NPs have displayed photothermal conversion efficiency of 93.4% when dispersed in water and illuminated with an 808 nm laser. Using these NPs for the *in vitro* photothermal heating of HeLa cells led to 100% cell death when using 808 nm laser irradiation and 70% cell death when using 730 nm laser after 4 min of irradiation (Xiao et al., 2014). Theoretically, other nanomaterials exhibit higher photothermal conversion efficiencies, such as Au rods, which exhibit a 98.6% photothermal conversion efficiency. However, the large size of Au rods is a huge disadvantage and results in lowering the theoretical 98.6% photothermal conversion efficiency to 85.6% when irradiated with a 730 nm laser. Despite having a higher theoretical photothermal conversion efficiency, the large size of Au rods (60.8 nm on average) compared to 20 nm porous Pd NPs resulted in showing lower experimental photothermal conversion efficiency due to the higher fraction of scattering in the extinction (Xiao et al., 2014).

In another study, porous 22 nm Pd NPs were coated with chitosan oligosaccharide to improve their biocompatibility and further functionalized with RGD peptide (Arginylglycylaspartic acid) to increase their accumulation in MDA-MB-231 breast cancer cells. In an animal model, they have shown very promising results in the *in vivo* photothermal therapy of breast cancer. The researchers injected these Pd NPs intravenously in BALB/c nude mice bearing MDA-MB-231 xenograft tumors, irradiated the tumor region with 808 nm laser for 5 min, and measured the tumour progression rate for 20 days. Impressively, on the 20th day, the thermally destructed tumor was reduced and healed completely (Bharathiraja et al., 2018). Interestingly, besides their photothermal conversion efficiency, Pd NPs also produce large signals in photoacoustic imaging, which is an emerging new non-invasive biomedical technique that combines ultrasound-based signals with optical contrast to image treated cancer tissues. In (Basavegowda et al., 2016), the researchers injected the coated and functionalized Pd NPs intravenously in the animal model and diagnosed the tumor region using photoacoustic imaging. After accumulating in the tumor region, the injected NPs acted as an excellent contrast agent and generated a clear image of the tumor tissue.

Pd NPs could also play an important role in improving current cancer treatment technologies such as chemo- and radiotherapy. Song et al. (2018) have demonstrated that porous hollow Pd NPs can deliver ^{131}I (a radioisotope that is commonly used in radiotherapy) and DOX (a chemotherapy drug that is commonly used in chemotherapy) *in vivo* in mice injected with MCF-7 breast cancer cells. Compared to other mesoporous nanocarriers, these NPs exhibited high drug loading and controllable drug release promoted by laser irradiation and acidic pH in tumor microenvironments. Moreover, Pd NPs have also shown promising results in other biomedical areas such as gene therapy (Kang et al., 2018), drug delivery (Gil et al., 2018), prodrug activation (Weiss et al., 2014), and biosensors applications (Yi et al., 2017).

Conclusion and future perspectives

The continuous growth of Pd NP applications have made it imperative to exploit novel methodologies for the efficient and

environmentally friendly synthesis of Pd NPs. Current chemical and physical production methodologies can synthesize particles with narrow size distributions and specific shapes, which are highly related to their remarkable catalytic properties. The downside of some of those approaches is the high cost, high energy consumption, and the involvement of toxic chemicals. Biological synthesis of NPs using a broad range of species and biomolecules has emerged as a powerful alternative to the classic methodologies. These processes can potentially result in more environmentally friendly approach and might become a key part of a cyclic Pd economy when included in recycling and wastewater treatment processes.

Today, the available knowledge on the mechanisms of Pd NPs formation from different biological sources is insufficient, and more dedicated research is necessary to exert even better control over important parameters such as NP size and shape. The vast number and diversity of possible application of Pd NPs in catalysis, medicine, and biomedical therapies highlights the importance of such studies, and risks related to the toxicity of nanoparticles should not be ignored in the course of this research. As for many other new nanomaterials, we will probably see even more new applications for this exciting material in the future.

Author contributions

NJ wrote the first draft on the manuscript and produced all figures. All authors edited and approved the manuscript.

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Conflict of interest

Author GK was employed by the company Inven2 AS.

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