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Review
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REVIEW

Application of biosynthesized metal nanoparticles in electrochemical sensors

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Abstract: Recently, the development of eco-friendly, cost-effective and reliable methods for synthesis of metal nanoparticles has drawn a considerable attention. The so-called green synthesis, using mild reaction conditions and natural resources as plant extracts and microorganisms, has established as a convenient, sustainable, cheap and environmentally safe approach for synthesis of a wide range of nanomaterials. Over the past decade, biosynthesis is regarded as an important tool for reducing the harmful effects of traditional nanoparticle synthesis methods commonly used in laboratories and industry. This review emphasizes the significance of biosynthesized metal nanoparticles in the field of electrochemical sensing. There is increasing evidence that green synthesis of nanoparticles provides a new direction in designing of cost-effective, highly sensitive and selective electrode-catalysts applicable in food, clinical and environmental analysis. The article is based on 157 references and provided a detailed overview on the main approaches for green synthesis of metal nanoparticles and their applications in designing of electrochemical sensor devices. Important operational characteristics including sensitivity, dynamic range, limit of detection, as well as data on stability and reproducibility of sensors have also been covered.

Keywords: biosynthesis; green synthesis; nanomaterials; nanotechnology; modified electrodes; review.

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1. INTRODUCTION

Nowadays green nanotechnology has remained at the forefront of scientific research due to its outstanding approaches and applications. Green nanotechnology involves the application of green chemistry principles to the design of valuable and sustainable nanosized materials in a more environmentally benign approach.[1]

The unique properties of nanomaterials such as catalytic potential,[2] optoelectrical properties,[3] magnetic behavior[4] and biological activity[5] are the main factors determining their extremely wide applications in various fields of science, technology and industry. Nanosized materials are widely used as catalysts[6] and nanoelectronic components,[7] in the composition of antibiotics, antiseptics and disinfectants,[8] in drug delivery,[9] food and material packaging,[10] targeted delivery of pharmaceuticals,[11] development of biosensors,[12] *etc*.

The main challenge in the development of catalyticaly active nano-sized materials is to prepare nanoparticles that are highly active, selective, stable, robust, and inexpensive. Classical synthesis of metal nanoparticles (MNPs) most commonly involves chemical reduction of metal ions from solutions of their salts in the presence of organic or inorganic reducing agent such as ethylene glycol, dimethylformamide and sodium borohydride ($NaBH_4$), followed by addition of a stabilizing agent.[13] The reagents used are usually expensive and toxic substances which could generate hazardous by-products harmful to health and environment.[14] Therefore, there is a growing concern to develop new, alternative and sustainable methods for MNPs preparation. Research on the possibilities of using biological systems (plants, bacteria, fungi, algae) to obtain stable MNPs and metal oxide NPs has been particularly intense in recent years. The so-called green synthesis has received more attention as a cost effective and valuable alternative for environmentally safe and energy-efficient production of nanoparticles with desired properties.[2,15–19] Unlike chemical and physical processes, bio-inspired synthetic methods restrict the use of sophisticated instruments, toxic chemicals and energy (high temperature, pressure, irradiation). Green synthesis of MNPs involves the use of plant extracts or microorganisms for the bioreduction of metal ions into their zero-valent elemental form. Biomolecules such as proteins, sugars, flavonoids, alkaloids, polyphenols, *etc*. (Fig. 1) act as reducing and capping agents. Regarding the process of metal oxide NPs synthesis in a

green way, researchers suggest that specific biomolecules react with the metal ions to reduce or to form complexes. The resulting product is subjected to thermal treatment to get final metal oxide NPs. Therefore, different mechanisms of metal oxide NPs formation were proposed considering the ability of the active compounds in reducing and chelating the metal ions.

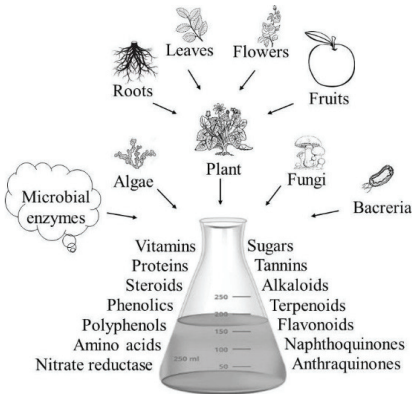

Fig. 1. Schematic illustration of the natural sources used to synthesize NPs in a green way.

Biological systems differ in their capabilities to supply MNPs, hence the production process highly varies depending on the choice of green material. The plant extracts are considered to be more suitable compared to microorganisms for green synthesis of MNPs. Plant extract mediated synthesis of MNPs is preferable due to its economic and ecological effectiveness – easily available plant material, aqueous solvents and normal conditions are used for the synthesis of nanoparticles in a simple one-step procedure. Extensive research shows that the plant-assisted synthesis is relatively fast and suitable for large-scale production of stable MNPs. At the same time, delicate, complicated and meticulous preparation steps are required for microbial synthesis of MNPs. Organisms such as bacteria and fungi need to be cultured or propagated in order to obtain sufficient starting materials. Thus, synthesis protocols include prior procedures such as microorganism isolation and identification, growth optimization and culture preparation. Other challenges are the slow reduction process (ranging from hour to days) and poor understanding of the mechanisms controlling the shape and dispersity of microbial synthesized MNPs. In addition, development of new green synthesis methods based on the use of waste products from agriculture and food-processing is one of the current research areas that has attracted a great deal of attention over the past years.[2] These waste derived MNPs have found a variety of applications in biotechnology, however, data on their applications in sensor technologies are still limited.

Current review features recent trends in electrode catalysts based on metal and metal oxide NPs synthesized by using plant extracts and microorganisms.

Even though research on the applications of biosynthesized nanoparticles in electrochemical sensors is actually at a really early stage, there are already promising opportunities for development of novel sensing platforms. Most relevant biosynthesis approaches, successful integration strategies, selected sensing applications and future prospects of these biosynthesized nanomaterials for the design of advanced sensor platforms are also highlighted.

2. GREEN SYNTHESIS OF METAL/METAL OXIDE NANOPARTICLES USING PLANTS

Due to the abundance of biomass and the diversity of species, plants are most suitable for large-scale biosynthesis and they are preferred for green synthesis of MNPs.[20–22] Plant leaf extracts are the most common choice for bio-inspired synthesis of MNPs but the use of seeds, bark, fruits, tubers and root extracts has also been reported.[20,23,24] It was established that experimental conditions such as temperature,[25–27] pH,[27,28] concentration and quantity of extract[27,29,30] and/or metal ions,[26,27] and contact time[27] affect the efficiency and rate of the process of metal reduction and nanoparticles with desired shape and size could be produced. Researchers suggested that various compounds such as amino acids, citric acid, heterocyclic compounds, flavonoids, polyphenols, terpenoides, enzymes, peptides, polysaccharides, saponins, tannins were responsible for reduction of metal ions and subsequent stabilization of the produced nanoparticles.[4, 32–41]

Green synthesis of MNPs based on the reduction of precious and non-precious transition metals including silver, gold, palladium, platinum and copper using plant extracts has been investigated by some authors.[20,21,25] Silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) are the most common ones used for chemical, electrochemical, biomedical and environmental applications.[42]

Owing to their high surface-to-volume ratio and unique physicochemical properties, AgNPs possess various important characteristics: high catalytic activity, electrical and thermal conductivity, as well as broad-spectrum bioactivities.[43,44] In medicine AgNPs have received tremendous attention for their excellent antimicrobial, antibacterial and anticancer potential. Antimicrobial properties of AgNPs caused the use of these nanomaterials in cosmetics, military, packaging, *etc*.

A large number of research groups have been reported completely green, feasible, renewable and inexpensive approaches for synthesis of stable AgNPs. A new, simplified and rapid methodologies for green synthesis of AgNPs using *Azadirachta indica*,[45] *Crotolaria retusa*[46] and *Terminalia arjuna*[47] plant extracts as reducing and stabilizing agents have been proposed. Experimental data show that the so-synthesized nanoparticles exhibit high catalytic activity as well as excellent antimicrobial properties against Gram-negative and Gram-positive bacteria. The extract of some grape by-products such as stalks, leaves, stems, seeds and dried fruits have been successfully used for synthesis of AgNPs,[48] bimetallic

Fe/Pd[49] and Fe_3O_4/Ag[50] nanoparticles. Recent studies on the chemical composition of grapes have revealed that the main components are polar compounds soluble in hot water with a high content of tannins and polyphenolic compounds.[51] This suggests that the grape extract will also contain polyphenolic compounds that could act as reducing and stabilizing agents in the formation of nanoparticles.

AuNPs have drawn the attention of researchers because of their extensive applications in areas such as electronics, catalysis, sensing/biosensing, medicine, controlled drug delivery, etc. Intensive studies have revealed that AuNPs possess potential to serve as building blocks for plasmonic devices, as well as being used as catalysts and antimicrobials against a wide range of microorganisms.[31,52] To date, a number of methods for synthesis of AuNPs including physical, electrochemical, photochemical and liquid chemical reduction have been developed. Krishnaswamy *et al.* have reported a single step green synthesis of AuNPs using agricultural wastes materials such as grape seed, skin and stalk.[53] Various methodologies for biosynthesis of AuNPs from plant extracts also have been reported – *Ginkgo biloba*,[54] sunflower (*Helianthus annuus*), *Chilopsis linearis*, *Medicago sativa*, *Brassica juncea*,[55] leaves of *Sphaeranthus indicus* and various parts from plants (bark, stem, root, etc.)[56] have been used to synthesize AuNPs.

Palladium nanoparticles (PdNPs) have broad application in heterogeneous catalysis due to their excellent catalytic/electrocatalytic ability, high surface-to--volume ratio and high surface energy. Recently, it has been reported that PdNPs could be synthesized by using extracts of *Filicium decipiens*[57] and *Hippophae rhamnoides Linn*.[58]

Research teams have reported production of nanoparticles of metal oxides (CuO and ZnO) using *Centella asiatica*[59] and aloe leaf,[60] respectively. Reddy has reported on a new green method for the synthesis of CuO nanoparticles (CuONPs) using *Calotropis procera*.[61] CuONPs are widely used as catalysts due to their excellent photocatalytic properties.[62] Ghidan *et al.*[63] also have described successful biosynthesis of CuONPs using *Punica granatum* bark extract, and Ijaz *et al.*[64] propose a method for synthesis of CuONPs from fresh leaves of *Abutilon indicum*.

Zinc oxide nanoparticles (ZnONPs) have aroused great interest due to their low cost, attractive properties and important role as semiconductor materials, in development of catalysts, ceramic resistors, gas sensors and energy-saving materials.[65] Due to their antimicrobial and antibacterial potential ZnONPs are widely used in medicine.[66,67] Matinise *et al.* have reported an eco-friendly method for the synthesis of ZnONPs using Moringa *Oleifera* extract.[68] Mechanisms of formation of the ZnONPs via the chemical reaction of the zinc nitrate precursor with the bioactive compounds of the Moringa *Oleifera* are proposed. The electrochemical analysis proved that ZnONPs have high electrochemical activity

without any modifications and therefore are considered as a potential candidate in electrochemical applications. Nava *et al.* also have used zinc nitrate as a source of the zinc ions and different peels extracts, from *Lycopersicon esculentum* (tomato), *Citrus sinensis* (orange), *Citrus paradisi* (grapefruit) and *Citrus aurantifolia* (lemon), for the green synthesis of ZnONPs.[69] The proposed formation mechanism is based on the chemical characteristics of the flavonoids, limonoids and carotenoids that present in the peel extracts. These biomolecules are believed to chelate Zn^{2+} and form metal coordinated complexes that are further thermally treated to form ZnONPs. Authors have analyzed the effect of the extract used on the surface morphology of the resulting ZnONPs, and tested the efficiency of ZnONPs in the photocatalytic degradation of methylene blue under UV irradiation. The presented results highlight that the chemical composition of the extract has a significant effect on the size and shape distribution of nanoparticles, which further is directly associated with their catalytic activity.

3. GREEN SYNTHESIS OF METAL/METAL OXIDE NANOPARTICLES USING MICROORGANISMS

A variety of microorganisms are utilized in nanoparticle synthesis. Prokaryotic bacteria, actinomycetes, yeasts, fungi and algae have been broadly employed for biosynthesis of metal/metal oxide nanoparticles. Bacterial synthesis of MNPs is accepted due to the relative ease of manipulation of bacteria.[41] Some examples of bacterial strains that have been widely used for synthesis of bioreduced AgNPs with different morphology are: *Escherichia coli*, *Lactobacillus casei*, *Bacillus cereus*, *Aeromonas* sp. SH10 *Phaeocystis antarctica*, *Pseudomonas proteolytica*, *Bacillus amyloliquefaciens*, *Bacillus indus*, *Bacillus cecembensis*, *Enterobacter cloacae*, *Geobacter spp.*, *Arthrobacter gangotriensis*, *Corynebacterium* Sp. SH09 and *Shewanella oneidensis.*[70] From bacterial strains such as *Candida guilliermondii*,[71] *Pseudomonas denitrificans*,[72] *Pseudomonas fluorescens 417*,[73] *Staphylococcus epidermidis*[74] and *Bacillus stearothermophilus*[75] spherical AuNPs with a diameter between 5 and 80 nm have been successfully synthesized.[76] AgNPs and AuNPs of various shapes (spherical and triangular) have also been synthesized using algal strains such as *Pithophora oedogonia*,[77] *Ecklonia cava*,[78] *Chondrus crispus* and *Spyrogira insignis*[79] and *Sargassum wightii* Greville.[80]

Fungi-mediated biosynthesis of metal/metal oxide nanoparticles is also a very efficient process for the production of monodispersed nanoparticles with well-defined morphologies.[70] Fungi act as good biological agents for the synthesis of nanoparticles of metals and metal oxides due to the presence of a variety of intracellular enzymes.[81] Compared to bacteria, fungi could be a source for a large amount production of nanoparticles.[82] The probable mechanism for the formation of MNPs is enzymatic reduction in the cell wall or inside the fungal cell. A variety of fungal species are used to synthesize metal/metal oxide nano-

particles such as AgNPs, AuNPs, TiO_2NPs, ZnONPs.[70] Successful synthesis of nanomaterials via yeast also has been reported by numerous research groups.[70]

4. ELECTROCHEMICAL SENSORS BASED ON BIOSYNTHESIZED METAL/METAL OXIDE NANOPARTICLES

Research on electrochemical sensors attracts lots of current interest because of their promising applications in food industry, ecology, medicine, pharmacy, etc. Electrochemical sensor systems offer advantages of a cost-effective, rapid, highly sensitive, selective, compact and convenient to handling method for quantitative detection of the target analyte. These devices provide the opportunity for an accurate and susceptible automation analysis, and are a promising alternative of the conventional analytical techniques where time-consuming procedures for sample pre-treatment and expensive instruments are required. Variety of electroanalytical techniques including cyclic voltammetry (CV), constant potential amperometry (Amp.), differential pulse voltammetry (DPV), square wave voltammetry (SWV), linear sweep voltammetry (LSV) and stripping voltammetry are available and applicable for electroanalysis. Advantages of these techniques over classical detection methods such as spectroscopy and chromatography are their accuracy, reliability, ease of use and low cost.

The general principle of electrochemical detection is illustrated in Fig. 2.

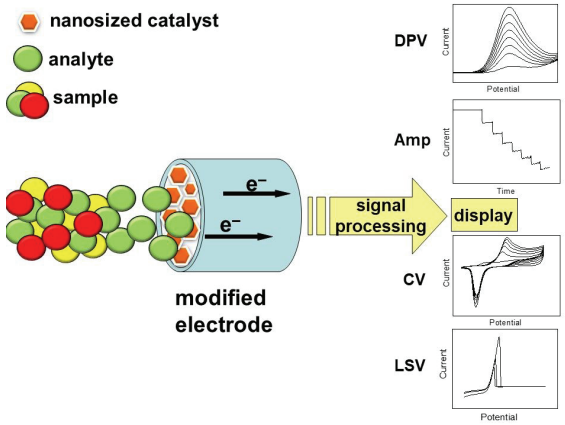

Fig. 2. Illustrative representation of electrochemical detection.

The analyte reacts at the surface of the sensing electrode (modified working electrode) involving either an oxidation or reduction mechanism. This reaction is catalyzed by the electrode material specifically developed for the analyte of interest. The current generated in the process is converted into a signal that could be amplified, processed and displayed easily by modern electrical instruments. By analyzing the magnitude of the electrical signal, we can obtain information about the concentration of the substance being analyzed.

The experimental setup used for electrochemical analysis consists of conventional three-electrode cell including working electrode (WE), reference electrode (RE) and counter electrode (CE), potentiostat and personal computer (Fig. 3). The working electrode is the electrode at which the reaction of interest occurs; as a reference electrode Ag/AgCl or saturated calomel electrode is usually used; an inert conducting material (Pt) is used as a counter electrode. During experiments, charge flow (current) occurs between the working electrode and the counter electrode while the potential of the working electrode is measured with respect to the reference electrode.

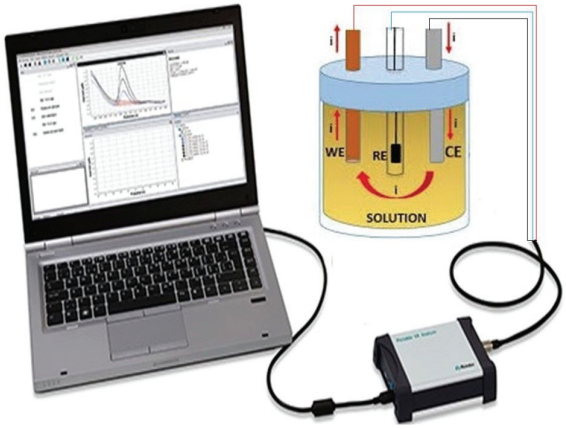

Fig. 3. Experimental setup used for electrochemical analysis.

In electrochemical sensors design, in order to enhance the effective electrode surface and to increase the sensitivity, various nanomaterials such as carbon nanoparticles, metal/metal oxide nanoparticles, nanosized alloys and binary nanocomposites are used for the functionalization of electrode surface as a direct active layer.[83–85] As a result, modified electrodes have extremely high catalytic efficiency due to the reduced overpotentials and faster electron transfer kinetics.

Therefore, the importance of developing nanostrustured highly active and selective electrode-catalysts applicable for quality and safety assessment of foods, for environmental monitoring, pharmaceutical analysis and clinical diagnostics, has received considerable attention nowadays.[86–91]

Physical, chemical and electrochemical methods including laser ablation, high energy ball milling, reactive sputtering, thermal salt decomposition, sol–gel method, electrodeposition, *etc*, have been developed to obtain nanosized metal or metal oxide particles. Although each one of the methods mentioned above had its merits, there are considerable disadvantages in terms of preparation and cost – multi-step time-consuming methodologies and requirement of sophisticated equipment. In this connection, recently biosynthetic approaches has received

great attention due to their capability to design alternative, environmentally friendly, safer, energy efficient and less toxic routes towards synthesis. The green synthesis of nanosized materials has found a wide range of applications in the field of electrochemical sensors/biosensors, revolutionizing this field.[92–94]

Fig. 4 shows the basic steps in the preparation of electrode modified with biosynthesized MNPs. In summary: 1) plant extract was mixed with the metal salt solution; 2) bio compounds reduce metal from positive oxidation state to zero oxidation state; 3) the working surface of electrode was modified through a drop-wise of the resulting colloidal solution.

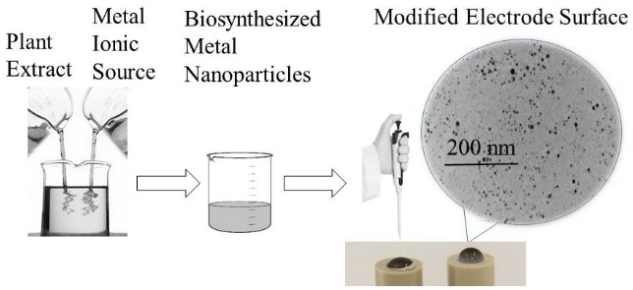

Fig. 4. Scheme of the basic steps in the preparation of electrode modified with biosynthesized MNPs.

In the next part of this review article we have summarized and discussed the recent progress, current challenges and future perspectives in green synthesis of different metal/metal oxide nanoparticles and their applications in the development of new electrode-catalysts for electroanalytical purposes.

The most commonly used metal nanoparticles as electron-transfer mediators are AgNPs and AuNPs due to their chemical stability, unique physicochemical properties, good conductivity and electrocatalytic activity. Relatively simple procedures for synthesis of AgNPs and AuNPs, facile electrode modification with AgNPs and AuNPs as well as their key role in reducing the overpotentials of electrocatalytic reactions make them extremely attractive to research groups.[95]

4.1. Electrochemical sensors based on biosynthesized AgNPs

Nowadays, considerable attention has been paid to the detection of hydrogen peroxide (H_2O_2) owing to its wide applications. H_2O_2 is used in industrial wastewater treatment, as a disinfectant in medicine, as an oxidant and bleaching agent in textile, paper, pharmaceutical and cosmetic industries. Due to its inherent bactericidal properties H_2O_2 is also used as a sterilizing agent in milk and dairy production[96,97] and in food aseptic packaging.[98] Reliable and rapid quantification of H_2O_2 is also important in various biological, medical and clinical studies since H_2O_2 is one of the by-products of enzyme-catalyzed reactions occurring in living organisms. H_2O_2 acts as a precursor in the formation of highly reactive and

potentially harmful hydroxyl radicals and it is one of the most important markers of oxidative stress. Excessive accumulation of H_2O_2 in the body causes various diseases such as cardiovascular disorders, Alzheimer's, DNA fragmentation, tissue damage and cancer.

A number of research groups have confirmed remarkable electrocatalytic activity of AgNPs for H_2O_2 reduction and successfully have employed AgNPs--modified electrodes as sensing interface to construct enzyme-free H_2O_2 electrochemical sensors.[99–104] In the cited articles electrode surface modification with AgNPs has been performed applying chemical or electrochemical methods in order to enhance the rate of electron transfer and to decrease the required high overpotential – the major barrier for effective electrochemical detection of H_2O_2 at ordinary solid electrodes.

Salazar *et al.* have investigated the catalytic activity of electrode modified with biosynthesized AgNPs in the reaction of electroreduction of H_2O_2.[105] They have presented a simple one-step eco-friendly strategy to obtain silver nanoparticle-modified reduced graphene oxide nanocomposites (rGO/AgNPs) using green tea extract for reducing both Ag^+ and graphene oxide sheets. TEM image and the size distribution for AgNPs confirmed the quasi-spherical shape of the AgNPs with an average size of about 25 nm (a size range distribution from 5 to 60 nm). Glassy carbon (GC) electrode was conveniently modified with rGO/ /AgNPs nanocomposite and electrochemical tests were carried out to study the electrocatalytic properties of the rGO/AgNPs/GC sensor towards H_2O_2 reduction. Basic analytical parameters such as selectivity, sensitivity, limit of quantification and limit of detection, time of response and stability of modified electrode in 0.1 M PBS under optimized conditions (pH 8.0; applied potential of –0.4 V *vs.* Ag/AgCl, 3 M) were also studied. It was determined that the electrode has a sensitivity of 236 μA mM^{-1} cm^{-2} (R^2 = 0.999) in the concentration range from 0.002 to 20 mM, rapid response (~2 s) and detection limit of 0.73 μM H_2O_2 estimated on the criterion signal-to-noise S/N = 3. After 7 months storage it was established that rGO/AgNPs/GC has no significant loss of sensitivity. The selectivity of the modified electrode was tested against different biological interferences including dopamine, glutamate, glucose and ascorbic acid with promising results. In addition, the applicability of this sensor for H_2O_2 detection in real samples was confirmed in antiseptic solutions, commercial milk and urine.

Tagates erecta (Marigold) flowers extract has been used for production of AgNPs in a green route.[106] Characterization of biosynthesized nanoparticles was done using different methods: ultraviolet–visible spectroscopy (UV–Vis), field emission scanning electron microscopy (FESEM), elemental dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The UV–Vis studies showed the occurrence of an absorption band at 430 nm which is specific

for AgNPs. FESEM analysis indicated that the biosynthesized AgNPs have a homogenous size distribution. The XRD patterns reflected that the particles are crystalline in nature, with a face-centered cubic structure. Using AgNPs and chitosan (CS), modified pencil graphite electrode (PGE) was fabricated by drop-casting method and the as-prepared hybrid material PGE/AgNPs/CS was used for supercapacitator and electrochemical sensing applications. It has been shown that PGE/AgNPs/CS electrode provided remarkable catalytic activity towards electrochemical reduction of H_2O_2. Quantitative analysis of H_2O_2 was performed in supporting electrolyte 0.1 M HCl/KCl (pH 2.0) using cyclic voltammetry (CV) and a linear graph was obtained in the concentration range of 1.0–10.0 μM (limit of detection was found to be 0.52 μM). Furthermore, the sensor was applied to real sample analysis. The results obtained suggested that the proposed electrochemical device can be used for traces analysis of H_2O_2 in cosmetic products.

Since the industrially steam distillation of essential oil crops never leads to complete extraction of the aroma substances, the essential oil industry wastes have a potential for extraction of residual volatile polar metabolites. The waste is rich in non-volatile polar metabolites (flavonoids, organic acids, carbohydrates, amino acids, *etc*.) and some of these compounds have also reduction properties and could influence the synthesis and stabilization of AgNPs. Dodevska *et al.*[107] have reported for the first time utilization of *Rosa damascena* waste for synthesis of AgNPs and applicability of the nanoparticles for development of electrochemical sensors for H_2O_2 and vanillin detection. The process of AgNPs synthesis takes place in one-stage and it is based on the utilization of abundant and cheap waste materials. The authors stated that the main functional groups involved in the AgNPs formation were aromatic hydroxyl groups and carbonyl groups and substances such as phenolic acids, flavonoids, proteins, terpenes, carbohydrates, etc. having important role in reduction of Ag^+. Furthermore, proteins, polysaccharides and carboxylic acids additionally participated in the process by capping the *in situ* generated nanoparticles. The data suggested that the ethanolic extracts have higher content of phenolic acids and flavonoids than water extracts. On the other hand, the water extracts were rich in carbohydrates (including reducing sugars), proteins and pectic substances (as suggested by the presence of uronic acids). TEM micrographs showed that using water extract of *Rosa damascena* AgNPs were obtained as sphere-like particles with an average size calculated to be 25.8±11.5 nm. Biosynthesized AgNPs were deposited onto a spectroscopic graphite (Gr) electrode and the electroactive layer was stabilized by applying thin film of chitosan onto the modified electrode surface. Chitosan is commercially available natural polymer and preferable material in designing sensors/biosensors. It is a linear amine-rich polysaccharide, biocompatible polymer distinguished by its ability to form flexible, strength, highly adhesive membranes. In electrochemical sensors chitosan is commonly used to enhance the stability of

nanoparticles. The coverage of chitosan on the biosynthesized AgNPs not only protected the nanoparticles against aggregation, but also stabilized surface properties of AgNPs while enhancing their catalytic activity. The electrochemical performance of the modified electrode AgNPs/CS/Gr was studied by means of CV, DPV and chronoamperometry at pH 7.0 and its applicability for amperometric detection of H_2O_2 and vanillin was investigated. Vanillin (4-hydroxy-3--methoxybenzaldehyde) has a specific aroma, pronounced antioxidant and antimicrobial properties and it is one of the most commonly used food supplements. For adults the permissible daily intake of vanillin is less than 10 mg kg^{-1} (the addition of vanillin in baby formula and infant food is not permited). The overweight content of vanillin in food products, as the excessive ingestion via the dietary intake has potential toxic effect – symptoms of a vanillin overdose can include nausea, vomiting and headache; in cases of severe intoxication vanillin can cause irreversible damage to the liver and kidneys. Therefore, the development of novel analytical techniques have been employed for fast and reliable quantitative detection of vanillin. Electrochemical studies suggested that graphite electrode modified with AgNPs, biosynthesized using *Rosa damascena* waste, possesses a stable response to vanillin up to 0.5 mM with a detection limit of 8.4 μM at an applied potential of 0.58 V (vs. Ag/AgCl, 3 M KCl). The developed electrode exhibited a sensitive and reproducible response for quantitative determination of H_2O_2 at applied potentials from –0.2 to –0.3 V. Constant potential amperometry measurements at –0.3 V showed highly sensitive response to H_2O_2 up to 6.6 mM. Electrochemical studies with AgNPs synthesized using flower aqueous extracts of *Achillea millefolium* and *Lavandula angustifolia* wastes as reducing agents, which is a novel simple approach, inexpensive and eco-friendly in nature, also were reported.[94] The representative electron micrographs of AgNPs showed that the nanoparticles grew very tiny with spherical shape. From the presented histograms it can be seen the size distribution of AgNPs and their mean sizes were 2.8 nm for AgNPs/*Achillea millefolium* and 3.1 nm for AgNPs/ /*Lavandula angustifolia*, respectively. Selected area electron diffraction (SAED) pattern represents the (111), (220) and (222) crystal planes of the cubic structure of AgNPs in both samples. Biosynthesized AgNPs were deposited onto a spectroscopic graphite surface, applying two different procedures, and stabilized using chitosan to build new electrocatalysts. The electrochemical performance of the modified electrodes was studied by means of CV and chronoamperometry in neutral medium and their applicability for amperometric quantitative determination of H_2O_2 was demonstrated. The modified electrodes showed a remarkable activity at applied potentials of –0.3 and –0.2 V *vs.* Ag/AgCl, 3 M KCl, rapid, stable and reproducible amperometric response. It was stated that amperometry at constant potential of –0.3 V is distinguished by extremely high sensitivity (533.5 μA mM^{-1} cm^{-2}) up to 4.3 mM H_2O_2. In order to study the selectivity, the amp-

erometric response was examined in the presence of common interfering species such as nitrate, glucose, uric acid, ascorbic acid and citric acid. The authentic record of the electrode signal clearly shows that the tested species had no effect on the H_2O_2 detection – no response was observed in the presence of the above mentioned substances and the current response for H_2O_2, registered after adding the substances, corresponds to the one determined in the calibration study. These results demonstrate that the modified electrode has good selectivity for H_2O_2 and reveal the application potential of the so-biosynthesized AgNPs for sensing of H_2O_2 in real samples.

Potassium and sodium nitrites (KNO_2, $NaNO_2$) are listed as permitted food additives (E249, E250). KNO_2 and $NaNO_2$ show important bacteriostatic and bacteriocidal activity against several spoilage bacteria and foodborne pathogens in meat products and are widely used as preservatives in the preparation of cured meat products.[108] Nitrite ions not only have a pronounced antimicrobial activity, but also act as a color fixative and inhibits lipid oxidation, thereby slowing meat spoiling. In addition, nitrite ion concentration is one of the most important indicators determining the quality of drinking water – according to the recommendation of the World Health Organization[109,110] the acceptable NO_2^- content is 0.2 mg L^{-1}; according to European Community regulation[111,112] the maximum permissible nitrite content of drinking water is 0.1 mg L^{-1}. Consumption of foods with excessive nitrite content poses a serious threat to human health. A number of clinical studies have shown that nitrite intake is associated with higher relative risk of breast cancer, gastric cancer, renal cell carcinoma, adult glioma, colorectal cancer, esophageal cancer and thyroid cancer.[113] Therefore, the importance of improved analytical methods for determination of nitrite in drinking water, cured food and environmental systems has received considerable attention. Nitrite ion is an electroactive and can be quantified electrochemically. In comparison with the conventional analytical techniques, electrochemical analysis has been considered as a fast, low-cost and effective way due to its intrinsic simplicity and high sensitivity.[114]

A promising electrochemical sensor for accurate, sensitive and selective detection of nitrites is developed by Shivakumar *et al.*[115] The authors reported on a facile, cost effective, green synthesis method of silver nanospheres (AgNS) by using pre-hydrolyzed liquor (PHL) from the *Nilgiri* wood generated from pulp industry without any pre-treatment. The synthesis was performed at room temperature within 3 h. The presented XRD pattern of AgNS evidences face centered cubic crystalline structure of metallic silver; the average crystallite size of AgNS calculated from Scherrer equation was found to be ~30 nm. It was suggested that hemicelluloses present in PHL were responsible for the reduction of silver ions and stabilization of AgNS. The GC electrode modified with biosynthesized AgNS has been shown to exhibit excellent electrocatalytic activity in nitrite oxid-

ation – extremely low detection limit (0.031 μM) and high electrode sensitivity of 580 μA mM^{-1} cm^{-2} in the concentration range from 0.1 to 8.0 μM. It is noteworthy that after 30 days storage the presented electrode retains up to 98 % of its initial activity.

Ascorbic acid (AA), known as vitamin C, is a naturally occurring organic compound with antioxidant properties – it is one of the strongest reductants and free radical scavengers in living cells that is suggested to decrease oxidative damage and lowering the risk of certain chronic diseases. The antioxidant activity of AA is the main reason to be frequently used in food industry to prevent unwanted changes in the color and aroma of foods. The use of AA in meat products, with the addition of nitrites, is important for the activity of reduction dependent upon nitrousmetamyoglobin-Fe (III) converted into nitrousmetamyoglobin–Fe (II), which maintains the colour of the product most brilliant.[116] Additives based on AA are widely used in the production of food and beverages (jam, candy, fruit juices, fish and meat products, beer, etc.). AA is used as well as in cosmetics as a skin conditioning agent and in pharmaceutical industry as a diet supplement in various forms.[114] The wide and effective therapeutic potential of AA in dermatology also has been proven. Vitamin C plays a key role in maintaining skin health, provides protection against UV-induced photodamage, participates in the formation of skin barrier lipids and collagen in the dermis, as well as in the modulation of cell signal pathways of cell growth and differentiation. Numerous clinical studies and *in-vitro* data support the use of topically applied AA for photoprotection, antiaging, anti-inflammatory and skin-lightening uses. A topical AA treatment of the epidermal surface suppressed UVB-induced cell death, apoptosis, DNA damage, reactive oxygen species (ROS) production, and the infammatory response by downregulating tumour necrosis factor-α (TNF-α) expression and release.[117]

Under normal physiological conditions, melanin is produced by the epidermal melanocytes in response to UV-irradiation. An excessive production of melanin causes dermatological problems such as freckles, age spot and melasma. These skin pigmentation disorders can be caused by various factors such as an excessive sun exposure, hormonal imbalance during pregnancy or menopause, side effects from certain medications. Emerging evidence has indicated that AA has therapeutic effects on facial hyperpigmentation, as it reduces melanin synthesis. AA suppresses the catalytic activity of tyrosinase, the rate-limiting enzyme in melanin biosynthesis.[118] Although the antipigmentary and skin-protective mechanisms of AA still need to be clarified, AA has been used widely as skin-lightening, anti-aging, anti-oxidant and anti-inflammatory agent in commercially available cosmetics (creams, lotions, dental care products, *etc.*).

Due to the important role of AA, recently there is a significant research interest to develop electrochemical sensors for detection of AA content in various

samples including foods, drugs, cosmetics and biological fluids.[114,119] In this regard crystalline silver face-centered cubic phase, spherical in shape, with mean particle size about 5.3–10.2 nm was synthesized using onion extracts.[120] The authors of this study believe that high phenolic content of the water extract of onion is responsible for production and stabilization of AgNPs. It was suggested that the formation of AgNPs was related to the reaction temperature, pH, duration, as well as concentrations of silver nitrate solution and onion extract. Modified carbon paste electrode (AgNPs/CPE) was prepared using the AgNPs phytosynthesized at optimal conditions (5 mM $AgNO_3$, 17 wt. % onion extract, temperature 35 °C, pH 10 and 18 h reaction time). The effect of synthesized AgNPs on AA electrooxidation was investigated by SWV. Voltammograms show that the peak current at 0.48 V remains linear in the concentration range 0.4 to 450 μM AA; detection limit was calculated to be 0.1 μM AA. The real sample analysis reveals the practical applicability of AgNPs/CPE for AA detection in fruit and vegetable juices.

Electrochemical sensor for dopamine (DA) based on biosynthesized AgNPs was developed by Sreenivasulu *et al*.[121] Dopamine (4-(2-aminoethyl)benzene--1,2-diol) is a neurotransmitter that affects numerous physiological processes and plays an important and diverse role in brain function. Dopamine molecule is biomarker for diseases such as Parkinson's, depression, schizophrenia and some brain tumors. Reliable detection of dopamine is important in research and clinical disease diagnosis and various types of electrochemical sensors have been developed due to its electroactive nature. Sreenivasulu *et al.* have used aqueous root extract of *Mimosa pudica* for facile and stable biosynthesis of AgNPs. The formation of AgNPs were identified using UV–Vis spectrophotometer and thoroughly characterized by using XRD, FTIR, SEM, EDAX and TEM. TEM analysis showed that the synthesized AgNPs have a spherical shape and average sizes from 35.0 to 42.5 nm. Amperometric studies revealed that the AgNPs-assembled-GC electrode possesses high sensitivity, low limit of detection (0.5 μM) and an excellent dynamic range (10–60 μM) for quantitative detection of DA. The authors stated that these results are comparable with those obtained by chemically modified GC electrodes previously reported in the literature.

Nitrobenzene (NB) is widely used as a precursor for aniline, pesticides, herbicides, insecticides, azo dyes, explosives, and drugs. Acute (short-term) and hronic (long-term) inhalation, oral, and dermal exposure of humans to NB result in effects on the blood, central nervous system, liver and kidney. Prolonged exposure may cause headache, nausea, fatigue, dizziness, impaired vision, cyanosis and anemia. Unfortunately, a huge amount of NB was exited into water, soil and sediments from industries. Therefore, the timely and accurate detection of NB is an important concern in public and environmental protection. Different analytical methods have been used for detection of NB and electrochemical methods are

considered simpler and more sensitive than available chromategraphic and spectrophotometric methods.[122] Shivakumar *et al.* have described eco-friendly synthesis of AgNPs using *Eucalyptus* extract as a reducing and stabilizing agent.[123] A GC electrode was modified with the so-synthesized nanoparticles and AgNPs/GC was tested for quantitative detection of NB. Two electrochemical techniques – CV and DPV were used to study the electrochemical behaviour of AgNPs/GC. The modified electrode exhibited good electrocatalytic activity in the reaction of electroreduction of NB – linear current response in the concentration range 5 to 40 μM, sensitivity of 2.262 μA μM^{-1} cm^{-2}, detection limit of 0.027 μM and good selectivity. Stability studies were carried out by running the CV of the modified electrode in the presence of 1 mM NB on the day of preparation and every alternate day up to 20 days. The authors stated that the sensor exhibited great storage stability retaining up to 92.8 % of preliminary current at the end of tested period. The practical applicability of developed electrode material to detect selectively NB in tap water and lake water was tested and satisfactory results were obtained.

In order to improve selectivity, sensitivity and detection limit for determination of NB, Karthik *et al.* have modified GC electrode with sphere-like AgNPs biosynthesized using *Camellia japonica* leaves.[124] The fabricated electrocatalyst AgNPs/GC have been shown to have ability to detect NB with an excellent selectivity, extremely low limit of detection (0.012 μM) and a wide linear range (up to 2.593 mM). The AgNPs/GC showed excellent selectivity towards the NB detection – the results from selectivity test showed that the addition of potentially interfering species (common metal ions, some anions and nitroaromatic containing substances) into the system in 500-fold concentration relative to the analyte does not affect the electrode signal. This result is remarkable given the fact that other nitroaromatic compounds usually significantly affect the peak current response of NB owing to their similar structural activity. The practical applicability of this catalyst for selective quantitative analysis of NB in real samples was tested successfully in contaminated waste water. The sensor device is simple, cost effective and portable and can be applied in a number of industrial and research measurements. An electrochemical sensor for NB based on reduced graphene oxide (rGO) and AgNPs, biosynthesized using *Justicia glauca* leaf extract, has been developed.[125] The modified rGO/AgNPs/GC electrode showed good efficiency for selective quantitative determination of NB, compared to other modified electrodes – the electrode signal retained its linearity in the concentration range from 0.5 to 900 μM, the sensitivity was determined as 0.836 μA μM^{-1} cm^{-2} with a detection limit of 0.261 μM NB. In addition, the reduction peak current response to 100 μM NB was examined up to 52 days by CV and rGO/AgNPs/GC was stored in phosphate buffer solution (PBS) when not in use. The modified electrode retained about 90.15 % of its initial current response after 52

days, which indicates the excellent storage stability of the sensor. The authors have reported that the fabricated sensor showed a satisfactory reproducibility with *RSD* of 3.8 % for determination of NB using 5 different sensors. The good recovery results and *RSD*s of the devepoled sensor obtained in waste water samples proved the practical applicability towards the determination of NB in real samples.

Bastos-Arrieta *et al.* have demonstrated that biosynthesized AgNPs may be useful in developing catalysts for electrochemical sensing of some heavy metal ions.[126] Heavy metal toxicity has proven to be a major threat and there are serious health risks associated with it.[127] Toxicity of heavy metals is due to accumulation in tissues, metabolic interference, mutagenesis and carcinogenesis. Arsenic, cadmium, mercury, chromium, lead and nickel induce oxidative stress, DNA damage, cell aging and cell death processes, resulting in increase the risk of cancer and cancer-related diseases.[128] Bastos-Arrieta *et al.* reported on synthesis of AgNPs by using an aqueous extract of grape stalk waste as a reducing and capping agent, thus leading to a reagent-free procedure and valorisation of agri-food waste.[126] Various factors affecting the AgNPs synthesis such as temperature, contact time, extract/metal solution volume ratio and pH have been studied. AgNPs with an average diameter of 27.7±0.6 nm were selected to proof their suitability for sensing purposes. Screen-printed carbon nanofiber electrode modified with biosynthesized AgNPs (AgNPs–SPCNFE) was tested for the simultaneous stripping voltammetric determination of Pb(II) and Cd(II). The good reproducibility, high sensitivity and low limits of detection (around 2.7 μg L^{-1} for both metal ions) make this electrocatalyst a promising sensing element in electrochemical sensor device for a fast and reliable simultaneous detection of Pb(II) and Cd(II).

Table I summarizes electrochemical sensors based on biosynthesized AgNPs. Important operational characteristics including sensitivity, dynamic range, limit of detection, as well as data on stability and reproducibility of sensors were presented.

4.2. Electrochemical sensors based on biosynthesized AuNPs

In nanotechnology AuNPs have attracted much attention due to their remarkable properties including high mechanical stability, unique tunable optical and distinct electronic properties, high electrical conductivity, strong binding affinity to thiols, and catalytic activity. Adhering to the principles of green chemistry, Mohd Taib *et al.* have described a new method for synthesis of AuNPs, using water extract of *Hibiscus sabdariffa* leaves (*H. sabdariffa* L.) as both reductant and stabilizer.136 The proposed procedure is reliable, environmentally friendly and cost-effective compared to other conventional synthesis methods. The authors suggested that chlorogenic acid (an ester of caffeic acid and quinic acid) in *H. sabdariffa* L. extract is the major compound involved in the reduction of Au^{3+} to Au.

TABLE I. Operational characteristics of electrochemical sensors based on biosynthesized AgNPs; Amp. (amperommetry); CV (cyclic voltammetry); DPV (differential pulse voltammetry); DPASV (differential pulse anodic stripping voltammetry); SWV (square wave voltammetry); SWASV (square wave anodic stripping voltammetry); *LOD* (limit of detection); AgNS (silver nanospheres); CS (chitosan); GC (glassy carbon); Gr (graphite); GO (graphene oxide); rGO (reduced graphene oxide); SPCNFE (screen-printed carbon nanofiber electrode); CPE (carbon paste electrode); NB (nitrobenzene); AA (ascorbic acid); DA (dopamine)

Modified electrode	Reducing agent	Method (E / V)	Analyte	Sensitivity, μA mM^{-1} cm^{-2} (linear range) (*LOD*)	Stability (*RSD*)
AgNPs/CS/Gr[94]	*Achillea millefolium*	Amp. (–0.3[a])	H_2O_2	533.5 (up to 4.3×10^{-3} M) (–)	– (6.8 %)
AgNPs/CS/Gr[94]	*Lavandula angustifolia*	Amp. (–0.3[a])	H_2O_2	374.7 (up to 3.5×10^{-3} M) (–)	– (–)
AgNPs/CS/PGE[106]	*Tagetes erecta*	CV (–0.55[a])	H_2O_2	0.129 mA μM^{-1} (1.0–10.0 μM) (0.52 μM)	4 weeks (1.4 %)
rGO/AgNPs/GC[105]	*Green tea*	Amp. (–0.4[a])	H_2O_2	236 (0.002–20.0 mM) (0.73 μM)	7 weeks (3.6 %)
AgNPs/CS/Gr[107]	*Rosa damascena*	Amp. (–0.3[a])	H_2O_2	115.2 (up to 6.6 mM) (–)	– (6.7 %)
AgNPs/Gr[107]	*Rosa damascena*	Amp. (–0.3[a])	H_2O_2	214.7 (up to 3.9 mM) (–)	– (6.7 %)
AgAu/rGO/GC[129]	*Azadirachta indica*	Amp. (–0.4[a])	H_2O_2	– (0.1–5.0 mM) (1.0 μM)	– (–)
rGO/AgNPs/GC[130]	*Plectranthus amboinicus*	Amp. (–0.32[a])	H_2O_2	– (1.0–800 μM) (0.312 μM)	– (–)
AgNPs/GO/GC[131]	*Callicarpa maingayi*	Amp. (–0.32[a])	H_2O_2	– (5.0–700 μM) (0.6 μM)	– (–)
AgNPs/GC[132]	*Bacillus subtilis*	Amp. (–0.35[b])	H_2O_2	236 (0.05–120 mM) (8.0 μM)	30 days (3.1 %)
AgNS/GC[115]	*Nilgiri* wood	Amp. (0.86[a])	NO_2^-	580 (0.1–8.0 μM) (0.031 μM)	30 days (3.6 %)
AgNPs/GC[133]	*Piper betle*	Amp. (1.0[a])	NO_2^-	1642.27 (1.0–6000 μM) (0.046 μM)	30 days (3.3 %)
AgNPs/GO/GC[134]	AA	SWASV (–0.6[a])	As^{3+}	180.5 μA μM^{-1} (13.33–375.19 nM) (0.24 nM)	90 days (–)
AgNPs/SPCNFE[126]	Grape stalk waste	DPASV (–0.42[a])	Pb^{2+}	62 nA μg^{-1} L (8.9–100.4 μg L^{-1}) (2.7 μg L^{-1})	– (–)
AgNPs/SPCNFE[126]	Grape stalk waste	DPASV (–0.55[a])	Cd^{2+}	46 nA μg^{-1} L (9.5–37.9 μg L^{-1}) (2.8 μg L^{-1})	– (–)
AgNPs/CPE[120]	Onion	SWV (0.45[a])	AA	– (0.4–450 μM) (0.1 μM)	– (–)
AgNPs/GC[121]	*Mimosa pudica*	DPV (0.1[a])	DA	– (10.0–60 μM) (0.5 μM)	– (–)
AgNPs/GC[135]	*Ocimum tenuiflorum*	Amp. (0.55[a])	glucose	895.8 (1.0–8.9 mM) (0.0048 μM)	10 days (1.15 %)
rGO/AgNPs/GC[125]	*Justicia glauca*	DPV (–0.458[a])	NB	0.836 μA μM^{-1} cm^{-2} (0.5–900 μM) (0.261 μM)	52 days (3.8 %)

TABLE I. Continued

Modified electrode	Reducing agent	Method (E / V)	Analyte	Sensitivity, μA mM^{-1} cm^{-2} (linear range) (*LOD*)	Stability (*RSD*)
AgNPs/GC[124]	*Camellia japonica*	Amp. (–0.42[a])	NB	– (0.05–21.0 μM) (23.0–2593 μM) (0.012 μM)	– (–)
AgNPs/GC[123]	*Eucalyptus*	DPV (–0.78[a])	NB	2.262 μA μM^{-1} cm^{-2} (5.0–40.0 μM) (0.027 μM)	20 days (–)
AgNPs/CS/Gr[107]	*Rosa damascena*	Amp. (–0.3[a])	vanillin	56.8 (up to 0.5 mM) (8.4 μM)	– (–)

[a]Reference electrode: Ag/AgCl, 3 M KCl (0.200 V *vs.* SHE); [b]reference electrode: saturated calomel electrode (SCE, 0.242 V *vs.* SHE)

Previous reports on AuNPs-synthesis have shown that the caffeic acid moiety of chlorogenic acid was essential to reduce Au^{3+}. TEM analysis confirmed that the so-biosynthesized AuNPs were formed with a narrow distribution and an average particle size of 7±2 nm. A glassy carbon electrode modified with the AuNPs was tested as a catalyst in electrooxidation of nitrite. AuNPs/GC showed good electrocatalytic activity in the target reaction – sensitivity was calculated to be 917±30 μA mM^{-1} cm^{-2} in the concentration range from 0.37 to 10 mM and detection limit of 0.11 mM (S/N = 3). The stability, reproducibility and repeatability of AuNPs/GC electrode were investigated by voltammetric measurements. After 21 days storage the prepared electrode possesses around 80 % of its initial response. An analysis for ten sequential prepared electrodes showed *RSD* of 4.27 % which confirmed the repeatability of AuNPs/GC. The sensor-to-sensor reproducibility was investigated by measuring the current responses of five diverse electrodes prepared independently by the same procedure. The results showed that the response produced by different electrodes had a good reproducibility with *RSD* of 4.21 % and authors concluded that the sensor fabrication methodology was reliable.

Emmanuel *et al.* have presented a green procedure for synthesis of AuNPs using *Acacia nilotica* twig bark extract at room temperature.[137] The synthesis protocol shows that the formation of gold particles is within 10 min, which implies a higher reaction rate. The size of biosynthesized AuNPs was calculated using Debye–Scherrer equation which showed that the nanoparticles were in the average size of 30 nm. The AuNPs modified glassy carbon electrode exhibited excellent reduction ability towards NB compared to the unmodified electrode. The developed sensor AuNPs/GC displayed a wide linear response from 0.1 to 600 μM with high sensitivity (1.01 μA μM^{-1} cm^{-2}) and a low detection limit of 0.016 μM in DPV mode. The modified electrode demonstrated exceptional selectivity in the presence of ions, phenolic and biologically active compounds. In

addition, the AuNPs/GC exhibited an outstanding recovery results towards NB in various real water samples.

Electrochemical sensor for quantitative detection of hydrazine – another environmentally hazardous pollutant, was devepoled by Karthik *et al.*[138] Their study envisages easy and innovative method for green synthesis of AuNPs on GC electrode; the fabricated modified electrode was used for the detection of hydrazine by using sensitive amperometric method. Hydrazine is an inorganic base, which is an important reagent in the production of polymer foams, pesticides, insecticides, pharmaceuticals, etc. Hydrazine is also used as rocket fuel – it is a high volumetric energy density liquid fuel (at room temperature and atmospheric pressure) that contains 12.6 wt. % of hydrogen. However, hydrazine is a highly toxic compound with mutagenic and carcinogenic effects. Serious effects on the reproductive system are observed in animals after hydrazine inhalation. Therefore, rapid and precise detection of hydrazine is of great importance. Karthik *et al.* have used *Cerasus serrulata* (*C. serrulata*) leaves extract for green synthesis of AuNPs. TEM images confirmed that biosynthesized AuNPs were spherical in shape and approximately in the range of 5 to 25 nm. DFT studies revealed that the coumarin present in the *C. serrulata* leaves extract demonstrated greater reducing and stabilizing properties compared to the properties of other compounds like butylhydroxytoluene and hydrocoumarin present in the extract. The electrochemical results showed remarkable electrocatalytic activity of the AuNPs-modified GC electrode towards oxidation of hydrazine. AuNPs/GC exhibited a wide linear range from 5 nM to 272 μM with a low detection limit of 0.05 μM. The fabricated electrode showed good selectivity towards the sensitive determination of hydrazine even in the presence of 1000-fold and 150-fold excess concentration of common ions and biological interferents (ascorbic acid, uric acid and dopamine), respectively. Thus the proposed electrode seems to be a potential candidate for developing a simple, rapid and cost-effective electrochemical sensor for hydrazine detection.

For the first time Karthik *et al.* report in electrochemical chloramphenicol (CAP) sensor using plant extract derived AuNPs.[139] CAP is an effective broad-spectrum antibiotic that has been widely used to treat mammalian, poultry, aquatic and bee diseases around the world. However, CAP is associated with numerous toxic and fatal side effects in human, especially bone marrow suppression, aplastic anemia and agranulocytosis. Therefore, development of fast, simple and reliable methods for CAP monitoring in food samples are extremely important in food quality control. Karthik *et al.* have presented a simple and rapid green synthesis using *Bischofia javanica Blume* leaves as reducing agent for the preparation of AuNPs. The biosynthesis procedure requires less than 40 s to reduce gold salts to AuNPs. They have used graphene oxide (GO) as support to anchor and stabilize AuNPs which also avoids aggregation. The successful formation of

the AuNPs/GO composite was revealed by morphological, elemental, spectroscopic and electrochemical methods. The green synthesized AuNPs/GO delivered high conductivity, surface area and porosity. AuNPs/GO composite film modified electrode has shown excellent electrocatalytic ability to CAP. The amperometric sensing platform possesses a sensitivity of 3.81 μA μM^{-1} cm^{-2} in the range of 1.5 μM–2.95 μM; *LOD* of the sensor was calculated as 0.25 μM CAP. The amperometric measurements proved that the modified electrode has a good anti-interference ability, a fast response (the current reached 95 % steady-state current within 5 s of CAP injection), satisfactory repeatability (*RSD* for five repeatable measurements was calculated to be 3.18 %) and reproducibility of the procedure (five different AuNPs/GO modified electrodes showed *RSD* 3.83 %). The long-term storage stability of the electrode was also reasonable – 92.15 % of the initial response current was retained over 15 days. The real sample analysis tested in milk, powdered milk, honey and eye drops samples validates excellent practical feasibilty of AuNPs/GO modified electrode to determine CAP content in food and pharmaceutical samples.

Table II provides an overview of the electrochemical sensors based on biosynthesized AuNPs.

TABLE II. Operational characteristics of electrochemical sensors based on biosynthesized AuNPs; SPE (screen-printed electrode); CAP (chloramphenicol). Other abbreviations are the same as Table I

Modified electrode	Reducing agent	Method (*E* / V)	Analyte	Sensitivity (linear range) (*LOD*)	Stability (*RSD*)
AuNPs/CPE[140]	Glycerol	SWV (0.65[b])	NO_2^-	0.268 A L mol^{-1} (0.2–15 μM) (0.2 μM)	60 days (4.0 %)
AuNPs/GC[136]	*Hibiscus sabdariffa*	Amp. (0.8[a])	NO_2^-	917 (370–10000 μM) (110 μM)	21 days (4.21 %)
rGO/AuNPs/GC[141]	*Abelmoschus esculentus*	SWASV (–0.791[a])	Cd^{2+}	19.05 μA μM^{-1} cm^{-2} (5–10 μM) (31.81 nM)	– (–)
rGO/AuNPs/GC[141]	*Abelmoschus esculentus*	SWASV (–0.54[a])	Pb^{2+}	47.7 μA μM^{-1} cm^{-2} (5–10 μM) (12.69 nM)	– (–)
rGO/AuNPs/GC[141]	*Abelmoschus esculentus*	SWASV (–0.064[a])	Cu^{2+}	22.10 μA μM^{-1} cm^{-2} (5–10 μM) (27.42 nM)	– (–)
rGO/AuNPs/GC[141]	*Abelmoschus esculentus*	SWASV (0.228[a])	Hg^{2+}	29.28 μA μM^{-1} cm^{-2} (5–10 μM) (20.70 nM)	– (–)
AuNPs/SPE[77]	*Pithophora oedogonia*	Amp. (0.77[a])	Carbendazim	– (0.05–25 μM) (0.0029 μM)	– (–)
AuNPs/GC[138]	*Cerasus serrulata*	Amp. (0.24[a])	Hydrazyne	– (0.005–272 μM) (0.05 μM)	– (–)
AuNPs/GC[137]	*Acacia nilotica*	DPV (–0.7[a])	NB	1.01 μA μM^{-1} cm^{-2} (0.1–600 μM) (0.016 μM)	8 days (2.1 %)

TABLE II. Continued

Modified electrode	Reducing agent	Method (E / V)	Analyte	Sensitivity (linear range) (*LOD*)	Stability (*RSD*)
AuNPs/GO/GC[139]	*Bischofia javanica Blume*	Amp. (–0.45[a])	CAP	3.81 μA μM^{-1} cm^{-2} (1.5–2.95 μM) (0.25 μM)	15 days (3.18 %)
AuNPs/GC[142]	Peanut seeds	CV (–0.3[a])	Sudan IV	– (10–80 μM) (4.0 μM)	20 cycles (–)

4. 3. Electrochemical sensors based on other biosynthesized metal and metal oxide nanoparticles

Copper nanoparticles (CuNPs) are particularly attractive because of high natural abundance of copper, low cost and the practical and straightforward multiple ways of preparing Cu-based nanomaterials.[143] Cu-based materials can promote and undergo a variety of reactions due to accessible oxidation states of copper which enable reactivity *via* both one- and two-electron pathways. Recently, copper oxide nanostructures have been given more attention as promising electrode materials for supercapacitores, gas sensors, electrochemical sensors and anode materials for lithium ion batteries. Many researchers have found that the electrochemical performance of CuO/Cu_2O composites has been improved due to their stable multiple oxidation states and integration of their catalytic capabilities. A simple, low cost, stable and sensitive electrochemical sensor based on biosynthesized copper oxide nanoparticles (CuO/Cu_2O NPs) was developed for formaldehyde detection.[144] Momeni *et al.* have successfully synthesized CuO/Cu_2O nanoparticles using Gum Arabic (highly branched complex polysaccharide, nontoxic and hydrophilic with abundant hydroxyl and carboxyl groups) as a stabilizing and capping agent. The CuO/Cu_2O NPs modified carbon ionic liquid electrode (CuO/Cu_2O/CILE) was designed and its catalytic activity was investigated towards formaldehyde oxidation in alkaline medium. Formaldehyde is one of the most widely used chemicals – it acquires applications in different areas, such as resin, adhesive and plastic industry, fuel cells and electroless plating industry, agriculture and food manufacturing, as an industrial disinfectant and a preservative agent in medical labs, *etc*. However, a number of studies have suggested that formaldehyde exposure is associated with certain types of cancer, particularly myeloid leukemia.[145] In the commented article the results showed that CuO/Cu_2O/CILE electrode possesses good electrocatalytic activity in the target reaction with a linear current response in the range from 0.1 to 110 mM formaldehyde and a detection limit of 10 μM. The authors have proven the good reproducebility and stability of modified electrode. The long term stability of CuO/Cu_2O/CILE electrode was tested by storing the electrode at room temperature for one month and the current response retained 94 % of its initial response. A simple and green route for synthesis of CuO/Cu_2O NPs together with enhanced electrocatalytic

activity toward formaldehyde oxidation show that the CuO/Cu_2O/CILE is one of the most promising systems for detection of formaldehyde.

Copper oxide nanoparticles (CuONPs) were synthesized using *Caesalpinia bonducella* seed extract *via* a green synthetic pathway and were evaluated for electrochemical detection of riboflavin (vitamin B2).[146] Riboflavin is a water-soluble vitamin needed for the proper functioning of human organs, such as it plays an essential role in the sequence of protein, carbohydrate and fat metabolism. The lack of vitamin B2 leads to skin disorders and eye lesions. At the same time excess of riboflavin in the human body is dangerous because leads to damage to DNA and tissues. Riboflavin cannot be produced by the human body – it is provided through dietary supplements and pharmaceutical products. Therefore, it is essential to monitor vitamin B2 in situ in real food and pharmaceutical samples. Sukumar *et al.* have reported on the development of modified paraffin-impregnated graphite electrode CuONPs/PIG as a suitable sensor for the determination of nanomolar concentration of vitamin B2 with an observed linear range of 3.13−56.3 nM and a limit of detection of 1.04 nM. The electrode showed satisfactory stability over a period of 4 months – 95 % residual activity was recorded after 80 days and 80 % after 120 days, respectively. The practical applicability of CuONPs/PIG was checked with real samples – egg yolk, milk powder and commercially available B-complex tablets. The concentration of vitamin B_2 was evaluated by the standard addition method, and the recovery values range from 99 to 99.75 %. The results showed high recovery and the authors stated that this method could be extended for further practical applications.

Kumar *et al.* have been demonstrated a facile and eco-friendly approach for the simultaneous reduction of graphene oxide as well as copper acetate to prepare Cu_2O decorated reduced GO (rGO/Cu_2O).[147] In this work an easily available and naturally occurring mango bark (*M. indica*) extract has been used as the reducing agent instead of hazardous and toxic chemicals. Fourier transform infrared and X-ray photoelectron spectroscopy have been performed to confirm the removal of oxygen functional groups from the surface of GO and the X-ray diffraction pattern reveals the formation of Cu_2ONPs. The electrocatalytic behaviour of the resultant rGO/Cu_2O composite has been carried by CV and constant potential amperometry. The utility of rGO/Cu_2O as an electrochemical sensor towards H_2O_2 detection was shown; the sensitivity and limit of detection were found to be 7.435 μA μM^{-1} and 42.35 nM, respectively.

Amanulla *et al.* have reported the development of a sensitive and selective amperometric sensor for H_2O_2, using for the first time biosynthesized iron nanoparticles (FeNPs).[148] A simple and facile green process was used for the synthesis of FeNPs decorated rGO nanocomposite using *Ipomoea pestigridis* leaf extract as a reducing and stabilizing agent. The physicochemical results confirmed the successful formation of rGO/FeNPs composite; TEM images showed

that the FeNPs were evenly distributed on rGO surface with an average diameter of 28±4 nm. The nanocomposite rGO/FeNPs was further modified on GC electrode and used for H_2O_2 sensing. CV data reveal that rGO/FeNPs nanocomposite has an excellent behavior to H_2O_2 electroreduction when compared to the response of FeNPs and rGO modified electrodes. Amperometry was further used to quantify selectively H_2O_2 using rGO/FeNPs nanocomposite: the electrode response at an applied potential of –0.5 V (vs. Ag/AgCl) was linear over the concentration range from 0.1 μM to 2.15 mM and exceptionally fast (2 s). The limit of detection and sensitivity of the proposed sensor were estimated as 0.056 μM and 0.2085 μA μM^{-1} cm^{-2}, respectively. The practical ability of the fabricated sensor was examined in commercial contact lens solution, human serum and urine samples.

Selenium nanoparticles (SeNPs) synthesis has been achieved by either physical or chemical methods, which suffer from drawback like high pressure, low yields and longer growth times which cannot be regarded as an eco-friendly process. Prasad *et al.* have developed an eco-friendly and simple method for SeNPs synthesis using a selenium-resistant bacterium identified as *Bacillus pumilus* sp. BAB-3706 cell-free extract.[149] A working electrode was modified by coating the surface of indium tin oxide (ITO) with resulting colloidal SeNPs (size 10–80 nm). The proposed sensor SeNPs/ITO exhibited good electrocatalytical activity towards the reduction of H_2O_2 and low detection limit. Hence, microbial SeNPs can be a promising source for the development of electrochemical sensor system for H_2O_2.

Among various metallic nanoparticles, platinum (Pt) and palladium (Pd) nanoparticles are the most widely studied due to their extremely high catalytic/ /electrocatalytic activity. Due to their extensive applications in sensors, biosensors and catalysts, production of PtNPs and PdNPs through environment friendly methods has a significant role. In this regard, Momeni *et al.* have presented green synthesis of PdNPs using natural and low-cost crude extract derived from the marine alga *Sargassum bovinum*.[93] TEM study confirmed the monodispersed and octahedral shape of PdNPs within the size ranges 5–10 nm. Electrocatalytic performance of the so-biosynthesized PdNPs towards reduction of H_2O_2 was investigated. PdNPs-modified carbon ionic liquid electrode (PdNPs/CILE) was developed as a nonenzymatic sensor for the determination of hydrogen peroxide. Amperometric measurements at potential of –0.2 V (*vs*. Ag/AgCl) showed that PdNPs/CILE has an excellent stability and it is a reliable sensor for the detection of H_2O_2 in a wide range of 5.0 μM–15.0 mM with a sensitivity of 284.35 mA mM^{-1} cm^{-2} and a detection limit of 1.0 μM H_2O_2. The method is reliable – *RSD* of current response to 1 mM H_2O_2 of five separate electrodes made with different CILE pastes was calculated to be 3.2 %, and a single electrode using five consecutive determinations showed average *RSD* of less than 2.5 %. The authors concluded that the interesting performances of the electrode coupled with its simple,

effective and green preparation procedure of PdNPs synthesis, without any surfactants and templates, make it a promising electrochemical sensing platform.

Rapid and eco-friendly synthesis of platinum nanoparticles (PtNPs) using aqueous leaves extract of *Quercus glauca* has been reported for first time for detection of hydrazine.[150] The prepared PtNPs were spherical in shape and size from 5–15 nm. The electrocatalytic performance of modified electrode PtNPs/GC for hydrazine has been studied by CV and amperometric techniques. Cyclic voltammogram of PtNPs/GC showed a sharp peak at a very lower onset oxidation potential of –0.3 V. The fabricated hydrazine sensor showed excellent selectivity, low detection limit of 7 nM, wide linear range from 0.01 to 283 μM and a sensitivity of 1.704 μA μM^{-1} cm^{-2}. The sensor was successfully used for the detection of hydrazine in spiked water samples.

Manganese oxide nanoparticles (MnONPs) of different sizes were synthesized in aqueous medium using clove, *i.e.*, *Syzygium aromaticum* extract (CE) as reducing and stabilizing agent. MnONPs with size ~4 nm were used for the electrochemical sensing of *p*-nitrophenol – a toxic pollutant released by textile and leather industries, iron and steel production, pharmaceutical manufacturing, rubber processing, production of electrical and electronic components.[151] Acute inhalation or ingestion of *p*-nitrophenol in humans leads to headache, drowsiness, nausea and cyanosis (result of methemoglobinemia). Endocrine disrupting effect and hypothalamic pituitary gonadal toxicity of *p*-nitrophenol on animals have been documented recently.[152] *p*-Nitrophenol exposure disrupted steroidogenesis during the ovarian development in female rats, reduced testosterone synthesis, caused morphological changes in testes, and ultimately decreased semen quality in the roosters.[153,154]

The MnONPs, prepared using CE-based green chemistry approach, were useful for *p*-nitrophenol sensing. MnONPs-modified gold electrode detected *p*-nitrophenol with good sensitivity (0.16 μA μM^{-1} cm^{-2}) and detection limit of 15.65 μM.

An overview on the main operational parameters of electrodes modified with biosynthesized metal NPs or metal oxide NPs is presented in Table III.

TABLE III. Operational characteristics of electrochemical sensors based on other biosynthesized metal NPs and metal oxide NPs; UA (uric acid); MGPE (modified graphite paste electrode); EGCG (epigallocatechin gallate); CILE (carbon ionic liquid electrode); PIG (paraffin-impregnated graphite electrode); ITO (indium tin oxide); BCA (butyl carbitol acetate). Other abbreviations are the same as Table I

Modified electrode	Reducing agent	Method (E / V)	Analyte	Sensitivity (linear range) (*LOD*)	Stability (*RSD*)
PdNPs/CILE[93]	*Sargassum bovinum*	Amp. (–0.2[a])	H_2O_2	284.35 (5.0–15000 μM) (1.0 μM)	– (2.5 %)

TABLE III. Continued

Modified electrode	Reducing agent	Method (E / V)	Analyte	Sensitivity (linear range) (*LOD*)	Stability (*RSD*)
rGO/FeNPs/GC[148]	*Ipomoea pes-tigridis*	Amp. (–0.5[a])	H_2O_2	0.2085 μA $μM^{-1}$ cm^{-2} (0.1–2150 μM) (0.056 μM)	– (3.6 %)
SeNPs/ITO[149]	*Bacillus pumilus*	Amp. (–1.0[b])	H_2O_2	16.54 (5.0–600 mM) (3.0 μM)	– (–)
Cu_2O/rGO[147]	*M. indica*	Amp. (–0.2[a])	H_2O_2	7.435 μA $μM^{-1}$ (0.2–3.6 μM) (42.35 nM)	15 days (–)
PdAg/CPE[155]	Fungi	DPV (0.3[a])	UA	– (up to 273.0 nM) (5.543 nM)	– (–)
Cu/Cu_2O/CuONPs/GC[156]	*Pomegranate*	CV (–0.3[a])	Ethanol	0.049 μA mM^{-1} (0.5–2.0 μM) (0.09 μM)	– (–)
CuO/Cu_2O/CILE[144]	Gum Arabic	CV (0.4[a])	Formal-dehyde	186.0 (0.1–110 mM) (10 μM)	30 days (4.6 %)
CoONPs/CPE[157]	Gelatin	CV (–0.34[a])	Glucose	609.04 mM^{-1} cm^{-2} (7.0–1000.0 μM) (5.3 μM)	4 weeks (2.9 %)
PtNPs/GC[150]	*Quercus glauca*	Amp. (–0.18[a])	Hydrazine	1.704 μA $μM^{-1}$ cm^{-2} (0.01–283.0 μM) (7 nM)	– (–)
MnONPs/BCA/Au[151]	*Syzygium aromaticum*	DPV (–0.69[a])	*p*-Nitro-phenol	0.16 μA $μM^{-1}$ cm^{-2} (200.0–550.0 μM) (15.65 μM)	– (–)
CuONPs/PIG[146]	*Caesalpinia bonducella*	SWV (0.03)	Riboflavin	– (3.13–56.3 nM) (1.04 nM)	120 days (–)

5. CONCLUSIONS AND FUTURE PERSPECTIVES

Over the past decade intensive research on the possibility of using plant extracts or microorganisms to produce stable metal nanoparticles with pronounced antibacterial and antitumor activity, as well as studies focused on biosynthesized nanoparticles as catalytically active components in the development of new electrocatalysts, have been observed. There is convincing evidence that green synthesis of metal and metal oxide nanoparticles has a potential to provide a new direction in the fabrication of cheap and highly effective electrocatalysts applicable in food, clinical, pharmaceutical and environmental analysis. In this review we have been summarized the main approaches for biosynthesis of metal nanoparticles and their use in the construction of novel electrochemical sensor platforms. It was shown that the biosynthesized metal nanoparticles produced by plants and microorganisms are successfully applied in designing of electrochemical sensors for detection of broad spectrum of analytes.

Currently, researchers have focused their attention on detection of biomolecules involved in the synthesis of metal nanoparticles as well as on understanding the principles/pathways and mechanisms of nanoparticle biosynthesis. Since the properties of nanomaterials strongly depend on their size and shape, efforts should also be focused on optimizing the experimental conditions to yield stable and reproducible size-controlled biosynthesis of nanoparticles. Therefore, researchers should refine the biological mediated synthesis protocols to ensure increasing the sustainability of the processes involved in the production of nanoparticles. Scalability of the production method also is a necessary – appropriate technologies need to be developed for safe and efficient production of these novel nanomaterials on a commercially sustainable scale while maintaining a satisfactory size distribution.

In terms of electrochemical sensing applications selectivity and reproducibility of the electrode signal in real complex matrices, as well as long-term stability of the modified material are extremely important. The experimental data show that the modified with biosynthesized nanoparticles surfaces still remain challenging as they are not often as reproducible and stable as one would hope. Further research needs to be done to address these issues and to improve the electrode performance. Consequently the emphasis should be on achieving a higher operational and storage stability of the electrode-catalysts modified with biosynthesized metal/metal oxide nanoparticles. Expectations in this area are also related with broadening the spectrum of target analytes, as well as development of surface modification methods capable of enhancing the electrode sensitivity and selectivity.

In summary, the significant development of electrochemical sensor platforms based on biosynthesized nanomaterials is giving rise to new impetus of generating novel sustainable bio-based technologies for analysis and securing the environmental and food safety.

ИЗВОД

ПРИМЕНА БИОСИНТЕТИСАНИХ МЕТАЛНИХ НАНОЧЕСТИЦА У ЕЛЕКТРОХЕМИЈСКИМ СЕНЗОРИМА

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У новије време развој еколошки прихватљивих, исплативих и поузданих метода синтезе металних наночестица привлачи значајну пажњу. Такозване зелене синтезе, које користе благе реакционе услове и природна средства као што су биљни екстракти и микроорганизми, успостављене су као погодан, одржив, јефтин и еколошки безбедан приступ синтези разноврсних наноматеријала. Током протекле деценије биосинтеза се наметнула као значајна метода којом се смањују штетни ефекти традиционалних метода синтезе наночестица које су уобичајене у лабораторијама и индустрији. Овај прегледни

рад наглашава значај биосинтетисаних металних наночестица у области електрохемијских сензора. Све је више доказа да зелена ситеза наночестица пружа нови правац у дизајнирању исплативих, високо осетљивих и селективних катализатора за електроде које се примењују у анализи хране, као и у клиничким анализама и заштити животне средине. Рад је базиран на 157 литературних навода и даје детаљан преглед главних приступа зеленој синтези металних наночестица и њиховој примени у електрохемијским сензорима. Такође су обухваћене значајне радне карактеристике укључујући осетљивост, динамички опсег, границу детекције, као и податке о стабилности и репродуктивности сензора.

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