



REVIEW ARTICLE

An overview of a sustainable approach to the biosynthesis of AgNPs for electrochemical sensors



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Abstract Mother nature furnishes various sources to synthesize nanomaterial's with different geometry, size, and functionality. In this outline, we aimed to discuss the biological source-mediated fabrication of Ag NPs because of their easy handling, yields, and economical and non-toxicity. The literature reveals that different plant species, fungi, and bacteria can employ biosynthesis, enabling the fabrication of nanoparticles with different features, notably size, geometry, and morphology. The exact mechanisms have not been understood well, even though it is trusted that bio-sourced is responsible for this process. The method of synthesis can be influenced by pH, concentration, time, and biomass. The optimized biosynthesized AgNPs can employ in various domains like sensors, nanomedicine, environmental pollution etc., The main objective of the paper is to elaborate on the biosynthesized AgNPS in electrochemical sensing and its surface modifications. Furthermore, these electroanalytical techniques are to be used for real-time sampling to allow the selective detection of the target analyte.

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1. Introduction

To attain the expanded applications of today and tomorrow's lifestyle, nano-biotechnology is one of the cutting-edge techniques with various applications like medicine, food cosmetics, environmental monitoring, soil, and water quality checking (Grieshaber et al., 2008), industrial chemicals, drug discovery, space equipment, photo-electrochemical, optical, electrical and

electronic applications (Mansur et al., 1995) (Wilmot, 1997) (Hoffman et al., 1992) (Schmid, 1998). In nanotechnology, the greener method also played a major role to synthesize metal nanoparticles (NPs) by using plants, bacteria, yeast, algae, enzymes, etc., the sustainable plant-based biosynthesized NPs are efficient for various applications and are eco-friendly and valuable substitutes for environmental management (Birla et al., 2013). Using plant parts to synthesize nanoparticles receives more attention due to the mystery of the plant world, still, the plants are surprising us with their unique properties, and the exact mechanisms for plant metabolites are challenging to researchers and not explored well. To improve in the medicinal field, nanomaterial plays a vital role in milestones and now it is the better substitute for biomedical applications (Balantrapu and Goia, 2009). In the current situation, the biggest challenge is to identify and treat new dis-

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eases, food adulterations, and environmental monitoring. However, Nano-sized functionalized NPs are an astonishing tool for such kind of identification (Khan, Saeed, and Khan, 2019).

This outline is an attempt to exhibit sustainable biosynthesized silver NPs towards electrochemical biosensors to track target analytes. Before concluding this outline shows the necessity of portable electrochemical biosensors with prospects.

2. Why green synthesis?

Green synthesis is the only way to avert harmful materials as compared to chemical synthetic procedures, toxic side products, and also the current and fascinating research domain (Hasan et al., 2015). Furthermore, it is reliable, sustainable, and eco-friendly. The synthesis procedure is also simple, and lesser time conception moreover the plants and the plant's medicinal properties and bioactive ingredients will be explored by using this method (Yousaf et al., 2019) (Hasan, 2019) (Hasan et al., 2013). To attain better, long-lasting, safe, and cleaner techniques for NPs synthesis, it is crucial to develop such strategies that aid to reduce the cost, boost the yield, and develop better ways that may be used at both industrial and commercial levels. Therefore, it is essential to research environmentally friendly, cost-effective, and high-production processes that use inexpensive reagents without compromising safety or the environment. Some key benefits of biological NPs production methods over physical and chemical methods (Hasan et al., 2018). The chemical composition which is present in the bio-sourced will act as a natural reducing agent without any hazards and environmentally friendly at a low cost.

2.1. The impetus of silver nanoparticles

Metals like Iron (Fe), Copper (Cu), platinum (Pt), Gold (Au), Palladium (Pd), and Silver (Ag) show engrossed in research, it has varying assets due to their physical and chemical properties. For millennia, silver has been used as an antibacterial to lessen microbial contamination and its claim to elevate our immune system. As silver is a valuable antibacterial and antioxidant, our ancestors also used it in vessels and ornaments. Ionic silver is also used to heal wounds in conjunction with this. A mechanism for silvers' antimicrobial activity remains a mystery. During the last decades, the utilities of Ag NPs are increased in many paths like medical devices, electronic equipment, drug delivery, and other applications (Tashi et al., 2016) (Slane et al., 2015). So silver gained much attention in every field, and also Ag is one of the best natural sources of abundance.

2.2. Importance of sensor

The sensor is one of the basic aspects of daily life just like the five senses of humans. The sensor is used for monitoring, security, maintenance, protection, and many more [12–14]. The accurate and rapid identifications of the target analyte are received more focus and demand (Li et al., 2019) (Kaviya, 2020a). Traditional techniques like atomic absorption spectroscopy, UV–visible spectroscopy, and mass spectroscopy are widely used for the identification of target analytes. The

drawbacks of these techniques are the need for trained manpower, skilled source, pre-treatment, expensive, long procedures, etc., (Akhgari et al., 2015). With this goal in mind, better precision, sensitivity, and budget-friendly sensors are the better technique to identify analytes such as toxic metal ions, dyes, gases, preservatives, drug discovery, water, and soil monitoring, etc., (Sapsford et al., 2008) (Chen et al., 2018).

2.3. Role of metal NPs in sensor

Noteworthy sensors are based on two basics: (i) analyzing the components for a specific analyte and (ii) a transducer compound for recording the better interaction event. These basics are in terms of selectivity, reproducibility, stability, time of response, noise ratio, and LOD (Saha et al., 2012). Furthermore in this outline, we focused on Ag NPs and their physical and chemical character and varying asset like antimicrobial (Kaviya et al., 2011) bio-imaging agent (Dayanand and Justyna, 2018) photocatalyst (Hashemi et al., 2022), etc., “The special properties of the metal make this asset possible, such as biocompatibility, chemical inertness, massive surface area, simple chemical synthesis, surface adaption, and optical properties as a result of its electron oscillation with the analyte” (Kaviya, 2020b).

2.4. Reason for bio-assisted NPs for sensor

A bio-assisted nanoparticle is eco-friendly, sustainable, cost-effective, and stable. Even though sensors have evolved over the years, the process has lost some of its affordability, biocompatibility, and greenness. Biosynthesis permits the identification of the target analyte with good selectivity without generating unwanted or harmful products. We are focused on revealing the bio-assisted metal NPs turned into the electrochemical sensor.

2.5. Fabrication of nanoparticle

Mainly metallic nanoparticles are fabricated by two methods: (i) Top-down and (ii) Bottom-up methods as shown in Fig. 1. Top-down techniques include processes like pulsed laser ablation (Zakaria et al., 2020), Arc discharge (El-Khatib et al., 2018), Spray pyrolysis (Kaya et al., 2020), Electro-explosion (Singh et al., 2016), Ball milling (Baláž et al., 2017), and lithography (Wang et al., 2019) that reduce large-scale materials into the minute, fine particles. However, these methods are better than chemical methods because of not use solvents or any toxic chemicals. Meanwhile, Bottom-up techniques, in contrast, involve shrinking the size of the material into the nanoscale through the process like micro-emulsion (Rivera-Rangel et al., 2018), photochemical (Gabriel et al., 2017), electrochemical pyrolysis (Chae, Lee, and Joo, 2019), microwave (Iqbal et al., 2014), solvothermal (Wani et al., 2010), Coprecipitation (Minh Dat et al., 2021), and sonochemical (Zhang and Li, 2012) as well as chemical reduction using reducing agents like sodium borohydride (Chouhan, Ameta and Meena, 2017), quinone based compounds (Jacob et al., 2008). The final method is the Bio-reduction process by using plant parts, bacteria, fungi, yeast, and algae. The chemical composition which is present in the bio-sourced will act as a natural reducing agent without any hazards and environmen-

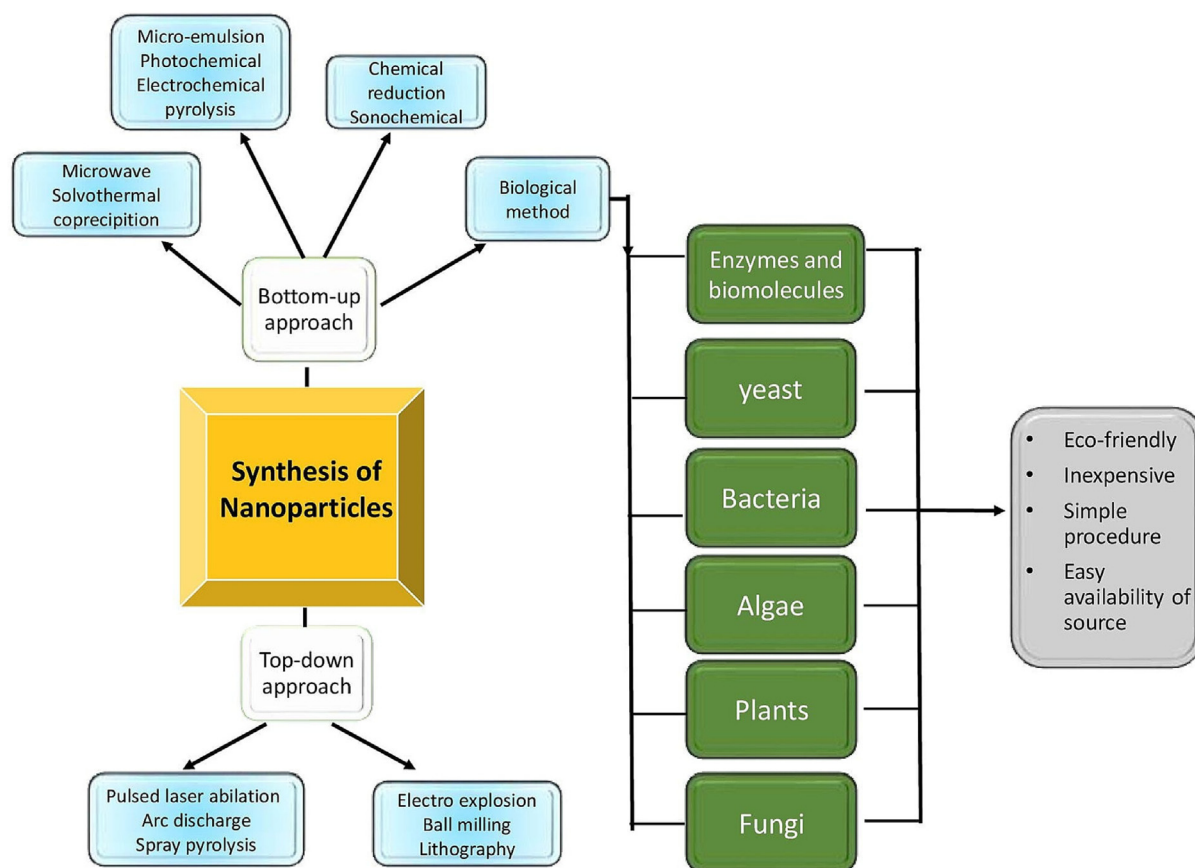


Fig. 1 Routes to synthesis nanoparticle.

tally friendly at a low cost. The bio-assisted NPs are named Green synthesized NPs with desired metal under optimal conditions.

2.6. Biological methods

The metal NPs can synthesize from various bio-sourced including bacteria, fungi, yeast, algae, and plant parts (Fig. 2). There is no need for an external stabilizing agent because the bio-sourced has the active property that makes it a bio-reducing agent in the fabrication of NPs synthesis. Since the fabrication is a harmless and prominent particle of metal NPs have received more focus from researchers (Iravani, 2011).

2.7. Bacteria-assisted synthesis of Ag NPs

Microorganisms are one of the best candidates for the bio-fabrication of NPs but it has contamination of culture medium, long procedure, and are not able to control the size of NPs (Rafique et al., 2017). However, bacteria-assisted synthesis of Ag NPs can able to reduce heavy metal ions, and it receives a better interest in NPs synthesis. Based on the location of synthesis in bacteria it can classify into distinct types (Li et al., 2011). Survey shows that *Pseudomonas stutzeri* and *Pseudomonas aeruginosa* have a better ability to overcome the toxicity of heavy metal ions and even can grow in higher heavy

metal concentrations (Iravani, 2014). Table 1 provides several studies related to the biosynthesis of Ag NPs by using bacteria. In 1999 Klaus et al. (Klaus et al., 1999) reported the bio-fabrication of Ag NPs by using *Pseudomonas stutzeri* strain and this is one of the earliest articles on the fabrication of triangular-shaped Ag NPs with 200 nm by using bacteria. Shivaji and Madhu et al., (Shivaji, Madhu and Singh, 2011) purposed the synthesis of Ag NPs by using *psychrophilic* bacteria. The recent article purposed by Garibo et al. studied the bio-fabrication of Ag NPS by using *Escherichia coli* (Garibo et al., 2020).

2.8. Fungi-assisted synthesis of Ag NPs

Fungi are one of the better potential biomass for the production of Ag NPs, nearly 6,400 bioactive ingredients are present in fungi and fungal species (Kim et al., 2017). Moreover, it can use for large-scale production with optimized parameters, and also it has several advantages over other microorganisms to produce a large amount of NPs. The biosynthesis of NPs by fungi can be classified into two parts: intracellular and extracellular (Azmath et al., 2016) (Khan et al., 2017). If the metal precursor is added in mycelial it is called intracellular whereas in extracellular, the metal precursor will be added in aqueous filtrate which contains only fungal biomass (Rose et al., 2019). Table 2 reported some illustrative examples of the bio-fabrication of Ag NPs by fungi-assisted.

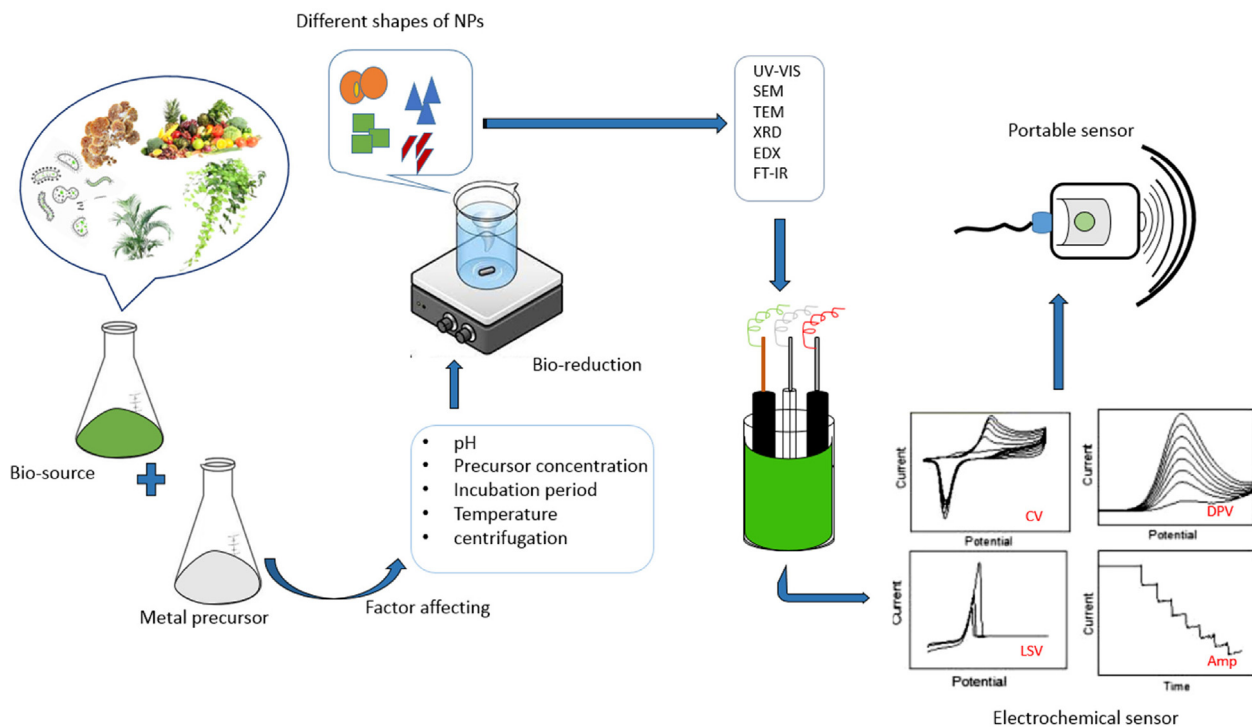


Fig. 2 Consequences of biogenic nanoparticle, b. Consequences of biogenic nanoparticle.

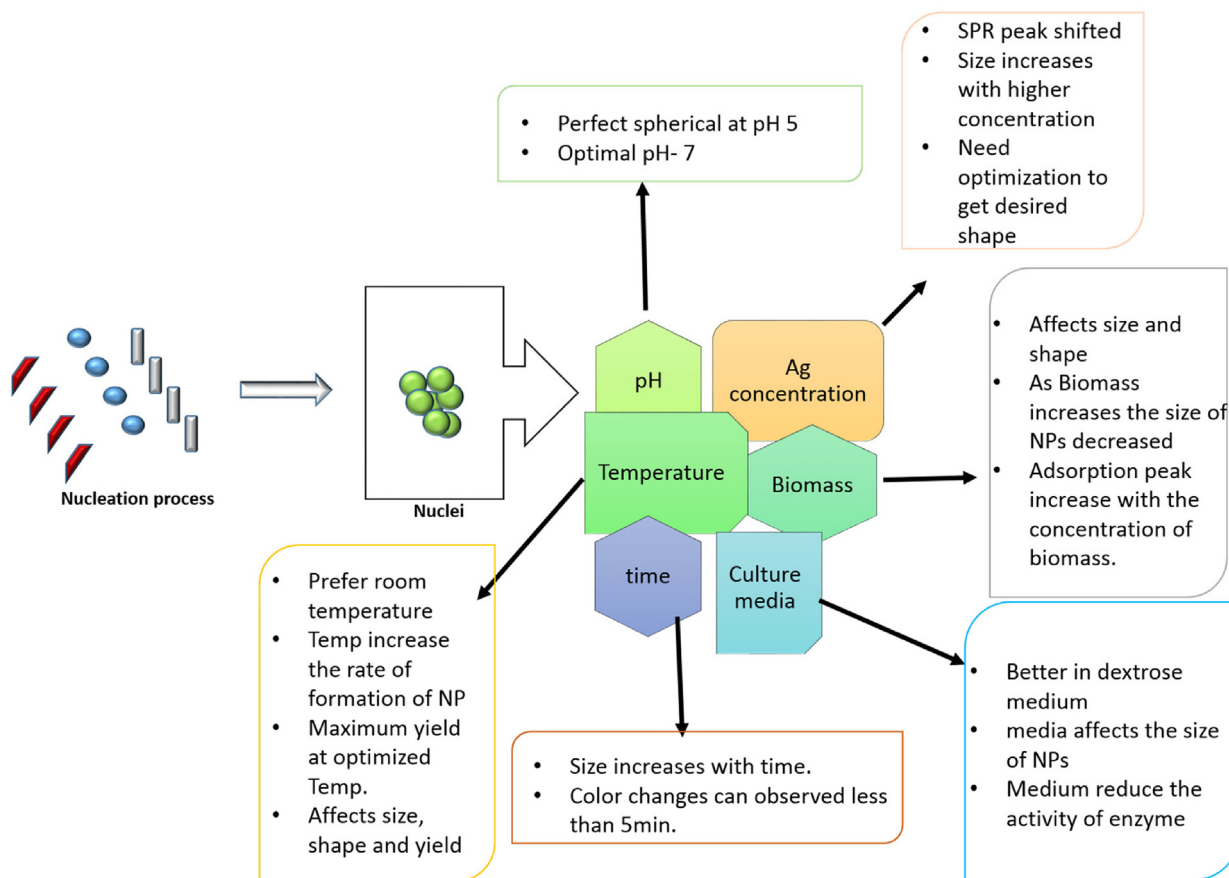


Fig. 2 (continued)

Table 1 Bacteria mediated synthesis of Ag NPs.

Bacteria species	Size (nm)	Shape	Reference
<i>Escherichia coli</i>	1.2–62	Spherical	(Garibo et al., 2020)
<i>Bacillus siamensis</i>	25–50	spherical	(Ibrahim et al., 2019)
<i>Serratia nematodiphila</i>	65–70	Spherical	(Malarkodi et al., 2013)
<i>Bacillus stearothermophilus</i>	65–70	Spherical	(Mohamed et al., 2009)
<i>Lactobacillus casei</i>	42–92	Spherical	(Iravani et al., 2012)
<i>Nocardiopsis</i> spp.	25–50	Spherical	(Manivasagan et al., 2013)
<i>Streptomyces hygroscopicus</i>	45 ± 0.15	–	(Sadhasivam et al., 2010)
<i>Staphylococcus aureus</i>	20–30	Irregular	(Nanda and Saravanan, 2009)
<i>Rhodococcus</i> spp.	160–180	Spherical	(Otari et al., 2015)
<i>Marine Ochrobactrum</i> spp.	5–50	Spherical	(Thomas et al., 2014)
<i>Escherichia coli</i>	38–85	Spherical	(Ghorbani and Rashidi, 2013)
<i>Lactobacillus</i> strains	1–100	Triangular/ hexagonal	(Nair and Pradeep, 2002)
<i>Bacillus methylotrophicus</i>	15–500	Spherical	(Wang et al., 2016)
<i>Vibrio alginolyticus</i>	50–100	Crystalline/spherical	(Garibo et al., 2020)

Table 2 Fungus mediated synthesis of Ag NPs:

Fungus	Size	Shape	Reference
<i>Colleotrichum</i> sp. ALF2-6	5–60 nm	Myriad shapes	(Azmath et al., 2016)
<i>Aspergillus oryzae</i>	7–27 nm	Spherical	(Phanjom and Ahmed, 2017)
<i>Rhizopus stolonifer</i>	2 nm	Spherical	(AbdelRahim et al., 2017)
<i>Aspergillus fumigatus</i> BTCB10	322.8 nm	spherical	(Shahzad et al., 2019)
<i>Fusarium oxysporum</i>	5–13 nm	Spherical	(Husseiny et al., 2015)
<i>Guignardia mangifera</i>	5–30 nm	spherical	(Balakumaran et al., 2015)
<i>Duddingtonia flagans</i>	30–409	spherical	(Costa Silva et al., 2018)
<i>Trichoderma longibrachiatum</i>	24	spherical	(Elamawi et al., 2018)
<i>Penicillium oxalicum</i>	36	spherical	(Du et al., 2015)
<i>Arthroderma fulvum</i>	20	spherical	(Xue et al., 2016)
<i>Sclerotinia sclerotiorum</i>	10–15	spherical	(Saxena et al., 2016)

Table 3 Yeast mediated synthesis of Ag NPs:

Yeast	Size (nm)	Shape	Reference
<i>Saccaromyces cerevisiae</i>	6.7	spherical	(Elnagar et al., 2021)
<i>Pichia kudriavzevii</i> HA NY2	12.4	round	(Ammar et al., 2021)
<i>Saccharomyces uvarum</i> HA NY3	20.6	cubic	(Ammar et al., 2021)
<i>Crataegus pinnatifida</i>	50–100	spherical	(Liu et al., 2021)
<i>Vitis vinifera</i>	50–100	spherical	(Liu et al., 2021)
<i>Saccharomyces cerevisiae</i>	11–25	Spherical	(Kthiri et al., 2021)
<i>Staphylococcus aureus</i>	13	Spherical	(Shu et al., 2020)
<i>Saccharomyces cerevisiae</i>	16	Oval	(Ibraheim et al., 2016)
<i>Rhodotorula</i> sp. strain	8–21	Oval	(Soliman et al., 2018)

2.9. Yeast-assisted synthesis of Ag NPs

Yeast is one of the simple processes in the bio-fabrication of NPs with mass production. Yeast is known as the eukaryotic microorganism of fungi, around 1,500 species are present now. Table 3 shows the reported bio-synthesis of Ag NPs by using various yeast.

2.10. Plant-assisted synthesis of Ag NPs

In greener synthesis, plant-mediated synthesis (Table 4) is the most believed route as it gives a plethora of merits over the

chemical and physical route. The extended research of plant-mediated synthesis is fractionating the crude extract of the plant-like ethanol–water mixture. Murtaza Hasan et al used *Fagonia Cretica* 50 % fractionation to achieve enhanced anti-oxidant, anti-tyrosinase, and antiurease. Whereas the plant extract's 90 % and 70 % ethanol fractions have greater anti-tyrosinase and anti-urease activities. Plant extract fractions with 50 % ethanol show potential for anti-oxidant and anti-urease properties. When diluted and doubled, the 30 % ethanol fraction of the plant extract gets stronger and exhibits anti-oxidant and antiurease activity. Only when employed in high concentrations do the 50 % and 30 % ethanol fractions

Table 4 Plant mediated synthesis of Ag NPs:

plant	Size (nm)	Shape	reference
<i>Salvadora persica</i>	37	spherical	(Arshad et al., 2021)
<i>Parthenium hysterophorus</i>	10	spherical	(Sivakumar et al., 2021)
<i>Populus ciliata</i>	4	Spherical	(Hafeez et al., 2021)
<i>Rosa canina</i>	150	spherical	(Ozlem Saygi and Usta, 2021)
<i>Cuminum cyminum L.</i>	50	spherical	(Chamkouri et al., 2021)
<i>Cleome viscosa</i>	20–50	spherical	(Lakshmanan et al., 2018)
<i>Ficus hispida</i> Linn. f.	20	spherical	(Ramesh et al., 2018)
<i>Acacia cyanophylla</i>	88	spherical	(Jalab et al., 2021)
<i>A. nilotica</i> Willd twig bark	10–50	circular	(Karuppiyah et al., 2014)
<i>Azadirachta indica</i> leaves	5	spherical	(Gnana Kumar et al., 2014)
<i>Callicarpa Mainga yi</i> leaf	15	sheet	(Chekin et al., 2014)
<i>Citrus sinensis</i> var. <i>Kozan yerly fruit</i>	4–10	spherical	(Khan et al., 2015)
<i>Plectranthus amboinicus</i> leaf	22	spherical	(Zheng et al., 2016)
<i>Mimosa Pudica</i> root	35–42	spherical	(Sreenivasulu et al., 2016)
<i>Convolvulus pluricaulis</i> leaf	10–11	spherical	(Sandeep et al., 2016)
<i>Piper betel</i> leaves	48	spherical	(Ramachandran et al., 2016)
<i>Onion extract</i>	10	Spherical	(Khalilzadeh and Borzoo, 2016)
<i>Ocimum tenuiflorum</i> leaves	20–25	Spherical	(Dayakar et al., 2018)
<i>Lithodora Hispidula</i> leaves	15	spherical	(Turunc et al., 2017)
<i>Salvia leriifolia</i> leaves	27	spherical	(Baghayeri et al., 2018)
<i>Camellia japonica</i> leaves	12–25	spherical	(Karthik et al., 2017)
<i>Oakleaf</i>	20–25	spherical	(Hemmati et al., 2018)
<i>Allium sativum</i> cloves	19	spherical	(Aravind et al., 2018a)

of the plant extract exhibit anti-tyrosinase activity. Therefore, among all fractions of plant extract, the 50 % ethanoic fraction contains more active chemicals that are involved in a variety of pharmacological activities (Hasan, 2019). This process is eco-friendly, simple, has no sophisticated equipment, and is non-toxic without any external capping, reducing, or stabilizing agent (Nadaroglu et al., 2017). Plants have free natural reducing, stabilizing, and capping activity in short it is a method of natural ingredients with modern technology. Moreover, the product formed by using plant extract is more stable with optimized shape and size (Shumin Yang and Yanqing Wu, 2013). The phytonutrients which are present in plant extract contain proteins, amino acids, terpenoids, flavonoids, and polyphenols are the basic metabolites for natural reducing properties (Silva, Pereira and Bonatto, 2019). Krishnaraj et al., (Krishnaraj et al., 2010) reveal the secret of *Acalypha Indica* plant nutrients, they reported quercetin is responsible for the Ag NPs formation and will act as a natural reducing agent in the bio-reduction process. Similarly, Ahmad et al., (Ahmad et al., 2011) synthesized Ag NPs by using *Desmodium triflorum* here ascorbic acid is the plant metabolite that serves as a natural reducing agent.

2.11. Characterization of NPs

Instrumentation of NPs is an important part of the material science domain, various analytical instrumentation will be carried out to confirm the production of NPs. Some basic analytical techniques like spectroscopy and microscopy are very fruitful to study scientifically and from the SEM, XRD, and HRTEM we can confirm the geometry of fabricated NPs with size. The techniques like UV-vis, FT-IR, Zeta potential, VSM, BET, Raman, Fluorescence, photoluminescence, AFM, EDX, etc., were used to study the nature of synthesized NPs.

2.12. Morphology control of the bio-assisted synthesis of NPs

Similar to chemical synthesis, parameters such as temperature, pH, solvent, nature/composition of the natural source present in the extract/bio-source, concentration of the biosource, reaction time/incubation period, gas atmosphere, stirring speed, calcination temperature, concentration/chemistry of the precursor, capping, reducing, and stabilizing agent, allows for fine-tuning of the size and shape of the biosynthesized nanoparticles (Fig. 2b). Due to the dense components in the bio-source, it is challenging to control the shape of the biosynthesized NP. The ratio between the concentration of the precursor and the capping agent typically controls the size and formation of nanoparticles. When the ratio is very high or low, the likelihood of aggregation increases, which can result in polydisperse or irregularly shaped particles. Biosynthesis of Ag NPs can also vary based on optimization including temperature, pH, time of reaction, agitation, metal salts, and plant concentration. With the help of optimized parameters, we can attain the desired shape and size of NPs. Since optimization is one of the important factors to get proper monodispersity, stability, and bio-compatibility of fabricated NPs (Balakumaran et al., 2015). In 2013 Hasan et al. attempted to synthesize AgNPs using dragon's blood (*Dracaena Cochinchinensis*, Lour. S.C. Chen) resin extract at various times and temperatures namely 4 h, 2 h, and 30 min of reaction at 30 °C, 60 °C and 90 °C and they achieved the size of nanoparticles varying from 10 nm to 30 nm (Hasan et al., 2013). The same group in 2015 reported the synthesis of AgNPs using dragon's blood with 1 mM of AgNO₃ and the main outcome of the results in the synthesis of round shaped AgNPs ranging from 5 to 50 nm in short time and also they revealed the main active ingredients which is present in the dragon's blood biosource like *pterostilbene*, *cinnabarone*, *Loureirin A*, and *Loureirin*,

etc., (Hasan et al., 2015). Hence the optimization plays a vital in the synthesis of nanoparticles.

2.12.1. The consequence of reaction time

The effect of time influences the quality of the NPs and also the structure and active properties can change (Darroudi et al., 2011). The duration of reaction time is incubated considerably affects the size, shape, and extent of nanoparticle formation. According to Nazeruddin et al. (Nazeruddin et al., 2014), *Coriandrum sativum* seed extract produces Ag nanoparticles rapidly, taking only 1 to 2 h as opposed to the 2 to 4 days needed by microorganisms. Similar to this, Noruzi et al. (Noruzi et al., 2011) observed that the Rosa hybrid petal-mediated Au nanoparticle manufacturing reaction was quick and finished in under 5 min. Although compared to microorganisms, plant-mediated biosynthesis of nanoparticles is often faster, some scientists have found that the production rate is still efficient at a fast reaction time (Darroudi et al., 2011). Within 15 min of the reaction beginning, Ag and Au nanoparticle production was detected by Dwivedi and Gopal (Dwivedi and Gopal, 2010a). Also, they discovered that an increase in contact time had a significant impact on how sharp the peaks in both Ag and Au nanoparticles were. A few investigations also suggested that the nanoparticles' size and shape change depending on how long it takes to react, Li et al. (Rousta and Ghasemi, 2019) found that five hours of reaction time resulted in spherical and polycrystalline-shaped nanoparticles (102 nm) when Ag nanoparticles were synthesized using Capsicum annum L. extract. The nanoparticles' sizes rose with an increase in reaction time to 9 h and 13 h, respectively, to 25 nm and 40 nm. NPs can experience size effects if the incubation time is increased beyond 10 min. (Velgosova et al., 2017).

2.12.2. The consequence of bio-mass

The amount of bio-mass plays a vital role to form desired size and geometry of the bio-fabricated NPs. Researchers also tried various concentrations of bio-mass to optimize the size and geometry of NPs like 0.5, 1, 2.8, and 4.8 mL of *Tanacetum vulgare* extract to fabricate Ag NPs (Dubey, Lahtinen and Sillanpää, 2010). They reported that the concentration of bio-mass increased with a decrease in the size of the synthesized NPs (Dwivedi and Gopal, 2010b), and the absorption peak of synthesized NPs increased with an increase in the concentration of bio-mass due to the presence of the dense molecule present in the biomass (Korbekandi et al., 2013). It can be stated that an appropriate balance between the amount of organic material, obtained from the fungus, and the amount of metal precursor is required for efficient nanoparticle synthesis, despite variances in the amount of biomass used depending on the species of fungus used (Shahzad et al., 2019).

2.12.3. The consequence of Ag-salt quantity

This factor is one of the important factors to make the synthesis route economical in the biotransformation process. This effect will optimize the level of agglomeration and the surface plasmon resonance (SPR). The SPR peak often shifts towards the higher wavelength area and gets narrower as concentration values rise. We conclude that increasing the concentration of the solution causes the formation of nanoparticles with smaller sizes because, assuming that the plasmon resonance peak shift indicates a change in the size of AgNPs, any shift of the peak

towards the higher wavelength is followed by a decrease in the size of the prepared AgNPs. On the other hand, the expansion of the surface plasmon resonance peak suggests that the solution contains a wider range of sizes (Bar et al., 2009). Dubey et al (Dubey, Lahtinen and Sillanpää, 2010) try to optimize the concentration of Ag salt varies from 1 to 3 mM and they observed the size of the NPs increases with increasing the concentration of Ag salt. Similarly, the other group use the *Chenopodium album* to optimize Ag salt, they also reported that the size of NPs increases with increasing the concentration of Ag salt (Dwivedi and Gopal, 2010b). However the gradual increasing the concentration of Ag salt and the size of NPs increases up to 10 mM, after 10 mM it starts to decrease the production. Hence the optimal concentration of Ag salt is 5 mM (Korbekandi et al., 2013).

2.12.4. The consequence of pH

In the production of nanoparticles by bio-source, pH is crucial. Researchers have found that pH affects the size, shape, and production rate of synthesized NPs (Armendariz et al., 2004). The creation of nucleation centres rises with an increase in pH. The reduction of metallic ions to metal nanoparticles increases along with the nucleation centre. Additionally, the solution pH affects the rate of reduction of a metal salt as well as the activity of the functional groups in the plant extract or bio-source (Bali and Harris, 2010). Furthermore, Jacob et al. (Jacob, Mukherjee and Kapoor, 2012) investigated the Au and Ag ion reduction rates at pH 3.3 and 10.8. According to their research, Ag ions reduced at pH 3.3 more slowly than Au ions, and the resultant nanoparticles precipitated in just two days. Nevertheless, both metal ions underwent simultaneous decreases at pH 10.8, and a single Surface plasma resonance band was seen. The homogeneous electron density visible in the TEM image suggests that alloyed nanoparticles were created. Additionally, they claimed that a high pH value helped create the molecules AgO^- and AgO , which bind strongly with the hydroxyl groups in plant extracts and efficiently cover the surface of nanoparticles. pH also depends on the reaction medium. Literature survey shows that the lower the pH favoured increasing the size of NPs (Gericke and Pinches, 2006). Spherical shapes of Ag NPs can get at pH 5 by using *Cinnamon zeylanicum* (Sathishkumar et al., 2009). Researchers show that the optimal pH value is 7 and also the maximum yield can get at pH 7.

2.12.5. The consequence of culture medium

In the bio-synthesis of Ag NPs by using fungi, the culture medium plays an important role and its different responses are based on the culture medium. Higher concentrations and smaller sizes of the nanoparticles were present in the nanoparticle dispersions made using the filtrate from the fungus growing in the enzyme induction medium. This was explained by the nitrogen source's stimulation of enzymatic activity in the modified medium, which increased nanoparticle production. In trials where various mediums for the growing of fungi were investigated, various behaviours were seen (Costa Silva et al., 2017). Ashrafi et al. discovered that the same medium prevented the formation of silver nanoparticles using *Rhizoctonia solani* filtrate, but the synthesis was effective when the fungus was grown in a potato dextrose medium. It was postulated that a component of the medium may have reduced the activity of

the enzyme responsible for the reduction process (Ashrafi et al., 2013). Conversely, Birla et al. tried with different media nearly 10 to optimize the better yield of Ag NPs (Birla et al., 2013). It was proposed that a component of the medium may have impeded the activity of the enzyme in charge of the reduction process.

2.12.6. The consequence of temperature

Another significant element that affects the size, shape, and rate of nanoparticles is temperature. Similar to pH, temperature increases cause more nucleation centres to develop, which in turn speeds up the biosynthesis process and gets the maximum yield of product. Most of the optimal temperature was room temperature (25 °C) with this temperature can get maximum yield (Zhang et al., 2013). To find the ideal temperature, Shen et al. (Shen, Mathew and Philip, 2011) studied the reduction processes of Au and Ag ions by *Anacardium occidentale* leaf extract at various values of time and temperature. The authors discovered that producing stable nanoparticles at low reaction temperatures required more leaf extract than when doing so at high temperatures. More specifically, 0.6 mL of leaf extract was all that was needed for biosynthesis to occur at 100 °C, whereas 2.5 mL of leaf extract was needed for synthesis to occur at 27 °C. The authors also noted that high-temperature nanoparticles were not only more stable but also greater in size. Irvani and Zolfaghari (Irvani and Zolfaghari, 2013) heated the reaction mixture to various temperatures to study the impact of temperature and the authors state that with increasing temperature whereas the size of Ag NPs decreases with increasing absorbance. Similar results are also get by using *Annona squamosa* peel to get a higher yield at higher temperatures (Kumar et al., 2012). Furthermore, temperature affects the absorption peak, at low temperatures the band was sharp whereas at the higher temperature the band became broad (Shahzad et al., 2019). Meanwhile, Raju et al., (Raju, Mehta, and Hazra, 2011) get the perfect geometry of spherical at a higher temperature. The ability of some fungal species to transfer electrons from free amino acids to silver ions at high temperatures is demonstrated. However, the proteins that make up the nanoparticle capping get denaturated at extremely high temperatures, between 80 °C and 100 °C. Ag⁺ ion nucleation is altered by this denaturation, causing the nanoparticles to aggregate and grow in size reported by Birla et al., [7]. Due to the low activity of the synthesis-related enzymes, Husseiny et al. (Husseiny et al., 2015) claim that suboptimal temperatures cause increased nanoparticle size and loss of stability.

In short, the varying factor of synthesis can vary the characteristics of NPs. however, the consequences are still unclear and need further pieces of information for each organism employed. It is important to reveal the optimized physico-chemical characteristics of NPs, in the flow to find the parameters used in the fabrication like pH, temperature, the concentration of Ag-salt, and bio-mass. The optimization only can enable achieving rapid large-scale NPs fabrication.

2.13. Plant-assisted synthesis of Ag NPs as sensors

The Ag NPs can be employed in various fields (Fig. 3) listed such as food and agriculture, textiles, electronics, health care, biomedical, environmental, etc. In sensors, there are different

types of sensors like SERS, Colorimetric, fluorescence, and electrochemical sensors. Electrochemical sensors are one important technique to analyze quantitatively and qualitatively any target material with good selectivity and sensitivity. The electrochemical sensors are portable and have good sensitivity with better selectivity with economical. It does not require any prolonged procedure, skilled power, pre-treatment for the mediator, etc., the various techniques in electrochemical like amperometry, cyclic-voltammetry, impedimetric, linear sweep voltammetry, potentiometric, etc., can be used to detect the specific target analyte. Table 5 reveals the elaborated bio-assisted Ag Nps utilized for electrochemical detection of the targeted analyte. To create an electrochemical sensor, a working electrode is either glassy carbon or screen printed. Reference electrodes (Ag/AgCl) must be used to maintain a stable potential, and counter electrodes (Au/Pt) will be used to connect to the electrolyte and provide current to the working electrode [70].

2.14. Bio-assisted synthesis of Ag NPs for electrochemical sensor

Huge effects have been required to build a sustainable sensor with high sensitivity and selectivity. To overcome this dilemma the utilization of bio-synthesized nanomaterials is one of the promising tools to build biocompatibility, the low-cost sensor which is prepared from natural sources. In this context, the main purpose of biosynthesized NPs is to develop highly sensitive, non-toxic sustainable sensors. The electrochemical sensor has a sophisticated facility and plays a vital role in the food industry, medical, pharmaceutical, etc., due to its inexpensive, rapid, simple procedure with good sensitivity and selectivity, and real-time analysis. This method is one of the promising alternative analyses over spectroscopy and chromatography with various techniques like cyclic voltammetry (CV), amperometry (Amp), differential pulse voltammetry (DPV), square wave voltammetry (SWV), and linear sweep voltammetry (LSV).

An electrochemical sensor design, requires a working electrode either glassy carbon or screen printed electrode it can transduction element for chemical reaction, a reference electrode (Ag/AgCl) for stable potential, counter electrode (Au/Pt) to form a link with electrolyte to give current to the working electrode (Grieshaber et al., 2008).

Biosynthesized AgNPs for H₂O₂ reduction: Generally, NPs have good conducting and catalytic properties due to their large surface area, the huge number of research groups were involved in the NPs employed electrochemical sensors (Table 5), especially the H₂O₂ sensor-H₂O₂ and its derivatives are highly oxidizing agent it cause several issues and is widely used in various domain like industry, food product, clinical, etc., it causes severe environmental issue. Turunc et al., (Turunc, Kahraman, and Binzet, 2021) use pollen extract for the detection of H₂O₂ by using amperometry and the square wave voltammetry method (Fig. 4). Pollen grains are collected from *C. Sempervirens* and treated with 1 mM AgNO₃ to form Ag NPs at room temperature. The experiment was carried out with a pre-treated glassy carbon electrode that was drop cast by 8 µL of synthesized Ag NPs and 5 µL of Nafion in 0.1 M PBS (pH 7). They show a linear range between 5 µM and 2.5 mM with a limit of detection of 0.23 µM in the detection

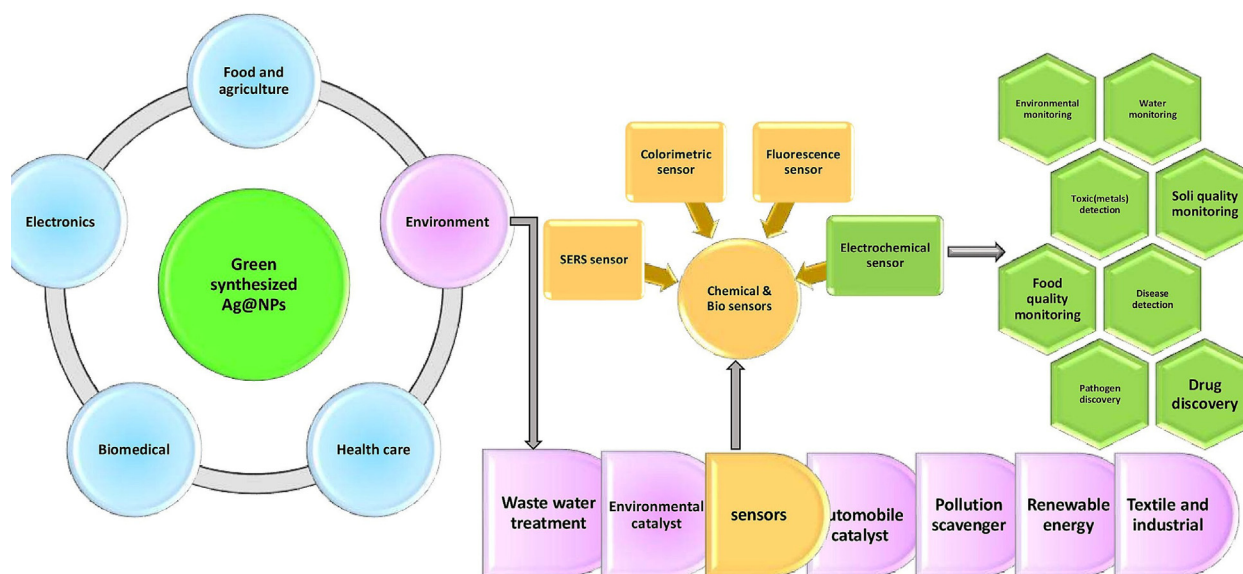


Fig. 3 Applications of biosynthesized Ag NPs.

of H_2O_2 and the interference was also carried out to find better selectivity. Similarly Mavaei et al (Mavaei et al., 2020) attempt to sensor H_2O_2 by using *Prangos ferulacea* roots extract. The isoimperatorin solution was isolated from *Prangos ferulacea* roots and it was treated with 1 mM AgNO_3 to synthesize spherical shape Ag NPs. The GCE was constructed by drop-casting of 5 μL of synthesized Ag NPs and the prepared electrode was characterized in 0.1 M PBS (pH 7) to catalyze H_2O_2 with a linear range of 0.1 μM – 4 mM and LOD was calculated and found to be 0.036 μM . In another work, *Tagetes erecta* (Salve et al., 2020) was used to synthesize Ag NPs with a 0.5 mM solution of Silver nitrate salt to catalyze H_2O_2 and supercapacitor application. They construct Pencil graphite electrode /AgNPs/Chitosan in HCl-KCl solution (pH 2). By adopting cyclic-voltammetry the H_2O_2 was catalyzed from the lower concentration of 1 μM to a higher concentration of 10 μM with 0.52 μM of the detection limit.

Biosynthesized AgNPs to detect toxic metals and drugs: Imatinib is a cancer drug to treat chronic myeloid leukemia however, it leads to a decrease in the plasma concentrations in inpatients. Hence it is mandatory to monitor the imatinib level in the body. By using *lycoris longituba* leaf extract, the Ag NPs were synthesized to detect imatinib (Wu et al., 2021) they chose graphene-based modified electrode to sense imatinib by adopting DPV technique with various concentration ranges from 10 nM – 280 μM and the LOD is 1.1 nM. They attempt to show better selectivity using real sample analysis and interfere effect with various analytes like sodium, potassium, and copper but imatinib only shows 10 times higher current value than the rest of all. In the list of toxic metal ions, mercury is one of the toxic heavy metals which cause drastic effects on the environment. *Mimosa diplotricha* assisted Ag NPs were synthesized for the electrochemical catalyze of mercuric ions (Punnoose et al., 2021) the analysis was carried out in a pH 6 acetate buffer solution. They chose the DPV technique to sense mercuric ions at pulse amplitude of 25 mV and 200 ms pulse width. The *Mimosa diplotricha* employed Ag NPs modified pt electrode was used to sense mercury ion with the linear range of 5–

45 μM and shows excellent selectivity over Ni^{2+} , Cu^{2+} , Mn^{2+} , Co^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} .

Araucaria angustifolia mediated Ag NPs was formed for the detection of paracetamol (Zamarchi and Vieira, 2021). Further, Graphite nanoplatelet electrodes were employed to form AgNP-xGnP/GCE as shown in Fig. 5. The modified electrode can detect up to 3.38×10^{-5} M paracetamol in PBS at pH7 conditions and it shows detection of limit (8.50×10^{-8} molL $^{-1}$). The modified electrode was employed to investigate the real sample of the commercially available pharmaceutical product.

Biosynthesized AgNPs for biosensor: In the other investigation 6 nM-sized round spherical-shaped Ag Nps were fabricated by using the endophytic fungus *Fusarium oxysporum*. Ag/Ag₂O NPs/GCE electrode was designed by bio-transformation of silver oxide micro powder into Ag/Ag₂O nanoparticles. The modified electrode was constructed by the process of 50 μL of micron Ag₂O and Ag/Ag₂O nanoparticles on GCE and 1 M KOH as an electrolyte to catalyze non-enzymatic glucose. They tried various concentrations of glucose ranging from 25 $\mu\text{mol/L}$ to 125 $\mu\text{mol/L}$ at 50 mVs $^{-1}$. The lack of the purposed work is they do not provide an exact linear range of detection and do not show the LOD value (Islam et al., 2021). The Ag NPs with reduced graphene oxide were immobilized on a glassy carbon electrode. Amperometric techniques were involved in the experiment to detect H_2O_2 , with concentrations ranging from 35 μM to 1.95 mM in pH 7 conditions in presence of 0.1 M PBS electrolyte. They also performed an interference effect to show better selectivity and stability of the modified electrode containing 800 μM H_2O_2 at 50 mVs $^{-1}$ checked along with this the relative standard deviation value was found to be 8.2 % (Chelly et al., 2021). In 2020 Bahareh et al., attempted to fabricate Ag NPs from pegalum harmala to make Ag-NP/Paraffin oil(PO)/*n*-hexyl-3-methylimidazolium hexafluoro phosphate(MIHP)/Carbon paste electrode(CPE), which demonstrated excellent performance for the electrocatalytic determination of quercetin with a detection limit of 5.0 nM. Finally, the Ag-NP/PO/MIHP/

Table 5 Biogenic synthesized Ag NPs in electrochemical sensor.

Bio-source	Size (nm)	Shape	Colour change	Modified electrode	Analyte	Linear range	LOD	Technique	Reference
<i>V. planifolia</i>	9–25	shell	Yellow to brown	CDA/Au-Ag/GCE	Vanillin	0.2–50 μM	40 nM	Amp-It	(Zheng et al., 2010)
<i>Bacillus subtilis</i>	50–100	rod	Yellow to brownish	Bio-Ag NPs/GCE	H_2O_2	0.05 to 120 nM mmol L ⁻¹	8 $\mu\text{mol/L}$	Amp-It	(Liu et al., 2013)
<i>A. nilotica</i> Willd twig bark	10–50	circular	Yellow to brown	Ag-NPs/GCE	4-nitro phenol	100 nM to 350 μM	15 nM	DPV	(Karuppiyah et al., 2014)
<i>Azadirachta indica</i> leaves	5	spherical	–	Ag–Au–rGO/GCE	H_2O_2	100–5000 μM	1 μM	Amp-It	(Gnana Kumar et al., 2014)
<i>Callicarpa Mainga yi</i> leaf	15	sheet	Yellowish green to dark brown	AgNPs-GO/GCE	H_2O_2	5 μM to 700 μM	0.6 μM	Amp-It	(Chekin et al., 2014)
<i>Citrus sinensis</i> var. <i>Kozan yerly fruit</i>	4–10	spherical	Yellow to dark black	Ag NPs/GCE	Catechol	–	–	CV	(Khan et al., 2015)
<i>Plectranthus amboinicus</i> Leaf	22	spherical	Brown yellow to black	RGO-Ag-GCE	H_2O_2	1 and 800 μM	0.312 μM	Amp-It	(Zheng et al., 2016)
<i>Mimosa Pudica</i> root	35–42	spherical	Pale yellow to dark brown	AgNPs/GCE	Dopamine	10–60 μM	0.5 μM	DPV	(Sreenivasulu et al., 2016)
<i>Convolvulus pluricaulis</i> leaf	10–11	spherical	Pale yellow to dark brown	Gr-AgNPS/GCE	–	–	–	CV	(Sandeep et al., 2016)
Piper betel leaves	48	spherical	Colourless to olive	Ag/GCE	NO_2^-	1–6000 μM	0.046 μM	Amp-It	(Ramachandran et al., 2016)
Onion extract	10	Spherical	Watery to brown	AG/CPE/GCE	Ascorbic acid	0.4–450.0 μM	0.1 mM	SWV	(Khalilzadeh and Borzoo, 2016)
<i>Ocimum tenuiflorum</i> leaves	20–25	Spherical	Pale yellow to dark brown	Ag/GCE	glucose	1 to 8.9 mM	0.0048	Amp-It	(Dayakar et al., 2018)
<i>Streptomyces</i> sp. BHUMBU-80	11–38	spherical	Light brown to dark brown	AgNPs/GCE	H_2O_2	50 μM to 1000 μM	50 μM	CV	(Gupta et al., 2017)
Nilgiri wood	30	spherical	Light yellow to reddish amber	Ag-NS/GCE	Nitrite	0.1–8 μM	0.031 μM	Amp-It	(Shivakumar et al., 2017)
Instant dry yeast	–	Core-shell	–	CDA/Au–AgNPs modified GCE	paracetamol	0.01–0.1 mM	2.6 μM	Amp-It	(Wei, 2017)
Lithodora	15	spherical	Yellowish brown to dark brown	AgPdNPs-GCE	H_2O_2	20 mM – 5.00 mM	0.52 μM	Amp-It	(Turunc et al., 2017)
<i>Hispidula</i> leaves	27	spherical	Light yellow to brown	AgNPs/GCE	Nitrite	1 to 3.75 μM	–	CV	(Baghayeri et al., 2018)
<i>Salvia leriifolia</i> leaves	27	spherical	Light yellow to brown	AgNPs/GCE	Nitrite	1 to 3.75 μM	–	CV	(Baghayeri et al., 2018)
<i>Camellia japonica</i> leaves	12–25	spherical	White into yellow	AgNPs/GCE	nitrobenzene	0.05 to 3637 μM	0.012 μM	Amp-It	(Karthik et al., 2017)
<i>Oak leaf</i>	20–25	spherical	Yellow to yellowish red	Hb-AG/GCE	H_2O_2	–	–	CV	(Hemmati et al., 2018)
<i>Allium sativum</i> cloves	19	spherical	Yellow to brown	AgNP-Pt	Cd	10–90 μM .	0.277 μM	DPV	(Aravind et al., 2018a)
Grape stalk water	27	spherical	Pale yellow to reddish brown	Ag-NPs-SPCNFE	Pb and Cd	3.3–100.4 and 16.0–39.7 $\mu\text{g L}^{-1}$	4 and 4.8 $\mu\text{g L}^{-1}$	DPV	(Bastos-Arrieta et al., 2018)

Table 5 (continued)

Bio-source	Size (nm)	Shape	Colour change	Modified electrode	Analyte	Linear range	LOD	Technique	Reference
<i>Lycopersicon esculentum</i> mushroom	10	spherical	Light yellow to brown	AgNP-Pt	Cr	10 to 90 μ M	0.804 μ M	DPV	(Aravind et al., 2018b)
Rosa damascena waste	10	spherical	–	Pd-Ag/CPE	Uric acid	4.6– 273 nM	5.54 nM	DPV	(Mallikarjuna et al., 2018)
<i>Convolvulus pluricaulis</i> leaf	30	irregular	Light brown	AgNPs/CS/GE.	H ₂ O ₂ and vanillin catechol	–	8.4 μ M	Amp-It & DPV	(Dodevska et al., 2019)
<i>Mangifera indica</i> leaves	–	–	Pale yellow to dark brown	Gr/PPy/AgNPs/PPO	Ascorbic acid	0.001 – 0.015 mM	0.47 μ M	Amp-It	(Sandeep et al., 2019)
<i>Achillea millefolium</i> wastes	–	spherical	Colorless to yellowish brown	Pt/AgNP	–	–	–	CV	(A. Mamuru et al., 2019)
<i>Eucalyptus bark</i>	2.8	spherical	Yellow to brown	AgNPs–CS/Gr	H ₂ O ₂	–	–	Amp-It	(Lazarova et al., 2019)
Moringa oleifera Extract	18	spherical	Yellow to brown	AgNPS/GCE	Nitro benzene	5–40 μ M	0.027 μ M	DPV	(Shivakumar et al., 2020)
Pistia stratiotes L. leaves	18–23	spherical	Yellow to brownish yellow	AgNPs/PE	Cu	10–90 μ M	0.530 μ M.	CV and DPV	(Sebastian, Aravind and Mathew, 2019)
Acacia Melanoxydon leaves	30	spherical	Yellow to deep brown	AgNPs/GO/SPE	Na	0–100 mM	9.344 mM	CV	(Traiwatcharanon et al., 2020)
<i>Peganum Harmala</i> Extract	10	cubic	Pale yellow to brown	Ag NP/CPE	Dopamine and H ₂ O ₂	50 to 500 μ M and 8 to 28 μ M	–	CV	(Shashanka and Kumara Swamy, 2020)
<i>Tagetes erecta</i> (Marigold) flowers	10	spherical	–	Ag-NP/PO/MIHP/CPE	Quercetin	0.01–550 μ M	0.005 μ M	Amp-It	(Davarnia et al., 2020)
<i>Opuntia-ficus-indica</i> stem	20–50	spherical	Red to orange	PGE/AgNPs/CS	H ₂ O ₂	1 μ M – 10 μ M	0.52 μ M	CV	(Salve et al., 2020)
<i>Prangos ferulacea</i> roots	10–20	spherical	Colorless to brown	AgNPs/GCE	glucose	0.01–2.2 mM	0.01 mM	SWV	(Khalifa et al., 2020)
<i>Rumex roseus</i>	79	spherical	Pale yellow to red	AgNPs/GCE	H ₂ O ₂	0.1 μ M – 4 mM	0.036 μ M	DPV	(Mavaei et al., 2020)
<i>Fusarium oxysporum</i>	50	round	Pale to yellow	AgNPs-rGO/GCE	H ₂ O ₂	35 μ M to 1.95 mM	1.1 μ M	Amp-It	(Chelly et al., 2021)
<i>Araucaria angustifolia</i>	6	spherical	Black to brown	Ag/Ag ₂ O NPs/GCE	glucose	–	–	CV	(Islam et al., 2021)
<i>Mimosa diplotricha</i> leaf	100	Spherical	Brownish yellow	AgNP-xGnP/GCE	paracetamol	4.98 \times 10 ⁻⁶ to 3.38 \times 10 ⁻⁵ M	8.50 \times 10 ⁻⁸ molL – 1	SWV	(Zamarchi and Vieira, 2021)
Lycoris longituba	33	spherical	Yellowish brown	AgNPs/GCE	Hg	5–45 μ M)	1.46 μ M.	DPV	(Punnoose et al., 2021)
<i>Cupressus sempervirens</i> L.	24	Spherical	–	G/Ag NPs/GCE	imatibin	10 nM- 280 μ M	1.1 nM	DPV	(Wu et al., 2021)
	11	Spherical	Yellow to dark brown	AgNPs-GCE	H ₂ O ₂	5.0 μ M – 2.5 mM	0.23 μ M.	SWV Amp-It and DPV	(Ersan Turunc, 2021) (Turunc, 2021)

CDA: Cellulose Diacetate; GCE: Glassy Carbon electrode; Gr: Graphite rod; CPE-Carbon paste electrode; NS: Nanosphere; Hb: Hemoglobin; SPCNFE: Screen printed carbon nanofibre electrode; CS: chitosan; PPy: Pyrrole electropolymerized; PPO: Poly phenol oxidase; Pt: Platinum electrode; GO: Graphene oxide; SPE-Screen printed electrode. MIHP- *Mihp n*-hexyl-3-methylimidazolium hexafluoro phosphate; PO: Paraffin oil; PGE: Pencil graphite electrode; GnP: Graphite nano platelets; G: graphene.

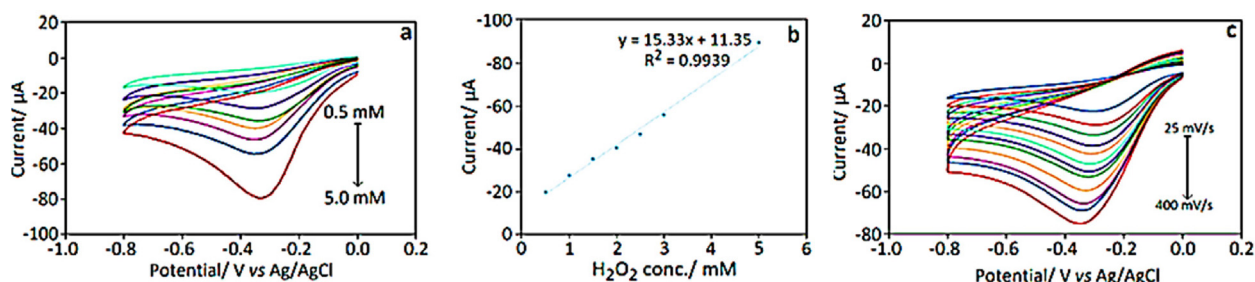


Fig. 4 (a) Cyclic voltammograms for various concentrations of H_2O_2 at AgNPs-GCE in 0.1 M phosphate buffer solution with $\text{pH} = 7.0$ (from top to down 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 5.0 mM, respectively), scan rate 50 mV/s, (b) variation of peak current versus concentration, (c) cyclic voltammograms of AgPdNPs-GCE in 0.1 M PBS containing 1.0 mM H_2O_2 at variable scan rates (from top to down 25, 50, 75, 125, 100, 150, 175, 200, 250, 300, 350 and 400 mV/s, respectively (Ersan Turunc, 2021)).

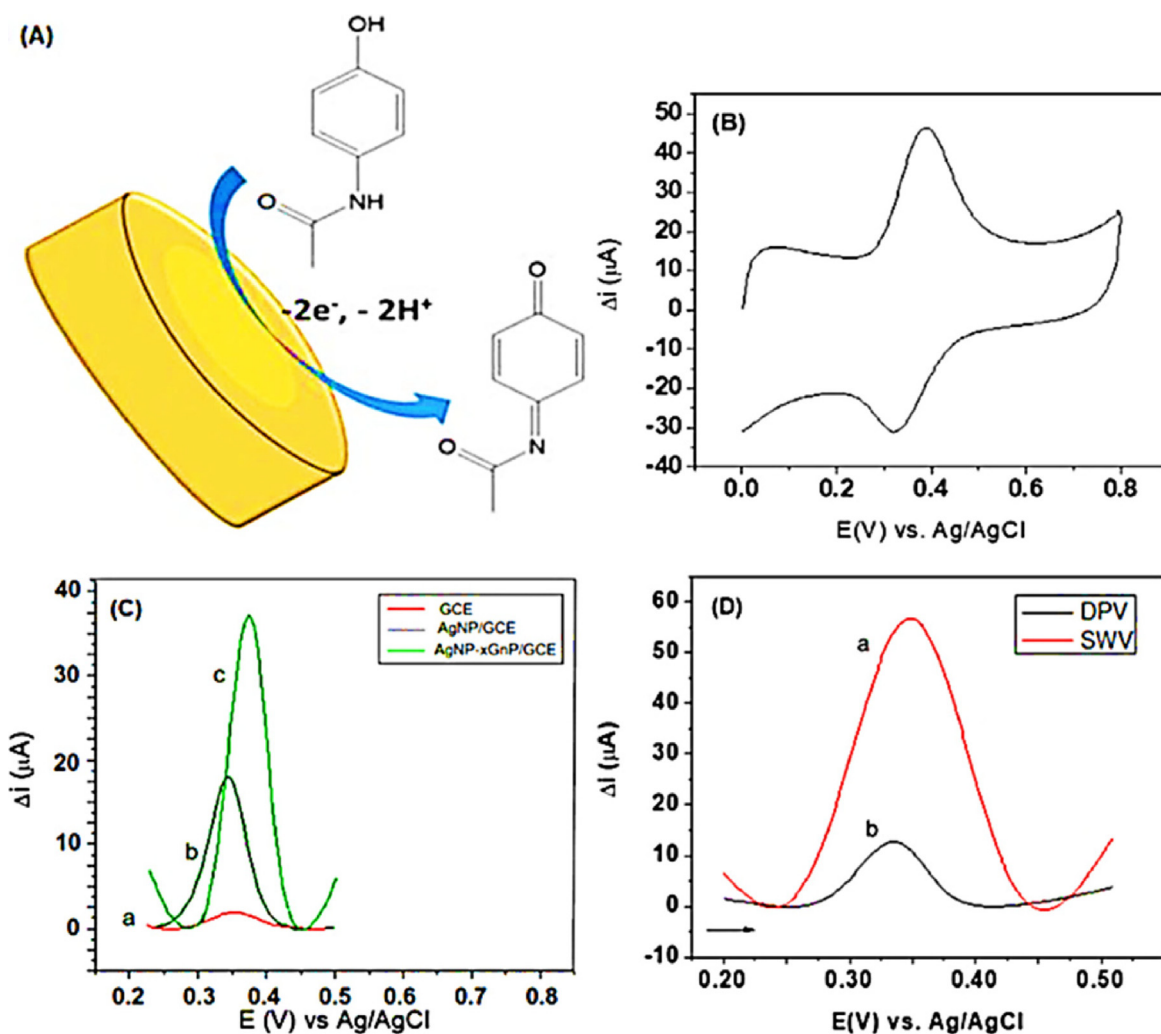


Fig. 5 (A) Schematic representation of the reaction involving paracetamol on the surface of the sensor; (B) cyclic voltammogram at 100 mV s^{-1} , (C) SWV using the (a) bareGCE, (b) AgNP/GCE, (c) AgNP-xGnP/GCE and (D) voltammograms obtained applying the electroanalytical techniques: (a) SWV and (b) DPV in PBS solution (0.1 mol L^{-1} , $\text{pH}7.4$) containing $1.48 \times 10^{-5} \text{ mol L}^{-1}$ paracetamol (Felipe Zamarchi, 2021).

CPE method was successful in determining quercetin in a variety of dietary samples, including hawthorn and onion (Davarnia et al., 2020). Sreenivasulu et al., (Sreenivasulu et al., 2016) developed an electrochemical sensor for dopamine

(DA) based on biosynthesized AgNPs. Dopamine (4-(2-aminoethyl)benzene-1,2-diol) is a neurotransmitter that influences a range of biological processes and has a wide range of functions in the brain. Parkinson's disease, depression, schizophre-

nia, and certain brain cancers all include dopamine as a biomarker. Because of its electroactive nature, reliable detection of dopamine is vital in research and clinical illness diagnosis, and many types of electrochemical sensors have been developed. For the production of AgNPs, Sreenivasulu et al. employed an aqueous root extract of *Mimosa pudica*. The UV–Vis spectrophotometer was used to identify AgNP form, and XRD, FTIR, SEM, EDAX, and TEM were used to completely describe AgNPs. The produced AgNPs had a spherical form with average diameters of 35.0 to 42.5 nm, according to the TEM examination. For quantitative detection of DA, amperometric tests demonstrated that the Synthesized nanoparticles electrode has a high sensitivity, a low limit of detection (0.5 μM), and an outstanding dynamic range (10–60 μM). These results, according to the authors, are equivalent to those previously reported in the literature utilizing chemically modified GC electrodes.

Biosynthesized AgNPs to detect toxic chemicals: Aniline, pesticides, herbicides, insecticides, azo colors, explosives, and pharmaceuticals all employ nitrobenzene (NB) as a precursor. Humans' blood, central nervous system, liver, and kidneys are affected by acute (short-term) and chronic (long-term) inhalation, oral, and cutaneous exposure to NB. Long-term exposure can result in headaches, nausea, tiredness, dizziness, cyanosis, and anemia. Unfortunately, companies released a large amount of NB into water, soil, and sediments. As a result, fast and precise detection of NB is critical for public and environmental safety. For the detection of NB, many analytical approaches have been utilized, with electrochemical methods being deemed easier and more sensitive than chromatographic and spectrophotometric methods. Using *Eucalyptus* extract (Shivakumar et al., 2020) as a reducing and stabilizing agent, Shivakumar et al. reported an environmentally friendly AgNP synthesis. The synthesized nanoparticles were used to modify a GC electrode, and AgNPs/GC was used to test for quantitative detection of NB. Fig. 7. Shows the electrochemical behaviour of AgNPs/GC was investigated using two electrochemical techniques: CV and DPV. The modified electrode had high electrocatalytic activity in the NB electroreduction reaction, with a linear current response in the concentration range of

5 to 40 M, a sensitivity of $2.262 \text{ AM}^{-1} \text{ cm}^{-2}$, a detection limit of 0.027 M, and good selectivity. The CV of the modified electrode was conducted in the presence of 1 mM NB on the day of preparation and every other day for the next 20 days to test stability. According to the scientists, the sensor had excellent storage stability, maintaining up to 92.8 percent of the initial current after the test time. The created electrode material's practical usefulness in detecting NB selectively in tap water and lake water was tested, and good results were achieved. Karthik et al. (Karthik et al., 2017) modified a GC electrode with sphere-like AgNPs biosynthesized using *Camellia japonica* leaves to increase selectivity, sensitivity, and detection limit for determining NB. The constructed electrocatalyst AgNPs/GC has been proven to have high selectivity, a low limit of detection (0.012 M), and a wide linear range for detecting NB (up to 2.593 mM). The AgNPs/GC showed excellent selectivity for NB detection – the results of the selectivity test showed that adding potentially interfering species (common metal ions, some anions, and nitroaromatic containing substances) into the system at a 500-fold concentration relative to the analyte did not affect the electrode signal. This is interesting since, due to their structural similarity, other nitroaromatic chemicals normally have a large impact on the peak current response of NB. In polluted wastewater, the catalyst's practical application for the selective quantitative determination of NB in actual samples was successfully evaluated. The sensor gadget is easy to use, inexpensive, and portable, and it may be used in a variety of industrial and research applications.

For the electrochemical detection of uric acid, a Pd–Ag bimetallic NP was constructed by using edible mushrooms (Mallikarjuna et al., 2018). The experiment was conducted in phosphate buffer solution (PBS) at various pH levels and scan rates. They compared the performance of carbon past electrodes (CPE) and Pd–Ag modified CPE electrodes and discovered that the Pd–Ag modified electrode had better electrocatalytic activity than the CPE electrode. For example, a cyclic voltammetry (CV) measurement of CPE yielded an oxidation peak current (I_{pa}) of 50 μA , but a CV measurement of Pd–Ag/CPE yielded an I_{pa} of 100 μA , owing to the composite's increased electrical conductivity. The probe responded lin-

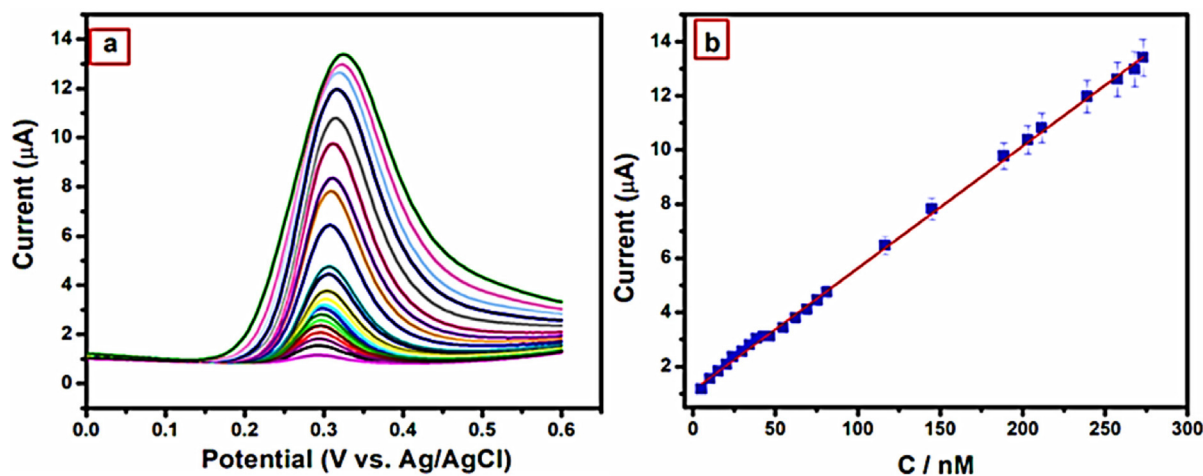


Fig. 6 Mechanism for the electrochemical oxidation of UA, (a). DPV obtained for Pd–Ag/CPE due to the addition of 4.69–273 nM UA into 0.1 M PBS (pH 7.0) and (b) Calibration plot of I_{pa} vs concentration of UA (Mallikarjuna, 2018),

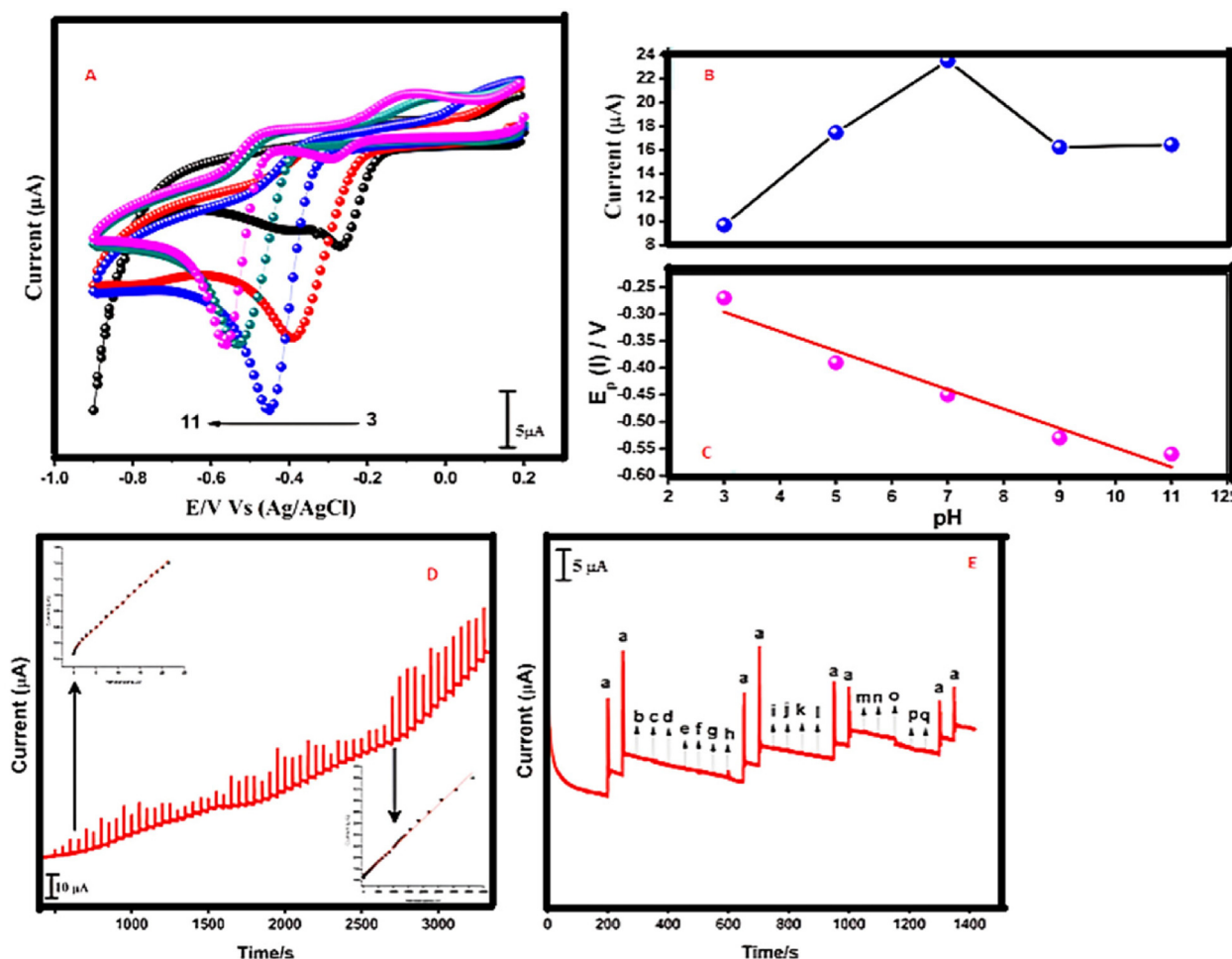


Fig. 7 (A) CVs of 300 μM nitrobenzene at green synthesized Ag-NPs modified GCE in 0.05 M PBS pH ranges from 3 to 11 (Right to left side). (B) Calibration plot of nitrobenzene reduction peak current (I_{pc}) vs different pH (C) Reduction peak potential (E_p) vs pH, (D) Amperometric ($i-t$) response at green synthesized Ag-NPs modified RDE upon successive additions of 0.05–3693 μM nitrobenzene into continuously stirred N_2 saturated PBS. Applied potential: -0.42 V ; Rotation speed: 1200 rpm. Inset (upper) is the plot of response current vs [nitrobenzene]. Inset (bottom) the plot of response current vs [nitrobenzene]. (E) Amperometric ($i-t$) response at green synthesized Ag-NPs modified RDE for addition of nitrobenzene (a) in the presence of 500 folds excess concentration of (b) Co^{2+} (c) Ni^{2+} (d) Na^+ (e) Ba^{2+} (f) Ca^{2+} (g) Pb^{2+} (h) Cd^{2+} (i) Cl^- (j) S^- (k) Br^- (l) I- and nitro aromatic compounds derivatives (m) 4-aminophenol (n) 4-acetamidophenol (o) 2- nitro aniline (p) 4- nitro aniline and (q) 4-nitrophenol in 100 fold excess, respectively (sivakumar, 2020).

early between 4.69 and 273 nM, with a detection limit of 5.543 nM (Fig. 6) and they used the probe in a real sample analysis of urine and retrieval of UA range of 93 % to 103 %.

For the detection of 40 nM vanillin, biosynthesized Ag–Au alloy NP was used (Zheng et al., 2010). They employed cellulose diacetate as a link material with modified glassy carbon electrodes by Ag–Au alloy NPs. According to the findings, the modified electrode has a performance that is roughly 5 times better than CCE when it comes to detecting vanillin. On the modified electrode, amperometric measurements were made at 1 V and a steady-state response for vanillin was obtained in the range of 0.2–50 μM . They also used 2.5×10^{-4} M caffeine, sucrose, l-arginine, hypoxanthine, barbitone, cholesterol, benzoic acid, vitamin B, xanthine, and ethyl vanillin (6.5×10^{-6} M), and glucose in an interference experiment to detect 6.5×10^{-6} M vanillin as shown in Fig. 8. Nonetheless, due to their similar structures and simple electrochemical oxidation, xanthine and ethyl vanillin cause substantial interference

with vanillin. They tested the probe's stability and repeatability by exposing it to air for a week and obtaining 93 % of its original performance. Furthermore, they investigated the probe's potential use for the real-time measurement of vanillin in vanilla bean and vanilla tea and obtained 99.86 % and 100.09 % responses, respectively.

An electrochemical sensor for NB has been constructed utilizing reduced graphene oxide (rGO) and AgNPs, which were biosynthesized using *Justicia glauca* leaf extract (Karuppiyah et al., 2015). When compared to other modified electrodes, the modified rGO/AgNPs/GC electrode performed well for the selective quantitative determination of NB: the electrode signal remained linear in the concentration range of 0.5 to 900 M, and the sensitivity was determined to be 0.836 A/M cm^{-2} with a detection limit of 0.261 M NB. rGO/AgNPs/GC was also kept in phosphate buffer solution (PBS) when not in use, and the decreased peak current response to 100 M NB was investigated by CV for up to 52 days. After 52 days,

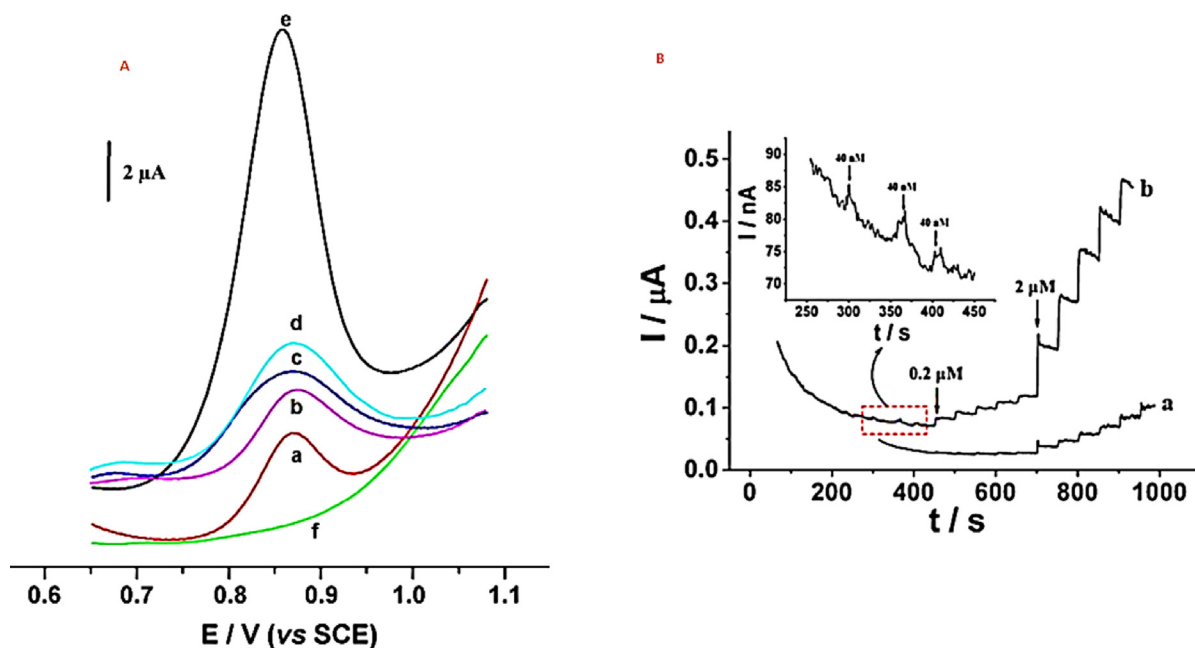


Fig. 8 (A) Square wave voltammograms of bare GCE (a), CDA/GCE (b), CDA/AgNPs/GCE (c), CDA/AuNPs/GCE (d) and CDA/Au-AgNPs/GCE (e and f) in the presence (a, b, c, d and e) and absence (f) of 6.6×10^{-5} M vanillin in phosphate solution (pH 2.0). Amplitude: 20 mV, frequency: 20 Hz. (B) Amperometric response of vanillin at bare GCE (a) and CDA/Au-AgNPs/GCE (b) with successive injections of 0.2 M and 2 M vanillin at the operational potential of 1.0 V. Inset: Amperometric response of 40 nM vanillin at CDA/Au-AgNPs/GCE (Zheng et al., 2010).

the modified electrode had kept roughly 90.15 percent of its initial current responsiveness, indicating exceptional storage stability. According to the scientists, the constructed sensor demonstrated good repeatability with an RSD of 3.8 percent when determining NB using five distinct sensors. The developed sensor's good recovery results and RSDs in wastewater samples demonstrated its practical utility for determining NB in actual samples.

AgNPs-GO for electrochemical sensor: Apart from the uses of plants, fungi, and bacteria to fabricate Ag NPs. Researchers used GO to reduce Ag ions by simple, green route synthesis with bio source (Table 6) (Fig. 9). The few reports of biosynthesis of Ag NPs with reduced GO with the simple and economical procedure to enhance the better results of the sensor. The oxidized form of graphene is graphene oxide (GO). It has a 2-D plane with a large number of oxygen-containing functional groups, along with this GO has better dispersibility and film-form capability. The covalent bond which is present in the GO enhances the tremendous mechanical strength of the molecular-level chemical sensor with good

selectivity. The combination of nanostructured metal particles or clusters with GO has been used for wide applications due to its functional groups such as $-\text{OH}$, $\text{C}-\text{O}-\text{C}$, $-\text{COOH}$ (Compton and Nguyen, 2010) (Atif and Inam, 2016).

Tryptophan is one of the essential amino acids for human nutrition, woefully it cannot be secreted in the human body and hence it should be taken via food and medicine. And also tryptophan will act as a precursor for the secretion of serotonin and melatonin which give better sleep and relaxation. However, an excessive amount of tryptophan created toxic to the brain, even causing hallucinations and delusion. Junhua Li et al., (Li et al., 2013) proposed Ag NPs/GO nanomaterial synthesized by reduction of Ag ion on graphene oxide surface in presence of glucose as reducing agent and they adopted Hummers' method to synthesize GO. The AgNPs/GO nanocomposite was first manufactured using a low-cost and environmentally friendly method and then utilized to fabricate a new electrochemical sensor. The nano-hybrid SEM, TEM, EDX, FTIR, and SEM were used to describe the composite film. Electrochemical research has shown that AgNPs/GO

Table 6 Graphene oxide based Ag NPs in electrochemical sensor.

Sensors	Applied potential (V)	Linear range	LOD	Analyte	Method	Reference
AgNPs/GO/GCE	0.38	50–800(μM)	0.002 μM	tryptophan	DPV	(Li et al., 2013)
β -CD/AgNPs-GO	-0.6	13–375(nM)	0.24 (nM)	As(III)	SW-ASV	(Dar et al., 2014)
NG-Ag NPs	-0.47	0.005-47X 10^{-3} M	0.56×10^{-6} M	H_2O_2	Amp-It	(Li et al., 2016)
GCE/rGOX/AgNPs	-0.4	0.002–20 (mM)	30–160 (mM)	H_2O_2	Amp-it	(Salazar et al., 2019)
AgNPs-rGO	-0.4	0.0015–100(mM)	1.90 (μM)	H_2O_2	Amp-It	(Bhangoji et al., 2021)

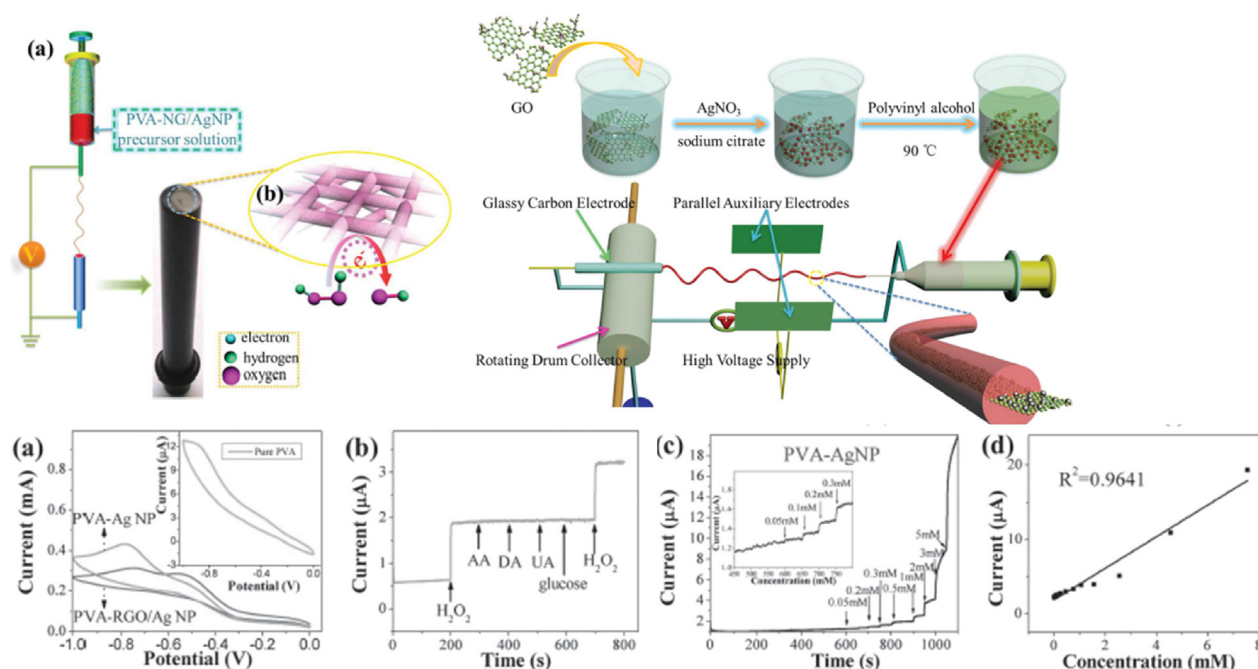


Fig. 9 (a) Schematic presentation for the fabrication mechanism of NG/AgNP hybrid membrane and MME. (b) Schematic fabrication of MMEs; (b) the possible detection mechanism of H₂O₂. (c) Electrochemical H₂O₂ biosensing: a) CVs of PVA, PVA-AgNP, PVA-NG, and PVA-NG/AgNP MMEs; b) selectivity of biosensor: amperometric responses upon successive addition of 1×10^{-3} M of H₂O₂, 0.10×10^{-3} M of AA, 0.10×10^{-3} M of DA, 0.10×10^{-3} M of UA, 5.0×10^{-3} M of glucose, and 1×10^{-3} M of H₂O₂; (c,d) I - T response and calibrated line of PVA-AgNP MME in 0.1 M PBS with successive addition of H₂O₂ at -0.47 V versus SCE (Yang et al., 2016).

had a synergetic catalytic impact on tryptophan oxidation and that the substantial Peak current has increased, whereas peak potential has decreased. The constructed sensor's analytical performance has substantially increased. The kinetic parameters, such as the number of transported electrons, for the oxidation of tryptophan, the electron transfer coefficient, surface coverage, and standard heterogeneous rate constant were measured and attained. Wider linear ranges and a lower detection limit were attained under optimal circumstances. To our knowledge, this is the first time an electrochemical sensor for tryptophan has been built with that kind of a low detection limit (2 nM), and its qualitative properties outperformed the majority of previously reported electrochemical sensors. Furthermore, the nanocomposite enhanced tryptophan and tyrosine oxidation peak separation, and DPV was able to determine tryptophan on-site in the presence of a high quantity of tyrosine.

Furthermore, the AgNPs/GO composite has several intriguing properties, including simplicity of synthesis, low toxicity, surface functions, and outstanding stability, all of which make it a promising candidate for biological and organic molecule electroanalysis and electrocatalysis. Another research group fabricated a new electrochemical sensor for As(III) detection employing Anodic stripping voltammetry using a green and simple technique to synthesize cyclodextrin (CD) stabilized AgNPs-GO composite. Because arsenic pollution of groundwater is a worldwide major concern that affects the safety of drinking water in various nations. Because of its interactions with enzymes in human metabolism, As(III) is regarded to be more hazardous than As(V). Many ailments are caused by this, including skin lesions, keratosis, lung

cancer, bladder cancer, and others. In January 2011, the United States Environmental Protection Agency (USEPA) set a new arsenic threshold for drinking water at 10 parts per billion (ppb). The created sensor had a low detection limit, a wide operating range, and analytical properties that exceeded most electrochemical sensors previously described. We were able to detect As(III) in the presence of Cu and other organics using the AgNPs-GO composite sensor. The findings suggest that As(III) and Cu(II) might be determined at the same time. As(III) was measured in-ground and river water samples using the newly designed sensor. The suitability of the material for As(III) measurements in mineral water and other samples containing As(III) was demonstrated by the high recovery of the analysis (Dar et al., 2014).

2.15. Outline and prospects

The creation of superstructures is simple by using a bio-sourced mediated nanomaterial synthesis process. The bio-functionalized NPs' inherent adaptability allows for a wide variety of analyte detection, making them a viable alternative to non-eco-friendly technologies. It also adheres to the principles of sustainability and biocompatibility. The nanoparticles' bio-driven genesis and biocompatibility make them valuable in a variety of biomedical applications.

The lack of the biosynthesis of NPs using biosource is understanding the exact mechanism and the major challenges are to control the shape and size to attain the monodispersity. It seems like various important technical steps must be taken to cross this bio-mediated route for industrial synthesis. We need to level up biosynthesis into large-scale synthesis and

provide portable sensors. Even though electroanalytical biosensors are highly effective and economical, it requires enhancing the performance likely step down the electrode surface modification steps and conversion of the portable sensor with gadgets, wireless technology will attain more attraction. Finally, the goal of this outline is to present a summary of the current research of the art in the domain of electrochemical sensors for pesticide, and heavy metals detection. We hope this study will serve as a useful resource, raising understanding and appreciation of the role that electrochemical biosensors may play in protecting our environment.

CRedit authorship contribution statement

Jayaprakash Meena: Writing – original draft, Formal analysis.
K. Santhakumar: Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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