Chapter 7

Applications of Metals, Metal Oxides, and Metal Sulfides in Electrochemical Sensing and Biosensing

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Contents

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Abstract Conventional working electrodes encounter several drawbacks, such as requirement of high overpotential, poor selectivity and sensitivity, and surface fouling or poisoning of the electrode surface due to adsorption of the oxidized/reduced products of molecules under investigation. Surface modifications indeed play a catalytic role in determining the sensitivity of measurement in electroanalytical applications. Particularly, the use of metal nanoparticles in electroanalytical chemistry is an area of research, which is continually expanding. Taking advantage of exceptional attributes, such as being easy to handle, cost effectiveness, user friendliness, maintenance free electroanalytical devices have been utilized for the development of environmental sensors, chemical sensors, and biosensors. This chapter represents a comprehensive attempt to summarize and discuss various electrochemical sensing and biosensing applications using metals, metal oxides, and metal sulfides. These materials have been widely used as working electrodes, due to their good conductivity, large surface area, fast diffusion kinetics, low resistance, ease of functionalization, offering the versatile option of controllable adjustment with proper choice of materials. In this review, we have concentrated on widely used metal electrodes with specific application.

Keywords Metals · Metal oxides · Metal sulfides · Electrochemical sensor · Biosensor

7.1 Introduction

There is no doubt that electrochemical sensors provide quick response, require low-power, and are easy to use, compact, cost-effective, and portable than other analytical tools (Thiruppathi et al. 2019; Thiyagarajan et al. 2014). Electrochemical sensors offer timely results for samples with complex matrices even outside of laboratories. Glucose meter, pH meter, and the other ion-selective meter exemplify the potential real-time applications of electrochemical sensors (Gooding 2008). According to the current IUPAC's definition (Devi and Tharmaraj 2019), a chemical or bio-sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. There are different electrochemical techniques available for sensing important chemical and biochemical targets, including, voltammetry, amperometry, potentiometry, and electrochemiluminescence. Among the various electrochemical techniques, voltammetry is one of the most widely employed electrochemical techniques, which includes cyclic voltammetry (CV), linear sweep voltammetry (LSV), square wave voltammetry (SWV), and differential pulse voltammetry (DPV) (Fig. 7.1). Basically, it is used to get electrochemical information of analyte by measuring the current response of analyte as the function of potential and/or time. In the voltammetric methods, variety of electrode substrates are used to improve sensing performance of electrodes. Metals, metal oxides, and

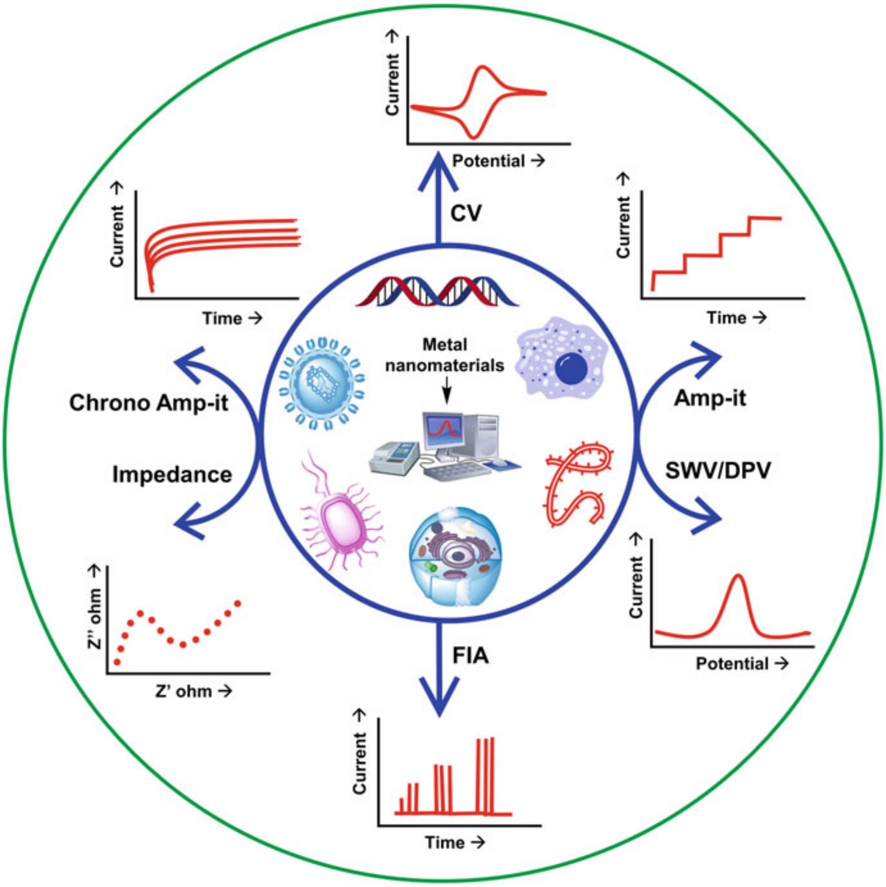

Fig. 7.1 Various available electrochemical techniques for sensing important chemical and biochemical targets (*CV* cyclic voltammetry, *SWV* square wave voltammetry, *DPV* differential pulse voltammetry, and *FIA* flow injection analysis)

metal sulfides are one of such substrates, and are widely used as electrode materials in electrochemical sensor field that transforms chemical signal of analyte into electrical signal (Alves et al. 2011). The following characteristics may be deemed necessary to be a good electrode material for sensing: (i) good conductivity, (ii) chemical inertness, (iii) high surface area, (iv) low resistance, (v) fast diffusion kinetics, and (vi) extraction and accumulation of an analyte at the electrode. More than half of the elements known today in the periodic tables are metals (Fig. 7.2).

Among the metals, d-block transition metals have been widely used in electrochemical analysis due to their good conductivity and a great range of catalytic activity (Gates 1993). Utilization of metal oxide nanoparticles in electrochemical sensing and biosensing has drawn a lot of attention and explored in the recent review (George et al. 2018). In this chapter, we highlight the widely employed transition

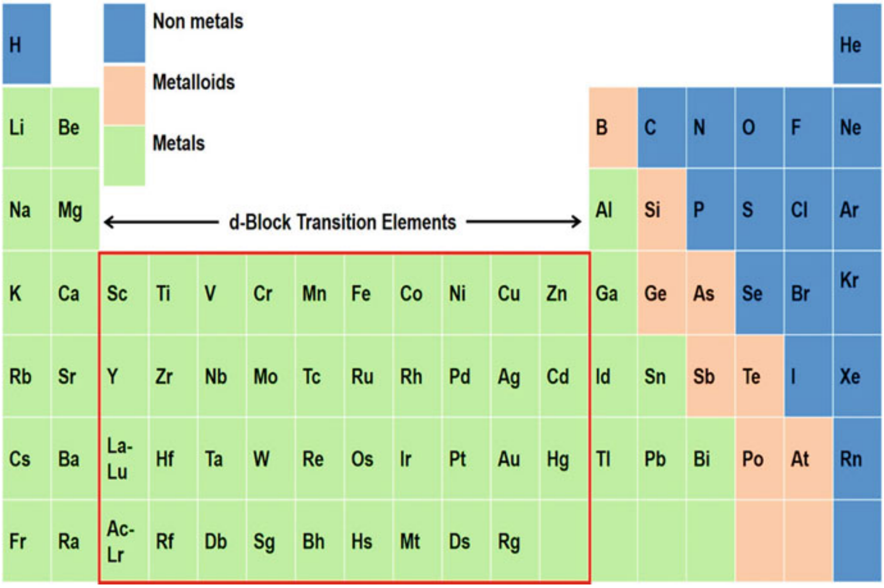

Fig. 7.2 Classifications of metals, nonmetals, and metalloid elements in the modern periodic table

metals/metal oxide/metal sulfide electrode properties along with their advanced applications in chemical and biological electro-sensing.

Though, metal-based electrodes are used for sensing analytes, they were largely restricted by poor kinetics and limited surface area. Surface modification for those oxides/sulfides of metals may be the solution to improve. Metal oxides are usually formed by the reaction of metal with oxygen, whereas metal sulfides, one of the broadly accepted and employed nanomaterials, are produced by the reaction of a metal and sulfide (Velmurugan and Incharoensakdi 2018).

$$\text{Metal} + \text{Oxygen} \rightarrow \text{Metal oxide},\ \text{Metal} + \text{Sulfide} \rightarrow \text{Metal sulfide}.$$

7.1.1 Modification of Nanomaterials on Electrode Surface

Surface modification is employed for two main purposes, either to protect an electrode that is not corrosion resistant under operating conditions or to incorporate specific properties to the surface. Conventional working electrodes encounter several drawbacks, such as requirement of high overpotential, poor selectivity and sensitivity, and surface fouling or poisoning of the electrode surface due to adsorption of the oxidized/reduced products of molecules under investigation. The concept of chemically modified electrodes (CMEs) was introduced to overcome aforementioned problems.

CMEs consist of a conductive substrate modified with electrochemically active, functional moieties; metals, metal oxides, metal sulfides, and polymers. CMEs are fabricated for a specific application that may not be feasible with a bare/unmodified metal electrode. Modification of the nano-metal oxide and sulfides onto the electrode surface may result in enhanced electron transfer kinetics, improved sensitivity, and reduced overpotential. These modifications involved irreversible adsorption (Thiruppathi et al. 2016), self-assembled layers, covalent bonding, electropolymerization (Thiruppathi et al. 2017), and others (Lane and Hubbard 1973; Murray 1980; Zen et al. 2003b). Surface modifications indeed played a catalytic role in determining the sensitivity of measurement in electroanalytical applications. Such surface modifications endowed the surface with new properties independent of those of the unmodified electrode. Modified electrodes in general led to the following:

1. Endowing with physicochemical properties of the modifier for the electrode
2. Improved sensitivity and electrocatalytic ability
3. High selectivity toward analyte due to special functional moieties and pores
4. Improved diffusion kinetics
5. Extraction and accumulation of an analyte at the electrode

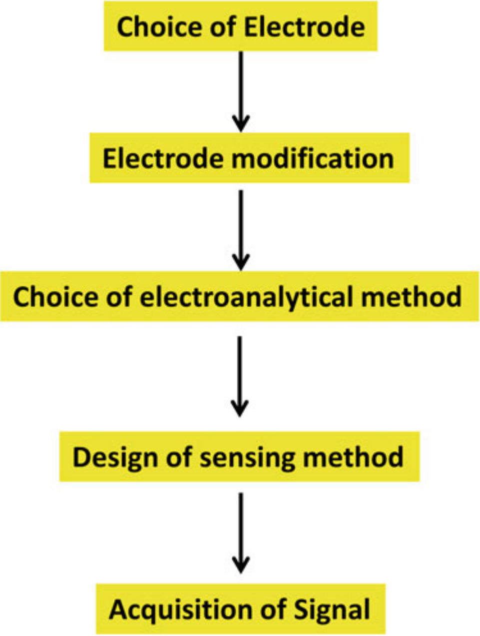

Fig. 7.3 Operational stages of the electrochemical sensor

7.1.2 Operational Stages of the Electrochemical Sensor (Fig. 7.3)

Overall, this chapter is divided into two parts (i) non-noble and (ii) noble metal-based sensors.

7.2 Non-noble Metals

7.2.1 Titanium (Ti)

Titanium is the strongest pure metal on earth. It is also an attractive material used in electrochemical analysis and mostly utilized in chemical sensors. Bukkitgar et al. 2016 have investigated the electrochemical oxidation of nimesulide at TiO_2 nanoparticles-modified glassy carbon electrode (Bukkitgar et al. 2016). Furthermore, Ti is largely used as a base substrate for deposition/immobilization of active catalyst materials. Kang et al. 2008 decorated a Gold–Platinum nanoparticle onto a highly oriented titania nanotube array surface by electrochemical method that was used for amperometric detection of H_2O_2 (Figs. 7.4 and 7.5) (Kang et al. 2008). A modified titanium electrode of nanoporous gold particles (Yi and Yu 2009) and silver nanoparticles (Yi et al. 2008) was utilized for the detection of hydrazine. Kubota and co-workers have tried to immobilize Meldola's Blue on titanium, and employed it for electrocatalytic oxidation of reduced nicotinamide adenine dinucleotide (NADH) (Kubota et al. 1996). Noble nanomaterials (Ag, Pt, Au) have been commonly seen in modifying Ti electrode, and subsequently utilized for chemical sensing. Some examples for the Titanium (Ti) electrode-based sensors are listed in Table 7.1.

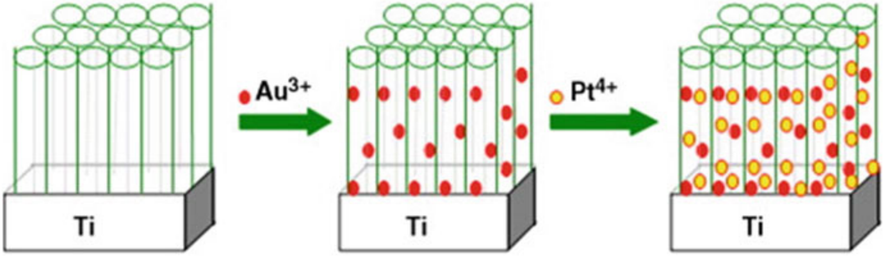

Fig. 7.4 Deposition process of Au and Pt nanoparticles (Reproduced with permission from Kang et al. 2008)

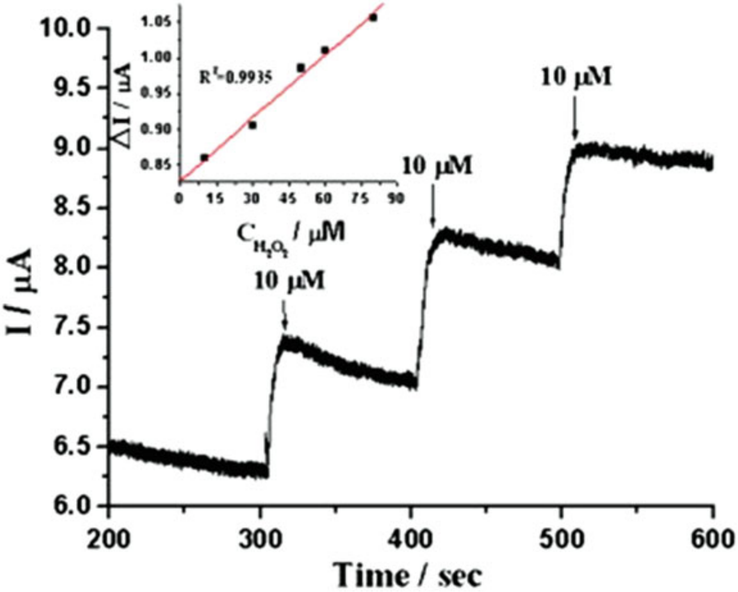

Fig. 7.5 Amperometric responses of the Pt–Au/TiOx NT electrode upon adding continuously 10 μM H_2O_2 in 10 mM PBS (pH 7.3) containing 0.1 M NaCl at −0.2 V vs Ag/AgCl (saturated by KCl). 10 μM H_2O_2 is the final concentration. The inset shows the calibration curve. (Reproduced with permission from Kang et al. 2008)

Table 7.1 List of Titanium (Ti) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	Reference
GCE-TiO_2	DPV	Nimesulide	pH 2, PBS	40–100 μM	3.37 nM	Bukkitgar et al. (2016)
Pt–Au/TiOx NT	Amperometry	H_2O_2	pH 7.3, PBS	0–1.8 mM	0.1 mM	Kang et al. (2008)
nanoAg/Ti	Amperometry	Hydrazine	NaOH	0–60 mM	–	Yi et al. (2008)
Au/Ti	Amperometry	Hydrazine	NaOH	5–40 mM	0.042 mM	Yi and Yu (2009)
Meldola's Blue/Ti	Amperometry	NADH	pH 7.4, PBS	10–50 μM	–	Kubota et al. (1996)

GCE-TiO_2 titanium oxide modified glassy carbon electrode, *Pt–Au/TiOx NT* gold-platinum nanoparticle modified onto a highly oriented titania nanotube array, *nanoAg/Ti* nano-silver-titanium electrode, *Au/Ti* gold titanium electrode, *DPV* differential pulse voltammetry, *PBS* phosphate buffer saline, *H_2O_2* hydrogen peroxide, *NaOH* sodium hydroxide, and *NADH* nicotinamide adenine dinucleotide

7.2.2 Vanadium (V)

Vanadium is the lightest, corrosion-resistant d-block transition metal, which exists in oxidation states ranging from −1 to +5 (Barceloux and Barceloux 1999b; Privman and Hepel 1995). Vanadium electrodes have been widely used in capacitors and batteries, only a little amount of success has been achieved in the sensor field. Cyclic voltammetric behavior of vanadium electrodes has been summarized by Privman and Hepel (1995) (Privman and Hepel 1995). A VO-polypropylene carbonate modified glassy carbon electrode prepared by casting method was described by Tian et al. (2006) and used for amperometric detection of ascorbic acid (AA) (Tian et al. 2006). Huang group developed a novel electrochemical biosensor for the determination of 17β-estradiol using VS_2 nanoflowers-gold nanoparticles modified glassy carbon electrode (Huang et al. 2014). Tsiafoulis et al. 2005 prepared vanadium hexacyanoferrate and casted onto the glassy carbon electrode, which was subsequently used as electro catalyst for H_2O_2 sensing (Tsiafoulis et al. 2005). Some examples for the Vanadium (V) electrode-based sensors are listed in Table 7.2.

7.2.3 Manganese (Mn)

Reports show that MnS can be utilized as one of promising active materials for pseudocapacitor and battery applications (Li et al. 2015; Zhang et al. 2008). Manganese oxide (MnO_2), however, was extensively used for electrochemical sensors than Mn and MnS. Several kinds of MnO_2 nanomaterials were employed to construct chemical sensors or biosensors in recent years (Bai et al. 2009). The reactivity of thiol group toward MnO_2 is higher than those of amine and carboxylic functional groups (Eremenko et al. 2012). Therefore, Bai and co-workers developed a sensing

Table 7.2 List of Vanadium (V) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	Reference
$VO(OC_3H_7)_3$-PPC/GCE	Amperometry	Ascorbic acid	pH 8.06, BRS	40 nM–0.1 mM	15 nM	Tian et al. (2006)
AuNPs/VS_2/GCE	DPV	17β-estradiol	pH 7, PBS	10 pM–10 nM	1 pM	Huang et al. (2014)
VHCF/GCE	Amperometry	H_2O_2	pH 7, Tris buffer	0.01–3 mM	4 μM	Tsiafoulis et al. (2005)

$VO(OC_3H_7)_3$-PPC/GCE vanadium tri (isopropoxide) oxide and polypropylene carbonate glassy carbon electrode, *AuNPs/VS_2/GCE* vanadium sulfide nanoflowers-gold nanoparticles modified glassy carbon electrode, *VHCF/GCE* vanadium hexacyanoferrate and casted onto the glassy carbon electrode, *BRS* Britton–Robinson solution, *PBS* phosphate buffer saline, *H_2O_2* hydrogen peroxide, *DPV* differential pulse voltammetry

method for cysteine using β-MnO_2 nanowires modified glassy carbon (GC) electrode (Bai et al. 2009), a manganese dioxide–carbon (MnO_2–C) nanocomposite was also applied in the development of sensors to detect cysteine (Xiao et al. 2011). MnO_2 was also used to prepare screen printed electrodes (Šljukić et al. 2011), enabling the development of point of care sensors. Additionally, the electrocatalytic behavior of MnO_2 was also adopted for non-enzymatic H_2O_2 sensor (Chinnasamy et al. 2015; Dontsova et al. 2008; Šljukić et al. 2011; Wang et al. 2013; Zhang et al. 2014). Hierarchical MnO_2 microspheres composed of nanodisks were once used for nitrite sensing (Xia et al. 2009). Moreover, Revathi and Kumar (2017) hydrothermally prepared polymorphs of alpha (α), beta (β), gamma (γ), epsilon (ϵ) MnO_2 and MnOOH under different conditions for H_2O_2 sensing (Revathi and Kumar 2017). Some examples for the Manganese (Mn) electrode-based sensors are listed in Table 7.3.

7.2.4 Iron (Fe)

Iron is the fourth most common element in the Earth's crust (Anderson 1989). A few review articles were highlighted below, showing how iron is useful for electrochemical sensor applications. The development of electrochemical biosensors based on Fe and Fe-oxide nanomaterials has been well summarized in the literature written by Hasanzadeh and Urbanova group (Hasanzadeh et al. 2015; Urbanova et al. 2014). Bank's group developed disposable screen printed electrodes modified with iron oxide nanocubes for meclizine, antihistamine (Khorshed et al. 2019). Iron and associated nanomaterials are known to exhibit electrocatalytic ability toward a wide range of analytes including hydrogen peroxide (H_2O_2) (Comba et al. 2010), sulfide (S) (Sun et al. 2005), nitrite (NO_2) (Bharath et al. 2015; Xia et al. 2012), phenyl hydrazine (Hwang et al. 2014), and hydrazine (Benvidi et al. 2015; Mehta et al. 2011). Šljukić et al. 2006 demonstrated that Fe-oxide particles existed at the multiwalled carbon nanotube were responsible for electrocatalytic detection of H_2O_2 (Šljukić et al. 2006). Some examples for the Iron (Fe) electrode-based sensors are listed in Table 7.4.

7.2.5 Cobalt (Co)

Cobalt is a relatively rare magnetic element with properties similar to iron and nickel (Barceloux and Barceloux 1999a). Cobalt oxide (Co_3O_4) nanowires exhibited glucose oxidase-like enzymatic activity. Chemical vapor deposition (CVD) method was employed to synthesize Co_3O_4 nanowires and subsequently used for enzymeless glucose sensor application (Fig. 7.6) (Dong et al. 2012; Wang et al. 2012). Reports have shown that Co and associated nanomaterials display high sensitivity and selectivity toward phosphate ion (Chen et al. 1997), and electrocatalytic ability

Table 7.3 List of Manganese (Mn) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	Reference
MnO_2/Chit/GC	Amperometry	Cysteine	pH 7.8 BBS	0.5–630 μM	70 nM	Bai et al. (2009)
MnO_2-C/chit/GC	Chronoamperometry	Cysteine	pH 7.8, BBS	0.5–680 μM	22 nM	Xiao et al. (2011)
MnO_2-SPC	Voltammetry	Ascorbic acid	pH 7, PB	20–100 μM	2.8 μM	Šljukić et al. (2011)
MnO_2-SPC	LSV	Nitrite	$HClO_4$ + $NaClO_4$	20–200 μM	2.5 μM	Šljukić et al. (2011)
MnO_2/nafion/Pt	Chronoamperometry	H_2O_2	NaOH	1–5 mM	–	Chinnasamy et al. (2015)
MnO_2NPs	Amperometry	H_2O_2	pH 7.4, KCl	78 nM −0.78 mM	78 nM	Dontsova et al. (2008)
Au-MnO_2-rGO/GCE	Amperometry	H_2O_2	pH 7, PBS	0.1 μM-12.6 mM	50 nM	Wang et al. (2013)
MnO_2 nanosheet	Amperometry	H_2O_2	pH 7, PBS	5 μM-3.5 mM	1.5 μM	Zhang et al. (2014)
MnO_2/QPOE composite electrodes	Amperometry	Nitrite	$HClO_4$ + $NaClO_4$	0.5 μM-3 mM	0.36 μM	Xia et al. (2009)
α-MnO_2/GCE	Amperometry	H_2O_2	KCl	0.67–20 μM	0.175 μM	Revathi and Kumar (2017)

MnO_2/Chit/GC manganese dioxide nanowires and chitosan modified glassy carbon electrode, *MnO_2-SPC* manganese oxide screen printed electrodes, *MnO_2/nafion/Pt* manganese oxide and nafion modified platinum electrode, *MnO_2NPs* manganese oxide nanoparticles, *Au-MnO_2-rGO/GCE-gold* manganese oxide-reduced graphene oxide modified glassy carbon electrode, *BBS* Borate buffered saline, *PB* phosphate buffer, *PBS* phosphate buffer saline, *H_2O_2* hydrogen peroxide, *$HClO_4$* perchloric acid, *$NaClO_4$* sodium perchlorate, *LSV* linear sweep voltammetry, *KCl* potassium chloride

Table 7.4 List of Iron (Fe) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	Reference
Fe_2O_3 NCs-SPEs	DPV	Meclizine	Sulfuric acid	6.6–196 μM	1.6 μM	Khorshed et al. (2019)
FeNPs	Amperometry	Hydrogen peroxide	pH 7, PBS	Up to 20 mM	0.2 mM	Comba et al. (2010)
α-Fe_2O_3	Chemiluminescence	Sulfide	–	–	10 ppm	Sun et al. (2005)
Fe_3O_4-rGO	DPV	Nitrite	pH 4, PBS	0.5 μM-9.5 mM	30 nM	Bharath et al. (2015)
Fe_2O_3	Amperometry	Nitrite	pH 7.5, PBS	9 μM –3 mM	2.6 μM	Xia et al. (2012)
α-Fe_2O_3	I-V	Phenyl hydrazine	pH 7, PBS	97 μM-1.56 mM	97 μM	Hwang et al. (2014)
Fe_3O_4NPs	DPV	Hydrazine	pH 7, PBS	0.12–0.6 μM	40 nM	Benvidi et al. (2015)
α-Fe_2O_3	Amperometry	Hydrazine	pH 7, PBS	–	3.84 μM	Mehta et al. (2011)
Iron oxide	CV	Hydrogen peroxide	pH 7.4, PBS	–	–	Šljukić et al. (2006)

Fe_2O_3 NCs-SPEs screen-printed carbon electrode modified with uniform iron oxide nanocubes, *FeNPs* iron nanoparticles, *α-Fe_2O_3* iron oxide, *rGO* reduced graphene oxide, *PBS* phosphate buffer saline, *DPV* differential pulse voltammetry, *CV* cyclic voltammetry

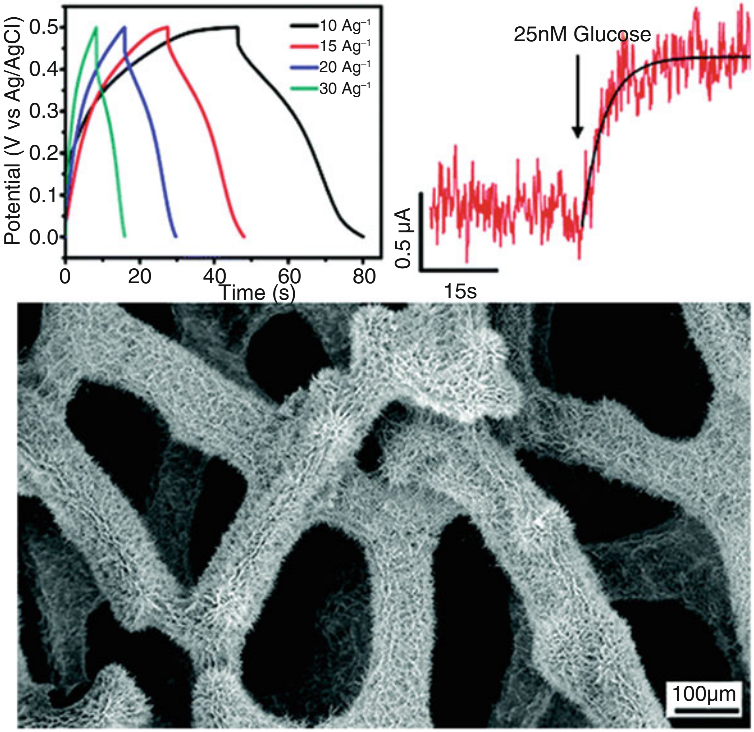

Fig. 7.6 Electro catalytic detection of glucose on cobalt oxide modified electrode. (Reproduced with permission from (Dong et al. 2012)

toward hydrogen peroxide (Salimi et al. 2007). Furthermore, numerous enzyme-free sensors are configured using various cobalt nanomaterials such as nanorod, nanosheet, and nanoparticles (George et al. 2018). Some examples for the Cobalt (Co) electrode-based sensors are listed in Table 7.5.

7.2.6 Nickel (Ni)

Nickel is an important metal and a possible alternative to the noble metals. Nickel and its composites are most active catalyst for glucose oxidation process in alkaline medium (Yuan et al. 2013). Nickel nanomaterials have been widely used for broad range of sensor applications. The Ni nanomaterials are pH dependent, and redox active in the alkaline environment; therefore, they are suitable for sensing glucose in alkaline pH. The previously published articles indicated that nickel oxide modified electrodes were capable of catalyzing the glucose oxidation reaction, as shown below:

Table 7.5 List of Cobalt (Co) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	References
Co_3O_4	Amperometry	Glucose	KOH	20–80 μM	100 nM	Dong et al. (2012)
Graphene/Co_3O_4	Amperometry	Glucose	NaOH	50–300 μM	10 μM	Wang et al. (2012)
Cobalt wire	Potentiometry	Phosphate	pH 5, potassium acid phthalate	50 μM–5 mM	1 μM	Chen et al. (1997)
Cobalt oxide/GC	Amperometry	H_2O_2	pH 7, PBS	4–80 nM	0.4 nM	Salimi et al. (2007)

Co_3O_4 cobalt oxide, *GC* glassy carbon

$$\mathbf{Ni(OH)_2 \rightleftharpoons NiOOH + H^+ + e^-}$$
$$\mathbf{NiOOH + Glucose \rightleftharpoons Ni(OH)_2 + Gluconolactone}$$

Yuan et al. (2013) electrochemically synthesized 3D nickel oxide nanoparticles (NiONPs) onto the surface of graphene oxide (GO) modified glassy carbon (GC), resulted in the development of the nonenzymatic glucose sensor and supercapacitor (Yuan et al. 2013). The catalytic ability of nickel electrode toward glucose was also useful for indirect detection of phosphate, as indicated in Fig. 7.7 (Cheng et al. 2010), Cheng et al. (2010) used activated nickel electrode to develop enzyme-free method for the detection of phosphate ($PO_4{}^{3-}$) anion with flow injection analysis (FIA) (Cheng et al. 2010). In this system, the activation of barrel plated nickel electrode (NiBPE) was found to initiate the adsorption of $PO_4{}^{3-}$ anion at the nickel electrode, which suppressed glucose oxidation current at the NiBPE in 0.1 M, NaOH solution induced by adsorption of phosphate.

Zen’s group constructed an electrochemical cell coupled with flow injection analytical system (FIA) using disposable NiBPE for the analysis of trivalent chromium (Cr^{III}), as illustrated in Fig. 7.8 (Sue et al. 2008). Some examples for the Nickel (Ni) electrode-based sensors are listed in Table 7.6.

7.2.7 Molybdenum (Mo)

Both Molybdenum sulfide (MoS_2) and Molybdenum oxide (MoO) were widely known as semiconductors, which are mostly utilized as electrode for energy generations. Experimental and theoretical studies have confirmed the catalytic activity of MoS_2 (Lee et al. 2010). Structural diversity of 2D/3D molybdenum disulfide (MoS_2) rendered them first choice for electrochemical sensors and biosensor applications

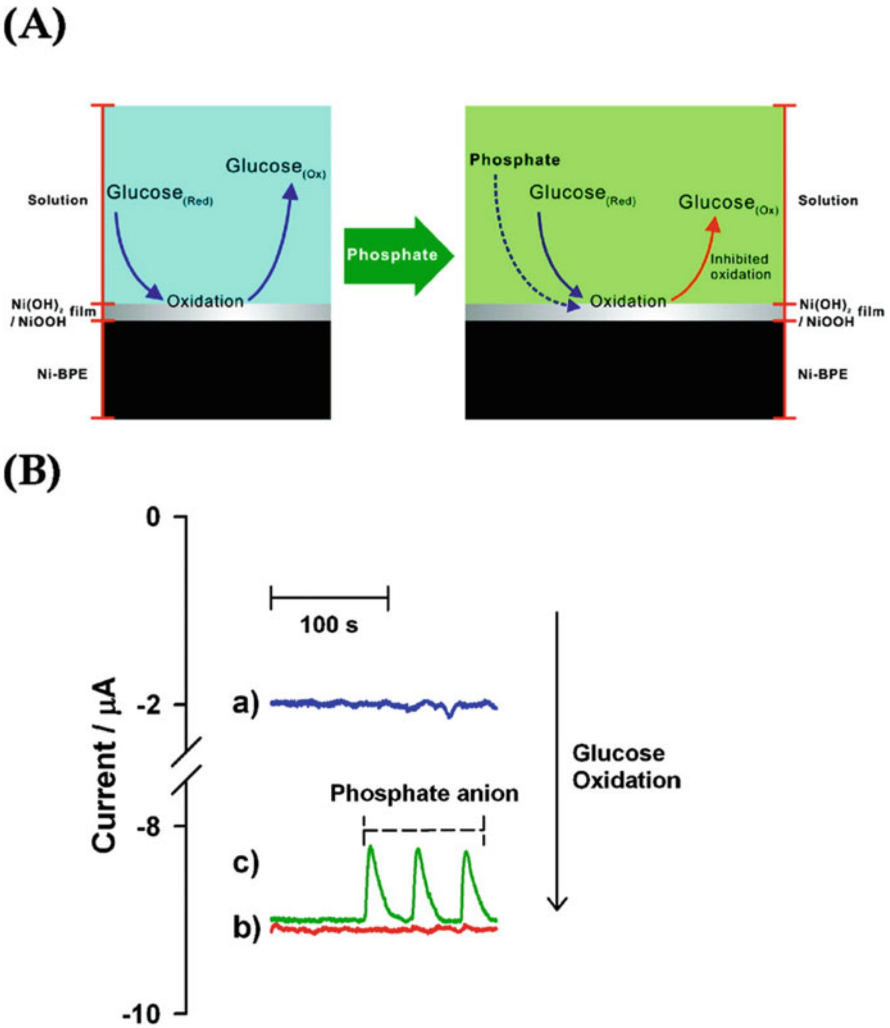

Fig. 7.7 (**a**) Detection scheme of the proposed system mentioned in Cheng et al. (2010). (**b**) FIA responses of the activated Ni-barrel plating electrode in 0.1 M NaOH (**a**), in 0.1 M NaOH with 25 μM glucose (**b**), and sequential injection of 500 μM PO_4^{3-} in 0.1 M NaOH with 25 μM glucose as carrier solution (c) at Eapp = +0.55 V vs Ag/AgCl. (Reproduced with permission from (Cheng et al. 2010)

than MoO (Figs. 7.9 and 7.10). In fact, MoO has not been explored much for sensor applications (Vilian et al. 2019).

Ezhil Vilian et al. (2019) have done an extensive review on MoS_2 based electrochemical sensors (Vilian et al. 2019). Mani and colleagues synthesized MoS_2 nanoflowers onto the CNTs decorated-graphene nanosheet (GNS) through hydrothermal method, followed by the utilization in developing an electrochemical sensor,

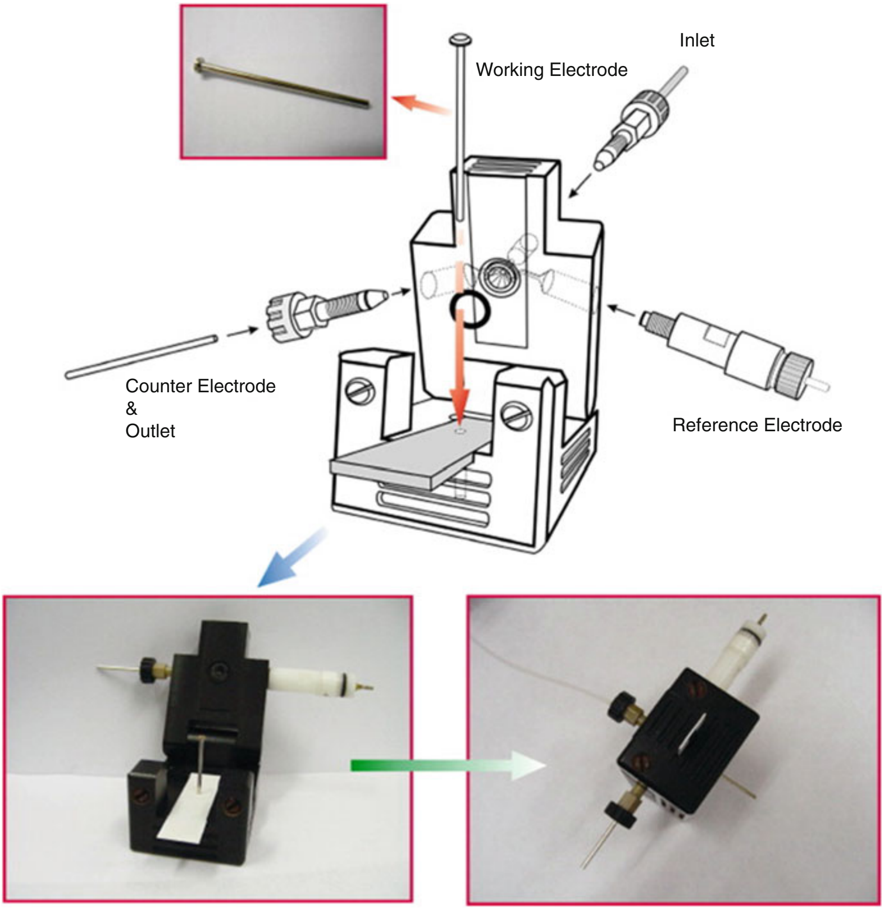

Fig. 7.8 Proposed flow injection electrochemical detector setup. (Reproduced with permission from Sue et al. 2008)

Table 7.6 List of Nickel (Ni) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	Reference
NiONPs/GO/GC	Amperometry	Glucose	NaOH	3.13 μM–3.05 mM	1 μM	Yuan et al. (2013)
Ni-BPE	FIA	Phosphate	NaOH	25 μM–1 mM	0.3 μM	Cheng et al. (2010)
Ni-BPE	FIA	Cr^{III}	NaOH	Up to 1 mM	0.3 μM	Sue et al. (2008)

NiONPs/GO/GC nickel oxide nanoparticles-graphene oxide modified glassy carbon electrode, *Ni-BPE* Ni-barrel plating electrode, *FIA* flow injection analysis, *NaOH* sodium hydroxide

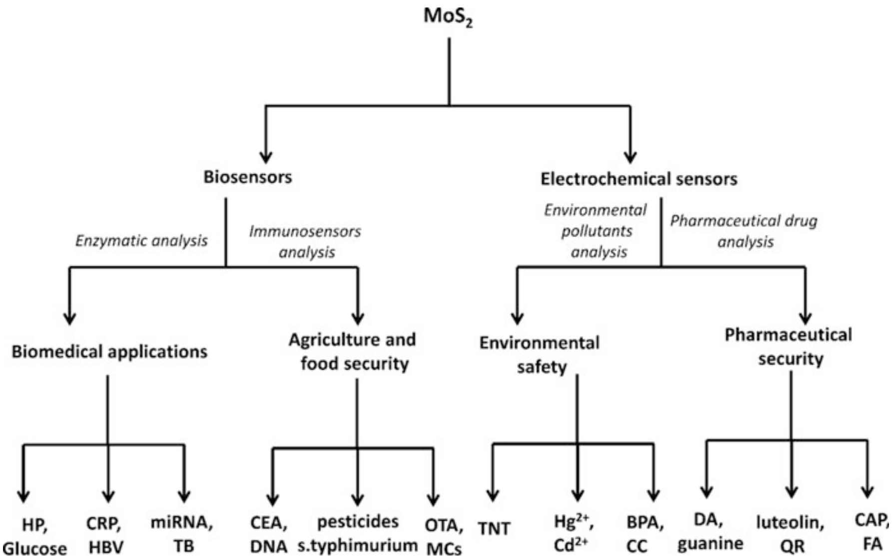

Fig. 7.9 Schematic illustration of the electrochemical sensing and biosensing applications of MoS_2-based detection devices.
MoS_2 molybdenum sulfide, *HP* hydrogen peroxide, *CRP* C-Reactive Protein, *HBV* Hepatitis B virus, *miRNA* micro RNA, *TB* tuberculosis, *CEA* carcinoembryonic antigen, *DNA* deoxyribonucleic acid, *OTA* Ochratoxin A, *MCs* microcystins, *TNT* trinitrotoluene, *BPA* Bisphenol A, *CC* Catechol, *DA* dopamine, *QR* quercetin, *CAP* Chloramphenicol, *FA* folic acid. (Reproduced with permission from Vilian et al. 2019)

which showed feasibility in detecting nanomolar level of dopamine (DA) in rat brain and serum samples, as illustrated in Fig. 7.11 (Mani et al. 2016). In addition, MoS_2 was also used to develop an electrochemiluminescence-sandwich type sensor for concanavalin A (Con A) (Fig. 7.12) (Ou et al. 2016).

7.2.8 Copper (Cu)

The redox chemistry of copper is interesting, and it has been involved in various biological and chemical processes (Lewis and Tolman 2004). Copper is an attractive material for sensing application, which was employed in the electrochemical analysis of o-diphenols, glucose, amino acids, and oxygen. Sivasankar et al. 2018 constructed a glucose sensor based on copper nanoparticles-decorated, nitrogen doped graphite oxide (NGO) (Sivasankar et al. 2018). In addition ~~of~~ to sugar detection, Cu nanomaterials (both CuO and CuS) were also used as an electrocatalyst in the H_2O_2 sensor (Dutta et al. 2014; Gu et al. 2010; Wang et al. 2008). Baskar et al. (2013) reported the complex forming ability of free amine group of poly(melamine) with Cu to enhance the electrocatalytic behavior of poly(melamine)-Cu nanoclusters

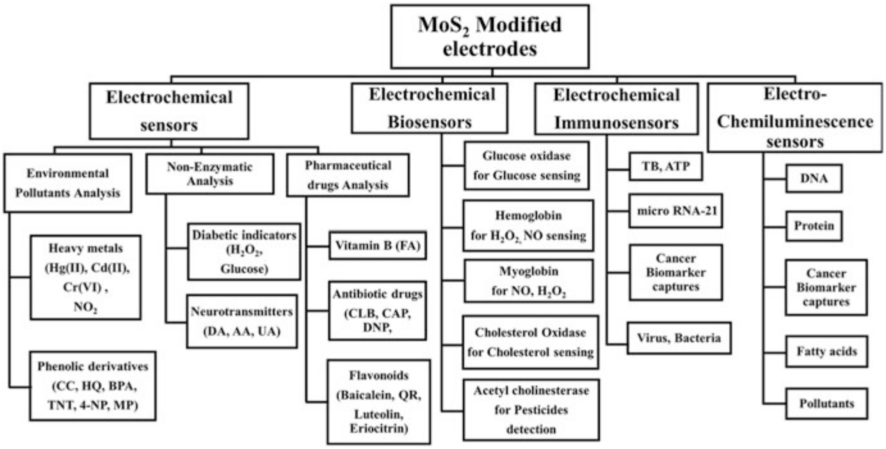

Fig. 7.10 Flowchart representing the applications of MoS$_2$-based modified electrodes toward their sensors and biosensors applications
MoS$_2$ molybdenum sulfide, *H$_2$O$_2$* hydron peroxide, *NO$_2$* nitrite, *HQ* hydroquinone, *BPA* Bisphenol A, *TNT* trinitrotoluene, *NP* nitrophenol, *MP* metaphenol, *CC* Catechol, *DA* dopamine, *AA* ascorbic acid, *UA* uric acid, *CLB* Clenbuterol, *CAP* Chloramphenicol, *DNP* diamond nanoparticles, *QR* quercetin, *TB* tuberculosis, *ATP* Adenosine triphosphate, *DNA* deoxyribonucleic acid. (Reproduced with permission from (Vilian et al. 2019)

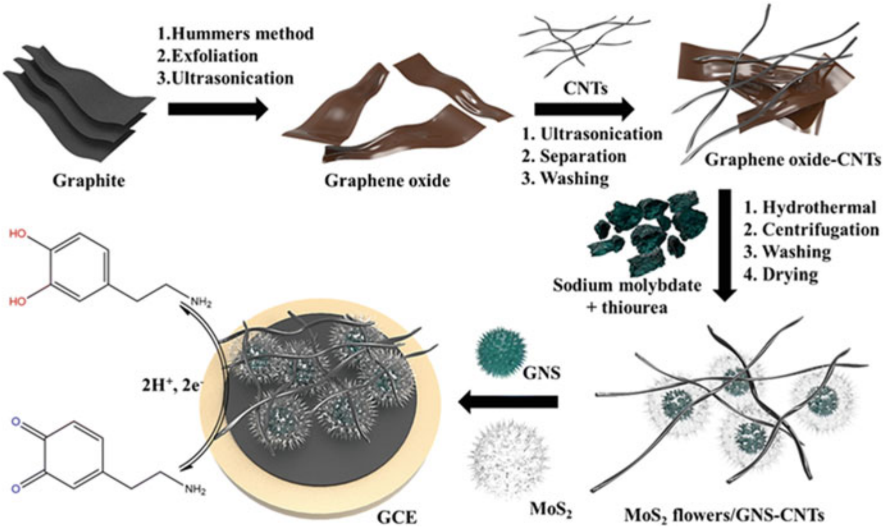

Fig. 7.11 Fabrication of a GNS-CNT/MoS$_2$ hybrid nanostructure, and its application in the electrochemical sensing of dopamine for biological and pharmaceutical samples (*CNTs* carbon nanotubes, *GCE* glassy carbon electrode, *GNS* graphene nanosheet. (Reproduced with permission from Mani et al. 2016))

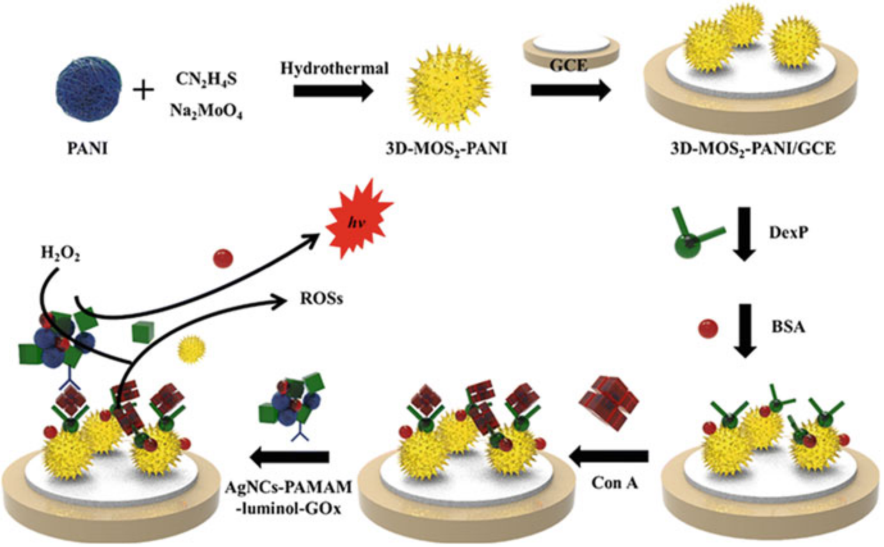

Fig. 7.12 3D-MoS$_2$-PANI-based ECL biosensor (*PANI* polyaniline, *BSA* bovine serum albumin, *GCE* glassy carbon electrode, *ECL* electrochemiluminescence, *Con A* concanavalin A, *H_2O_2* hydron peroxide. (Reproduced with permission from Ou et al. 2016))

that was efficient for H_2O_2 sensing, and the system showed excellent stability (Baskar et al. 2013). In addition, Cu nanoparticle-plated disposable electrodes were also utilized for amino acid detection (Zen et al. 2004).

Ling et al. (2018) reported a novel method to prepare 3D porous Cu@Cu$_2$O aerogel networks by self-assembling method. The resultant Cu@Cu$_2$O aerogel networks displayed excellent electrocatalytic activity toward glucose oxidation at a low onset potential. The Cu@Cu$_2$O aerogels were found to be electroactive, pH dependent, and stable, possess horseradish peroxidase (HRP)-like and NADH peroxidase-like enzymatic activities, demonstrating sufficient electro/photo catalytic activities toward the oxidation of dopamine (DA), o-phenylenediamine (OPD), 3,3,5,5-tetramethylbenzidine (TMB), and dihydronicotinamide adenine dinucleotide (NADH) in the presence of H_2O_2 (Fig. 7.13) (Ling et al. 2018).

Copper-plated electrodes were capable of selectively detecting the O-diphenols, such as catechol (CA), dopamine (DA), and pyrogallol (PY), in the presence of the other inferring species, including diphenol and ascorbic acid, for clinical and biochemical examination (Zen et al. 2002a). The o-diphenols have been detected amperometrically through electrochemical oxidation, of which the possible mechanism and detection signal were shown in Fig. 7.14. Zen's group also developed photoelectrocatalytic based o-diphenol sensor, its reaction mechanism and amperometric signal were shown in Fig. 7.15 (Zen et al. 2003a). Some examples for the Copper (Cu) electrode-based sensors are listed in Table 7.7.

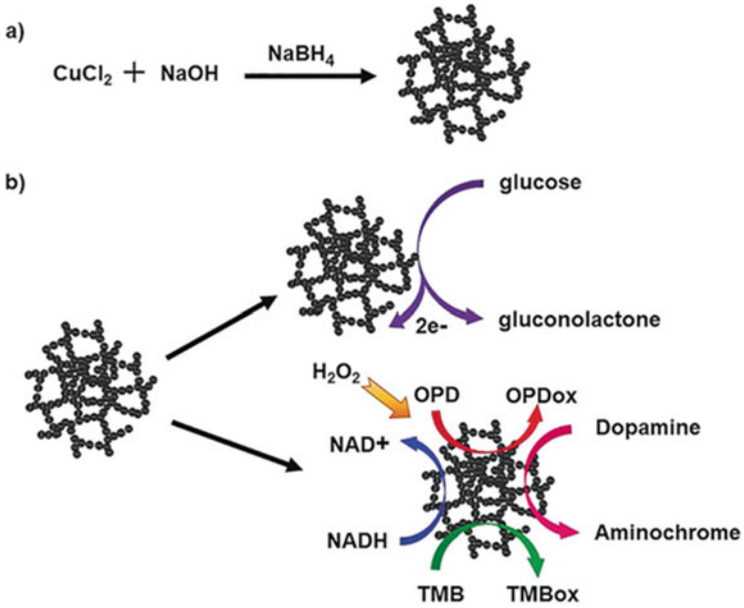

Fig. 7.13 Illustration of (**a**) the preparation and (**b**) versatile biomimetic catalytic properties of 3D Cu@Cu$_2$O aerogel networks. (Reproduced with permission from Ling et al. 2018)

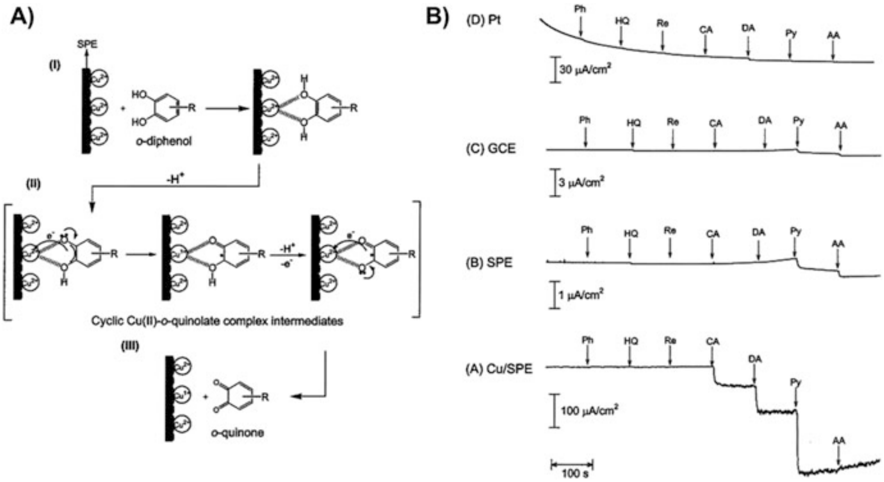

Fig. 7.14 (**a**) Reaction mechanism for the selective oxidation of o-diphenol on the screen printed electrode. (**b**) Typical amperometric hydrodynamic response for the copper screen printed electrode (**a**), screen printed electrode (**b**), glassy carbon electrode (**c**), and Pt electrode (**d**) with a spike of 2 mM various phenolic and o-diphenol derivatives in pH 7.4 PBS at an applied potential of −0.05 V (vs Ag/AgCl). (Reproduced with permission from Zen et al. 2002a)

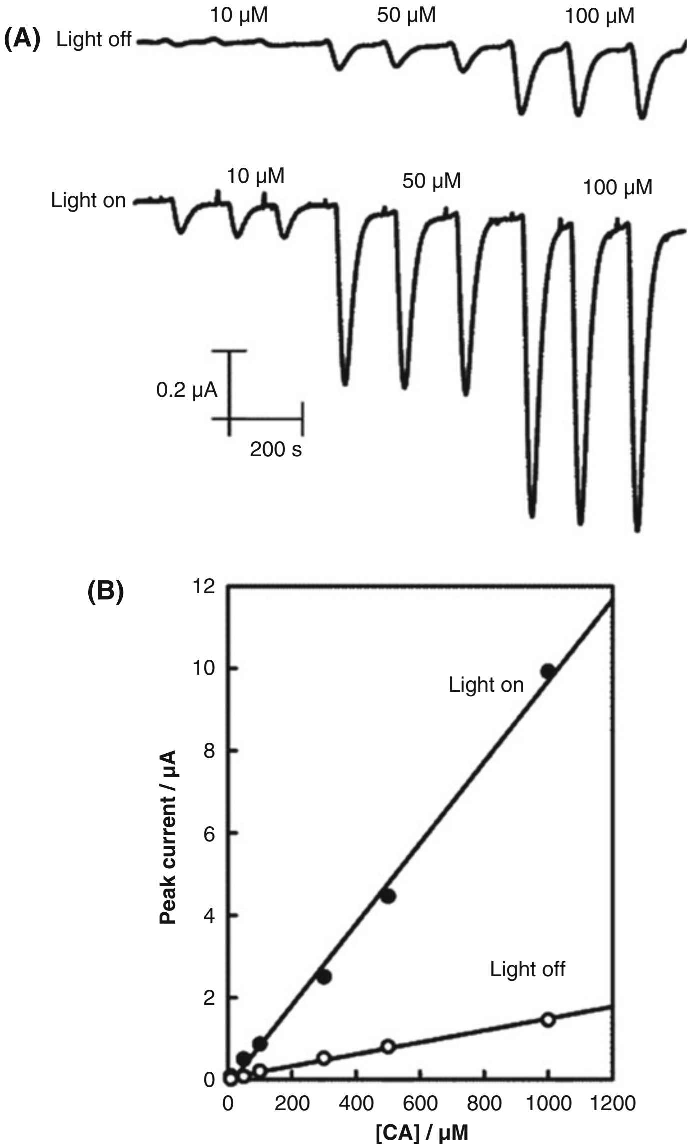

Fig. 7.15 (**a**) Amperometric responses for the analyses of 10, 50, and 100 μM Catechol (CA). (**b**) Calibration curve for CA. Experimental conditions: flow rate 100 mL/min, Ep = −0.1 V (vs Ag/AgCl), and light power 120 W. (Reproduced with permission from Zen et al. 2003a)

Table 7.7 List of Copper (Cu) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	References
CuNPs/NGO	Amperometry	Glucose	NaOH	1–1803 µM	0.44 µM	Sivasankar et al. (2018)
CuS/GCE	Amperometry	H_2O_2	pH 7.4, PBS	10–1900 µM	1.1 µM	Dutta et al. (2014)
CuO/Au	Amperometry	H_2O_2	pH 7.2, PBS	50–750 µM	5 µM	Gu et al. (2010)
Cu/CHIT/CNT/GC	Amperometry	H_2O_2	pH 7, PBS	0.05–12 mM	0.02 mM	Wang et al. (2008)
Cu/poly (melamine)-SPCE*	FIA	H_2O_2	pH 7, PBS	1 µM-10 mM	0.21 µM	Baskar et al. (2013)
Cu^n-$SPE_{100\text{-nm}}$	FIA	Amino acids	pH 8, PBS	5–500 µM	24 nM-2.7 µM	Zen et al. (2004)
Cu@Cu_2O	Amperometry	Glucose	NaOH	50 µM to 8 mM	15 µM	Ling et al. (2018)
CuSPEs	FIA	Catechol	pH 7.4, PBS	10–200 µM	3 µM	Zen et al. (2002a)
CuSPEs	FIA	Dopamine	pH 7.4, PBS	10–300 µM	5 µM	Zen et al. (2002a)
CuSPEs	FIA	o-diphenols	pH 8, PBS	10–100 µM	0.84 µM	Zen et al. (2003a)

CuNPs/NGO copper nanoparticles/nitrogen doped graphene oxide, *CuS/GCE* copper sulfide modified glassy carbon electrode, *CuO/Au* copper oxide modified gold, *Cu/CHIT/CNT/GC* copper chitosan carbon nanotube modified glassy carbon electrode, *Cu/poly(melamine)-SPCE** copper polymelamine modified preanodized screen printed carbon electrode, Cu^n-$SPE_{100\text{-}nm}$ copper modified screen printed electrode, *Cu@*Cu_2O copper oxide modified on copper, *CuSPEs* copper screen printed electrodes, *FIA* flow injection analysis H_2O_2-hydron peroxide, *NaOH* sodium hydroxide, *PBS* phosphate buffer solution

7.3 Precious/Noble Metal Electrodes (Pd, Ag, Au, Pt)

7.3.1 Palladium (Pd)

Palladium metal has properties similar to those of platinum (Campbell and Compton 2010). Determination of dissolved dioxygen (O_2) through electrocatalytic oxygen reduction reaction at a preanodized screen-printed carbon electrode (SPCE*) modified with Pd nanoparticles (PdNPs) was explored by Zen and his co-workers (Yang et al. 2006). They also electrochemically deposited copper–palladium alloy nanoparticle onto the screen-printed carbon electrodes (SPE/Cu–Pd) for the electrocatalytic hydrazine (NH_2-NH_2) sensor (Yang et al. 2005). Gupta and Prakash 2014a developed a method that took only 90 seconds to prepare uniform sized of Pd nanocubes electrochemically without using template (Gupta and Prakash 2014a). Electrochemically synthesized palladium nanocubes were used for chronoamperometric detection of cefotaxime drug. It was also confirmed that PdNPs can be utilized as highly efficient catalyst toward the reduction of hydrogen peroxide (H_2O_2) (Ning et al. 2017). Some examples for the Palladium (Pd) electrode-based sensors are listed in Table 7.8.

7.3.2 Silver (Ag)

Silver is a relatively abundant metal that is less expensive than gold and platinum. Silver oxide electrodes have been used for detection of halides in the field of biomedical, food, and environment samples. Zen's group developed a single strip three-electrode configuration using silver working, auxiliary, and reference electrodes, and that was used for simultaneous determination of halides, such as chloride, bromide, and iodide in aqueous solutions (Chiu et al. 2009). Moreover, the same group also developed a powerful tool based on Ag electrodes for the measurement of trace levels of heavy metals, such as, lead ion (Pb^{2+}) (Zen et al. 2002b), mercury (Hg) (Chiu et al. 2008), and H_2O_2 (Chiu et al. 2011). Silver metal possesses the highest electrical conductivity but is susceptible to oxidation. The stability of silver across a range of pH and potentials is outlined in Fig. 7.16.

Therefore, capping agents/stabilizing ligands were largely used to improve the stability of the AgNPs. For example, SiO_2 was functionalized with two different carboxylate ligands to stabilize silver nanoparticles, and used as electrochemical sensors for non-enzymatic H_2O_2 and glucose detection (Ensafi et al. 2016). Raymundo-Pereira et al. (2016) prepared nano-carbons-silver nanoparticle composites for sensitive estimation of antioxidant activity (Raymundo-Pereira et al. 2016). Silver oxides in silver-reduced graphene oxide (Ag-rGO) nanocomposites showed an electrocatalytic and electrosensing activity for hydroquinone (H_2Q) and ascorbic acid (AA) (Bhat et al. 2015). AgO was also employed for detection of cefotaxime (Gupta and Prakash 2014c) and nitrite (Gupta and Prakash 2014b). Some examples for the Silver (Ag) electrode-based sensors are listed in Table 7.9.

7.3.3 Gold (Au)

Gold is also an efficient electricity conductor and is known for its biological applications. Due to the good conductivity and chemical inertness, gold electrode becomes an attractive material in electrochemical analysis. Many publications revealed that the electrocatalytic ability of gold is dramatically increased with the decreasing particle size (Burke and Nugent 1998). Thus, AuNPs-modified electrode led to many developments in the enzyme-based biosensors, DNA sensors, and immunosensors. The flat gold electrode is one of the favorable characters to develop the immunosensor; since thiol, pyridine, and amine groups are relatively easy to be modified onto the surface of gold.

Table 7.8 List of Palladium (Pd) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	References
SPE*/Pd	CV	O_2	pH 7.4, PBS	1–8 ppm	–	Yang et al. (2006)
SPE/Cu–Pd	FIA	Hydrazine	pH 7.4, PBS	2–100 μM	270 nM	Yang et al. (2005)
ITO/Pd nanocubes	Chronoamperometry	Cefotaxime	pH 7.2, Tris buffer	0.1–0.7 μM	0.062 μM	Gupta and Prakash (2014a)
Pd/$ZnFe_2O_4$/rGO	Amperometry	H_2O_2	pH 7, PBS	25 μM –10.2 mM	2.12 μM	Ning et al. (2017)

SPE/Pd* palladium modified preanodized screen printed carbon electrode, *SPE/Cu–Pd* copper–palladium alloy nanoparticle onto the screen-printed carbon electrodes, *ITO* indium tin oxide, *Pd/*$ZnFe_2O_4$*/rGO* palladium, zinc-iron oxide-reduced graphene oxide

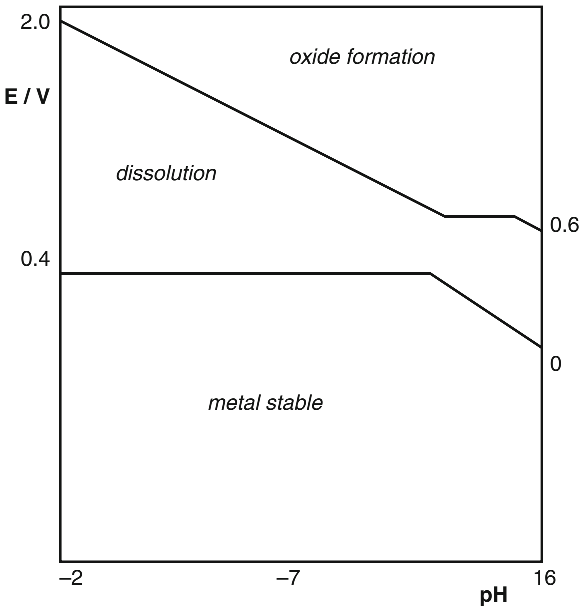

Fig. 7.16 Silver metal stability reported across a range of pH and potential values. (Reproduced with permission from Campbell and Compton 2010)

Our group utilized Au-S biding for the development of various biochemical sensors including a rapid electrochemical assay for L-dopa in urine samples (Viswanathan et al. 2007), a DNA electrochemical sensor for the detection of *Escherichia coli* O157 (Fig. 7.17) (Liao and Ho 2009), a rapid and sensitive diagnostic method for human lung cancer maker enolase 1 (ENO1) (Figs. 7.18 and 7.19) (Ho et al. 2010a), a biotin sensor (Ho et al. 2010b), a formaldehyde and glucose sensor (Tanwar et al. 2012), a Cu ion and H_2O_2 sensor (Tanwar et al. 2013), a nonenzymatic detection of H_2O_2 and glucose (Jou et al. 2014), and Tyramine sensor (Li et al. 2017).

To date, many commercial disposable screen-printed gold electrodes are available for electroanalysis. As a typical example, a highly toxic heavy metal ion chemical sensor, based on poly(L-lactide) stabilized gold nanoparticle (PLA–AuNP), was developed for the detection of As(III) by differential pulse anodic stripping voltammetry (Song et al. 2006).

Kesavan et al. (2012) synthesized β-D-Glucose capped gold nanoparticles (Glu-AuNPs) on an aminophenyl grafted GC electrode for the selective determination of norepinephrine (NEP) in the presence of uric acid (UA). The schematic representation of the interactions between NEP and Glu was shown in Fig. 7.20 (Kesavan et al. 2012). Huang's group also developed a highly sensitive detection method for copper using nanoporous gold electrode via mercury-free anodic stripping voltammetry (ASV) (Huang and Lin 2009). Some examples for the gold (Au) electrode-based sensors are listed in Table 7.10.

Table 7.9 List of Silver (Ag) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	References
Screen-printed silver strip	LSV	Chloride	pH 6, PBS	0.1–20 mM	18.83 μM	Chiu et al. (2009)
Screen-printed silver strip	LSV	Bromide	pH 6, PBS	0.01–20 mM	2.95 μM	Chiu et al. (2009)
Screen-printed silver strip	LSV	Iodide	pH 6, PBS	0.01–20 mM	3.05 μM	Chiu et al. (2009)
AgSPE	SWV	Pb^{2+}	pH 3, KNO_3/HNO_3	5–80 ppb	0.46 ppb	Zen et al. (2002b)
AgSPE	LSV	Hg	H_2SO_4	500–4500 ppb	98 ppb	Chiu et al. (2008)
SPAgE-Bi^{nano}	CV	H_2O_2	pH 7, PBS	100 μM –5 mM	56.59 μM	Chiu et al. (2011)
AgNPs-ligand 1	Amperometry	H_2O_2	pH 7, PBS	3.6–1460 μM	0.28 μM	Ensafi et al. (2016)
AgNPs-ligand 2	Amperometry	H_2O_2	pH 7, PBS	1.0–1618 μM	0.094 μM	Ensafi et al. (2016)
AgNPs-ligand 1	Amperometry	Glucose	NaOH	4.28–5492 μM	0.62 μM	Ensafi et al. (2016)
AgNPs-ligand 2	Amperometry	Glucose	NaOH	1.43–3202 μM	0.33 μM	Ensafi et al. (2016)
GC/PC-Ag	DPV	Gallic acid	pH 7, PBS	0.5–8.5 μM	63.3 nM	Raymundo-Pereira et al. (2016)
Ag/Ag_2O-rGO/GCE	CV	Hydroquinone	pH 7, PBS	–	–	Bhat et al. (2015)
Ag/Ag_2O-rGO/GCE	DPV	Ascorbic acid	pH 7, PBS	–	–	Bhat et al. (2015)
Ag–DTZH	Chronoamperometry	Cefotaxime	pH 7.2, Tris buffer	0.1–0.8 μM	15.32 nM	Gupta and Prakash (2014c)
Ag–PTZH	Amperometry	Nitrite	pH 7.2, Tris buffer	5–45 nM	2.3 nM	Gupta and Prakash (2014b)

AgSPE silver screen printed electrode, *SPAgE-Binano* Screen printed silver-nano bismuth electrode, *AgNPs* silver nanoparticles, *GC* glassy carbon, *GCE* glassy carbon electrode, *Ag/*Ag_2O*-rGO/GCE* silver, silver oxide-reduced graphene oxide modified glassy carbon electrode, *Ag–DTZH* silver colloids dithizone (DTZ)/its oxidation products (DTZH), *Ag–PTZH* nanoscale silver capped with phenothiazine and its oxidation product (PTZH), *CV* cyclic voltammetry, *LSV* linear sweep voltammetry, *SWV* square wave voltammetry, and *DPV* differential pulse voltammetry

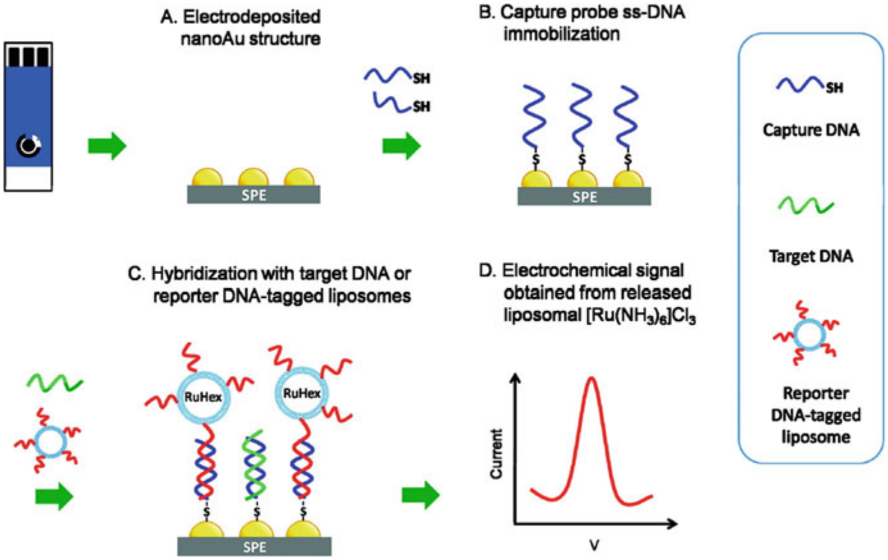

Fig. 7.17 Flow diagram displaying the concept behind the competitive assay-based performance of the developed genosensor. (Reproduced with permission from Liao and Ho 2009)

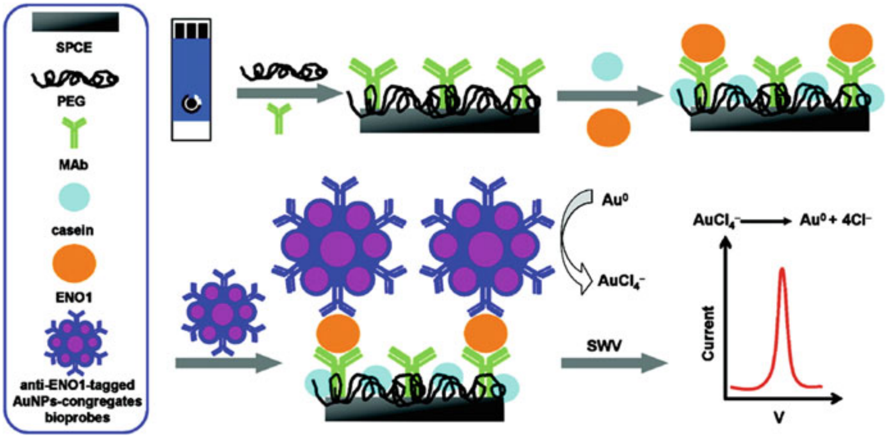

Fig. 7.18 Operation of the electrochemical immunosensor for the detection of enolase 1. (Reproduced with permission from Ho et al. 2010a)

7.3.4 Platinum (Pt)

Platinum is more expensive than both silver and gold. Platinum wires are often employed in electroanalysis owing to their excellent stability, chemical inertness, and high conductivity (Campbell and Compton 2010). Pt electrodes have been long

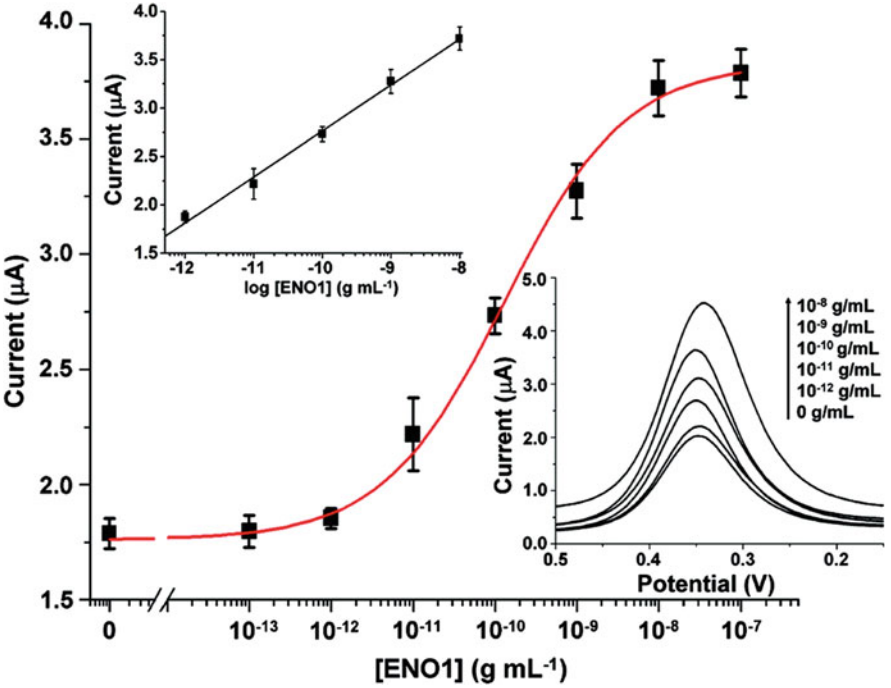

Fig. 7.19 Dose-response curve for the enolase 1 target using the PEG-modified SPCE. Insets: (lower right) Square wave voltammograms for the electrochemical detection of enolase 1 upon serial dilutions of the enolase 1 stock from 10^{-8} to 10^{-12} g/mL; (upper left) linear fit to the central data of main curve. (Reproduced with permission from Ho et al. 2010a)

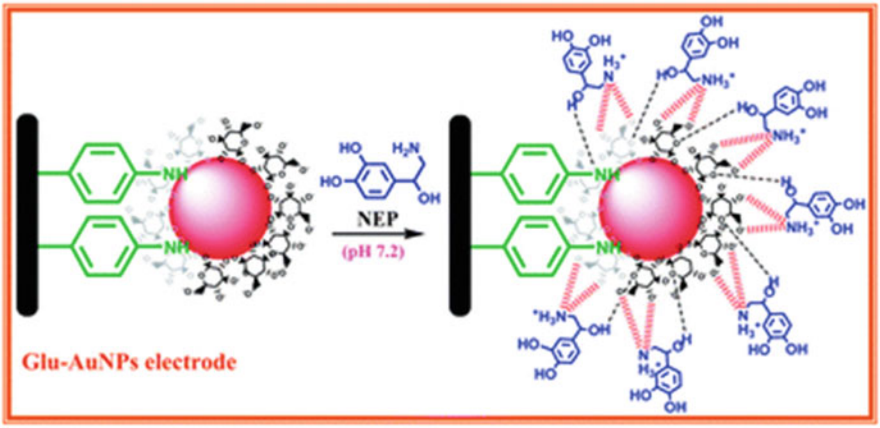

Fig. 7.20 Interactions between norepinephrine and Glu-AuNPs electrode. (Reproduced with permission from Kesavan et al. 2012)

Table 7.10 List of gold (Au) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	References
GNEE	FIA	L-dopa	pH 7, PBS	5–300 ng/mL	3 ng/mL	Viswanathan et al. (2007)
Nano Au/SPE	SWV	E-coli O157	Tris-HCl, pH 7.4	1–106 fM	0.75 aM	Liao and Ho (2009)
AuNP	SWV	Enolase 1	HCl	10^{-8}–10^{-12} g/mL	2.38 pg/mL	Ho et al. (2010a)
AuNP/SPGE	SWV	Biotin	$K_4Fe(CN)_6$-$K_4Ru(CN)_6$	1×10^{-3}–1×10^{-10} M	1.6×10^{-10} M	Ho et al. (2010b)
Au-calix-PPY	LSV	Formaldehyde	NaOH	–	–	Tanwar et al. (2012)
Au-calix-PPY	LSV	Glucose	NaOH	–	–	Tanwar et al. (2012)
Au-PANI-calix	SWV	Cu^{2+}	pH 7.12, PBS	1 μM–5 mM	10 nM	Tanwar et al. (2013)
Au-PANI-calix	Amperometry	H_2O_2	pH 7, PBS	5–50 μM	1 μM	Tanwar et al. (2013)
CNT@GNB	Amperometry	Glucose	NaOH	1–10 mM	0.07 mM	Jou et al. (2014)
CNT@GNB	CV	H_2O_2	pH 7.2, PBS	1–100 μM	0.8 μM	Jou et al. (2014)
SPCE/PEDOT: PSS/AuNP/1-m-4-MP	DPV	Tyramine	NaOH	5–100 nM	2.31 nM	Li et al. (2017)
PLA-AuNP/SPE	DPSV	As^{3+}	HCl	0–4 ppm	0.09 ppb	Song et al. (2006)
Glu-AuNPs/GCE	Amperometry	Norepinephrine	pH 7.2, PBS	30 nM-0.1 mM	0.147 nM	Kesavan et al. (2012)
Nanoporous gold	ASV	Cu^{2+}	$NaNO_3$	0.1–5 μg L^{-1}	0.002 μg L^{-1}	Huang and Lin (2009)

GNEE gold nanoelectrode ensembles, *Nano Au/SPE* nanogold screen printed electrode, *AuNP* gold nanoparticles, *AuNP/SPGE* gold nanoparticles screen printed graphite electrode, *Au-Calix-PPY* gold calix polypyrrole, *PANI* polyaniline, *CNT@GNB* Gold nanobone/carbon nanotube hybrids, SPCE/PEDOT: PSS/AuNP/1-m-4-MP-PEDOT:PSS/AuNPs/1-methyl-4-mercaptopyridine modified screen-printed carbon electrode with molecularly imprinted polymer, *PLA-AuNP/SPE* PLA capped gold nanoparticle modified screen printed electrode, *Glu-AuNPs/GCE* glucose capped gold nanoparticle modified screen printed electrode, *CV* cyclic voltammetry, *LSV* linear sweep voltammetry, *SWV* square wave voltammetry, and *DPV* differential pulse voltammetry

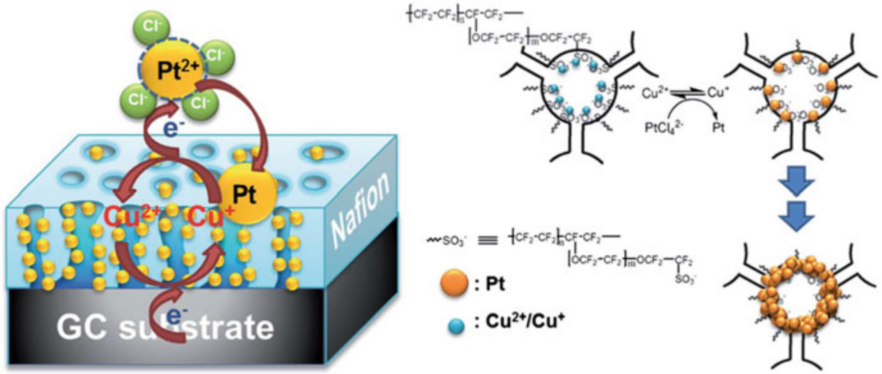

Fig. 7.21 Schematics of the process for Cu^+ assisted formation and self-assembly of Pt nanoparticles in the micro-framework of Nafion. (Reproduced with permission from Huang 2014)

used as a working electrode in energy generation field, such as methanol oxidation, oxygen reduction, and hydrogen evolution. Jing-Fang Huang (2008) developed a simple and effective way to prepare a highly stable mesoporous platinum electrode with large surface area, the as-prepared PtNPs were utilized for developing non-enzymatic glucose sensors (Huang 2008).

A facile electrochemical followed by chemical (EC) catalytic process, involving a Cu^+ mediated Pt reduction (CMPR), was developed by Huang et al. (Huang 2014). The proton conducting polymer nafion's porosity was utilized as a template for preparation of nanostructured mesoporous platinum composites for non-enzymatic determination of glucose (Fig. 7.21). Pt electrode has also used in gas sensor. Zen's group developed formaldehyde gas sensor based on platinum working electrode, screen printed edge band micro carbon electrodes were used for deposition of homogeneous PtNPs, and Nafion polymer was used as a solid electrolyte. The sensor setup was shown in Fig. 7.22. The results suggested that it is possible to monitor gaseous formaldehyde continuously down to the ppb level with the present approach (Chou et al. 2010). Some examples for the Platinum (Pt) electrode-based sensors are listed in Table 7.11.

7.4 Conclusion

Metals, metal oxides, and metal sulfides have been used for construction of various chemically modified electrodes for the use of developing electrochemical sensors or biosensors. With this chapter, we provide a summary on several electrochemical sensing processes with many types of analytes. All the aforementioned sensors prove the ideality and benefit of metal nanomaterials. However, designing and developing new types of metal nanoparticles (MNPs) for electrochemical-sensor applications with good stability and selectivity remains a challenge. Electrochemical application

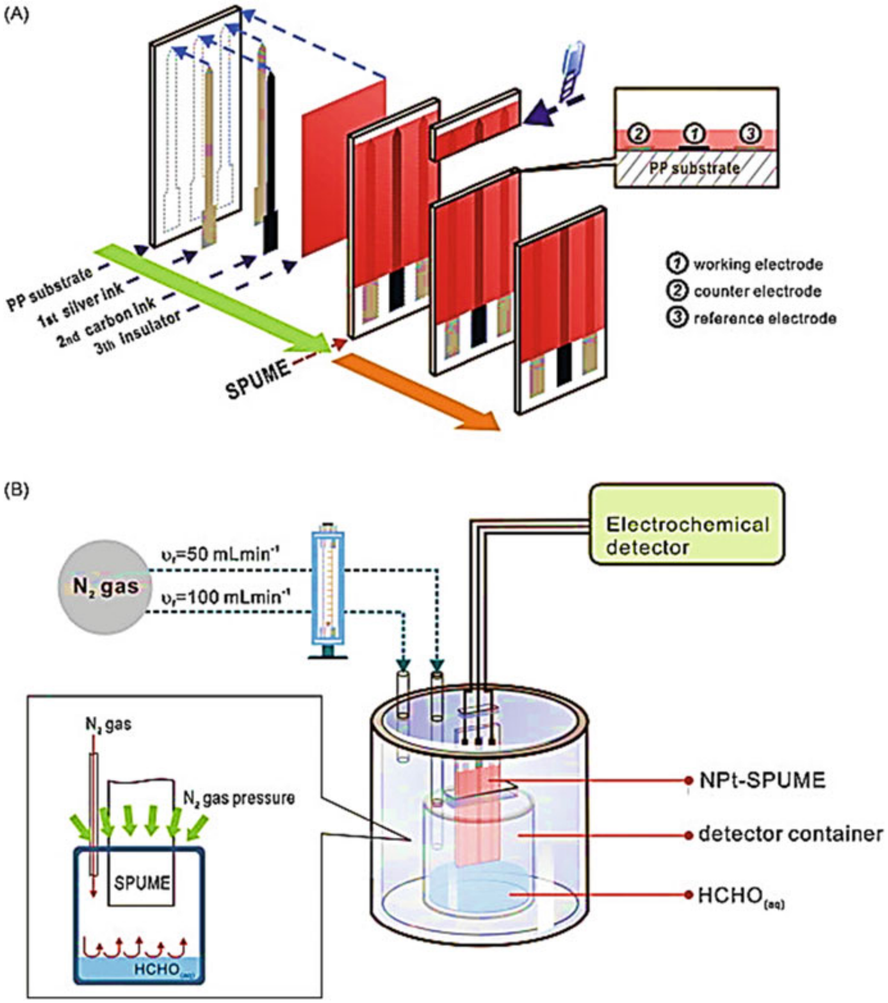

Fig. 7.22 (**a**) The structure of the SPUME assembly with a built-in three-electrode configuration and (**b**) schematic representation of the detecting system. (Reproduced with permission from Chou et al. 2010)

Table 7.11 List of Platinum (Pt) electrode-based sensors

Electrode material	Detection method	Analyte	Electrolyte	Linear range	Detection limit	References
PtNPs	Amperometry	Glucose	pH 7.4, PBS	0.1–1.5 mM	–	Huang (2008)
NF(Pt$_{nano}$)/GC	Amperometry	Glucose	pH 7.4, PBS	0.1–20 mM	–	Huang (2014)
NPt-SPUME	SWV	Formaldehyde	Gas phase	0–5.1 ppm	80 ppb	Chou et al. (2010)

PtNPs Platinum nanoparticles, *NF(Pt$_{nano}$)/GC* Pt–nanoparticle-embedded Nafion composites modified glassy carbon, *NPt-SPUME* platinum-deposited screen-printed edge band ultramicroelectrode, *SWV* square wave voltammetry of metal nanomaterials in environmental and biological/biomedical monitoring are still evolving. Numerous efforts are required to design many other new MNPs, such as highly stable nanostructured copper material, metal organic frame work (MOF), or metal based covalent organic frame work, to be employed in the development of various biosensors that function efficiently at biological pH 7.4 and physiological condition. The application of these materials should enable strong driving forces for the development of more advanced electrochemical-sensor systems. At last, we must be aware that the renovation of lab sensor to an integrated self-powered portable or wearable device is in high demand, a robust chemically modified electrodes therefore become indispensable.

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