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Reduction of 4-nitrophenol using green-fabricated metal nanoparticles

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Noble metal (silver (Ag), gold (Au), platinum (Pt), and palladium (Pd)) nanoparticles have gained increasing attention due to their importance in several research fields such as environmental and medical research. This review focuses on the basic perceptions of the green synthesis of metal nanoparticles and their supported-catalyst-based reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). The mechanisms for the formation of these nanoparticles and the catalytic reduction of 4-NP are discussed. Furthermore, the parameters that need to be considered in the catalytic efficiency calculations and perspectives for future studies are also discussed.

1 Introduction

In recent years, one issue that has generated significant concern due to its adverse effects, mainly on human health, is the contamination of water (surface and groundwater), including the ocean.[1–3] The principal cause of this event is the high amounts of toxic and refractory pollutants, mainly 4-nitrophenol (4-NP),[1,4–6] which is widely used in the pharmaceutical and textile industries[7,8] for the production of herbicides, insecticides, synthetic dyes, and paints, and as a corrosion inhibitor and pH indicator, among other applications.[4,9,10] Therefore, the reduction of 4-NP to 4-aminophenol (4-AP) has become a crucial issue, given that 4-AP is a compound with a lower degree of toxicity.[6,11] Among the various 4-NP reduction reactions, the reaction with sodium borohydride ($NaBH_4$) as a reducing agent (H_2 source) in conjunction with metal catalysts, such as Pd,[12–14] Ag,[15,16] Pt,[8,17] Cu,[18] Au[4,9,19] and their assemblies on dendrimers, polymeric matrices, microgels, metal-immobilized silica-coated supports, and graphene oxide,[20] has gained more attention due to its eco-friendly and straightforward reduction process. Furthermore, chemical and green methods are widely employed for the fabrication of nanomaterials as catalysts for the 4-NP reduction reaction[21] in aqueous and semi-solid media.[5,11,21–23] Pradhan *et al.*[23] primarily introduced 4-NP reduction as a model reaction using Ag nanoparticles. The catalytic reduction reaction was real-time monitored *via* UV-visible spectroscopy by observing the decrease in the absorption band at 400 nm belonging to the 4-

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nitrophenolate ion (intermediate product) and increase in the band at 300 nm related to 4-AP.[4,22] Subsequently, many studies have been reported, but compared to other techniques, green-synthesized catalysts play a vital role in the 4-NP reduction reaction due to their biocompatibility, low toxicity, low cost, and easy preparation process. Also, several green reducing agents, such as ascorbic acid,[24] formic acid,[23] tetramethyl disiloxane,[25] plant or seed extracts, and microorganisms,[26] have been studied.[19,27–29]

The purpose of this review is to present the scientific advances in the green synthesis of noble metal nanoparticles and their application in the reduction of 4-nitrophenol in aqueous media, clearly explaining the reaction mechanisms of both metal nanoparticle synthesis and 4-NP reduction.

The overall publication trend in the last two decades is presented in Fig. 1. During the first decade (2000 to 2010), only less than 200 articles were published annually. On the contrary, during the second decade (2011 to 2020), a significant increase (almost four-fold higher) in the number of annually published articles was observed. During the pandemic period, many articles were published, which can be explained by the growing recognition and importance of 4-NP.

1.1 History of 4-nitrophenol

The three-step procedure to synthesize paracetamol was first proposed by J. von Mering in 1893, which was advertised in 1953 considering that it safer than aspirin. The steps in synthesis of paracetamol are as follows: nitration of phenol → conversion of nitro group (4-NP) → amino group (4-AP) and acetylate amino group → paracetamol (Fig. 2).

4-Nitrophenol is also called *para*-nitrophenol (*p*-nitrophenol) or 4-hydroxynitrobenzene. It has a nitro group at the *para* position in a phenolic compound (*i.e.*, hydroxyl (–OH) group attached to a carbon atom in a benzene ring). In general, it is used in pharmaceutical drugs and insecticides. Moreover, 4-NP is an intermediate product in the production of acetaminophen (paracetamol) from phenol (as mentioned above). Human beings may be exposed to 4-NP by drinking polluted water.

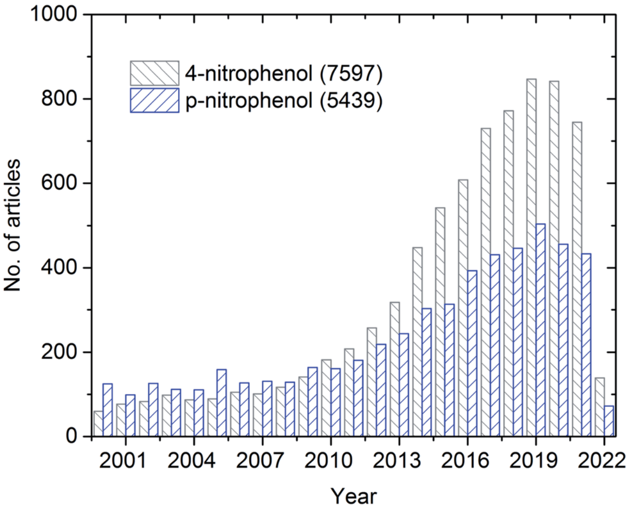

Fig. 1 Schematic representing the history of publications from 2000–2022 (up to 8th March) on 4-nitrophenol/*p*-nitrophenol from Web of Science search results.

2 Update on 4-nitrophenol reduction using green-synthesized metal nanoparticles

There are few reports on the reduction of 4-nitrophenol. Pengxiang *et al.*,[21] Maryam *et al.*,[22] and Muhammad *et al.*[23] mainly focused on the synthesis-dependent fabrication of AuNPs and their nanocatalyst assemblies to reduce nitrophenol. In this review, we focus on green-fabricated monometallic, bimetallic Ag, Au, Pt, and Pd NPs and their assembled structures to reduce 4-NP using $NaBH_4$ as the model reaction.

3 Catalyst fabrication and characterization

3.1 Green synthesis-mediated metal nanoparticles as catalysts

The fabrication of nanoparticles (from different metals) *via* green synthesis has achieved great importance due to the fact that it "reduces" the use and formation of toxic compounds.[29,30] The use of biological materials such as bacteria, fungi, algae, and plant extracts (roots, leaves, fruits, flowers, and seeds)[30–32] avoids the use of intermediate base groups, making it a cost-effective, accessible, eco-friendly, and biocompatible method compared to other synthesis methods (*i.e.*, chemical and physical).[26,33] Plant extracts contain phytochemicals (polyols, terpenoids, polyphenols, carboxylic acids, flavones, amides, *etc.*) that are capable of bioreducing metal ions to metal NPs.[32,34,35]

For the fabrication of NPs *via* green synthesis, most studies report the extraction of the substrate from plant matter, as shown in our previous study, where *Coffea arabica* seed (CAS) powder was used as a green precursor, where 50 mL of distilled water was mixed with 0.6 g of CAS power at 85 °C.[28] After this process, the extract was filtered and metallic salts were added. When the reducing agents from the CAS extract came in contact with the metal salts, a visual color change was observed (the color variation depends on the metal ions), revealing the formation of NPs.[32,36]

However, the reaction conditions such as the type of feedstock (microorganisms, plant material, *etc.*), temperature, pressure, pH, reaction time, reducing agent and metal ion concentration directly affect the chemical, physical, and optical characteristics (particle size, shape, and texture) of the nanoparticles.[35,37–43] For example, pH plays an essential role in the synthesis of NPs, affecting their size, shape, and reaction rate. Moreover, these nanoparticles are used for various applications, such as antimicrobial agents (*e.g.*, AgNPs),[44,45] cell imaging in cancer detection (*e.g.*, AuNPs),[46] alternative energy generation (*e.g.*, AuNPs),[47,48] remediation of oily sewage,[49,50] sensors (*e.g.*, AgNPs),[51,52] and moreover, as sustainable catalysts for environmental remediation (*e.g.*, AuNPs and AgNPs).[28,53] Environmental

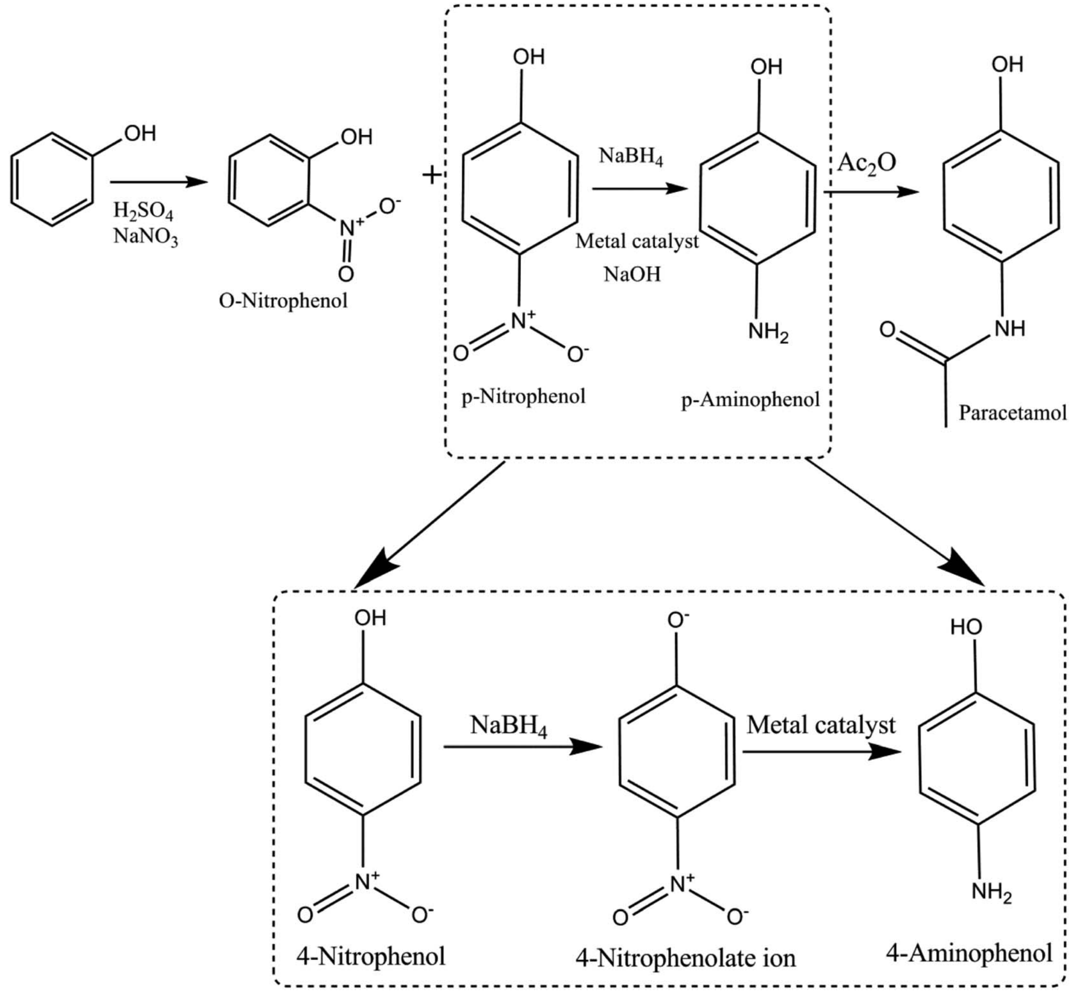

Fig. 2 Schematic representing the history of 4-nitrophenol acquired during the production of paracetamol from phenol as an intermediate product.

remediation has become important due to the negative impacts caused by pollution,[54] as mentioned above .[55–67] Water is one of the resources with the greatest impact due to the release of pollutants by industry and mining. Therefore, NPs obtained by green synthesis are an alternative for reducing toxic organic compounds (as mentioned in the Introduction). The possible mechanism for the formation of green-synthesized metal nanoparticles catalyst is still under debate. Various studies[68–71] have reported that the green precursors act as multifunctional agents with both reducing and capping capabilities, but limited efforts have been made to explore their chemistry. Some research groups proposed a possible understanding based on HPLC and FTIR results.

3.2 Catalyst characterization

The catalytic activity of metal nanoparticles depends on several properties, such as their synergistic effect, particle size, quantum effects, and surface properties. These properties can be investigated using several traditional characterization techniques. Primarily, the reduction of 4-NP is monitored using the absorption spectrum obtained by UV-visible absorbance spectroscopy and to identify the electronic transition bands of metal nanoparticles.[35] The particle size of metal nanoparticles plays a significant role in the removal of 4-nitrophenol. These particle size measurements have been achieved using dynamic light scattering[27]-based particle size analyzers and high-resolution transmission electron microscopy.[37] As is known, the surface charge and functional groups present on the catalyst can improve the adsorption of the organic pollutant, followed by the fast catalyst reduction of 4-NP, which have been obtained from zeta potential and Fourier transform infrared spectroscopy (FT-IR) studies, respectively.[39]

4 Reduction of 4-nitrophenol using green-synthesized metal nanoparticles

4.1 Gold nanoparticles (AuNPs) as catalysts

Briefly, Xin Huang *et al.*[72] fabricated gold nanoparticles (AuNPs) for the first time using plant tannins. The resultant AuNPs were supported on the porous γ-Al_2O_3, and the formation of multiple hydrogen bonds with γ-Al_2O_3 and self-cross-linking interactions among the stabilized AuNPs were observed. Further, the fabricated Al_2O_3–AuNPs were used as a reusable catalyst to reduce 4-nitrophenol in aqueous medium. Initially, the Al_2O_3–AuNP catalyst was mixed with a 4-NP solution, which was bubbled with N_2 to remove the dissolved O_2 in the solution. Subsequently, $NaBH_4$ was added to the mixture, which initiated the catalytic reduction, and the reduction of 4-NP was monitored by measuring the characteristic absorption peak of 4-NP at 400 nm. In addition, the porous Al_2O_3–AuNPs exhibited better reusability than the conventional Au–Al_2O_3 catalyst.

Daizy Philip's group[86] also proposed the fabrication of gold nanoparticles using an aqueous extract of fenugreek (*Trigonella foenum-graecum*) given that it is simple, efficient, economical, and nontoxic. The synthesized gold nanoparticles were characterized and tested for their size-dependent catalytic activity towards the reduction of 4-NP. The smaller nanoparticles showed faster activity.

Sanoe Chairam *et al.*[88] reported the preparation of mung bean starch (MBS)-mediated gold nanoparticles (AuNPs) through a green synthesis method, which were found to be efficient and recyclable catalysts for the reduction of 4-NP in the presence of $NaBH_4$.

Recently, Mustaffa Shamsuddin's[90] group presented the use of thioctic acid-functionalized SiO_2-coated Fe_3O_4-supported *P. macrocarpa* fruit extract-mediated AuNPs as a reusable catalyst for the reduction of 4-nitrophenol under various conditions. The optimization of the 4-nitrophenol reduction process was studied using the Box–Behnken design. Under the optimal conditions, the percentage reduction of 4-nitrophenol was 92% after 1 h, and the catalyst also maintained highly stable catalytic activity after five successive cycles.

Several other groups employed fungal *Aspergillus* sp. WL,[73] *Citrus maxima* (fruit),[74] fungus *Mariannaea* sp. HJ,[75] longan polysaccharides,[76] aspartame,[77] Jujube polysaccharides,[78] *Mimosa pudica* flower,[79] *Mimusops elengi* (bark),[80] *Cotoneaster horizontalis* leaves,[81] catechin-capped,[82] *Konjac glucomannan*,[83] caffeic acid,[84] *Coffea arabica* seed,[20] *Hedysarum* polysaccharides,[87] and *Sterculia acuminata* (fruit)[68] as precursors to obtain AuNPs (as an unsupported catalyst) for the reduction of 4-NP. The AuNPs obtained by green synthesis used to reduce 4-NP and their respective characteristics and reaction conditions are presented in Table 1.

Table 1 AuNPs obtained by green synthesis used for the reduction of 4-NP with their respective characteristics and reaction conditions[a]

			Reaction conditions				
Feedstock	Size (nm)	Shape	Catalyst conc.	$NaBH_4$ conc. (mM)	4-NP conc. (mM)	Time (min)	Rate constant (K_{app}) $\times 10^{-3}$ s^{-1}
Unsupported NPs							
Fungal *Aspergillus* sp. WL[73] (2017)	4–29	Spherical	114.72 mg L^{-1}	30	2	2–6	9.8–25[b]
Citrus maxima (fruit)[74] (2016)	25.7	Rod and spherical	1 mM	NR	0.25	20	1.5[b]
Fungus *Mariannaea* sp. HJ[75] (2017)	11.7	Spherical, hexagon, and irregular shapes	0.195 g L^{-1}	100	2	3.3	24.7
Longan polysaccharides[76] (2020)	7.8–15.6	Spherical	1.416 μM	500	0.6	42	4.65
Aspartame[77] (2015)	1.2–50	Spherical	1.0 mM	100	4.0	9	6.84[b]
Mushroom *Pleurotus florida*[78] (2013)	5–16	Spherical	3.5 mg	15	2	30	1.9–33[b]
Jujube polysaccharides[79] (2019)	8–13	Spherical and monodisperse	6.67 nM	NR	NR	18	1.17
Mimosa pudica flower[80] (2017)	∼24	Spherical	0.25 mM	250	5	15	5.0[b]
Mimusops elengi (bark)[81] (2016)	9–14	Spherical	0.42 mM	13–14	0.05	5–8	6.53–7.33
Cotoneaster horizontalis leaves[82] (2017)	18	Spherical	1 mM	30	2	10	NR
Catechin-capped[83] (2014)	16.6	Polydisperse	0.5 mM	5.5	0.15	8.6	1.5[b]
Konjac glucomannan (KGM)[84] (2014)	12–31	Uniform spherical	10 mM	10	0.05	8.6	6.03
Caffeic acid (CA)[85] (2017)	38.61	Spherical	0.2 mM	200	0.4	15	5.73
Coffea arabica seed[20] (2018)	28	Spherical	10 mM	100	10	38	0.8[b]
Trigonella foenum-graecum[86] (2012)	15–25	Spherical	1.3×10^{-4} M	250	0.25	7	NR
Hedysarum polysaccharides (HPS)[87] (2021)	5–8	Spherical	20 μL of 10% (stock Au salt)	11.34 mg	0.6	7	NR
Sterculia acuminata (fruit)[68] (2015)	26.5	Spherical	5 mM	20	1	36	1.8[b]
Supported NPs							
Mung bean starch-AuNPs[88] (2017)	10	Spherical	20–100 mg	0.1–0.9 g	1	13	0.36[b]
Al_2O_3-Bayberry tannin-AuNPs[89] (2011)	4.63–5.08	Spherical	2.5 μM	10	0.2	5	NR
Phaleria macrocarpa (Scheff.) Boerl. (*P. macrocarpa*) AuNPs supported on –NH–SiO_2–Fe_3O_4 nanoparticles[90] (2020)	2.4 ± 0.7	Spherical	2 mg	100	0.05	60	NR

[a] NR = not reported. [b] Denoted values were recalculated for uniformity in the corresponding units with respect to other reports.

4.2 Silver nanoparticles (AgNPs) as catalysts

Abilash *et al.*[91] reported the use of *Breynia rhamnoides* stem extract-mediated spherical AgNPs to reduce 4-NP. The synthesized AgNPs exhibited relatively lower catalytic rates than Au NPs due to their relatively large size and the formation of a surface oxide layer. Further, Natarajan Sakthivel's group[92] reported the preparation of AgNPs using a fungus (*Cylindrocladium floridanum*), which were tested for the reduction of 4-NP as a homogeneous catalyst.

The reduction reaction rate was dependent on the reaction conditions such as concentration, size, and number of surface atoms of the catalyst. Later, Muniyappan *et al.*[95] fabricated silver nanoparticles using *Dalbergia spinosa* leaves and tested them to reduce 4-nitrophenol. In addition to absorbance studies, they used ^{1}H NMR spectroscopy to confirm the reduction of 4-nitrophenol and the formation of 4-aminophenol.

Recently, several other groups also devoted their efforts to the reduction of 4-nitrophenol using green-fabricated silver nanoparticles, such as *Psidium guajava* leaves,[93] Tulsi leaves,[94] polyphenol,[97] pestle curcumin,[101] seaweed *Fucus gardneri*,[103] and others.[102–109] The green-fabricated AgNPs used as catalysts to reduce 4-NP and their respective characteristics and reaction conditions are shown in Table 2.

4.3 Platinum and palladium nanoparticles as catalysts

In addition to Ag and Au nanoparticles, Pt and Pd NPs have been tested to reduce 4-NP to 4-AP with a similar mechanism understanding to that of Au and AgNPs. However, there are less reports on green-fabricated Pt and Pd NP-based 4-NP reduction probes than Ag and Au NPs. Generally, Pd and Pt NPs are among the most efficient catalysts for various organic reactions with fast reaction rates, high turnover frequency, and high yields.

Table 2 AgNPs obtained by green synthesis used for the reduction of 4-NP and their respective characteristics and reaction conditions[a]

			Reaction conditions					
Feedstock	Size (nm)	Shape	Catalyst conc.	$NaBH_4$ conc. (mM)	4-NP conc. (mM)	Time (min)	Rate constant (K_{app}) $\times 10^{-3}$ s^{-1}	Ref.
Unsupported NPs								
Psidium guajava leaf (2019)	20–30	Polydisperse	10 µL	100	10	8	2.6[b]	93
Fungus Cylindrocladium floridanum (2013)	25	Quasi spherical	4.63–27.81 $\times 10^{-4}$ M	6.67	0.1	60	1.1[b]	92
Tulsi leaves (2018)	5–10	Globular	10 µL	200	5	30	34.1[b]	94
Dalbergia spinosa leaves (2014)	18	Quasi spherical	200 µL	0.1	0.1	NR	NR	95
Thymbra spicata leaves (2018)	7	Spherical	2 mg	250	2	60	64.5[b]	96
Polyphenol (2019)	2–10	*R*	0.2 mg L^{-1}	10	0.1	16	2.8[b]	97
Salmalia malabarica gum (2016)	7	Spherical	10 µL	15	0.2	60	0.9[b]	98
Kollicoat-capped Ag NPs (2016)	∼20	Spherical	20 µL	100	0.1	60	NR	99
Leaf extract of *Peronema canescens* (2021)	19	Spherical	150 µL	30	2	30	NR	100
Pestle curcumin (2019)	15–40	Spherical, rods, and hexagonal	500 µL	15	0.15	5	NR	101
Extract of *Breynia rhamnoides* (2011)	27	Spherical	0.3 mL	30	2	∼7	9.19	91
Sterculia acuminata fruit (2016)	10–50	Spherical	10–100 µg mL^{-1}	0.1 N	10^{-4} N	22	0.95[b]	68
Stemona tuberosa Lour (2018)	25	Spherical	20 µL	1 mg	1	2880	NR	102
Seaweed *Fucus gardneri* (2021)	19.39	Quasi spherical	1 mg mL^{-1}	0.03	2	5	9.3[b]	103
Supported NPs								
Herbal tea from *Stachys lavandulifolia* (Fe_3O_4@S) (2018)	20–40	Quasi spherical	2 mg of catalyst (0.008 mol%)	0.3	3	0.5	63.4[b]	104
AgNPs decorated with hydroxyapatite (2018)	14.79	Rod	2 mg	200	100	9	2.0–7.3	105
AgNPs decorated with SnO_2 microsphere (2017)	5	Spherical	1.5 mg	1.5 mg	20 mg L^{-1}	300–2160	4.7–51.7[b]	106
AgNPs synthesized with polyphenols and supported on modified graphene (Ag-TPG) (2015)	5	Spherical	0.5 mg mL^{-1}	10	0.1	13	3.35	107
AgNPs supported on cellulose nanocrystals (CNC@PDA-Ag) (2015)	∼10 nm	R	20 µg mL^{-1}	38	0.12	18	0.76[b]	108
AgNP-decorated halloysite nanotubes using dopamine (2018)	10–20	Rod	1 g	200	1	7	4.45[b]	109

[a] NR = not reported. [b] Denoted values were recalculated for uniformity in the corresponding units with respect to other reports.

However, the metal aggregation and precipitation result in catalyst decomposition and considerable loss in catalytic activity. Therefore, from the viewpoint of practical application, the use of green-fabricated Pd and Pt NP probes is desirable, similar to Au and Ag NPs.

When stable and uniform-sized Pd and Pt NPs are fabricated, they possess tremendous catalytic efficiency for the conversion of 4-nitrophenol to 4-aminophenol, better than other metal nanoparticles. In addition, our group found that self-assembled PtNPs demonstrated significant catalytic efficiency for the reduction of 4-NP. The rate constant of *Coffea arabica* seed-mediated self-assembled Pt nanoparticles (60×10^{-3} s^{-1})[70] was almost two-times higher than that of mushroom *Pleurotus florida*-mediated AuNPs,[78] where due to the presence of sharp edges in their corners, the number of active surface sites in the anisotropic PtNPs is very high compared with bare NPs, and the small molecules from biomass could readily adsorb on the Pt surface.

For instance, even with only 5–50 μg of *Sterculia acuminata*-mediated PdNPs,[71] the rate constant obtained was 3.0×10^{-3} s^{-1}. The superior catalytic activity of Pd and Pt NPs than that of equivalent Au and Ag NPs may be attributed to several other properties, such as their particle size and electron structure on the surface of their atoms (encourages the temporary sticking of molecules). The overall electron cloud changes shape, allowing the stuck molecules to rearrange into new compounds; however, catalyst does not change. Subsequently, the rearranged molecules are eventually pushed out by new input ones (temperature-caused motion).

Several other green precursors such as guar gum,[110] sodium rhodizonate,[111] *Maytenus royleanus*,[112] *Sterculia Acuminata* fruit extract,[69] *Equisetum arvense* L/walnut shell,[113] and *Silybum marianum*[114] have been used to obtain Pt and PdNPs (as unsupported catalysts) for the reduction of 4-NP. Still, there is room to develop supported catalysts using Pt/Pd NPs for the reduction of 4-NP. Table 3 shows the Pt and PdNPs obtained by green synthesis used to reduce 4-NP and their respective characteristics and reaction conditions.

4.4 Bimetallic nanoparticles as catalysts

As is well known, the reduction of 4-nitrophenol using metal nanoparticles is mainly dependent on the size and shape of the NPs, and thus nanoengineering plays a crucial role in tailoring catalysts. Consequently, the presence of two or more metals in a single catalyst may increase the number of active sites in bimetal catalysts than single-metal catalysts. Also, there is the possibility of the synergistic effect in bimetal catalysts.[115–127]

In 2013, Bihua Xia *et al.*[115] presented green-fabricated spherical Au/Ag bimetallic nanoparticles using degraded *Pueraria mirifica* starch as both a reduction and stabilizing agent. Further, the authors tested the catalytic efficiency of the fabricated bimetallic Au/Ag nanoparticles towards the reduction of 4-nitrophenol. Interestingly, the Au/Ag bimetallic nanoparticles exhibited rapid 4-NP reduction reaction catalytic efficiency compared to the bare Ag and Au NPs. The reaction time for the Au/Ag bimetallic nanoparticles was almost 14-times higher than that for the mono metal NPs fabricated using the same degraded *Pueraria mirifica* starch. Similarly, the Daizy Philip group[116] reported the preparation of pomegranate fruit juice-mediated core–shell Au–Ag NPs and their use as catalysts for the reduction of 4-NP. They also obtained better catalytic efficiency with core–shell Au–Ag NPs than their monometallic NPs. The obtained apparent rate constant (13.3×10^{-3} s^{-1}) of the core–shell Au–Ag nanoparticles was higher than that of the unsupported bimetal catalysts presented in the table.

The superior catalytic efficiency of bimetallic NPs may be due to the existence of two metals (Au and Ag) in their composition and their morphological changes, where due to their synergistic

Table 3 Platinum and palladium NPs obtained by green synthesis used for the reduction of 4-NP and their respective characteristics and reaction conditions[a]

				Reaction conditions					
Feedstock	Metal	Size (nm)	Shape	Catalyst conc.	$NaBH_4$ conc. (mM)	4-NP conc. (mM)	Time (min)	Rate constant (K_{app}) $\times 10^{-3}$ s^{-1}	Ref.
Platinum nanoparticles (PtNPs)									
Guar gum (2014)	Pt	∼6	Spherical	2.5 mM	100	1	240	7	110
Sodium rhodizonate (2018)	Pt	26	Quasi spherical	50 μL	5 mg in 0.5 mL of water	0.2	10	18.1[b]	111
Maytenus royleanus (2017)	Pt	5–8	Spherical	5 mg	20	1	20	2.1[b]	112
Sterculia Acuminata fruits extract (2018)	Pt	∼3.4	Irregular spherical	10–100 μL	100	2	8	0.1[b]	69
Coffea Arabica seed (2021)	Pt	2	Spherical	10 μL	0.76 mg	1	3–5	60	70
Palladium nanoparticles (PdNPs)									
Equisetum arvense L/walnut shell (2017)	Pd	5–12	Spherical	5 mg	250	2.5	1	NR	113
Sterculia acuminata (2018)	Pd	∼26.5	Spherical	5–50 μg	100	2	20	3.0	71
Silybum marianum (2017)	Pd	<20	Spherical	0.5 mL	15	20	27	NR	114

[a] NR = Not Reported. [b] Denoted values were recalculated for uniformity in the corresponding units with respect to other reports.

effect, electrons can transfer from one metal to the other metal NPs (*i.e.*, the ionization potential of Au/Ag is 9.22/7.58 eV, respectively). This is important to enhance the electron cloud on the bimetallic NP surface in a kinetically favorable manner with more active sites. Table 4 demonstrates the bimetallic nanoparticles obtained by green synthesis to reduce 4-NP and their characteristics and reaction conditions.

Yinan Wang *et al.*[117] fabricated a template (*i.e.*, lipid as a tube-like template) based on palladium–platinum nanotubes using ascorbic acid. The fabricated Pd–Pt nanotubes (15 μg) showed an improved catalytic activity for the reduction of 4-NP. The calculated apparent rate constant ($8.3 \times 10^{-3}\ s^{-1}$) of Pd–Pt NTs was almost 2.5-times higher than that of the Pt NTs ($3.3 \times 10^{-3}\ s^{-1}$) presented in the same report. Furthermore, the fabricated Pd–Pt NTs were also tested for their recyclability over six cycles, and the authors did not observe any loss in their activity. Similar to the above-mentioned reports, the better catalytic efficiency of the PdPt NTs than Pt NTs is ascribed to the electron transfer effect.

Recently, Ye *et al.*[126] synthesized lichen-reduced graphene oxide (LrGO)-AgAu composites using *Cetraria islandica* (L.) Ach. Extract. The fabricated LrGO–AgAu nanocomposites were examined for the reduction of 4-NP. Similar to previous reports on bimetallic NPs, higher catalytic activity was observed for the reduction of 4-NP than that with the monometallic nanocomposites related to the preparation of small-sized homogeneous particles, which give a significant amount of active sites on the nanocomposite surface.

The superior catalytic activity of bimetallic nanoparticles than that of monometallic nanoparticles may be attributed to several other properties, such as the synergic effect, particle size, quantum effects, and surface properties of the metal nanoparticles. Alternatively, rapid and easy procedures are essential to improve the reusability of catalytic probes.

4.5 Suggested studies during the 4-nitrophenol reduction process

4.5.1 Effect of $NaBH_4$ concentration on 4-nitrophenol reduction. According to Fig. 2, $NaBH_4$ plays a vital role in the reduction of 4-NP. However, besides the rigorous reaction, at higher concentration, it leads to toxicity due to the presence of boron. Even though numerous studies employed higher concentrations of $NaBH_4$ than 4-NP to achieve a higher reaction rate and get a perfect fit in the pseudo-first-order reaction plot during the process, it is time to think about the Environmental Protection Agency (EPA)/World Health Organization (WHO) toxicity limit of boron, which is supposed to be under 2.4 μg

Table 4 Bimetallic nanoparticles obtained by green synthesis used for the reduction of 4-NP and their respective characteristics and reaction conditions[115–127,a]

				Reaction conditions					
Feedstock	Metal	Size (nm)	Shape	Catalyst conc.	$NaBH_4$ conc. (mM)	4-NP conc. (mM)	Time (min)	Rate constant (K_{app}) $\times 10^{-3}\ s^{-1}$	Ref.
Unsupported NPs									
Ascorbic acid (2019)	Pd–Pt	∼57	Nanotubes	15 μg	100	0.009	10	3.4[b]	117
Morganella psychrotolerans and *Desulfovibrio alaskensis* (2019)	Pd–Pt	NR	NR	0.1 mM	10	0.1	10	NR	118
Waste tea leaves extract (2021)	Ag–Au	20	Spherical	20 μL	20 μL	0.1	6–7	NR	119
Pulicaria undulata (2020)	Au–Ag	5–12	Spherical	0.3 mL	30	2	∼5	NR	120
Salvia officinalis (2021)	Ag–Fe	30	Quasi spherical	5 mg	20	0.2	45	1.1[b]	121
Polysaccharide extracted from*Ramaria botrytis* mushroom (2020)	Ag–Au	150	Spherical	30.27 mg mL^{-1}	30	0.057	14	3.6[b]	122
Punica granatum extract (2015)	Au–Ag	12	Core–shell	NR	100	5	6	13.3[b]	123
Silybum marianum seed extract (2015)	Au–Ag	20–200	Spherical	0.5 mL	15	2	24	NR	124
Ginger rhizome powder (2018)	Cu–Ag Cu–Ni	NR	Spherical	10 mg	500	1	10	4.05–6.08	125
NPs supported on degraded *Pueraria mirifica* starch (DPS) (2013)	Au–Ag	1.6–26	Spherical	0.3 mL	15	0.2	35	NR	116
Supported NPs									
NPs synthesized with *Cetraria islandica* (L.) ash and supported on graphene oxides (2020)	Ag–Au (LrGO–AgAu)	6–30	Spherical	2.7 mL	100	9.6×10^{-5}	2–3	7.5–11.4	126
NPs supported on polydopamine-functionalized graphene (2016)	Pt–Au	2.7–6	Spherical	3 mg mL^{-1}	100	0.1	16	9.5	127
NPs decorated on graphene nanosheets (2014)	Au–Pd	2.67–3.15	Spherical	1.25 μg	10	0.1	25	14.5	115

[a] NR = not reported. [b] Denoted values were recalculated for uniformity in the corresponding units with respect to other reports.

mL^{-1}.[1,128] Obviously, the catalytic reduction reaction may take more time if the concentration of $NaBH_4$ is lower, but it is essential to evade boron purification.

4.5.2 Effect of reaction temperature on 4-nitrophenol reduction. To determine the ability of green-fabricated metal catalysts for 4-NP reduction, it is necessary to consider environmental conditions and it is essential to perform temperature-dependent studies. Based on the temperature-dependent 4-NP reduction reaction kinetics, we can also estimate thermodynamic parameters such as entropy, enthalpy, and Gibbs free energy. Sanoe Chairam *et al.*[88] tested mung bean starch-mediated AuNPs for the reduction of 4-NP at different temperatures and calculated the activation energy (E_a), enthalpy and entropy of 47.42 kJ mol L^{-1}, 44.78 kJ mol L^{-1}, and 261.49 kJ mol L^{-1}, respectively.

4.5.3 Experiments mimicking environmental conditions. To test the efficiency of the fabricated catalysts, the reaction needs to be performed in real (river, marine, agriculture, industry, *etc.*) water samples. As mentioned in the introduction, 4-NP is also used as a pH indicator, and thus the real water samples contain different pH and several contaminants such metal ions and pesticides. Thus, the changes in the absorption spectrum can confirm the pH of the real water solution. As is well known, the faster catalytic reduction of 4-NP happens in basic pH medium. On the one hand, there is a possibility of undergoing a faster reaction rate in real water samples (most samples above neutral pH). On the other hand, slower reaction kinetics can be observed due to the presence of unwanted systems such as heavy metals and other pollutants.

Moreover, interference studies need to be performed before using NPs in real-world applications. To the best of our knowledge, there are no studies on real water sample testing using green-fabricated metal nanoparticles.

4.6 Catalytic performance estimation parameters

The kinetics of the reaction can be estimated using the pseudo-first-order reaction, as follows:

$$\ln(C_t/C_0) = -kt$$

The regression factor (R^2) and rate of the reaction can be obtained from the slope (k, units: s^{-1} or $\min^{-1}$).

$$\ln(C_t/C_0)\ vs.\ t$$

where, C_0 and C_t indicate the initial and concentration of 4-NP at time t, respectively, and k is the apparent rate constant.

Thermodynamic parameters

$$\text{Gibbs free energy } (\Delta G) = \Delta H - T\Delta S \tag{1}$$

From the Arrhenius equation

$$\ln(k) = \left(-\frac{E_a}{R}\right)\frac{1}{T} + \ln(A) \tag{2}$$

$$\ln(k)\,vs.\,\frac{1}{T}$$

and

$$-\frac{E_a}{R} = \text{slope}$$

Eyring equation

$$\ln\left(\frac{k}{T}\right) = \left(-\frac{\Delta H}{R}\right)\frac{1}{T} + \ln\left(\frac{K_B}{h}\right) + \frac{\Delta S}{R} \tag{3}$$

$$\ln\left(\frac{k}{T}\right) vs.\ \frac{1}{T};\ \left(-\frac{\Delta H}{R}\right) = \text{slope}$$

and

$$\ln\left(\frac{K_B}{h}\right) + \frac{\Delta S}{R} = \text{constant } (c)$$

where A = Arrhenius constant, change in enthalpy (ΔH) and entropy, $R = 8.314$ J k^{-1} mol^{-1}, $K_B = 1.381 \times 10^{-23}$ J k^{-1}, $h = 6.626 \times 10^{-34}$ J k^{-1} mol^{-1}, T = absolute temperature in Kelvin, and $k = k_{app}$ = pseudo-first-order rate constant.

Activity parameter

$$k' = k/m \text{ units: } s^{-1}\ mg^{-1}$$

where m is the catalyst mass and k rate of the reaction.

Reduction/degradation capacity

$$Q_t = (C_0 - C_t) \times M/m$$

where C_0 is the initial and C_t is the concentration of 4-NP at time t, m is the mass of the catalyst and M is the mass of the organic pollutant.

Turnover number (TON): the TON is calculated using the number of moles of substrate that 1 mol of catalyst can convert into product.

Turnover frequency (TOF): the TOF is calculated simply by TON/reaction time.

Conversion efficiency

$$\text{Conversion efficiency } (\%) = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 and C_t are the initial absorbance of the 4-nitrophenol solution and with time (t), respectively.

5 Possible mechanistic understanding for the conversion of 4-nitrophenol to 4-aminophenol

The catalytic reduction of 4-NP by $NaBH_4$ and metal catalysts was investigated with the possible reaction mechanism presented in Fig. 3 initially following the LH model. The ionization of sodium borohydride in the liquid phase results in the production of borohydride ions (BH_4^-) and their adsorption on the surface of the metal catalyst to form a metal hydride

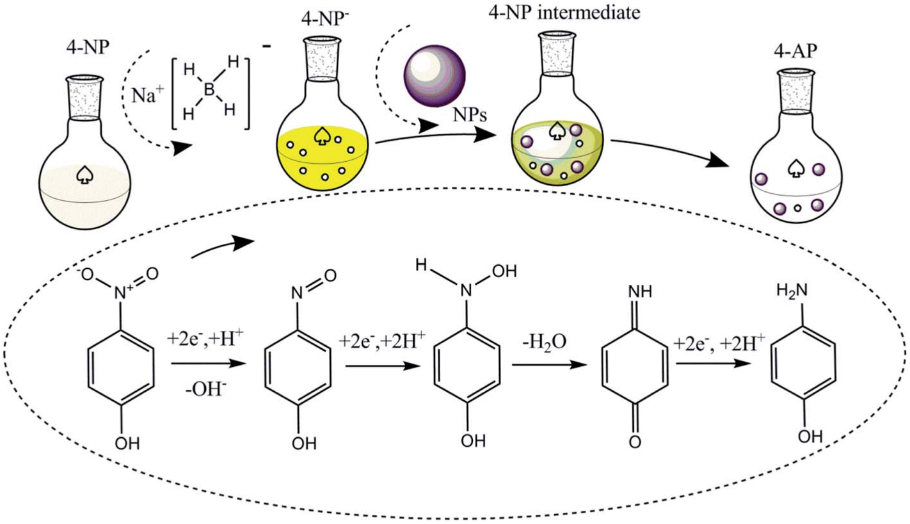

Fig. 3 Possible understanding of the conversion of 4-nitrophenol to 4-aminophenol using $NaBH_4$ and metal nanoparticles as an H_2 source and catalyst, respectively.

complex.[20,27,70,75,78] Simultaneously, 4-nitrophenol adsorbs on the metal hydride complex surface. Given that the progress is reversible, adsorption is followed by the desorption process. Thermodynamic equilibrium on the hydride complex surface allows H_2 transfer from the hydride complex surface to 4-NP, followed by the formation of the 4-nitrophenolate ion (4-NP$^-$).

Even though the specific mechanism still needs to be understood, according to the available hypothetical concepts, two (direct and condensation) paths can be proposed for the conversion of 4-nitrophenol to 4-aminophenol in the presence of $NaBH_4$ and catalyst. In the direct path, there is a possibility to obtain two consecutive fast reactions, *i.e.*, nitro group to nitroso group formation, and then amine group. Similarly, the condensation path involves the formation of azoxy compounds through the condensation of hydroxylamine with the nitroso compound. This is followed by its reduction, azoxy to hydrazo and hydrazo to 4-AP.

6 Challenges and future perspectives

In conclusion, green-fabricated metal nanoparticles and their up-to-date advancements in the reduction of 4-nitrophenol exhibited escalated progress in the past two decades. However, some challenges still need to be addressed for their possible scalability and application as economically viable water purifiers. Besides the production approach for developing highly stable and efficient metal nanoparticles, absorption in the entire visible spectrum and narrow bandwidth of metal nanoparticles with monodispersity and uniformity are required for specific applications and enhanced catalytic activity. Incredibly, researchers are still struggling to find possible economically viable techniques/methods for purifying metal nanoparticles and confirming the reduction of 4-nitrophenol.

The use of green materials from recycled waste needs to be assessed to produce metal nanoparticles. In addition, it is necessary to understand the effect of the presence of biomass on the development of metal nanoparticles. Alternatively, rapid and simple procedures are essential to develop recyclable catalytic probes to the boost catalytic efficiency. We suppose that the forthcoming investigation of catalytic probes using sustainable precursor-based metal nanoparticles will expand the general audience and scientific community awareness of their pollution removal application because of their simplicity, accessibility, and compatibility.

Conflicts of interest

There are no conflicts to declare.

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