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Applications of Metallic nanostructures in electrochemical sensors

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This review reports recent advances in Metallic nanostructures based electrochemical sensors.
Interesting aspects of NPs include size and shape-dependent interatomic bond distances, melting points, chemical reactivity, and optical and electronic properties. The small size of Metallic nanostructures has allowed nanoscale electrochemical processes to be probed. Electrochemical characteristics can be related directly to other properties of the Metallic nanostructures. The challenge of ultimately measuring the electrochemical behavior of individual Metallic nanostructures is leading to imaginative experiments that have an impact on electrochemistry in general, as well as broader surface and colloid science, as we highlight in this Review. One of the largest applications of Metallic nanostructures is in electrocatalysis, the field of catalysis concerned with reactions that involve charge transfer at the interface between a solid catalyst and an electrolyte.
A key aspect to the study of Metallic nanostructures as electrocatalysts is the preparation and characterization of nanoparticulate electrodes, which often consist of Metallic nanostructures dispersed on a support material. In such electrodes, the Metallic nanostructures support plays a number of roles. It acts as a conductive bridge, contacting the Metallic nanostructures to an external electronic circuit. The support acts to disperse the Metallic nanostructures, to limit agglomeration, and maintain the high surface-to-volume ratio desired.

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Introduction

Nano-science is a technology which is based on the manipulation of individual atoms and molecules to produce materials from them for applications well below the sub-microscopic level. This technology involves physical, chemical and biological knowledge at scales ranging between individual atoms and molecules below the nanometer, up to 100 nm. The subject also can generalize the integration of the resulting structures to larger systems. The most definitions of nanotechnology are based on dimensions: for instance, according to the National Nanotechnology Initiative (NNI) in the United States, for instance, "nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications". Often only one or two dimensions are in the nano region, as in quantum wells and nanowires but in some cases all three dimensions are nanoscale, as in quantum dots and nanocrystals [1].

The development of nanotechnology has been growing very fast over the last few years. Traditional areas of technology have been improved due to the great advantages that nanoparticulate based materials may offer. In the electrochemistry area, these advantages are gained by both the enhancement of the total rate of diffusion processes due to the surface to volume ratio and/or leading to a higher number of molecules that can be attached or adsorbed on the inorganic nanoparticles [2].

In biotechnological systems, the expanding availability of a variety of nanostructures with highly controlled properties in the nanometer size range has sparked widespread interest in their use .Size does matter the fact that nanoparticles are similar in size range to many common biomolecules makes them appear to be natural companions in hybrid systems. Beside, the unique properties of nanostructures can be entered in to biotechnological applications. By controlling structure precisely at nanoscale dimensions, the properties of nanostructures, such as semiconductor nanocrystals and metal nanoshells, in a very accurate manner. In addition, one can make modifications to nanostructures to match their integration much better with biological systems; for example, modifying their surface layer for enhanced aqueous solubility, biocompatibility, or biorecognition. With selected biomolecules bound to nanostructure surfaces, new 'hybrid' nanostructures can be obtained for applications such as biosensing and imaging, or nanostructures can be embedded in other biocompatible materials to modify material properties or expose new functionality [3].

The synthesis and the study of nanotools enhanced with properties (physical or chemical) have the capacity to be the base of any research related to nanosciences [5].

Nanostructured materials have attracted dramatic interests and have become a favorite research area for the past decade due to their unique properties [6]. The emergence over the last 10–15 years of the ability to controllably synthesize, purify, and analyze new nanoscale materials has driven intense research into the optical, electrical, thermal, and mechanical properties of both individual pieces of these materials. Typically, these films approach the high levels of in-plane conductivity of their bulk counterpart, with the extra benefits of flexibility/ durability and ease of processing. According to the relatively small size of the nanoscale forms of highly conducting "wires" or "sheets", it is somehow easy to solve these materials by fairly straight forward and inexpensive techniques. This ability of nanoscale conductors to be cast into films from solution can cause a model shift in thin film electronics away from high temperature, high vacuum, expensive processes, and towards high volume, high throughput, and solution coating methods. These methods leverage the existing roll-to-roll coating equipment and infrastructure from the ink and paint coating industries. The combination of inexpensive starting materials, high volume and inexpensive roll-to-roll coating techniques, superior film mechanical properties, and suitable electro-optical performance is driving the industry to spur continued research into these nano-materials. One of the first and most accessible applications for these materials is as transparent electrodes. Several emerging nanoscale materials are showing great potential as transparent electrodes. Such as nanoscale forms of carbon such as CNTs and graphene, as well as nanostructured metals, which we take to include metal grids, thin metal films, and metallic nanowires [7].

Metal nanoparticles have been applied to the fabrication of nanocomposites. They have properties such as good electrical properties, strong adsorption ability, high surface reaction activity, small particle size and good surface properties [8].

The usefulness of these materials as transparent electrodes may be resulted largely from their intrinsically high dc conductivity which enables ultrathin, optically transparent films on the order of 1–100 nm thick to have suitable conductance. This fact, coupled with the typically high aspect ratios of these materials and web-like topology, yields films with low material density, adequately low sheet resistance, and superior mechanical flexibility. These material properties, techniques, make these emerging nanomaterials very attractive for use as printed transparent electrodes. An intense electromagnetic field on the surfaces of metals can be generated by the resonant excitation of plasmons in metallic nanostructures, which in turn provide dramatic increases in the detected spectroscopic signals for molecules located in the close vicinity of metal surfaces [9-13].

Electrochemical Sensors

In recent years, nanoscale electronic devices created by using organic and inorganic materials such as single molecule, supramolecules, carbon nanotubes, self-assembled monolayers and metallic clusters and sol–gel composites have attracted much attention for the construction of fast, inexpensive and dimensionally ultimate devices as a bottom-up approach[14].

CNTs are important in the last years due to their unique structural, mechanical, geometric and chemical properties [15]. Their closed topology and tubular structure have made them very attractive materials [16]. CNTs have demonstrated to be extremely useful for the development of new electrode materials. Their electrocatalytic properties have been widely demonstrated in connection with several compounds of clinical, biological and environmental interest. Also, the application of chemically modified electrodes in electroanalysis offers several advantages. They can lower the over- potential, increase the reaction rate and sensitivity and improve selectivity [17, 18].

Researchers continually improve electrochemical based-chip sensors, reducing costs and lowering sample volumes, and the time required to take measurements, attempting to make them more relevant over traditional techniques such as liquid/gas chromatography, HPLC, and mass spectroscopy [19].

Electrochemical methods have the advantages such as being simple, sensitive, and selective for small amounts of sample. Also electrochemical sensors can be fabricated with small dimensions suitable for placement directly into biological samples. Yet, it is still of prime importance to search for new electrodes that do not need any treatment or pretreatment for prevention of electrode fouling [20]. Construction of them with modified electrodes were continues to be an area of great interest and relatively large amount of electrochemical research has been devoted to the development and application of these sensors for the analysis of biologically active compounds [21].

Modification of electrodes with suitable materials facilitates the electrochemistry of the redox biological compounds, which generally results in increased selectivity and sensitivity of the determinations [22]. The ability to variant the size, shape and structure of transition metals is an important goal in the current material synthesis, and there has been increasing interested in the synthesis of nanostructures of transition metal compounds with special shape and structure and due to their potential applications in catalysts and electrocatalysts, sensors and biosensors, photonics and optoelectronics, drug delivery and formulation, biomedical diagnostics, treatment and equipment, and energy producing and accumulating devices [23].

Some examples of different metallic nanostructured electrochemical sensors in various applications are represented here which can be categorized into four branches of metallic, metallic oxide, bimetallic and flower shape nanostructured electrochemical sensors.

Electrochemical sensors modified with metallic nanostructure

Electrochemical sensors modified with Gold nanoparticles

Over the past decade, the use of nanoparticles, specifically colloidal gold nanoparticles (AuNP) in connection with electrochemistry has been gaining interest. Manipulation of both physical and chemical properties allows AuNPs the allocation of a vast amount of applications in a wide variety of fields [24].

Daniel Fiorella et al. have demonstrated the electrochemical detection of Acetylcholinesterase AChE-mediated Au nanostructure formation on gold disposable chips for the first time. Detection involved measuring the Au reduction current signal upon the growth of the Au nanostructures on the electrode surface in the presence or absence of $HAuCl_4$. Acetylcholinesterase, isolated from Electrophorus electrics, is a 280 KDa glycoprotein responsible for the regulation of cholinergic synapses.

This technique is quick, inexpensive, and requires small sample volumes. Since the formation of Au nanostructures did not require any additional immobilization, the sensing method lends itself to be applicable to the detection of Acetylcholinesterase inhibitors for environmental and pharmaceutical analyses [25].

In another study, Li et al. have synthesized a novel magnetic graphene oxide @ gold nanoparticles-molecular imprinted polymers MGO@AuNPs composite with a MIPs outer layer for selective recognition of dibutyl phthalate (DBP) successfully. Owing to the unique mechanical properties and extremely large area of MGO@AuNPs, the resulting MGO@AuNPs-MIPs composite possesses high selectivity compared with other analogues, and good sensitivity toward template molecules [26].

In another study by Arkan et al. a graphen based carbon ion liquid electrode modified with gold nanoparticles fabricated. The advantages of nanoparticles caused large surface area and increased electron transfer abilities. Differential pulse voltammetry and cyclic voltammetry was applied to the determination of celecoxib in real samples [27].

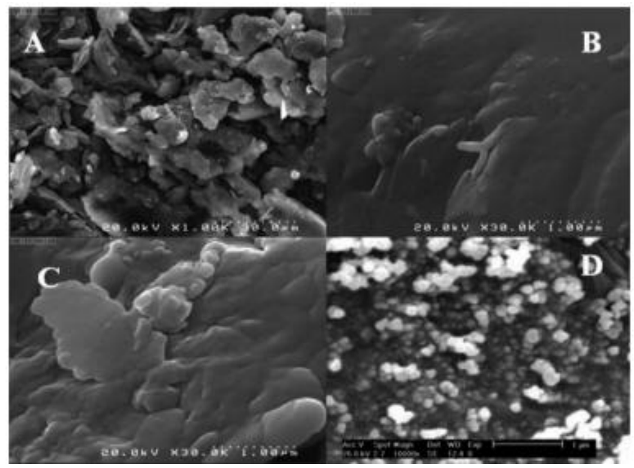

Fig.1. SEM images of (1) CPE, (2) CILE, (3) GR-CILE and (4) GR-CILE/Au NPs.

Electrochemical sensors modified with Silver nanoparticles

Recently, graphene with Ag, Pt and Au nanoparticles have been used in sensor applications [28]. Among these materials, silver nanoparticles (AgNPs) demonstrated excellent catalytic activity in sensor fields. The sensor performance of composites could be affected by the shape, size, and dispersion of metal particles on them [29]. Therefore, the composite matrix plays an important role in gaining high dispersion of AgNPs, as well as its respective size and shape. For example, Yang et al. and the Compton group discussed the chemical and physical methods that have been employed to fabricate AgNPs composites [30].

Other reported methods to produce AgNPs composite including templates, chemical reagents, irradiations, electrode position method [31]. The AgNPs were reduced to MWCNT surface, causing a good dispersion of AgNPs in the AgNPs–MWCNT composite and displayed good performance toward sensing H_2O_2 at high sensitivity levels [32]. The uniform distribution of nanometer-sized silver nanoparticles on graphene-oxide sheets could be achieved using silver ammonia complex as the precursor, instead of silver nitrate which is commonly used [33].

In a study, Lorestani et al. have synthesized silver nanoparticle-carbon nanotube reduced-graphene oxide nanocomposite (AgNPs–MWCNT–rGO) successfully by a simple and environmentally friendly one-step hydrothermal method. The advantage of this method is that it did not require any toxic solvent or chemical to reduce the graphite oxide. Ag nanoparticles that exist on the composite were synthesized from silver ammonia complex instead of silver nitrate were well-dispersed with small and narrow-sized distributions. The AgNPs–MWCNT–rGO composite exhibited excellent sensitivity for electrochemical detection of hydrogen peroxide in a cyclic voltammetry curve. This work provides a low cost, simple preparation, one-step, environmentally benign and green synthetic method of preparing AgNPs–MWCNT–rGO/GCE nanocomposites, which ultimately works as an effective enzymeless electrochemical H_2O_2 sensor [34]. In a pharmaceutical study, based on silver nanoparticles, Arkan et al. have used an electrochemical sensor based on Graphene–Chitosan Composite Film Modified Glassy Carbon Electrode was used to investigate the electro-oxidation behavior of amlodipine besylate in 0.1 M PBS of pH 7.4. As amlodipine besylate is an electroactive compound, which can be easily subjected to oxidation on different working electrodes, it can be investigated by electrochemical methods [35].

The proposed voltammetric sensor possessing high sensitivity, short response time, low cost and high stability for months without any significant divergence was successfully applied to the determination of tablets and, more importantly, to monitor the therapeutic or toxic levels of the drug and to investigate its pharmacokinetics in serum samples and urine samples[20].

In another work, by Arkan et al., An electrochemical sensor based on a silver nanoparticle (AgNP) modified carbon ionic liquid electrode (CILE) was prepared for the determination of ultra-trace levels of levetiracetam (LEV) in human plasma and pharmaceutical tablets. The AgNPs were electrodeposited on the CILE surface using a double pulse potentiostatic technique, which can suitably control the size and morphology of AgNPs electrodeposited on the electrode. The AgNPs deposited on the CILE surface revealed an excellent electrocatalytic activity towards the oxidation of LEV. The possible interference from several common ions and drugs that usually accompany LEV was tested. The method was successfully applied to the determination of LEV content in real samples such as tablets and human plasma samples with good recovery, and the obtained results were checked by HPLC. The proposed sensor is suitable for routine analysis of LEV in plasma samples to monitor the therapeutic or toxic levels of LEV and for drug pharmacokinetic studies [36].

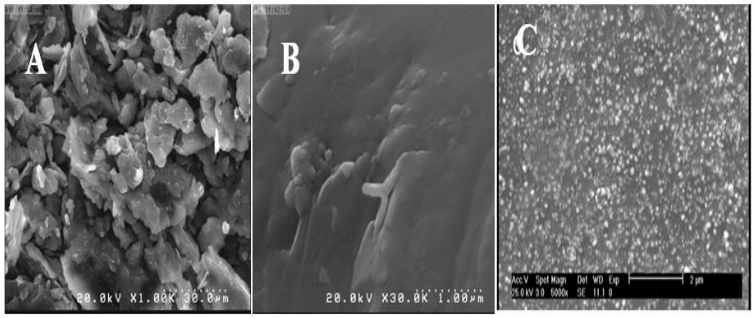

Fig. 2. SEM images of the (A) CPE, (B) CILE and (C) AgNP/CILE.

Electrochemical sensors modified with metallic oxides

In recent decades, resistive gas sensors based on metal oxide semiconductor materials have attracted special attention due to their good reproducibility, compact size, ease of use, real-time detection and low cost. These characteristics have led to their wide spread applications for monitoring poisonous and hazardous gases in air quality control, environmental protection, healthcare and security in domestic and industrial areas[37]. 10 More specifically, metal oxide semiconductor sensors such as SnO_2, TiO_2 and ZnO are used to detect both reducing and oxidizing gases. These sensors exhibit a high sensitivity. However, these sensors are not selective to a particular gas in a gas mixture. Moreover, the operating temperatures for them are quite high and needs to be lowered by some means [38].

Zno nanostructure

ZnO nanostructures, due to their excellent electron transfer rate, are able to evoke the hidden electrochemical ability of biomolecules, and facilitate their direct electrochemistry according to their excellent electron transfer rate [39]. Based on Previous studies, depending on their structural characteristics, rare earth (RE) elements could be introduced into metal oxide structures depending on their structural characteristics. This may lead to dominating their drawbacks such as low sensitivity [40].

High surface to volume ratio, non-toxic, low cost, chemical stability, eco-friendly and high electron communication features than their bulk counterpart are the main advantages of the synthesized ZnO nanostructures [41]. For instance in gas sensing, ZnO is a proper candidate for potential applications due to its thermal/chemical stability, good oxidation resistance, great bio-compatibility and high conductivity [42, 43]. Zinc oxide is known as an n-type semiconductor with a wide band gap energy of 3.37 eV [44] which can be used at typical working temperatures of about 200–450°C [45]. Zinc oxide also has interesting properties such as the capability of low temperature growth with many different kinds of morphologies including wires, rods, tubes and flower shape at nanoscale [46, 47]. In the gas sensor, especially in ZnO-based sensors, the morphology of the sensing materials has an important role on their gas sensing properties [48]. The method of preparation and the structure of directing agents used in the process of synthesis have significant impact on the morphology of nanostructures [49].

There are lots of ZnO nanostructures synthesis methods, such as vapor phase transport, magnetron sputtering, laser ablation, wet chemical methods including simple solution and hydrothermal and/or microwave treatment ,depending upon their application. Microwave-assisted synthesis is considered as a simple and fast technique which has been employed for many years for a variety of applications. The sensitivity and/or selectivity of the sensors such as optical, electronic and magnetic properties of ZnO can significantly be affected by additives [50].

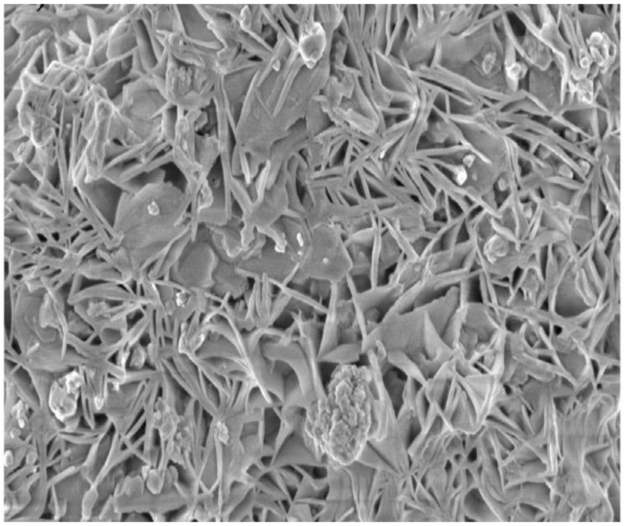

Fig. 3. SEM images of the ZnO nanostructure **[41]**.

TiO_2 nanostructures

TiO_2 nanostructures also can be used on electrochemical sensors for medical and pharmaceutical applications. For example, Durrant and co-workers immobilized a range of proteins into nanoporous TiO_2 film electrodes and successfully used this strategy to develop electrochemical and optical biosensors [51]. Luo and co-workers used nanocrystalline TiO_2 films on electrodes to entrap heme proteins such as cytochrome c, myoglobin, and hemoglobin, and observed the direct electrochemistry of these proteins [52].
In a pharmaceutical paper by Ardakani et al., the use of a carbon paste electrode modified by meso-tetrakis (3-methylphenyl) cobalt porphyrin and TiO_2 nanoparticles for the determination of levodopa in the presence of carbidopa was described. Differential pulse voltammetry investigations showed effective electrocatalytic activity of the modified electrode in lowering the anodic overpotential for the oxidation of levodopa and complete resolution of its anodic wave from carbidopa [53].

Leaf template Hierarchical porous cobalt oxide nanostructures

The leaves can be used easily for scale-up production of biotemplated materials as they are cheap, reproducible and abundant biomasses and because of their 3D architecture of the highly interconnected, nano-layered thylakoid membranes at the nanoscale [54], and the porous frame work of veins at the micro meter, they exhibit excellent light-harvesting efficiency [55].
In a work by Han et al. a novel three-dimensional (3D) hierarchical porous cobalt oxide (Co_3O_4) architecture was first synthesized through a simple, cost-effective and environmentally friendly leaf-templated strategy. Cobalt oxide (Co_3O_4), an important transition metal oxide, was selected as model for the application of leaf-templated materials in to electro catalysis and biosensing. The synthesis is simple, cheap, and environmentally friendly. The prepared Co_3O_4 inherited the 3D hierarchical porous and interconnected structure from leaves (Fig. 4). Further, it was applied to the direct electrochemical non-enzymatic sensor for hydrogen peroxide (H_2O_2) and glucose, which was cost-effective, rapid, sensitive, selective, reliable and stable. The prepared sensor was simple in preparation, rapid in response, and high sensitive toward glucose and H_2O_2. Meanwhile, it also exhibited good anti-interference performance and application potential for detection of blood glucose [56].

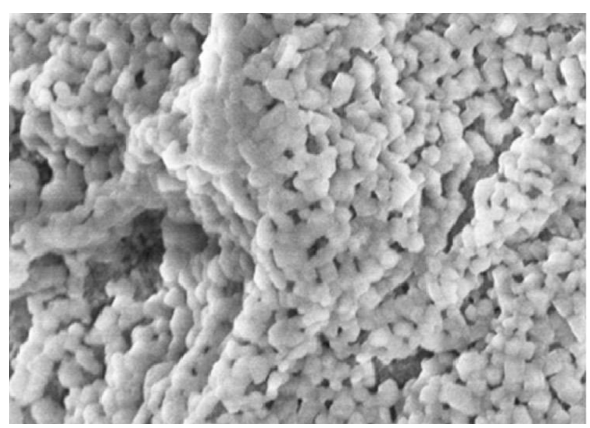

Fig.4. SEM images of leaf template Co3O4.

Bimetallic nanostructured electrochemical sensors

Since bimetallic nanoparticles lead to many interesting size-dependent electrical, chemical, and optical properties, they attracted a wide interest. Bimetallic nanoparticles are of wide interest since they lead to many interesting size-dependent electrical, chemical, and optical properties. These hybrid nanomaterials displayed superior electrochemical performance in comparison with that of alone nanomaterial.
Recently, zero-valent iron (ZVI, Fe^0) is commonly utilized in bio technological and biomedical industry, due to its nontoxic, paramagnetic behavior. According to the literature, the reductive activity of ZVI nanoparticles get enhanced in combination with some other metals [57]. A number of combinations have been reported so far to produce bimetallic ZVI systems like Pd/Fe [57], Cu/Fe [58], Ni/Fe [59], and Ag/Fe [60]. Among these alloys, Fe/ Pd nanoparticle modification was preferred due to their biocompatibility, high electrical conductivity and inexpensiveness [57].

Bimetallic Fe/Pd nanoparticles

In a work by Roy et al., a novel electrochemical-sensing platform based on imprinted bimetallic Fe/Pd (BI-Fe/Pd) nanoparticle has been fabricated for point-of-care diagnostics of oxidative stress marker (3-nitrotyrosine) in biological fluids. In this work, BI-Fe/Pd nanoparticles are used as a platform on which 3-nitrotyrosine imprinted cavities are created using acrylamide as monomer and N-N0-methylene bisacrylamide as cross-linker. Cyclic, differential pulse and square wave voltammetry in stripping mode are the methods which can be used for investigation of the obtained imprinted sensor ' performance. The performance of the obtained imprinted sensor is investigated by cyclic, differential pulse, and square wave voltammetry in stripping mode. The imprinted sensor exhibits high recognition ability and affinity for 3-nitrotyrosine in comparison with the non-imprinted one. In addition, the proposed sensor is capable of measuring 3-nitrotyrosine in aqueous as well as in human blood serum, plasma, and urine samples. Imprinted BI-Fe/Pd nanoparticle modified sensor shows high affinity and no interference from blood or urine components. They can be considered as attractive alternative to the enzyme-linked immunosorbent assay (ELISA) technique due to their high affinity and the lack of requirement for cold chain logistics [61].

Bimetallic Pt/Pd nanoparticles

Due to the unique catalytic activity and chemical selectivity of the bimetallic nanoparticles, the Pt/Pd nanoparticles-doped grapheme hybrid nanomaterials were found to play the dual roles of catalyzing cholesterol redox reactions and also assisting direct electron transfer from the redox enzyme to the electrode surface [62].
In a study, Cao et al. tried to fabricate platinum (Pt) and palladium (Pd) nanoparticles-doped graphene hybrid nanomaterials for the preparation of the electrochemical choles terol biosensor. Use of the Pt/Pd–CS–GS hybrid nanocomposites accelerated direct electron transfer from the redox enzyme to the electrode surface, greatly improved the electrochemical properties of the biosensor interface. Moreover, the sensitivity of the biosensor could be enhanced greatly. Moreover, it is possible to enhance the sensitivity of the biosensor greatly. The biosensor also demonstrated excellent stability and resistance to interference [63].

Bimetallic Pd/Cu nanoparticle

As mentioned above, Bimetallic nanoparticles can be used in electrochemical biosensors.For example, the outstanding catalytic ability of the Pd/Cu/GE hybrid is to quantitatively detect glucose in a wide range with a low detection limit without common interference from dopamine (DA), ascorbic acid (AA), uric acid (UA), acetamidophenol (AP) and monosaccharide (fructose). The PdCu/GE hydrogel are able to be used as non-enzymatic amperometric glucose sensors because of their easy fabrication procedure, fast response, high catalytic activity and good specificity in the presence of common interference such as dopamine, ascorbic acid, uric acid, acetamidophenol and some monosaccharides favor potential application [64].

Flower-shape nanostructures

Flower-shape nanostructures have been synthesized in recent years via different methods of oxidation, reduction, decomposition and electrode position due to interesting structure, shape and proper- ties and have potential applications in electrochemical, electrical, optical and magnetic devices .These applications are due to low density, large active surface area, and surface permeability of these nanostructures[65].

Nickel oxide flower-shape nanostructures

The special size and shape of nickel oxide nanostructures lead to its unique physical and chemical properties. Nanoflakes and nanoplatelet [66], hollow spheres, nanoparticles [67], nano ribbons [68] and nano flowers [69] of nickel oxide have been synthesized up to now.

The synthesis of nickel oxide has attracted great scientific and technological interests among various metal oxides because of its useful applications in different electrochemical devices, such as electrocatalysts sensors and biosensors. The main known characteristics of this metal oxide includes: conductivity (as a p-type semiconductor with a wide band-gap energy range),high specific energy, low cost, chemical and electrochemical stabilities, outstanding durability, near-reversible redox properties ,large span optical density and electrochromic properties, and high resistance to anodic corrosion of this compound [70].

Zinc oxide flower-shape nanostructures

There are many kinds of morphologies for ZnO but among them, nanorods and flower-likes have been used more in many sensors [48]. Method of preparation and the structure of directing agents used in the course of synthesis,have significant role on the morphology of nanostructures [49]. Various methods are defined to synthesize ZnO nanostructures according to their application, such as vapor-phase transport [71], magnetron sputtering [72], laser ablation [73], wet chemical methods including simple solution and hydrothermal and/or microwave treatmentcourse of synthesis [49]. Depending upon their application, ZnO nanostructures are synthesized using various of methods such as vapor-phase transport[71], magnetron sputtering[72], laser ablation[73], wet chemical methods including simple solution and hydrothermal and/or microwave treatment[74]. Microwave-assisted synthesis is considered as a simple and fast technique which has been utilized for many years for a variety of applications [75]. Sensitivity and/or selectivity of the sensors and also optical, electronic, and magnetic properties of them can significantly be influenced by additives [50]. In Fig.1 SEM images of Zinc oxide flower-shape nanostructures is shown.

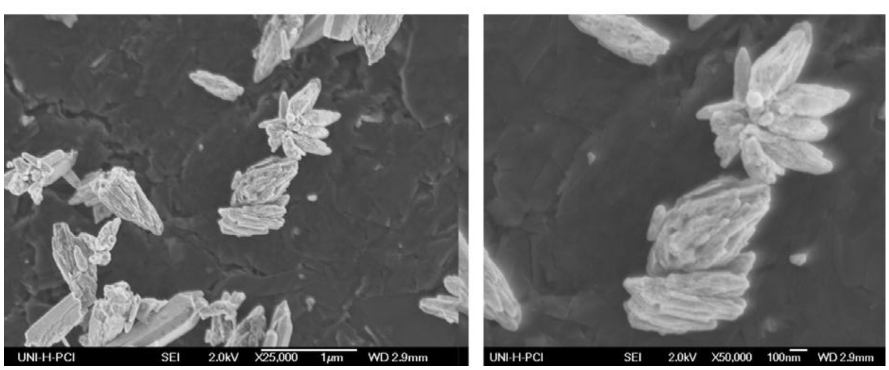

Fig.5. SEM images of flower shape ZnO nanoparticles [77].

Screen-printed electrodes (SPEs)

One of the other acknowledged effective devices for the development of disposable sensors are Screen-printed electrodes (SPEs) which can be used in electroanalysis. Being highly-versatile, easy to use, cost-effective analytical tools and also suitable to miniaturization are the advantages that are counted for these devices. In order to improve their electrochemical performance, SPEs have been coated with Au, Bi and Hg films [78, 79].

More complicated metallic nanostructured sensored

As mentioned previously, Some carbon nanomaterials have been considered as ideal supports for catalyst and enzyme, including carbon nanotubes, nano-diamond,and grapheme [80, 81]. Among them, graphene, has captured considerable attention of scientists as an interesting two-dimensional (2D)material, due to its unique physical and chemical properties, such as extremely high electric and thermal conductivity [82], high strength and large surface area [83, 84].In a work by Liu Z et al.a new nanocomposite was successfully synthesized by chemical deposition of nickel nanoparticles (NiNPs) on polyvinylpyrrolidone (PVP) stabilized graphene nanosheets (GNs) with chitosan (CS) as the protective coating. It can act as an enhanced electrochemical material for the determination of glucose [85].

Conclusion

In this Review, we have discussed recent reports on the electrochemical sensors modified with metallic nanostructures. Much progress in electrochemistry has been made in controlling the shape and size of metallic nanostructure, particularly during the colloidal synthesis of NPs. Many different shapes can be made reliably and these shape-tailored NPs typically show electrocatalytic responses reminiscent of their dominant exposed surface facets in single-crystal measurements. However, most shape-controlled NPs are still very large compared to commercial catalyst NPs and, therefore, have suboptimal mass activity.

Additionally, the morphological stability has not been demonstrated sufficiently. For the possible application of such promising particles, it will be very interesting to see if the mass activity can be increased by decreasing the NP size, while retaining high NP stability.

When NPs are used as electrocatalysis in electrochemitry, it is of paramount importance that best practices are followed with respect to immobilization, cleaning, and characterization of the NPs on support electrodes. If these aspects are not properly considered, results obtained in different laboratories and experiments are difficult to compare. Additionally, this Review has highlighted that when real catalysts are studied in model environments it is essential to control mass transport and ohmic losses to understand the intrinsic behavior. Mass transport is also a very important consideration when studying model NP ensembles in model environments, particularly for reactions that have soluble intermediates that may re adsorb on adjacent NPs, depending on the prevailing mass-transport rate and the inter particle separation. A major aspect of this Review has been to highlight emerging innovative techniques that hold considerable promise for a breakthrough in understanding the fundamentals of metallic nanostructures electrocatalysis through the study of individual nanoparticles. This type of approach is particularly effective when the activity and structure can be determined and correlated at an individual NP. The main technical challenges are the spatial isolation of a single NP and the measurement of the (often) very low electrochemical current generated at individual NPs. Three techniques were distinguished and discussed. First is the immobilization of individual particles on inert and ultrasmall probes, such as by electrodeposition. The use of this approach to study the ORR revealed how NP size influenced the electrocatalytic activity and the outcome (products) of electrochemical processes.

Conflict of interest

Authors certify that no actual or potential conflict of interest in relation to this article exists.

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