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Review

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Application of nanoparticles in electroanalysis

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ABSTRACT

The use of nanoparticles in electroanalysis is an area of great research interest, which is rapidly growing. There are enormous amount of work carried out on the synthesis, characterization and applications of nanoparticles. This review article summarizes the recent advancement of nanoparticle research in electroanalysis.

KEYWORDS

Nanoparticle;
Nanomaterials;
Nanotechnology;
Electroanalysis;
Surface to volume ratio.

INTRODUCTION

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. Nanoparticles are sized between 1 to 100 nm, though; the size limitation can be restricted to two-dimensions. Nanoparticles may exhibit size-related intensive properties that differ significantly from bulk materials. TABLE 1 shows the size range of some common nanoparticles. As shown in the table, the sizes of the nanoparticles are comparable to that of biological molecules such as enzymes, receptors and antibodies. As a result, these nanoparticles can offer unprecedented interactions with biomolecules both on the surface and inside the cells. Nanoparticles made of semiconductors like CdS, CdSe may be labeled as quantum dots if they are small enough (< 10 nm) to provide the quantization of electronic energy levels. Such quantum dots are used as drug carriers and imaging agents. Semi-solid nanoparticles like liposomes are currently used clinically as delivery systems for anticancer drugs and vaccines.

A number of physical properties (mechanical, optical, electrical etc.) changed significantly, as the dimension of the system decreases. A bulk material should have constant physical properties regardless of its size. Size dependent properties such as quantum confinement in semiconductor nanoparticles, surface plasmon resonance in some metal nanoparticles are observed in nanomaterials. The nanoparticles such as quantum dots exhibit quantum-mechanical behaviour. They are sometimes called artificial atoms due to the similar behaviour of free electrons in them. These free electrons can only occupy certain permitted energy states. A nanoparticle with dimensions below the critical wavelength of light renders them transparent. Nanoparticles have very high surface area to volume ratio. The large surface area to volume ratio imparts excellent catalytic property to gold nanoparticles. The large surface area of nanoparticles leads to strong interaction between the intermixed materials in the composites to provide special properties such as increased material strength/ increased heat resistant. Moreover, nanoparticles have been found to impart some extra properties to various day to day products. Nano zinc oxide (ZnO) has superior UV blocking properties compared to bulk matter. They are used in sunscreen lotions. Clay (silica) nanoparticles incorporated into polymer matrices enhance re-inforcement leading to stronger plastics, verified by a higher glass transition temperature and other mechanical property tests.

Nanoparticles of metals, semiconductors and inorganic compounds (e.g., oxides, sulphides, etc.) are of a few nanometers (1-50 nm) in size containing a finite number of atoms and comparable to large biomolecules like enzymes and antibodies. They are mostly obtained as colloidal sols. Michael Faraday was the first to synthesize a gold hydrosol in the mid-19th century[1]. In 1951, Turkevich and co-workers had carried out the synthesis and characterization of water soluble gold colloids of 18 nm size by electron microscope[2]. In early 1990's Brust and Schiffrin[3] reported the synthesis of alkanethiolate-protected gold nanoparticles, which are also known as monolayer-protected clusters (MPCs). They are different from metal colloids because they can be repeatedly dried and isolated from common organic solvents without decomposition and aggregation. Thus, nanoparticles can offer a method whereby a surface can be multifunctionalized to create a broad spectrum of functionality. MPCs are synthesized using a bottom-up approach, suggesting that a wide variety of nanomaterials are possible from a small number of building blocks[4]. Nanoparticles are created with a variety of core types and capping ligands to create water or organic solvents soluble products with desired functions. The most well-studied nanoparticles include semiconductor quantum dots, carbon nanotubes, paramagnetic nanoparticles, liposomes, gold nanoparticles and many others[5,6].

The unique properties of nanoparticles such as enhanced mass transport, high surface area, high surface to volume ratio, excellent catalytic property and improved signal to noise ratio can provide several advantages in electroanalysis. Thus, nanoparticles can be utilized for electroanalytical applications.

Enhanced mass transport of nanoelectrodes facilitates the study of fast electrochemical processes. Crystal planes are exposed at the nanoscale to provide improved current response and catalytic property.

The electroanalytical applications of such nanoparticles have been found to be quite extensive. The aim of this paper is to provide updated overview of applications of nanoparticles in electroanalysis. Due to space limitations, a complete review of all recent work on this important subject is not possible. However, we only summarize a few representative examples, including our own work. Fabrication of nanoparticle-based devices is cost-effective compared to conventional macroelectrode based devices. Thus, there is a great deal of scope for further study in this area of electrochemistry.

DISCUSSION

In this review, we have discussed the synthesis and practical electroanalytical applications of silver, gold, palladium and platinum nanoparticles.

Silver nanoparticles

Silver (Ag) is the most common materials used as electrode. It has the highest electrical conductivity of all metals and is highly stable. It can catalyze many reactions including the decomposition of hydrogen peroxide (H_2O_2). Ag nanoparticles can be synthesized by various methods as given below.

Reduction of a silver salt in the presence of a stabilizing agent is the most common method to synthesize colloidal Ag nanoparticles. Stabilizing agents like citrate, oleate, humic acid and cetyl trimethylammonium bromide (CTAB) are commonly used[7-9]. Recently, α-cyclodextrin has been used as stabilizing agent to produce Ag nanoparticles in water[10]. The common reducing agents are ascorbic acid, sodium borohydride and glucose. The size and the shape of the nanoparticles can be controlled by varying different parameters. A mixture of ethylene glycol (EG) and polyvinylpyrolidone (PVP) and a suitable reducing agent can be used to produce cubic nanoparticles[11]. Nanoparticles of various morphologies have been synthesized, including prisms, rods, wires, plates and belts. Microwave heating and biomolecules can be employed to prepare Ag nanoparticles[12]. Stabilizing agents such as starch and basic amino acids such as L-lysine and L-arginine as reducing agents have been employed to synthesize Ag nanoparticles. Synthesis by a reverse microemulsion system has also been employed[13].

The biocompatibility of certain colloidal nanoparticles makes them ideal to study the electron transfer processes of biomolecules. Oleate stabilized Ag nanoparticles of average diameter 15 nm have been applied in the analysis of cytochrome c[14]. The nanoparticle can enhance the electron transfer process between cytochrome c and the electrode as compared with bulk Ag. DNA immobilized Ag nanoparticles have been produced by a modified version of the famous Turkevich method. This method involves an Ag salt ($AgNO_3$) and sodium citrate as reducing agent with mild heating. Charged citrate ions adsorb onto the nanoparticle surface to prevent their aggregation, and thus, can stabilize. Predominantly spherical nanoparticles of average diameter 66 nm were synthesize and applied for the electrochemical sensing of Ag-tag-labelled DNA, immobilized on a pencil graphite electrode[15].

Ag nanoparticles can also be synthesize by electrochemical methods such as electrochemical deposition, typically by potentiometric techniques, such as pulsed or constant potential application. Dominguez-Renedo et al.[16] have determined Cr (VI) by using Ag nanoparticle screen-printed electrodes. Wu et al.[17] have synthesized Ag-DNA hybrid nanoparticles by template electrodeposition method, where DNA molecule can act as a template. DNA molecules can prevent the aggregation of Ag nanoparticles with enhancement of catalytic activity for the reduction of H_2O_2 and glucose. Casello and Contursi[18] have used Ag nanoparticles modified glassy carbon (GC) electrode to study the electroreduction of nitrophenolic compounds. Biocatalytic deposition of Ag nanoparticles has been utilized in electrochemical immunoassays to provide an ultrasensitive, low limit of detection method for the determination of immunoglobulin G (IgG)[19]. Yang et al.[20] have studied the electroanalysis of H_2O_2 using composite films of nanoscale Ag on multiwalled carbon nanotubes. Similarly, Ag nanoparticles can be electroplated onto carbon nanotube to detect DNA hybridization process[21]. Oyama and his group had been carried out a lot of experiments on the attached Ag nanoparticles onto indium tin oxide (ITO) surfaces[22]. They used the Ag nanoparticles modified ITO electrode to study various electron transfer processes.

Gold nanoparticles

Gold (Au) nanoparticles are very useful as they can replace bulk gold electrode in various electroanalytical application due to the biocompatibility as well as excellent catalytic property of Au nanoparticles. Recent reviews focus the Au-nanoparticle based biosensors. Au nanoparticles can be synthesized both by chemical as well as electrochemical methods.

Brust and Schiffrin[3] reported the synthesis of alkanethiolate-protected gold nanoparticles, which are also known as monolayer-protected clusters (MPCs). Thiol-capped MPCs have received more attention because of their ease of creation, water and air stability, electrochemical and optical properties and their ability to be surface-functionalized by the addition of biologically relevant ligands. These MPCs find potential applications in sensors and other devices. They have intense colors due to surface plasmon resonance phenomenon and their energy levels are quantized due to small size. Gold MPCs can range in size from 1 to 10 nm, containing approximately 55-1000 gold atoms with molecular weights between 10 and 200 kDa.

Inspite of the considerable progress in synthesizing monodispersed thiol-capped MPCs, there have been only one report on their electrochemical synthesis in literature[23]. Lakshminarayanan et al.[23] have synthesized thiol-monolayer protected gold nanoparticles by the process of electrochemical dissolution of gold in an ethanol-water mixture. The major advantage of the electrochemical method over traditional Brust method, is the synthesis of MPCs in the absence of a phase-transfer catalyst and the in-situ formation of a controlled number of nanoparticles stabilized by thiol monolayers. The ability of the Au nanoparticles to provide stable environment to immobilize biomolecules has led to the development of various biosensors such as enzyme biosensors, DNA sensors and immunosensors. Enzyme-based electrodes can be fabricated by immobilizing enzymes such as glucose oxidase, horseradish peroxidase and tyrosinase on colloidal Au nanoparticles. Electropolymerization techniques are also employed to fabricate immobilization matrices for the nanoparticles and appropriate biomolecules. Common polymers like polypyrrole, polyaniline and chitosan are used to immobilze Au nanoparticles. Jena and Raj[24] adopted a sol-gel derived thiol-functionalized silicate network on a Au macroelectrode to facilitate the self-assembly of au nanoseeds. They used this system for the

TABLE 1 : Nanoparticle size range

Nanoparticle	Size in nm
Fullerenes	1
CdSe Quantum dots	8
Dendrimers	10
DNA (width)	2
Proteins	5-50
Viruses	75-100

amperometric detection of toxic Cr (VI).

The electrodeposition of Au nanoparticles has been employed to immobilize various enzymes for the fabrication of Au-nanoparticle based biosensors. A tyrosinase biosensor was fabricated the electrodeposition of Au nanoparticles on GC electrode followed by the attachment of appropriate enzyme by cross-linking with glutaraldehyde. This biosensor was used to detect phenolic compounds like phenol, catechol and caffeic acid[25].

Similarly, an amperometric biosensor for hydoxanthine was fabricated by the electrodeposition of Au nanoparticles on a carbon paste electrode[26]. Xanthine oxidase was immobilized by cross-linking with glutaraldehyde and bovine serum albumin, which allows a detection potential of 0.0V to be employed instead of typical detection potential of 600 mV. Thus, the interference by ascorbic acid during the detection can be minimized. This method can be applied to the determination of hypoxanthine in foodstuffs.

Compton and his group[27] fabricated a system by depositing mesoporous gold on the surface of boron-doped diamond (BDD) electrode to detect arsenic (III) in phosphate-buffered media.

Zhang et al.[28] studied the electrocatalytic activity of three-dimensional monolayer of 3-mercaptopropionic acid assembled on Au nanoparticle arrays towards biomolecules such as NADH, ascrobic acid (AA), uric acid (UA) and dopamine.

Zhang et al.[29-31] also studied attached Au nanoparticles on ITO surfaces through an electrochemical method. The Au nanoparticle-ITO electrodes can provide interesting electrochemical and electrocatalytic properties towards various heterogeneous electron transfer reactions. These electrodes were used for the electrooxidation of UA, AA, dopamine, norepinephrine and epinephrine[30].These electrodes can provide biocompatible matrix for the immobilization of hemoglobin (Hb). Similarly, a mediator free H_2O_2 sensor was developed by immobilizing myoglobin onto the surfaces of Au nanoparticle/ITO matrix[32].

Oyama and his group in collaboration with Goyal's group in India used these Au nanoparticle modified ITO electrode surfaces for the electrochemical analysis of various biomolecules such as UA, paracetamol, atenolol, using a differential pulse voltammetric technique[33-35].

Palladium nanoparticles

Palladium (Pd) is a transition metal, which can be used as a potential device for hydrogen storage due to its ability to adsorb hydrogen. Pd can also be used as multilayer ceramic capacitors, CO detection, catalysis and organic synthesis. Pd can behave as a catalyst in the famous Suzuki and Heck reaction.

There are a few examples of colloidal synthesis of Pd nanoparticles. Guy et al.[36] and Burton et al.[37] had carried out the synthesis of colloidal Pd nanoparticles. Pd nanoparticles integrated with a multi-walled carbon nanotube network fabricated on the surface of a GC electrode exhibits biocompatibility and can be used as a highly sensitive DNA hybridization biosensor[38].

Xia's group succeeded in the synthesis of monodisperse Pd nanocubes in EG/PVP organic system, through a seed etching process by using $FeCl_3$ as etchant where the cube dimension was found to be dependent on the concentration of this etchant[39]. Such kind of cubic nanostructures can be employed as a template for the formation of nanoboxes and nanocages used as SERS substrates[40]. Most recently, Rafailovich and co-workers synthesized the rectangular Pd nanoparticles, including nanocubes and nanorods, under the assistance of CTAB and trisodium citrate[41]. Berhault et al. investigated the factors influencing kinetic or thermodynamic controlled Pd nanocrystals synthesis on the basis of seed-mediated growth with CTAB[42].

Tian and his group[43] took a simple approach to synthesize nearly monodisperse Pd nanocubes and nanodendrites in water at room temperature with moderate yield (60-70%). The morphology can be tuned by the addition of some different concentration of foreign halides. Moreover, the synthesized nanocubes and nanodendrites are single crystal with face-centered cubic (fcc) structure and different sizes can be obtained. They have also utilized these Pd nanocubes and nanodendrites as possible SERS substrates.

Pd nanoparticles have been electrochemically deposited on a BDD electrode from a solution of $PdCl_2$ in 1 M H_2SO_4 by potential sweep technique and fixed potential deposition[44]. Atomic force microscopic analysis was used to image the size of the Pd deposits and an average nanoparticle diameter of 100 nm was reported.

Single-walled carbon nanotubes have been used as a substrate for electrodeposited Pd nanoparticles for the fabrication of a hydrogen gas sensor by Mubeen et al.[45] with improved sensitivity and limit of detection over other reported findings.

Platinum nanoparticles

Platinum (Pt) metal has properties similar to those of palladium (Pd), ruthenium (Ru), osmium (Os), rhodium (Rh) and iridium (Ir). Pt can be used as industrial catalysts and can be found in the catalytic converters of vehicles. It is more expensive than both Au and Ag. Pt wires are often used in electrochemistry as electrodes due to their stability and conductivity. Pt nanoparticles are synthesized in a similar way to Ag and Au nanoparticles. Colloidal Pt nanoparticles are synthesized by the reduction of H_2PtCl_6 in the presence of a citrate capping agent. The colloidal Pt nanoparticles can then be functionalized with nucleic acids. These materials were used as labels for the amplified biorecognition of DNA hybridization, aptamer/protein recognition events and tyrosinase activity. The electrocatalyzed H_2O_2 reduction at Pt nanoparticle-labels enabled the amplified analysis of tyrosinase via the oxidation of tyrosine methyl ester functionalized Pt nanoparticles, in association with a boronic acid functionalized gold electrode[46].

Pt nanoparticles can be deposited on an electrode substrate by electrochemical deposition from an aqueous solution of Pt salts. Pt macroelectrodes have been shown to be useful in the detection of highly toxix arsenic, exhibiting low limit of detection with anodic stripping voltammetry. However, metals such as copper, lead, zinc and iron can interfere, as these metals get co-deposited during stripping voltammetry alongside arsenic. This problem can be solved as the catalytic oxidation of As (III) to As (IV) by Pt is not affected by the presence of copper. The use of nanoparticles in particular can also help to improve the selectivity of the system. Due to the resulting potential shift, the analytical peaks can be distinguished from common interference.

Pt is known to be an excellent catalyst for methanol oxidation. It can be also applied at the nanoscale, which has implications for the direct methanol fuel cell. However, it is important to overcome the associated problems of methanol fuel cells such as catalyst poisoning and slow electrode kinetics. Pt nanoparticles were deposited on a multi-walled carbon nanotube paste electrode at a constant potential (1 mM K_2PtCl_4 + 0.1 M K_2SO_4) and the resulting electrode was implemented as working electrode in methanol oxidation.

Nanoparticle-based electrochemical DNA sensors

Nanoparticle offers versatile ways for interfacing DNA hybridization recognition events with electrochemical signal transduction process. By successfully addressing the issues of high sensitivity, selectivity and multi-target detection capabilities, this nanoparticle based electrochemical DNA biosensors will have a major impact upon clinical assays, environmental monitoring and food safety.

Recent studies have focused at developing nanoparticle based electrical DNA biosensors for gene detection. This particle- based protocol for electrochemical detection of DNA is based on the use of colloidal gold tags, semiconductor quantum dots or magnetic beads. These nanoparticles offer a versatile way for interfacing DNA recognition with electrochemical signal transduction and amplification of resulting electrical signal. Most of these protocols are commonly dependent on a highly sensitive electrochemical stripping measurement of the metal tracers. Stripping Voltammetry is a powerful electroanalytical technique for the detection of trace amount of metals in the range of ppb (parts per billion), its high sensitivity is attributed to the pre-concentration step, during which the target metals are accumulated/deposited on to the working electrode. Compared to the pulse-voltammetric method, stripping voltammetry can exhibit a lower detection limit of three or four orders of magnitude for detecting DNA hybridization events. Such ultra-sensitive electrical detection of metal tags can be utilized to provide a versatile and elegant tool for the detection of

DNA.

Several groups have developed nanoparticle-based electrochemical DNA hybridization assays[47-49]. Such protocols are based on capturing the gold[47] or silver[49] nanoparticles to the hybridized targets, followed by acid dissolution and anodic stripping voltammetric measurement of the metal tracer. The target immobilization has been accomplished in connection to streptavidin-coated magnetic beads[47], through the use of chitosan or polypyrrole surface layers[49]. Picomolar and sub-nanomolar level of the DNA target have thus been detected.

Wang et al.[50] described an electrochemical protocol to detect DNA hybridization based on the fabrication of the metal marker along the DNA backbone. This new protocol relies on DNA-template induced fabrication of conducting nanowires as a mode of capturing the metal tags. Such approach was applied to grow Ag, Pd or Pt clusters on DNA templates.

Mirkin and his co-workers have developed an array based electrical detection utilizing oligonucleotide functionalized gold nanoparticles and closely-spaced interdigitated microelectrodes[51]. The oligonucleotide probe was immobilized in the gap between two microelectrodes. The DNA hybridization event thus localized gold nanoparticle in the electrode gap, and along with subsequent Ag deposition leads to measurable conductivity signals. This technique can offer high sensitivity with 0.5 picomolar detection limit.

Magnetic beads have also been used for triggering the electron-transfer reactions of DNA. Willner and co-workers have carried out bio-electrochemical processes such as DNA oxidation using external magnetic field[52].

Due to their tunable electronic properties, semiconductor quantum dots such as CdS, CdSe nanoparticles have generated a lot of interest for optical DNA detection. Willner et al. reported a photoelectrochemical transduction of DNA sensing events in connection to DNA cross-linked CdS nanoparticle arrays[53]. Wang et al.[54] reported on the detection of DNA hybridization in connection to CdS nanoparticle tracers and stripping voltammetric measurements of Cd. A nanoparticle-promoted Cd precipitation was used to enlarge the nanoparticle tag and amplify the stripping DNA hybridization signal. This method have shown low detection limit of 100 femtomolar. Such protocol was also extended to ZnS or PbS nanocrystals.

It is possible to further enhance the sensitivity by employing multiple tags per binding events. This can be accomplished in connection to polymeric microbeads carrying multiple tracers externally or internally. Combining the additional amplification units and processes, such bead-based multi-amplification protocols meet the high sensitivity demands of electrochemical DNA biosensors.

There are some excellent review articles based on the use of metal nanoparticles in electroanalysis[55-58]. Most of these reviews dealt with the utilization of metal nanoparticles to modified electrode surfaces, which can be further effective in electrochemical analysis. In a recent review article by Oyama[59], he mainly focused the recent development of nanoarchitectures or nanostructures based on metal nanoparticle modified electrodes for electroanalysis. Our review article focused on the synthesis and electrochemical applications of metal nanoparticles and nanoparticle modified electrodes.

Summary

This review article illustrates an updated version of the recent development on the applications of nanoparticles in electroanalysis. From consideration of the work discussed in this review, it can be concluded that nanoparticles play an important role in the field of electroanalysis. The unique properties of nanoparticles can be exploited to enhance the response of various electroanalytical techniques. At present, most of the work is empirical in nature. It is expected that systematic voltammetric and structural characterization will provide a more systematic basis to future work.

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