



MINI REVIEW

Metallic Nanoparticles for Modification of Electrodes for Heavy Metals Detection

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Metallic nanoparticles are an active area of research showing great potential to increase competitiveness of electrochemical sensors. The high active surface area, higher catalytic properties possess by these nanoparticles makes it an inquisitive area of research for environmental analysis. These unique properties increase the sensitivity and selectivity when applied on electrochemical sensors making it possible to achieve the lowest detection limits. This paper provides an overview of the various metal nanoparticles.

Keywords: Metallic nanoparticles, Modified electrode.

INTRODUCTION

Nanoparticles are normally found in the range of 1-100 nm in size, nanoparticles possess unique chemical, physical and electronic properties that are different from those of the bulk materials¹⁻³ and thus can be used to construct novel and improved sensing devices, in particular, electrochemical sensors and biosensors⁴⁻⁹.

In present years, the study of nanoparticle materials is gaining more attention particularly with respect to metallic nanoparticles. Subsequently, it has become an active area of research in environmental analysis, owing to their unique properties such as high active surface area, increased mass transport, lower detection limit and better signal-to-noise ratio. Nanoparticles are mostly applied on electrode surface by chemical synthesis using different methods that include; reduction¹⁰, UV light or electron-beam irradiation¹¹ and electrochemical techniques¹²⁻¹⁴, where the latter provides an easy and rapid alternative for the preparation of metallic nanoparticle electrodes in short period of time. Table-1 provides a list of various nanoparticles applied for heavy metals determination.

Gold nanoparticle (AuNPs): Much interest was focused on gold nanoparticles due to its electronic, thermal and optical properties, high catalytic properties, good biocompatibility, excellent conducting capability and high surface-to-volume ratio. Unfortunately the major drawback of gold based electrode is the well-known phenomenon of structural changes on the surface caused by amalgam formation in mercury detection.

Some researchers have tried solving this problem using different approaches. From Table-1, gold nanoparticles were applied with different materials such as amino acid^{15,16} carbon, carbon nanotubes, graphene oxide¹⁷. Commercial gold nanoparticle screen printed electrode was used for Hg(II) detection, achieving a detection limit of 0.8 ng/mL. The author pointed out the better performance of the electrode where efficient analyte deposition was observed in the absence of stirring during deposition. Alternatively there was no need for deaeration when running square wave sweep because of the renewable active surface of gold nanoparticles screen printed electrode (AuNPs-SPE) which minimizes the problem of memory effects, good recoveries was achieved for real samples¹². Lead(II) and copper(II) were determined using AuNPs/L-cys/L-asp on SPAuE achieving a detection limits of 1 µg/L for both metals¹⁵. Mercury was also determined using nanohybrid materials; carbon/AuNPs, carbon nanotubes/AuNPs (CNTs/AuNPs) and graphene oxide/AuNPs (GO/AuNPs) which gave a detection limit of 3.3, 0.2 and 1.9 µg/L, respectively. The use of first under potential deposition (UPD) with AuNPs make it possible to avoid pretreatment and the interesting aspect was the simultaneous detection of Hg(II) and Pb(II) due to the separation in the first under potential depositions of these two metals, giving detection limits of Hg(II) and Pb(II) as 1.9 µg/L and 2 µg/L, respectively¹⁷. Monodispersed AuNPs graphene hybrid nanocomposite was used on SPCE for detection of Hg(II), a detection limit of 6 ppt with (S/N) = 3 was achieved. However the use of graphene hybrid nanocarbon greatly facilitate the

electron transfer process. The method was applied on river water sample achieving a value lower than WHO value for drinking water¹⁸. Bimetallic Au-Pt nanoparticles was used with organic nanofiber on GCE, giving a detection limit of 0.04 nM for Hg(II). Additionally the used of bimetallic NPs show better performance, due to higher catalytic property and higher conductivity than monometallic¹⁹.

Silver nanoparticles (AgNPs): Silver nanoparticles are also being explored due to their unique properties, good physical and chemical properties and inexpensiveness. Silver nanoparticles was used as modifier on screen printed carbon electrode (SPCE) for detection of Sb(III) achieving a detection limit of 6.79×10^{-10} M. It was observed that AgNPs deposition was influenced by concentration and deposition time where lower concentration and deposition time gave a much better response¹³. A detection limit of 8.5×10^{-7} and 4×10^{-7} M for Cr(VI) was observed when AgNPs and AuNPs were applied on SPCE respectively¹⁴. Silver nanoparticles was used with Nafion to determine Cr(VI), achieving a detection limit of 0.67 ppb, nafion was employed as a conducting matrix for the attachment of AgNPs to the electrode²⁰.

Bismuth nanoparticles (BiNPs): The toxicity and hazardous nature of mercury has invalidated the use of mercury electrodes and better alternative are sought after. Metals like bismuth and antimony which are less toxic are replacing mercury electrode due to their attractive and unique behaviour combined with the special properties of metallic nanoparticle based electrodes. Bismuth film nanoparticles (BiNPs) was used on glassy carbon electrode (GCE) for detection of Pb(II), Cd(II) and Cr(III) achieving a detection limit of 87 nM, 98 nM and 2.3×10^{-15} M, respectively²¹. Detection limit of 2.5 µg/L for Pb(II) was reported using BiNPs as modifier on screen printed electrode²². Bismuth film nanoparticles modified boron doped diamond (BDD) electrode was used for the determination of Cd(II)

and Pb(II) giving a detection limits of 1.9 and 2.3 µg/L, respectively. The used of BiNPs-BDD electrode allows detection of Pb(II) to a 10 fold lower detection limit and 3 fold increase peak current, when compared with bare boron doped diamond electrode. The authors point out that the ability to control the particle size on the boron doped diamond surface was yet to be investigated²³. Bismuth film nanoparticles modified screen printed carbon electrode (SPCE) was explored using two hydrodynamic configurations base on stirring (convective cell) and flow (flow cell) in order to enhance the analyte deposition during the accumulation step, lower detection limits was found at the flow cell for Zn(II), Cd(II) and Pb(II) as 2.6, 1.3 and 0.9 ng/mL, respectively. The method was tested on waste water and tap water with good recoveries but with high interference from copper affecting both Cd(II) and Pb(II)²⁴.

Other nanoparticles: Functionalized mesoporous silica nanoparticle has been used to modify a SPCE for Pb(II) determination, achieving a detection limit of 0.1 µg/L as a result of high surface area and high porosity of the silica³². Antimony nanoparticles modified boron doped diamond electrode has been successfully used for the simultaneous determination of Pb(II) and Cd(II). The authors applied a low concentration of antimony (8.21 µM) on the surface of electrode, which improve the simultaneous detection of both Cd(II) and Pb(II) with a detection limit of 38.1 and 25.4 µg/L, respectively, although much higher concentration of the analytes (Pb and Cd) had to be used because analysis with lower concentration of the analytes did not gave a good response. Important point by the authors was the prospect of increasing the concentration of antimony on the surface of electrode, which was not investigated³³.

SPE: Screen printed electrode, GCE: Glassy carbon electrode, CNT/AuNPs: Carbon nanotube gold nanoparticles, GO/AuNPs: Graphene oxide gold nanoparticles, AuNP/GHNC: Gold nanoparticle graphene hybrid nanocomposite,

TABLE-1
METALLIC NANOPARTICLES APPLIED ON ELECTROCHEMICAL SUBSTRATE FOR HEAVY METALS DETECTION

Electrochemical platform	Technique	Analyte	LOD (limit of detection)	Sample	Reference
AuNPs SPE	SWASV	Hg(II)	0.8 ng/mL	Rain, river and industrial water	12
AuNPs/L-cys/L-asp SPE	SWV	Pb(II), Cd(II)	1 µg/L, 1 µg/L	-	15
AuNPsThiolamino acid	SWV	Hg(II)	2.3 nM	Tap and waste water	16
Carbon/AuNPs SPE	SWV	Hg(II)	3.3 µg/L	Tap and river water	17
CNTs/AuNPs SPE	SWV	Hg(II)	0.2 µg/L	Tap and river water	17
GO/AuNPs SPE	SWV	Hg(II)	1.9 µg/L	Tap and river water	17
AuNP/GHNC	SWASV	Hg(II)	6 ppt	River water	18
AuNPs-PtNPs GCE	SWASV	Hg(II)	0.04 nM	-	19
Functionalized mesoporous silica SPE	SWASV	Pb(II)	0.1 µg/L	Tap, river and waste water	20
BiNPs SPE	SWASV	Zn(II), Cd(II), Pb(II)	2.6, 1.3 and 0.9 ng/mL	Waste and tap water	24
AuNPs SPE		Pb(II)	0.8 ng/mL	-	25
GNEE	SWASV	As(III), Hg(II), Cu(II)	0.27 nM, 0.1 nM, 0.31 nM	-	26
AuNPs amplified DNA-Au electrode	SWASV	Hg(II)	0.5 nM	Buffer	27
AuNPs amplified DNA-Au electrode	DPV	Hg(II)	0.5 nM	Tap and lake water	28
AuNPs amplified DNA-Au electrode	CV	Hg(II)	10 nM	-	29
AgGNF	CV	Cr(VI)	0.65 ppb	-	30
PtNPs SPE	CV	As(III)	5.68 µg/L	Tap water	31

AuNPs/L-cys/L-asp: Gold nanoparticles/L-cystiene/L-aspartic, AuNPs-PtNPs: Gold nanoparticles Platinum nanoparticles, GNEE: Gold nano electrode ensemble, AgGNF: silver nanoparticles-coated gold nanoporous film, SWASV: Square wave anodic stripping voltammetry, SWV: Square wave voltammetry, CV: Cyclic voltammetry.

Conclusion

This paper has provided an overview of various literatures on the application of different heavy metals on modified electrodes, for their electrochemical detection. The draw backs of using some of the metals have been explained and some possible ways of enhancing electrode modification system for better detection limits were pointed out. It was observed in the review that very little or no research was performed using metals like silica and platinum. We therefore, recommend for their proper use due to their observed good response, thereby giving much better lower detection limit.

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