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REVIEW ARTICLE

Electrochemical nonenzymatic sensing of glucose using advanced nanomaterials

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Abstract
An overview (with 376 refs.) is given here on the current state of methods for electrochemical sensing of glucose based on the use of advanced nanomaterials. An introduction into the field covers aspects of enzyme based sensing versus nonenzymatic sensing using nanomaterials. The next chapter cover the most commonly used nanomaterials for use in such sensors, with sections on uses of noble metals, transition metals, metal oxides, metal hydroxides, and metal sulfides, on bimetallic nanoparticles and alloys, and on other composites. A further section treats electrodes based on the use of carbon nanomaterials (with subsections on carbon nanotubes, on graphene, graphene oxide and carbon dots, and on other carbonaceous nanomaterials. The mechanisms for electro-catalysis are also discussed, and several Tables are given where the performance of sensors is being compared. Finally, the review addresses merits and limitations (such as the frequent need for working in strongly etching alkaline solutions and the need for diluting samples because sensors often have analytical ranges that are far below the glucose levels found in blood). We also address market/technology gaps in comparison to commercially available enzymatic sensors.

Keywords Electrochemical sensors · Bimetallic nanoparticles · Electrocatalysis · Nonenzymatic sensing · Nanoporous · Glucose biosensor · Transition metal oxides · Glucose oxidation · Carbon nanomaterials · Diabetes management

Introduction

Diabetes mellitus is a chronic metabolic disorder, which is one of the most common and deadliest diseases and it is affecting by several millions of people worldwide. According to the latest report from the World Health Organization (WHO) and the International Diabetes Federation, an estimated 422 million people were living with diabetes and it is going to rise to 642 million by 2030. Precise and tight monitoring of blood glucose level is essential to manage diabetes effectively. With this huge demand, it is estimated that the 85% of the biosensor market is dominated by the analytical devices for blood glucose detection. Quantitative determination of glucose is also important in various fields such as food industry, fuel cells, environmental and pharmaceutical industries. With many important applications of glucose, various methods have been applied for the quantitative detection of glucose. Electrochemical sensors are the industry standard for glucose sensing because these sensors exhibit low detection limits, higher reliability, rapid response, operational simplicity, and are of much lower cost compared to the sensors based on other detection mechanisms. Over the past two decades the progression of non-enzymatic glucose sensors has risen at a considerable rate. The fabrication of a wide variety of nanomaterials has introduced an excess of selective and highly responsive glucose sensors. In 2013 and 2014 two extensive critical reviews of nonenzymatic electrochemical glucose sensors were published [1, 2]. In these, nonenzymatic systems are briefly discussed. In this review, we hope to assess the current situation with respect to the practical application of non-enzymatic glucose sensors. With superiority of good sensitivity and novel fabrication methods, extensive efforts have been made to explore high-performance non-enzymatic sensors. It was confirmed by the increasing number of relevant papers in the past few years are shown in Fig. 1.

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Enzyme based sensing: advantages and drawbacks

The history of electrochemical biosensors research is an excellent example of how a very simple and elegant idea resulted in an innovative breakthrough in biomedical and food industry, which is currently influencing all areas of our life. In 1962, Clarks and Lyons proposed an electrochemical oxygen electrode coupled with glucose oxidase (GOD) enzyme incorporated on dialysis membrane to demonstrate the capability to quantitatively measure glucose in aqueous media [3]. The first enzyme electrode was developed by Updike and Hicks by covering the Clarks oxygen electrode with polyacrylamide gel membrane containing glucose oxidase enzyme for the rapid and quantitative determination of glucose [4]. Guilbault and Montalvo used a glass based pH electrode with immobilized urease to measure urea concentration [5]. Nilsson et al. reported the first potentiometric glucose assay by coupling GOD with a pH meter [6].

The commercially available enzymatic sensors are operated based on the catalytic activity of the immobilized enzyme. Fast and efficient cyclic regeneration process is the basic criteria of an enzyme for the proper catalytic activity to take place [7]. The regeneration can occur either by natural co-factors/mediators or by additional compounds such as artificial mediators. The mediator based approach acts as an indirect route for monitoring the catalytic activity of the enzyme. Based on the evolution of the enzyme based biosensing schemes, the biosensors can be classified in three generations. First generation glucose biosensors are based on the consumption of molecular oxygen (O_2) or generation of hydrogen peroxide (H_2O_2). The decrease in concentration of O_2 is measured using Clark's oxygen electrode, or the increase in the concentration of H_2O_2 is measured by applying a constant potential to the electrode. H_2O_2 based sensing has the advantage that the sensor can be miniaturized. The major drawbacks associated with this generation biosensors, they are highly dependent on the oxygen concentration and a large oxidation potential is required to oxidize H_2O_2. To overcome the drawbacks of the first-generation glucose biosensors, the natural mediators are replaced with artificial mediators [8, 9]. With the use of mediators, the glucose measurements are made independent of the partial pressure of oxygen and can be carried out at a lower potential that does not produce the interfering reactions from the other electroactive species. The drawbacks associated with these second-generation biosensors are that the mediator leakage affects the sensor performance. A further improvement in glucose sensing is achieved by eliminating the usage of mediator. The third-generation glucose sensors facilitate the direct electron transfer between the redox center of an enzyme and the electrode, leading to a high sensitivity and reproducibility [10–12]. The chemical-relay groups anchored GOD networks increases the electron transfer kinetics and offers high output current [13]. Figure 2 explains the mechanism of first, second and third generation glucose biosensors.

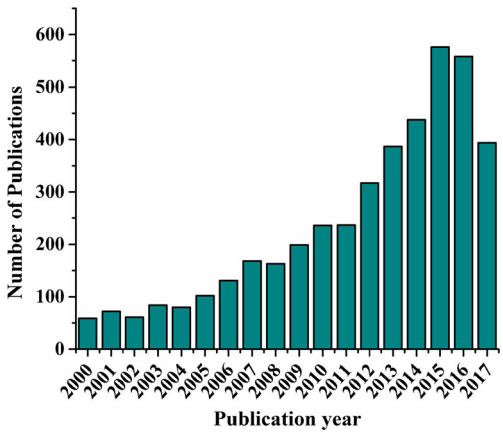


Fig. 1 Numbers of publications in the recent period about glucose biosensors based on records from Web of Science with the keyword "Electrochemical glucose sensors"

The first glucose monitoring device (Ames Reflectance Meter) emerged in 1969. It was based on the catalytic activity of glucose oxidase enzyme and evaluated glucose levels in a 50 μL blood sample. Later in the 1970s, self-monitoring of diabetes became accessible with the construction of the personal glucose monitor, which allowed multiple capillary blood glucose tests, insulin dose adaptation and, thus, better glucose control in terms of both hyper and hypoglycemia. Self-monitoring of blood glucose (SMBG) devices were widely introduced in the early 1980s and became commonplace in the 1990s as a replacement for urine testing to allow diabetic patients to assess their current level of glycaemia. Patients were trained how to use these SMBG readings to guide their decisions for immediate treatment. It has been shown to be an essential component in the intensive management of type 1 diabetes (T1D).

Enzymatic glucose biosensors have dominated the glucose sensor industry for more than twenty years. However, many critical drawbacks hinder its further development. The lack of chemical, thermal stability and the cost of the GOD prevent the enzymatic sensors in continuous monitoring applications. Even though GOD is more stable when compared to other enzymes, but still it is restricted to pH ranges from 2 to 8, the temperature below 44 °C and at ambient humidity levels. Apart from that GOD gets easily deactivated by a variety of detergents such as in the presence of sodium n-dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide at low and high pH respectively. Despite the contributions

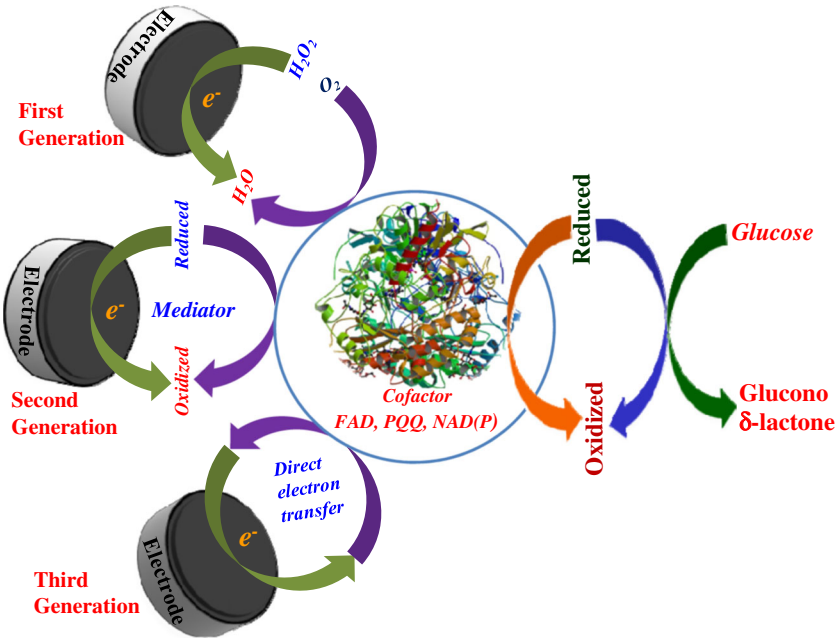


Fig. 2 Summary of enzymatic glucose oxidation mechanisms in the first, second and third generation biosensors

having alleviated the problem of enzyme-based electrodes to a certain extent, the glucose sensor based on GOD is easily exposed to harsh thermal and chemical conditions during fabrication, storage, and usage. In addition, as diabetes continues to rise in the developing countries, the glucose biosensor with a high fabrication cost and short shelf-life become less viable.

Nonenzymatic sensing with nanomaterials based electrodes

Considering the intrinsic drawbacks of insufficient stability and reasonable repeatability for enzyme-based biosensors, one moves interest to develop new electrochemical glucose sensors without using any biological catalysts, specifically non-enzymatic sensors. Functionalized nanomaterials act as catalyst or immobilization platform or as electro-optical labels for enhancing the sensitivity and specificity of the detection [14–16]. The use of non-enzymatic electrodes based on the direct electro-oxidation of glucose promises the fourth-generation glucose sensor. These sensors were fabricated by incorporating nanostructured metal [17, 18] or metal oxide [19–21] on the electrode surface and they have a significantly improved electrocatalytic activity towards glucose comparable to enzyme counterparts. Choosing the right catalyst for the direct electrochemical oxidation of glucose is the key step involved in the design of nonenzymatic sensors. Through extensive research, it has been well-established that certain nonenzymatic electrochemical glucose sensors have a very high sensitivity, specificity and favorable long-term storage stability [22, 23]. They also offer numerous advantages like cost effectiveness, stability, reproducibility and simplicity in development and avoids complex enzymatic immobilization techniques. Nonenzymatic electrocatalysts come in various forms such as metals, metal oxides, bimetallic/alloys, carbon nanomaterials, metal/metal oxide heterogeneous nanocomposites, metal/carbon nanomaterial based composites layered double oxides.

Metal and metal oxide based glucose sensors

Research in the field of biosensor has advanced significantly with the development of nanotechnology. Various metal/metal oxide based electrodes have been employed for application in glucose sensors over the past several decades [24–26]. The oxidation mechanism involved in the nonenzymatic sensors is poorly understood. Researchers came up with different possible mechanisms. Studies revealed that the mechanism of direct electrooxidation of glucose varied considerably depending on the catalyst used on the electrode [10]. With respect to this, various metals, metal oxides have been thoroughly investigated for the electrochemical oxidation mechanism for glucose under different reaction conditions. The following subsections have discussed about the electrochemical glucose sensors with various electrode materials such as different categories of noble metals/metal oxides, transition metals/metal oxides, bimetallic/alloys and carbon metal/metal oxide nanocomposites.

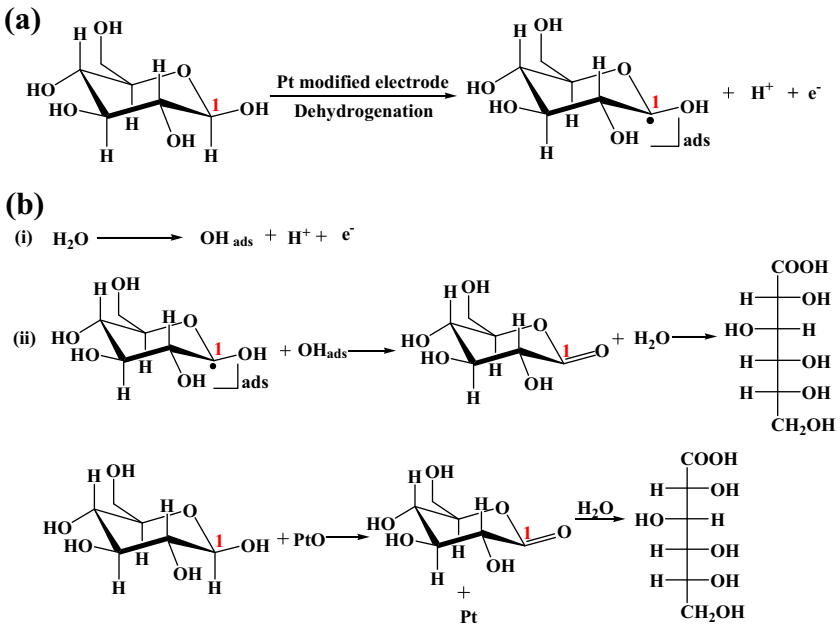
Noble metals

In this subsection, we will discuss the oxidation mechanisms, benefits, drawbacks, and advances in common metal-based glucose sensors. The noble metal nanoparticles (NP) may be the ideal candidate material for substitution of enzymes. The reasons are as follows: (i) noble metal NP have a good electrical performance and biocompatibility which results in potential application in bioelectronics. (ii) They possess unique catalytic properties, which can catalyze a wide range of organic reactions with lower activation barrier. The first electrochemical oxidation of glucose was studied one hundred years ago by Walther Loeb in H_2SO_4 electrolyte using lead anode [27]. After that, a large amount of work was carried out on the direct electrooxidation of glucose on platinum and gold electrodes in acidic, neutral and basic media. A possible mechanism proposed and proven by many researchers on the platinum electrode regardless of pH of the solution is the production of glucono-δ-lactone and its further hydrolyses to gluconic acid (Scheme 1).

In the first step, glucose is adsorbed on a platinum surface followed by hydrogen abstraction at the C1 position. In the next step, the water dissociates to produce hydroxide anions followed by the subsequent oxidation of adsorbed glucose by the adsorbed hydroxide anions. In the final step, glucose gets oxidize by PtO, which is formed by the evolution of oxygen [28, 29]. Park et al. used a mesoporous platinum electrode to develop a method for nonenzymatic, electrochemical monitoring of glucose in human whole blood and serum [30]. Different platinum nanostructures such as Pt nanoporous structures [31, 32], nanoflowers [33], nanotubule array [34], nanoparticle [35] and dendritic platinum nanostructures [36] have been extensively studied for direct electrooxidation of glucose.

Gold electrodes displayed better electrocatalytic activity than the platinum electrodes. This might be due to the filled d orbitals of gold and the poor adsorption/electro-adsorption of organic species participating in the electrooxidation on the gold surface [37, 38]. Au-NP may also be used to enhance charge transport through conductive matrices, and thereby accelerate bio-electrocatalytic processes. Many Au nanomaterials based sensors were developed, for example, Au nano coral [39], porous Au [40], urchin-like Au submicrostructures [18], nanoporous Au [41], Au nanowire arrays [42], Au nanotube arrays [43], Au nanoparticles [44], Au nano fract film [45] and 3D gold film electrode [46, 47]. But the mechanism of glucose oxidation on gold electrodes is poorly understood.

Palladium is a very important metal for electro-catalysis due to its various advantageous properties. Different methodologies have been investigated to incorporate Pd particles into polymer matrices, porous metal/metal oxide substrates and conducting carbon nanomaterials for the construction of Pd modified electrodes. Up to now many efforts have been stimulated toward the design and synthesis of Pd NP owing to their size- and shape- dependent electrocatalytic performance. Here we are mentioned some of the Pd based nonenzymatic glucose sensors, they are Pd nanocubes [48], Pd nanotubes/glassy carbon electrode (GCE) [49], Pd nanoparticles incorporated inside the poly(3,4-ethylenedioxythiophene) nanofibers (Pd-



Scheme 1 Mechanism of glucose oxidation on Pt electrode [28]

PEDOTn) and tested for glucose sensing application [50]. Few of the important literature on nonenzymatic glucose sensors based on noble metal are listed in the Table 1.

Following is the major problems encountered in the direct electrooxidation of glucose on the noble metal electrodes [30],

1) The activity of the noble metal is often impaired by the irreversibly adsorbed oxidation intermediates and the adsorbed chloride ions.
2) The sensitivity on the noble metal electrodes is relatively low due to the sluggish kinetics.
3) The selectivity of the sensor is also poor since some endogenous interfering species and other sugars also undergo oxidation in the potential range of glucose oxidation.

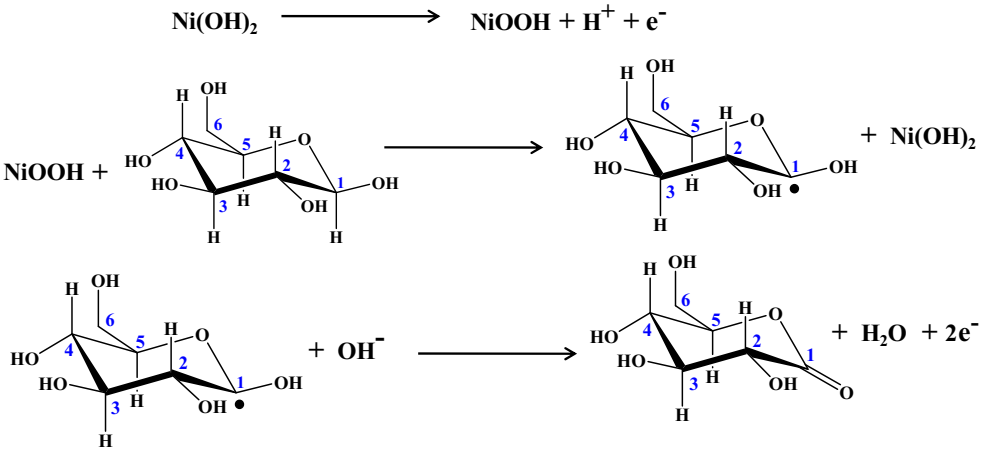
Transition metal/metal oxide, hydroxides, sulfides

Transition metals have been extensively studied for the electrooxidation of glucose. Metals such as Cu, Ni, Mn, Co, Fe and Zn and their oxides [57, 58] and sulfides [59] attracted much attention due to their enhanced catalytic properties. Fleishmann et al. reported the detailed mechanism and the performance of a nickel electrode on the electrooxidation of various organic molecules including glucose [60]. Luo et al. reported that the Ni electrode shows an anodic response corresponding to the oxidation of glucose [61]. Several reports on nonenzymatic sensing prove that the Ni-based electrodes exhibited very high current densities for glucose oxidation [62–64]. Zhao's group established that the oxidation of glucose to gluconolactone on nickel electrode is catalyzed by Ni(III)/Ni(II) redox couple according to the following mechanism [65], it is presented in Scheme 2.

Table 1 Comparison of noble metal based nonenzymatic glucose sensors

Electrode Material	Potential (V)	Linearity (mM)	Sensitivity μA mM^{-1} cm^{-2}	LOD (μM)	Response time	Ref.
Urchin Au sub-microstructures	+0.32	0.2–13.2	16.8	10	3 s	[18]
Mesoporous platinum	+0.4	0–10.0	9.6	–	–	[30]
Pt nanoporous	+0.4	0.1–1.5	642.0	–	–	[31]
Pt nanoflowers	+0.03	1.0–16.0	1.87	48	–	[33]
Pt nanotubule array	+0.4	2.0–14.0	0.1	1	–	[34]
Pt nanoparticles	–	0.2–3.2	137.7	5	–	[35]
Dendritic platinum nanostructures	+0.5	1.0–20	12.10	1.2	< 2 s	[36]
Electrochemically roughened platinum	+0.4	1–10	5.67 ± 0.18	0.8	–	[51]
Au branched belt	+0.2	0.05–40	11.9	10	–	[38]
Au nanocoral	+0.2	0.05–30	22.6	10	–	[39]
Porous Au	+0.35	2.0–10	11.8	5	2 s	[40]
Nanoporous Au	−0.15 +0.2	1.0–14.0 0.01–11.0	232.0 66.0	53.2 8.7	5 s	[41]
Au nanowire arrays	−0.4	1.0–10.0	309.0	50	–	[42]
Au nanotube arrays	+0.25	1.0–42.5	1.13	10	–	[43]
Au nanoparticles	+0.25	0.5–8.0	160.0	–	–	[44]
Fractal gold nano-structured film	+0.3 −0.15	0–57.5 0–30.0	– –	0.75 3.6	2 s	[45]
3 D inverse-opal gold film	−0.3	0.005–10.0	46.6	3.2	–	[46]
3D gold film electrode	+0.15	0.002–1.375 1.375–15.0	– –	0.5	–	[47]
3D hierarchical porous Au networks	+0.1	0.001–0.5 4.0–12	–	0.2	< 2	[52]
Au nanowires	+0.35	0.1 5.0	3700	33	–	[53]
Pd nanocubes	−0.05	1.0–10.0	34	–	–	[48]
Pd nanotubes	+0.4	0.005–10.0	6.58	1	–	[49]
Pd-PEDOTn	−0.1	0.04–9.0	24.04	1.6	–	[50]
Pt spheres	+0.4	1–15	66.5	40	–	[54]
AuNP/GA/APBA	–	0.5–50.0	–	25	–	[55]
PdNP/HNT	+0.4	0.001–2.0 2.0–15.0	362.98 86.28	0.425	< 3	[56]

LOD, Limit of detection; *HNT*, Halloysite nanotubes



Scheme 2 Schematic representation of glucose oxidation mechanism on Ni electrode

Various nickel nanostructures have been synthesized and tested towards the oxidation of glucose [66, 67] and they showed very good catalytic activity. Nickel electrodes were extensively studied for its catalytic properties towards the electrooxidation of different organic molecules including glucose in the alkaline medium. Nickel oxide catalyzes the oxidation of glucose by Ni(II)/(III) pair. Ni(II) gets electrochemically oxidized to Ni(III) in an alkaline medium which releases electron resulting in a peak current. At this region, glucose gets oxidized to gluconic acid by Ni(III), which gets reduced to Ni(II) at the same time. Ni(III) species rapidly activates the nickel surface and acts as a strong oxidant, with suitable d-orbitals to rapidly adsorb glucose molecule. Glucose undergoes hydrogen abstraction at the surface to form radical intermediate and reforming the $Ni(OH)_2$ species. The hydroxyl ions in the electrolyte rapidly convert the radical intermediate to gluconolactone.

A tremendous amount of work has been reported on glucose sensors based on nickel oxide nanostructures for the enhancement of the sensor characteristics. NiO modified carbon microspheres are found to have a sensitivity of 30.19 mA mM^{-1} cm^{-2}, that is one among the highest reported. The linear detection range is only up to 1.279 mM and does not meet the physiological range of glucose levels [68]. Yang et al. obtained a high sensitivity response to glucose with nanocomposite of NiO and silicon carbide (SiC) modified GCE in a basic medium [69]. NiO nanoparticles modified graphene showed enhanced capacitance behavior and glucose sensing properties [70]. Zhang et al. studied the sensing ability of electrospun NiO nanofibres on graphene and found that it detects glucose with good sensitivity and selectivity [71]. NiO and Pt modified reduced graphene oxide is found to be an excellent materials for the fabrication of glucose sensors [72]. NiO nanostructures developed by Mu et al. [73], hedgehog NiO nanoparticles [67], NiO hollow spheres [74], porous nickel nanostructures on screen printed electrodes [75], Ni foam [76], NiO on mesoporous carbon [77], NiO on MWCNT [78], NiO nanoflakes [79], NiO microfibers [80], 3D flower-like Ni_7S_6 [81] are among the other developments in glucose sensors based on NiO electro-catalyst.

By looking at the overview of literature on nonenzymatic glucose sensors, it is evident that more economical electro-catalyst without compromising the sensitivity and selectivity have gained considerable attention. Metallic copper based electrodes have been explored due to the catalytic activity and ready availability [82, 83]. Copper oxide, which is a p-type semiconductor with a narrow band gap of 1.2 eV has been widely studied for its electrocatalytic applications [19, 84]. Nonenzymatic glucose biosensors using copper oxide (CuO) gained great attention due to its excellent stability, ease of synthesis and post-synthesis handling, low cost and different redox properties of the oxide at different reaction conditions. The catalytic properties of CuO in the alkaline medium are due to the formation of thermodynamically unstable Cu(III) species. The species responsible is CuOOH formed from CuO that catalyzes the oxidation of glucose molecules [85]. The reported oxidation peak for copper near +0.6 V in an alkaline medium is due to copper(II)/(III) transition [86]. The voltammetric analysis also shows the corresponding reduction peak for the metal oxide. Glucose oxidation occurs at the same region and the fact that during the cycle the reduction peak current decreases with an increase in the concentration of glucose that suggests that Cu(III) is consumed during the oxidation. The other redox peaks for copper are clearly defined with the oxidation to Cu(I) and Cu(II) states, and the corresponding reduction, evident in voltammetric studies, which does not alter in the presence of glucose, suggests that they are not involved in glucose oxidation. The oxidation can be a complete breakage of C-C bonds in glucose to get $12e^-$ which was demonstrated by coulometric technique [82]. This is the reason for the high faradaic current density obtained from nonenzymatic

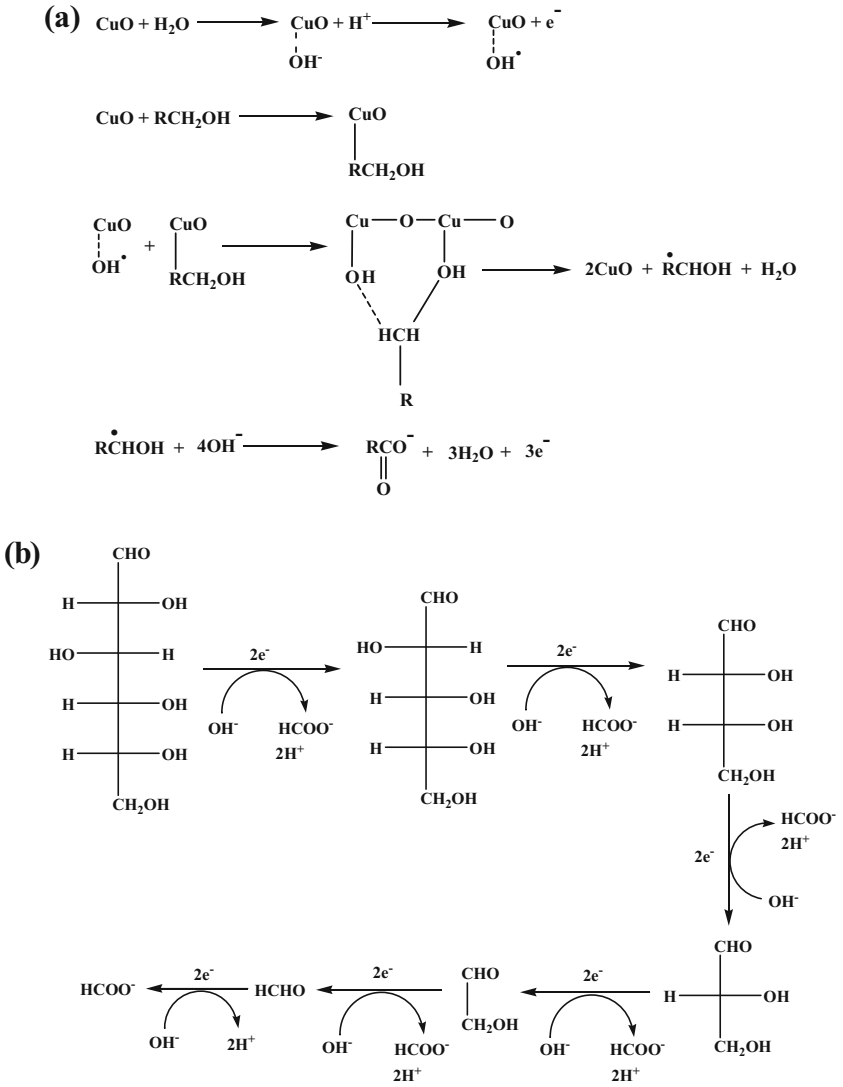
glucose sensors. Xie and co-workers proposed a mechanism for the carbohydrate oxidation on Cu electrode. According to them, the first step is the simultaneous adsorption of the active hydroxyl radicals and carbohydrate onto the electrode surface at the adjacent active sites. In the next step, an adjacent hydroxyl abstracts the hydrogen atom from the C1 carbon of beta-D-glucose and generates an organic radical. This is the rate-determining step in this mechanism. The organic radical further undergoes oxidation in presence of hydroxyl anion to the acid product [87].

Marioli and Kuwana investigated a detailed mechanistic study on initial steps involved in the electrooxidation of glucose on copper electrode. According to them, the oxidation reaction is activated by the deprotonation of the carbohydrate, isomerization to its enediol form and then adsorption on electrode surface followed by oxidation via Cu(I), Cu(II) and Cu(III) surface states [88]. From these two controversial mechanisms, the oxidation of glucose on copper electrodes remains unanswered. But a majority of the studies supports mechanism proposed by Xie and Huber [87] which involves, first the chemisorption of hydroxide ions on CuO surface lattices followed by oxidation of hydroxide to hydroxide radical. Then the glucose moiety absorbs on the CuO surface. Here the rate determining step is that the formation of bridge cyclic intermediate and the abstraction of a hydrogen atom from the carbon in the alpha position to the functional group. Scheme 3a shows the mechanism of glucose oxidation on CuO modified electrodes. Kenji Kano et al. proposed an alternative mechanism for electrocatalytic oxidation of glucose on copper oxide modified electrode [89] and mechanism is presented in Scheme 3b.

Copper [82], copper oxide (CuO) [57, 90, 91], cuprous oxide (Cu_2O) [92, 93] and cuprous sulfide (Cu_2S) [59, 94] were successfully employed for the oxidation of glucose. Zhuang et al. developed a highly sensitive nonenzymatic glucose sensor based on CuO nanowires on Cu electrode [95]. Huang and his co-workers fabricated a glucose sensor based on CuO nanobelt. The CuO nanobelt was directly grown on the carbon electrode by electrochemical deposition [96]. A CuO modified Cu electrode for the highly sensitive (791.9 μA mM^{-1} cm^{-2}) and wide detection range (up to 20 mM) was developed by Babu et al. [97]. From these studies, tuning the nano architectures of CuO improves the sensor performance. Microfibers of CuO modified fluorine tin oxide (FTO) based nonenzymatic glucose sensor was developed by Fei Cao et al. The sensor is highly sensitive (2321 μA mM^{-1} cm^{-2}) and selective to glucose with a lower limit of detection of 2.2 nM. But the linear detection range of the sensor was found to be below the physiological level [98]. Sen Liu et al. successfully synthesized highly stable CuO nanoparticles by heating copper acetate with urea in presence of the poly[(2-ethyldimethylammonioethyl methacrylate ethyl sulfate)-co-(1-vinylpyrrolidone)] [99]. The sensor showed remarkable catalytic activity towards glucose in 0.1 M NaOH solution with a linear detection range from 5 μM to 2.3 mM and detection limit is estimated to be 0.5 μM at an applied potential +0.55 V.

A wide variety of CuO with different size and shape were thoroughly investigated for the nonenzymatic sensing of glucose. Most of the studies were found to be novel and interesting in some features such as their synthetic methodology, electrode fabrication and sensor characteristics. Chen et al., and Zhao et al. studied the glucose oxidation on CuO micro dendrites [100, 101]. Nanofibers of CuO are also employed for the nonenzymatic glucose detection [102, 103]. One dimensional CuO nanowire arrays were found to be very sensitive due to the high aspect ratio of CuO nanowires [84, 90, 95, 104]. Similarly, nanorods [105, 106] and nanoflowers [107, 108] have been tried for the glucose oxidation. CuO nanorods and nanoflowers based glucose sensors exhibited reasonable sensitivity but the linearity was poor. Several nanoscale architectures of CuO such as nanospheres [57, 109], nanoplatelets [110], nanowalls [111], nanoleafs [112, 113], nanoleaves [114, 115], nanoneedles [116], nanoparticles [117, 118], nanosheets [119, 120], nanourchin [121], hollow polyhedron [122], sandwich [123] and porous copper foam [124] have been investigated. CuO microcubes on Cu electrode were successfully employed for the glucose detection by Zhang et al. [92]. The sensor output was linear up to 1.5 mM with a sensitivity of 50.6 μA mM^{-1} cm^{-2}. Wide linearity and very high sensitivity were achieved by increasing the surface roughness and converting it to nanoporous structure [125]. The copper oxide nanoflowers on screen printed electrode (SPE) based glucose sensor was designed by Dhara et al. [126]. The sensor exhibited a linear range of detection up to 15 mM with a very high sensitivity of 3225 μA mM^{-1} cm^{-2}.

The direct growth of vertically aligned $Cu(OH)_2$ nanotube arrays were grown on the copper substrate by one step method. The nanotube arrays are characterized thoroughly and utilized for the catalytic oxidation of glucose in alkaline medium at a lower over potential [127]. The sensor copper oxide based glucose sensors different nanostructures have been investigated for the glucose sensing. In-situ flower like copper oxide nanostructures were grown on screen-printed electrode and employed for glucose quantification [126, 128]. Randomly oriented copper oxide nanowire networks on a flexible transparent PET sheet were developed for the detection of glucose in solution volume of 2 μL. The sensor can detect the changes in glucose levels up to 12 mM and lower detection limit is 0.05 mM at an applied potential +0.6 V [129]. A template free biscuit like CuO has been synthesized by a precipitation cum thermal annealing process and used for glucose detection. The



Scheme 3 Mechanism of glucose oxidation on CuO electrode proposed by **a** Xie and Huber [87] and **b** Kano et al. [89]

CuO modified SPE exhibited a linear detection range from 0.0005 to 4.03 mM with a sensitivity of 308.71 μA mM^{-1} cm^{-2} and lower detection limit is 0.1 μM [130]. Alireza Molazemhosseini et al. constructed a non-enzymatic glucose biosensor based on a printed CuO nanoparticles film on thin gold film electrode with a high sensitivity of 2419.8 μA mM^{-1} cm^{-2}, linear range of detection from 0.1 to 6.5 mM and detection limit of 0.8 μM [131]. Large scale green synthesis of unique sandwich-structured CuO was synthesized under microwave mediated homogeneous precipitation method and used for the glucose sensing [123]. The oxidation of glucose on sandwich-structured CuO is followed by diffusion controlled process at an applied potential of +0.6 V with extremely high sensitivity of 5342.8 μA mM^{-1} cm^{-2}, linear range up to 3.2 mM, detection limit of ~1 μM and response time of ~0.7 s.

Cobalt is found to be an excellent electro-catalyst due to its different oxidation states in alkaline medium. Various reports discuss the electrooxidation of glucose on cobalt oxide based electrodes in alkaline condition. Glucose electrooxidation on cobalt also follows the similar mechanism that on copper and nickel. The electro-catalyst formed is CoOOH which further gets oxidized to CoO_2 and mediates oxidation reaction [132]. At an applied potential, Co forms CoOOH, which gets further oxidized from CoO_2 Co(III) to Co(IV). This Co(III)/(IV) redox couple catalyzes the glucose oxidation.

Cobalt oxide nanomaterials incorporated on various platforms are reported for the highly sensitive and selective detection of glucose. CoO on graphene is used for detection of glucose with a sensitivity of 669 μA mM^{-1} cm^{-2} and detection up to 8 mM by Ci et al. [132]. Electrodeposited CoOOH on Ti platform exhibited a high sensitivity of 526 μA mM^{-1} cm^{-2} and high stability. The macroporous structures surrounded by the nanosheets and the mesoporous in the nanosheets lead the electrodes to show hierarchical mass transport channels and adequate active sites for detecting glucose with high sensitivity [133]. Well oriented CoOOH

nanosheets prepared on cobalt substrate produce highly sensitive glucose sensor [134]. Cobalt oxide nanoparticles with reduced graphene detect glucose with high sensitivity [135]. Cobalt oxide on 3D graphene [136], electrospun Co_3O_4 nanofibres [137], Co_3O_4 nanoparticles, cobalt oxide acicular nanorods [138] are among the reports on Co based nonenzymatic electrochemical sensors for glucose. Tong Wang et al. reported a glucose sensor on Cobalt nanoparticles modified indium tin oxide electrode (CoNP/ITO) and it was fabricated using ion implantation technique [139].

Transition metal oxides of Fe, Mn, are reported for the nonenzymatic glucose oxidation. Manganese oxide is found to be sensing glucose at very low overpotential because of its different oxidation states in alkaline medium. It is found that Mn shows oxidation states $Mn(OH)_2$(II), which can further oxidize to MnO_2(IV) and then to MnO_4^{2-}(VI). These transitions from Mn(II) to Mn(VI) not only act as an electron transfer mediator but also as a catalyst for glucose oxidation. Multiwalled carbon nanotubes electrochemically modified with MnO_2 are used for sensing glucose at a lower applied potential. Carbon nanotubes-MnO_2 nanocomposite is reported to have good sensitivity [21]. Mn_3O_4 on 3D graphene detects glucose up to 8 mM with a sensitivity of 360 μA mM^{-1} cm^{-2} [140]. The electrode modified with FeOOH, mediate the heterogeneous redox reactions and the Fe(III) species get regenerated subsequently which mimic the enzymatic oxidation reactions [141]. ZnO is one of the most important and multifunctional material candidate due to its excellent physical, chemical, electrochemical and mechanical properties. The properties of wurtzite hexagonal phase ZnO include its wide bandgap, cost effective synthesis high electron features and biocompatibility, easy and better electrochemical performance, optical transparency. Dar et al. fabricated a nonenzymatic glucose sensors based on ZnO rods with a linear detection range of 0.001–10 mM and sensitivity of 5.601 ± 0.02 μA mM^{-1} cm^{-2} [142]. Table 2 summarizes the transition metal, metal oxide, hydroxides, and sulfides based nonenzymatic glucose sensors.

Bimetallic nanoparticles and alloys of copper, nickel and cobalt

To overcome the limitations faced by the metal electrodes due to the poisoning and interference, combinations of metals such as alloys and bimetallic systems for the determination of glucose have been reported. The platinum based alloys received great attention due to the improved sensitivity, selectivity, and anti-poisoning properties. Alloys of copper, nickel, and cobalt, which are of low cost with improved sensing characteristics in alkaline medium were reported [167]. The properties of alloys and bimetallic nanomaterials have been widely explored for the fabrication of glucose sensors which show excellent sensing characteristics. A brief outline of various studies on glucose sensors based on bimetallic and alloys are given below.

Noble metal-based bimetallic nanoparticles

To overcome the problems associated with the single noble metal based sensors, a combination of bimetallic/core shell and metal alloys of noble metal nanoparticles were attempted [168]. Bimetallic or core-shell nanoparticles were prepared by the successive reduction of one metal over the other [169]. The literature available proves the vast research scope associated with glucose sensors fabrication based on multimetallic/alloy particles as the catalyst. It is also seen that compared to pure metal based catalysts, bimetallic and alloys catalysts exhibit enhanced and superior catalytic performance with high sensitivity and good stability. This is due to its resistance in surface poisoning due to adsorbed intermediates, enhanced electrocatalytic performance, hindering the oxidation of other interfering endogenous biomolecule species at the potential window of glucose oxidation.

Mallouk and co-workers examined the catalytic activity of alloys of noble metals. The Pt-Pb exhibited glucose oxidation at a very low potential neutral solution [170]. Bimetallic nanoparticles with alloys or core-shell nanoparticles such as Au-Pd [171], Pt-Au, Pt-Ru [172] and Pt-Ir [173] often exhibited a better catalytic activity, non-toxicity and long-term stability than their monometallic counterparts. Pt-containing bimetallic nanomaterials such as Pt-Ni [174], Pt-Pd [175], Pt-Au [176] have been demonstrated with enhanced electrocatalytic properties towards glucose oxidation. Li et al. compared the electrocatalytic properties of two different nanostructures, Pt-Pd nanowires, and nanotubes for glucose sensor application and achieved good linear response and specificity [177]. Xu et al. fabricated Pt-Co alloy electrode by dealloying process for the sensing of glucose with good selectivity [178]. Pt-Pb alloy [179, 180], Pt-Ru nanoparticles on CNT [181], Pt-Ir nanoparticles [182], nanoporous Pt-Ag, Pt-Cu alloys [183] and Pt-Au alloy [184], Pt-Co/C composite [185] are found to have enhanced sensor characteristics. Li Wang et al. reported a glucose sensor based on Pt-Ni composite on rGO [186]. The sensor exhibited linear range from 0.008 to 14.5 mM with a sensitivity of 832.95 μA mM^{-1} cm^{-2}. Pt/Ni nanowire modified GCE was employed for glucose sensing at a low applied potential with a LOD of 1.5 μM [187]. Mahshid et al. constructed a glucose sensor based on Pt/Ni–Co nanowire modified GCE [188]. The sensor has a wide linearity with a reasonable sensitivity. Pt-Cu nanochain decorated GCE [189] and Pt-Ni/C nanostructures [190] were also reported for efficient glucose sensing.

Table 2 Comparison of transition metal/metal oxide based glucose sensors

Electrode material	Sensitivity $\mu A\ mM^{-1}\ cm^{-2}$	Linearity (mM)	LOD (μM)	Potential (V)	Ref.
Ultrathin nickel film	5070.9	0.001–10.0	–	+0.4	[58]
Nickel Nanoflakes	7320	0.05–0.6	1.2	+0.5	[62]
Ni foil	670	0.02–10.0	1.8	+0.5	[64]
Metallic nickel	–	0.10–2.50	40	+0.55	[65]
hedgehog-like NiO	1052.8	0.5–4.5	1.2	+0.49	[67]
NiO nanoparticles	2037.0	0.004–7.5	0.32	+0.5	[69]
Nano NiO	55.9	0.001–0.11	0.16	+0.7	[73]
	66.0	0.001–0.01			
NiO hollow spheres	–	0.002–0.01	0.3	+0.5	[74]
	–	0.05–3.3			
3D porous NiO	2900.0	0.0005–4.0	0.07	+0.5	[75]
Ni foam	–	0.05–7.35	2.2	+0.45	[76]
NiO nanoparticles	834.8	0.002–1.0	0.65	+0.55	[77]
Porous NiO nanoflakes	8500.0	0.01–0.8	1.2	+0.5	[79]
NiO microfibers/FTO	1785.41	0.001–0.27	0.033	+0.5	[80]
Cu film/ITO	699.45	0.001–0.5	0.5	+0.4	[83]
3D flower-like Ni_7S_6	271.80	0.005–3.7	0.15	+0.45	[81]
CuO nanowires/GCE	64.1	0.0005–0.488	0.045	+0.6	[84]
	–	0.988–5.488			
CuO nanoclusters	17.76	0.7–3.5	0.21	+0.65	[85]
CuO/SPE	–	0.5–6.0	4	+0.6	[86]
Cu-CuO nanowires	–	0.1–12.0	50	+0.3	[90]
Porous Cu_2O microcubes	–	0.0015–0.5	0.8	+0.61	[92]
Cu_2O nanoparticles	629.0	Up to 6	2.4	+0.75	[93]
CuS nanotube/Cu	3135	0.0002–2.5	0.045	+0.45	[94]
	2205	2.5–6.0			
CuO nanowires	490	0.0004–2.0	0.049	+0.33	[95]
Cu nanobelt	4433.33	0.01–1.13	10	+0.6	[96]
CuO/Cu	761.9	0.002–20.0	1	+0.7	[97]
CuO microfibers	2321	0.0002–0.6	0.002	+0.4	[98]
CuO nanoparticles	1397	0.005–2.3	0.5	+0.55	[99]
Cu microdendrites	–	0.0014–3.8	1.4	+0.4	[100]
Cu microdendrites	–	0.04–12.6	17	+0.35	[101]
CuO nanofibers	873.0	0.0002–1.3	0.04	+0.48	[102]
Copper oxide nanofibers	183.3	0.06–3.0	8	+0.35	[103]
CuO nanowires/GCE	119.9	Up to 12.34	5	+0.3	[104]
	648.2	Up to 5.64	2	+0.55	
CuO nanorod bundles	–	Up to 1	1.2	+0.6	[105]
Copper nanorods	1490	0.0001–0.8	0.008	+0.55	[106]
CuO nanoflower	789.3	0.000095–3.13	0.007	+0.5	[107]
CuO hierarchical nanoflowers	2657	0.01–5.0	1.71	+0.5	[108]
CuO spheres	164.25	0.039–2.5	–	–	[109]
CuO nanoplatelets	3490.7	Up to 0.8	0.5	+0.55	[110]
CuO nanowall	556.3	0.00005–0.01	–	+0.1	[111]
Leaf-like CuO nanoparticles	246	0.001–0.17	0.91	+0.6	[112]
CuO nanoleafs	1392.9	0.01–1.08	1	+0.5	[113]
Nanoleave-shaped copper oxide	664.3	Up to 9.0	5.7	+0.35	[114]
CuO nanoleaves	–	0.01–20	5	–	[115]
CuO nanoneedles	912.7	0.001–5.3	0.1	+0.6	[116]
Inkjet printed CuO nanoparticles	2762.5	0.05–18.45	0.5	+0.6	[117]
CuO nanoparticles	450.2	Up to 4.4	0.7	+ 0.59	[118]

Table 2 (continued)

Electrode material	Sensitivity $\mu A\ mM^{-1}\ cm^{-2}$	Linearity (mM)	LOD (μM)	Potential (V)	Ref.
CuO nanosheets	2792.64	0.0008–2.2	0.8	+0.5	[119]
CuO nanosheets	520	0.5–10.0	0.1	+0.5	[120]
CuO nanourchins	2682	0.1–3.0	1.52	+0.5	[121]
CuO polyhedron	1112	Up to 4.0	0.33	+0.55	[122]
Archetypal sandwich-structured CuO	5342.8	0–3.2	1	+0.6	[123]
CuO nanowires/3D copper foam	2217.4	0.001–18.8	0.3	+0.35	[124]
Microporous CuO	1890	0.002–15.0	0.05	+0.7	[125]
CuO nanoparticles	3225	0.0005–15.0	0.06	+0.65	[126]
$Cu(OH)_2$ nanotube array	418	Up to 3.0	0.5	+0.4	[127]
Flower-like CuO/SPE	1460	0.04–2.0	2.5	+0.6	[128]
CuO nanowires/PET	–	0–12.0	50	+0.6	[129]
Biscuit-like CuO	308.71	0.0005–4.03	0.1	+0.5	[130]
CuO nanoparticles film	2419.8	0.1–6.5	0.5	+0.5	[131]
Cobalt oxide microspheres	669.78	0.00083–8.61	0.46	+0.55	[132]
Rose-like CuO nanostructures	4.640	0.78–100	0.95	–	[143]
Porous CoOOH nanosheet arrays	526.8	0.003–1.109	1.37	+0.52	[133]
CoOOH nanosheet arrays	341.0	0.03–0.7	30.9	+0.4	[134]
	967.0	0.01–0.5	10.9	+0.5	
Co_3O_4 nanofibers	36.25	Up to 2.04	0.97	+0.59	[137]
Acicular cobalt oxide nanorods	571.8	0.2–3.5	0.058	+0.5	[138]
Cobalt nanoparticles/ITO	1720	0.005–0.18	0.25	+ 0.59	[139]
Co_3O_4 porous film	366.03	Up to 3.0	1	+0.6	[144]
MnO_2 nanoparticles	33.19	0.01–28.0	–	+0.3	[21]
FeOOH nanowires	12.13	0.015–3.0	7.8	–	[141]
Hollow $Ni(OH)_2$ nanorod arrays	1569	0.002–3.8	0.6	+0.6	[145]
Ni nano foam	2370	0.005–0.7	5	+0.5	[146]
$Ni(OH)_2$ nanoboxes/GCE	487.3	0.0005–5	0.07	+0.58	[147]
Ni_3S_2 nanosheet arrays	6148.0	0.005–3.0	1.2	+0.55	[148]
NiO hollow cages	2476.4	0.1–5.0	0.1	+0.48	[149]
Porous Cu_2O/nafion	11.0	0.002–0.35	1.3	+0.4	[150]
CuS nanotube/nafion/GCE	7842	0.00005–0.005	–	+0.2	[151]
CuS nanoflowers	2519	0.001–1	0.3	+0.46	[152]
Hollow CuS microsphere	64.97	0.01–1.55	3.78	+0.7	[153]
CuS micro flower	1007	0.02–5.4	2	+0.5	[154]
Copper sulfide dendrite	8337	0.001–4.9	0.05	+0.55	[155]
Octahedral Cu_2O	241	0.3–4.1	128	+0.6	[156]
3D porous CuO nanowire arrays	1420.3	Up to 2.55	5.1	+0.35	[157]
Nanoporous Co_3O_4–70	16,387	–	0.025	+0.6	[158]
1D Fe_3O_4 nanorod arrays	406.9	0.0005–0.766	0.1	+0.6	[159]
	134.1	0.766–3.67			
CuO nanowires	3502.4	0.2–1.5	0.11	+0.65	[160]
NiO pores	315.4	0.2–3.0	0.32	+0.55	
CuO nano ellipsoids	2555	0.1–3	0.072	+0.55	[161]
Nanoporous copper	33.75	0.006–3.369	2.6	+0.6	[162]
3D hierarchical porous Co_3O_4/GCE	471.5	0.001–0.3	0.1	+0.59	[163]
		4–12.5			
Co_3O_4 nanocrystals	743.6	0.1–0.9	50	+0.55	[164]
	270.9	1.0–7.0			
Co_3O_4 nanoparticles	520.7	0.005–0.8	0.13	+0.59	[165]
ZnO nanorods	2.97	0.1–13.8	1000	−0.4	[166]
ZnO nanorods/GCE	5.601 ± 0.02	0.001–10	0.5	–	[142]

Pt-based alloys are the most reported ones for glucose sensing. Alloys of Pd and Au also possess very good sensing characteristics. An alloy of Pd with Fe was used for the nonenzymatic detection of glucose [191]. Pd-Cd network structures [192], Pd-Cu nanoparticles on graphene hydrogel [193], Pd-Ni 3D nanomaterial [194], Pd-Ni nanoparticles modified silicon nanowires [195], Pd–Au bimetallic cluster [196] were among this category. Nanoporous Au-Cu alloy [197] Au-Ag alloy with different metal ratios [198] and Pt-Au/C based nanocomposite [199] are some of the bimetallic systems containing Au for glucose sensing. Hetero-structured Pd-Pt core-shell NC was synthesized and used for nonenzymatic amperometric glucose sensing [200].

Alloys of copper, nickel and cobalt

A variety of bimetallic or alloys of Cu, Ni and Zn have been fabricated with a goal of increasing the sensor performance in terms of sensitivity, selectivity, and linearity. Marioli reported the Ni-Cu and Ni-Cr-Fe alloy as a catalyst for glucose and other carbohydrates oxidation. The glucose oxidation occurs at +0.45 V with a lower detection limit of 15 and 1 picomoles at the Ni-Cu and Ni-Cr-Fe alloy electrodes respectively [201]. Many bimetallic glucose sensors such as Cu-Ni dendritic electrode [202], Pt-Ni nanowire array electrode [187], CuO-NiO microfibers [203], NiO/CuO on polyaniline (PANI) [204], Ni-Cr [205], Ni-Cu [206], Ag-Ni alloy [207] were studied for the glucose oxidation. Ni-Cu nanoparticles decorated highly ordered TiO_2 nanotubes (Ni-Cu/TiO_2NT) were fabricated by potential step method. This alloy modified TiO_2NT electrode exhibited better catalytic activity and high sensitivity in the alkaline medium when compared to Ni/TiO_2 and Cu/TiO_2 electrodes [208]. Similarly, there are several alloy/bimetallic sensors of Cu-Co [209], Cu-Ag [210, 211] and Pt-Cu [189] were reported. CuO and Pt nanoparticles electrodeposited on tantalum oxide honeycomb structure showed a wide linearity up to 31 mM with a reasonable sensitivity [212]. NiO-CuO nanoparticles on Ti substrate [213] and nickel-cobalt hydroxide (Ni-Co)$(OH)_2$ [214] were investigated. It is established that the alloys/bimetallic nanoparticles exhibit a synergistic response, in which the catalytic abilities of both metal and metal oxide got enhanced to form a super catalyst [215, 216]. Ni-copper oxide (CuO) -decorated cerium oxide (CeO_2) nanoparticles were synthesized and used for nonenzymatic glucose sensing [217]. Various bimetallic based nonenzymatic glucose sensors are summarized in the Table 3.

Other composites

A new sensing material, Cobalt phosphide nanorods was synthesized and used for glucose sensing in alkaline medium by Sun et al. [247]. The sensor exhibited good linearity up to 5.5 mM with a reasonable sensitivity of 116.8 μA mM^{-1} cm^{-2} and lower detection limit of 9 μM. A nonenzymatic glucose biosensor was constructed by gold nanoparticles on a ternary Ni-Al layered double hydroxide/single-walled carbon nanotubes/graphene nanocomposite (Au/LDH-CNT-G) matrix [248]. The sensor gives a wide linear range from 10 μM to 6.1 mM, a low detection limit of 1 μM and with a high sensitivity of 1989 μA mM^{-1} cm^{-2}. Gao et al. described a nonenzymatic amperometric nanomolar level detection of glucose on the molybdenum disulfide and copper sulfide (MoS_2-CuS) hybrid material at physiological pH [249]. The hybrid structure was synthesized by classical one post method. The sensor showed linearity up to 1 mM with a lower detection limit of 0.3 μM. Cobalt nitride nanowire arrays on Ti mesh (Co_3N NW/TM) electrode based high efficient glucose sensor was developed by Fengyu Xie et al. [250]. The sensor responds linearly to glucose from 0.1 μM to 2.5 mM, with a high sensitivity of 3325.6 μA mM^{-1} cm^{-2} and a lower detection limit of 50 nM. The sensor was used to determine the glucose in human blood serum samples. Similarly, monolithically integrated copper phosphide nanowire on copper foam (Cu_3P NW/CF) based glucose sensor exhibits good sensor characteristics [251]. Fe_3N-Co_2N nanowires array were used as sensing material for glucose with a high sensitivity of 333.7 μA mm^{-1} cm^{-2} and lower limit of detection of 77 nM [252]. Cu nanoparticles are encapsulated on a porous metal-organic framework (MOF), zeolitic imidazolate framework 8 (ZIF-8)) matrix for nonenzymatic glucose sensing in alkaline medium [253]. The sensor sensitivity was calculated as 4120 μA mM^{-1} cm^{-2} for the concentration scope of 0–0.7 mM, with a lower detection limit of 2.76 μM.

Carbon nanomaterial-based glucose sensors

Carbon nanomaterials such as fullerene, carbon nanotubes (CNT), carbon nanofibers, doped diamond-like materials, carbon black, nanodiamonds and graphene exhibits a unique physical and chemical properties and are very promising materials for chemical and biological sensors [254–256]. With all the interest in cutting-edge nanotechnologies, numerous glucose sensors based on carbon nanomaterials have been developed. Carbon nanomaterials decorated metal/metal oxide nanoparticles have materialized as a new kind of catalysts for electrochemical sensors [257–259]. Single, multi-walled carbon nanotubes and graphene-coated metal/metal oxide nanoparticles such as palladium nanoparticles [260], platinum nanoparticles [261], iron oxide (Fe_2O_3) [262], manganese dioxide (MnO_2) [263], cadmium oxide (CdO) [264] etc. have been studied.

Table 3 Comparison of bimetallic nanoparticles based glucose sensors

Electrode material	Potential (V)	Linearity	Sensitivity $\mu A\ mM^{-1}\ cm^{-2}$	Response time (s)	LOD (μM)	Ref.
Pt-Au alloy	+0.6	0.2–5.4 mM	–	< 2	0.5	[184]
Pt/Ni–Co nanowires	+0.4	0–0.2 mM 0.2–8 mM	1125 333	<3	1	[188]
Pt-Cu	−0.01	0.01–17 mM	135	–	2.5	[189]
Pt-Ni/C	−0.05	2.0–420 μM 0.5–8.5 mM	1795.1 707.72	–	1	[190]
PdFe alloy	+0.35	1–32 mM	2.7	< 2	1.6	[191]
Pd–Au cluster	−0.1	0.1–30 mM	75.3	5	50	[196]
Au-Cu alloy	+0.4	Up to 12 mM	374	10	2.8	[197]
Pd-Pt core-shell nanocubes	−0.05	0.3–6.8	170	–	41.1	[200]
Ni-Cu	+0.5	1 μM–0.5 mM	–	–	–	[201]
Nanoporous gold/ruthenium	−0.1	0–6 mM	240	–	1.7	[218]
Pt-Ni nanowire arrays	+0.45	2 μM–2 mM	920	3	1.5	[187]
CuO-NiO microfibers	+0.5	3 μM–0.51 mM	3165.53	3	0.001	[203]
Ni-Cu/TiO_2NT	+0.6	10 μM–3.2 mM	1590.9	5	5.0	[206]
AgO-Ni alloy	+0.6	Up to 2.63 mM	170.2	5	0.72	[207]
Cu/CuO/ZnO nanostructures	+0.5	Up to 1 mM	408	–	18	[219]
Ag/CuO–ITO	+0.5	0.5–500 μM	1347	–	0.052	[210]
Cu-Co	+0.65	0.5 μM–14 mM	–	5	0.05	[209]
Cu-Ag	+0.50	0.5–500 μM	1347	3	0.05	[210]
NiO-CuO NP/Ti	+0.42	0.1–1200 μM	1600	< 4	0.1	[213]
(Ni-Co) $(OH)_2$	+0.47	0.25 μM–3.7 mM	122.45	–	–	[214]
CuO/CeO_2/ITO	+0.4	Up to 4 mM	2.77	–	10	[217]
Pt-Fe/Carbon	+0.05	10 μM–18.9 mM	481.24	< 3	3	[220]
Au–Ni coaxial nanorod array	+0.4	27.5 μM–27.5 mM	769.6	13	5.5	[221]
CeO_2/Au	–	0.01–20 mM	44	–	10	[222]
NiO/CuO/PANI/GCE	+0.6	20–2500 μM	–	< 5	2.0	[204]
Cu_2O@Pd/GCE	+0.6	0.49 μM–8 mM	19.44	5	0.16	[223]
$NiMoO_4$ nanorods	+0.5	0.05–14 mM	389.9	4	0.36	[224]
NiO–Pt NFs	+0.6	0.02–3.67 mM	180.80	4.1	0.313	[225]
NiO-Au nanobelt/GCE	+0.2 +0.6	0.02–2.79 mM Up to 4.55 mM	23.88 48.35	–	0.65 1.32	[226]
5% NiO@Ag nanowires	+0.6	0.02–1.28 mM	67.51	7	1.01	[227]
Co@Pt core-shell NP	−0.05	1.0–30 mM	2.26	< 1	300	[228]
Ni-ZnO/GCE	+0.5	0.001–8.1 mM	824.34	< 4	0.28	[229]
3D NiO-Au foam	+0.6	Up to 0.5 mM	6302.25	4	1.16	[230]
$NiCo_2O_4$ nanowires	+0.4	0.001–0.88 mM	4710	3	0.063	[231]
Ni-CuO nanowires	+0.67	0.2–3.0 mM	5610.6	< 3	0.07	[160]
Cu-Cu_2O/TiO_2 NTA/Ti	+0.65	0.1–2.5 mM	4895	–	8.6	[232]
Pd–Ni/Si	−0.06	Up to 20 mM	190.72	8	2.88	[195]
Pt-Ir/Ti	+0.1	0–20 mM	93.7	–	–	[182]
$Ni(OH)_2$ NP/Ni	+0.45	0.6–6 mM	1950	–	0.16	[233]
Cu nanowires-Ti foil	+0.7	0.001–6.053 mM	4984.6	–	0.33	[234]
$NiMoO_4$ nanofibers	+0.6	0.01–8 mM	193.8	2	4.6	[235]
Cu foam- supported Cu_2O nanothorn arrays	+0.55	0.001–11.4 mM	97,900	–	0.005	[236]
Pd_2-Ag alloy nanocrystals	+0.5	0.04–46 mM	–	–	20	[237]
Co_3O_4/PbO_2 nanorod arrays	+0.55	0.005–1.2 mM	460.3	< 2	0.31	[238]
Nanoporous gold/cobalt oxide	+0.26	Up to 70 mM	12,500	< 1	0.005	[239]
Cobalt oxide/Au hierarchically nanostructure	+0.3	2 μM − 0.2 mM 0.5–20 mM	6000	–	0.1	[240]

Table 3 (continued)

Electrode material	Potential (V)	Linearity	Sensitivity $\mu A\ mM^{-1}\ cm^{-2}$	Response time (s)	LOD (μM)	Ref.
Ni–Cu/TiO_2 NTA	+0.6	10 μM–3.2 mM	1590.9	5	5	[208]
Nafion/SBA-15-Cu (II)/GCE	+0.5	0.5 μM–2 mM	598	–	0.076	[241]
Ag&Pt hallow NP-TiO_2	–	30–180 mM	3.99	–	22.6	[242]
Au-Cu_2O/GCE	–	0.05–2.0 mM	715	–	18	[243]
Nickel cobalt sulfide nanosheet	+ 0.55	0.001–3.0 mM	3291.5	< 5	0.12	[244]
$CoWO_4$ Nanospheres	+0.52	0.05 μM − 4.5 mM	1416.2		0.7	[245]
Cu/Ni NP/SPE	+0.55	2–400 μM	1590	–	0.6	[246]

NTA, Nanotube arrays; *SBA-15*, Santa Barbara amorphous-15 nanomaterial

Carbon nanotubes

CNT have excellent electrical, mechanical, thermal and optical properties [265–268]. The conductivity of the nanotubes is one of the potential issues. From the density functional theory (DFT) calculations of electronic band structures and molecular dynamic simulations of SWCNT by Britto et al. [269] proved that approximately one-third of nanotubes are metallic in nature and another two-third are semiconducting in nature. Vertically aligned carbon nanotubes (VACNT) are more advantageous for sensor application since the edges of the nanotubes are exposed and they exhibit a higher electrocatalytic activity and fast electron transfer.

Carbon nanotubes and their hybrid materials are widely used in the fabrication of electrochemical sensors because of their unique physical and chemical properties, high aspect ratio, low cost, biocompatibility, minimal surface fouling, their large electronic conductivity, excellent electron transfer kinetics and the fact that they are generally electrochemically inert. Hence, CNT-based sensors typically exhibit faster electron transfer kinetics, very high sensitivities and lower detection limits [270]. The CNT hybrid based sensors showed remarkable electrocatalytic activity for the detection of various analytes including DNA, viruses, antigens, disease markers and whole cells [270–274]. Noble metal nanoparticles anchored CNT are popular in the fabrication of nonenzymatic glucose sensors with a good sensitivity [275]. Alloys and bimetallic nanoparticles modified CNT such as PtRu [172], PtPb [179, 180] nanoparticles have been extensively applied for direct electrooxidation of glucose. A novel glucose sensor was developed by Chen et al. using carbon nanotube coupled with MnO_2, which shows wide linear range up to 28 mM, high tolerance to electrode fouling, anti-interference ability to chloride ions and common interfering electroactive species [21]. Transition metal nanostructures of copper [276–278], nickel [78, 279, 280] and MnO_2 [263] decorated CNT have been thoroughly studied. From the literature, the carbon nanotube is a promising base material for sensor fabrication due to simple modification, high catalytic response, and fast electron transfer. Also, the unmodified and modified CNT-based electrodes presented a very high sensitivity and selectivity, but the major limitation lies in the detection range. Syeda Ammara et al. reported a glucose sensor based on Cu/CNT. The electrophoretic deposition of copper nanoparticles on CNT was carried out to fabricate Cu/CNT nanocomposite sensor for glucose detection [281]. Table 4 represents the combination of carbon nanotubes with various metal nanoparticles based nonenzymatic glucose sensors.

Graphene, graphene oxide, carbon dots

Graphene is very attractive in biosensing due to its very high surface to volume ratio and unique physical and chemical properties. Application of graphene in biosensing has been demonstrated as well. Graphene and its composites have been used for the modification of electrodes in electrochemical sensors. Electrochemical detection of glucose, dopamine, proteins, etc. has been demonstrated using graphene-modified electrodes.

Graphene decorated with Pt nanoparticles have been employed for the nonenzymatic glucose sensing [302, 303]. Kong et al. fabricated a glucose sensor based on Au nanoparticles and thionine modified GO composite [304] which is used as the matrix to accommodate more number of Au nanoparticles. The composite modified glassy carbon electrode exhibited remarkable electrocatalytic activity and sensitivity to glucose detection. The linearity is from 0.2 to 13.3 mM and with a lower detection limit of 0.05 μM. Similarly other noble metals such as Pd [305, 306], Ru and Rh [170] decorated graphene nanocomposites have been synthesized and tested for glucose. Bimetallic or alloys of precious metals modified graphene such as Pt-Pd [307, 308], Pt-Au [309] and Co@Pt NP [228] were used for the fabrication of sensitive glucose sensors.

Table 4 Comparison of carbon nanotubes/metal nanoparticles based glucose sensors

Electrode material	Potential (V)	Linear detection range	Sensitivity $\mu A\ mM^{-1}\ cm^{-2}$	LOD (μM)	Ref.
PtRu–MWNT/GCE	−0.1	Up to 15 mM	10.6	50	[172]
PtPb NP/Nafion/MWCNT	−0.15	Up to 5 mM	18	7.0	[179]
PtPb/CNT	−0.99	Up to 18 mM	–	–	[180]
Au NP/MWCT/Nafion	+0.3	50 μM – 20 mM	0.4	20	[282]
MnO_2/CNT	+0.3	10 μM – 28 mM	33.19	–	[21]
Pt-MWCNT-Nafion/Au	0.0	1.0–11.7 mM 11.7–26.5 mM	–	–	[276]
CuO–MWCNT	+0.55	Up to 3 mM	2190	0.8	[277]
MWCNT/PEI/Cu/GCE	+0.35	10 μM – 0.5 mM	19.22	0.5	[278]
GC/MWCNT/NiO	+0.6	0.2–12 mM	436	160	[279]
NiO/MWCNT	+0.5	10 μM – 7 mM	1768.8	2	[78]
Ni NP-MWCNT/Cu	+ 0.53	2 μM – 10 mM	3822	0.7	[280]
MnO_2/VACNT	+ 0.45	1.2 μM −1.8 mM	1.08	0.8	[263]
Cu_2O/MWCNT	+0.4	0.5 μM – 2.5 mM	2143	0.2	[283]
Cu/CNT	+0.65	0.02–3.0 mM	314	10	[281]
Pd-SWCNT	−0.35	0.5–17 mM	160	0.2 ± 0.05	[284]
Pd NP-MWCNT	+0.025	1–10 mM 11–20 mM	11 6.3	4	[285]
Pt-Au/MWCNT	+0.3	0.04–24.4 mM	10.71	10	[286]
CuO/MWCNT	+0.4	Up to 1.2 mM	2596	0.2	[19]
Ni/Cu/MWCNT	+ 0.575	25 μM – 0.8 mM 2–8 mM	2633 2437	0.025	[287]
Ni–MWCNT	+0.6	3.2 μM – 17.5 mM	67.19	0.89	[288]
Ni/SWCNT	+0.4	1 μM – 1 mM	1438	0.5	[289]
Cu nanocubes/MWCNT	+0.55	1 μM – 7.5 mM	1096	1	[290]
MWCNT–RuO_2	+0.5	0.5–50 mM	–	33	[291]
CuO/Oppy/MWCNT	+0.55	0.2 μM – 2 mM	3922.6	0.05	[292]
Ni_3S_2/MWCNT	+0.54	30–500 μM	3345	1.0	[293]
$NiCoO_2$/CNT	+0.5	0.01–1.55 mM	1424.41	1.14	[294]
Ni on VACNT	+0.5	0.05–1.0 mM	950	30	[295]
NiO–MWCNT/CPE	+0.5	1–200 μM 0.5–9.0 mM	1696 122.1	0.01104 31	[296]
Au-Pt NP/SWCNT	− 0.45	50–750 μM	–	–	[297]
CNT-Ni nanocomposite	+0.5	0.005–2 mM	1384.1	2	[298]
Nano CuO/MWCNT	+0.35	0.5 μM – 2 mM	3968.42	0.07	[299]
Screen-printed flower-like CuO/MWCNT	+0.55	4 μM – 5 mM 5–10 mM 10–14.5 mM	1221 619 335	4	[300]
MWCNT/AuPd@Cu	+0.34	0.03–9.31 mM	744.98	1	[301]

PEI, Polyethyleneimine; *Oppy*, Overoxidized polypyrrole; *CPE*, Carbon paste electrodes

Previous studies showed that the inexpensive transition metal and metal oxides were the good catalysts for nonenzymatic glucose sensing. Zhang et al. fabricated a glucose sensor based on NiO nanofibers and graphene nanocomposite (NiO-NF/rGO). The nanocomposite is prepared by facile electrospinning technique followed by calcination. The sensor exhibited a detection limit of 0.07 μM and linear range up to 600 μM which was much below the physiological level [20]. To increase the linear detection range of the NiO/graphene-based sensor, different nanostructured NiO nanoparticles decorated graphene hybrid material were synthesized and employed for the glucose sensing [70, 310].

Nanocomposites of graphene and CuO nanocubes were prepared by Luo et al. through electrochemical deposition [311] and Yang et al. by chemical reduction method Both the composites exhibited good sensitivity and selectivity but the linear range was 4 mM and 7.5 mM respectively. Liu and co-workers studied graphene, and cuprous oxide (Cu_2O) nanocubes based nonenzymatic glucose sensor [312]. CuO nanoneedles were

synthesized by electrodeposition on the reduced graphene oxide (rGO) and carbon nanotube modified GCE [116]. The sensor showed rapid response and lower detection limit of 0.1 μM with a linear range up to 5.3 mM. Hsu et al. prepared CuO nanoparticles by chemical reduction method and employed for glucose sensing [313] with the linear range up to 8 mM. To improve the linear detection range, various CuO nanoparticles modified graphene hybrid materials are synthesized and tested with glucose [314, 315]. Fan et al. developed a glucose sensor based on CuO nanowires anchored graphene transparent electrode (GTE) composite [316] and the sensor showed linearity up to 6 mM with a sensitivity of 1100 μA mM^{-1} cm^{-2}. A disposable glucose sensor is fabricated using direct laser engraved graphene (DLEG) decorated with pulse deposited copper nanocubes (CuNC) [317]. Graphene and ZnO nanohybrid [318, 319], and graphene and cobalt oxide nanoparticle [320] have been employed for glucose sensing with good sensitivity and selectivity. Hybrid nanomaterials of graphene with NiO-CuO [321], Cu-NiO [322], Ni-Co nanostructures [323] have been studied. In all the above-mentioned sensors, the linearity was not enough for physiological glucose detection.

A combination of noble metal-transition metal nanoparticles has been used to increase the linear detection range of the sensor. Pt-Ni nanoparticles were electrodeposited on electrochemically reduced graphene oxide (E-rGO) and was used for the wide linear detection (up to 35 mM) of glucose [324]. More rapid and high sensitive current response was obtained for the oxidation of glucose. Similarly, hollow Pt-Ni/reduced graphene oxide [325] and Pt-NiO/graphene [72] were developed. Yuan et al. synthesized Pd-Cu on graphene hydrogel and tested for glucose sensing [193]. The applied potential for glucose oxidation on Pd-Cu/graphene hydrogel electrode is −0.4 V. Because of this lower overpotential, the interference from the other electroactive substance does not affect the sensor efficiency. From these studies, it is well understood that the graphene-based metal-metal oxide nanoparticles exhibited excellent sensitivity, wide linear range, lower detection limit with a good selectivity. Mn-Cu alloy on graphene detects glucose at a very low applied potential of −0.05 V with linearity up to 32.0 mM [326]. $Ni_{0.31}Co_{0.69}S_2$ decorated reduced graphene oxide was synthesized by Li et al. using hydrothermal method and applied for active material for glucose detection [327].

Mn_3O_4 nanoparticles decorated nitrogen-doped graphene (N-GR) was synthesized and modified on CPE for glucose sensing [328]. 3D rambutan-like CuO and CuO/rGO electrodes has been fabricated by a fast microwave method for nonenzymatic glucose detection. The CuO and CuO/r-GO glucose sensors owing to their high sensitivity and specificity under alkaline conditions [329]. Copper nanowires decorated reduced graphene oxide (CuNW/rGO) was synthesized by one-step wet-chemical process. The CuNW/rGO hybrid exhibits catalytic activity to glucose oxidation with a high sensitivity and specificity [330]. A sensitive electrode material nanoneedle-like CuO on nitrogen-doped reduced graphene oxide (NN-CuO/N-rGO) fabricated for nonenzymatic glucose sensing [331]. The characteristic combinations of graphene with various metal nanoparticles for the development of nonenzymatic glucose sensors are summarized in Table 5.

Other nanomaterials

Ordered mesoporous carbon matrices embedded with ultrafine Co_3O_4 nanocrystals were synthesized by environmental friendly method and used for glucose detection [164]. The sensor exhibited the two linear ranges first one is 0.01–0.8 mM with a sensitivity of 2597.5 μA mM^{-1} cm^{-2} and second range is from 0.9 to 7.0 mM with a sensitivity of 955.9 μA mM^{-1} cm^{-2}. Bimetallic nanoparticles (Cu, Ni, Fe and Mn) doped carbon nanofibers were synthesized by electrospinning method and employed for glucose detection [367]. Zhihong Zhu group synthesized nanoflower-like CoS-decorated 3D porous carbon skeleton (CoS@C) by one-pot solvothermal method [368]. The CoS@C coated on the GCE and tested for glucose detection in 0.1 M NaOH solution at +0.45 V. The sensitivity of the sensor was 697 μA mM^{-1} cm^{-2}, linear detection range is up to 0.96 mM. Phosphomolybdic acid/single walled carbon nanohorn based amperometric glucose sensor was constructed by Chen et al. [369]. Similarly, Cu microdendrites decorated on carbon nanohorn composite was studied for glucose sensing [101]. CuO dispersed on nitrogen-doped electrospun carbon nanofibers modified GCE (CuO/N-CNF/GCE) have demonstrated for direct electrocatalytic oxidation of glucose [370]. The CuO/N-CNF material has synthesized by two steps. First the N-CNFs were prepared by carbonizing electrospun polyacrylonitrile@polyaniline core–shell nanofibers. Later the CuO nanoparticles were decorated on N-CNF support by the facile solvothermal reaction. The sensor exhibited two linear detection ranges to glucose concentration with a good sensitivity: 0.25 to 2 mM (sensitivity of 968 μA mM^{-1} cm^{-2}) and 2 to 4 mM (sensitivity of 484 μA mM^{-1} cm^{-2}). Mian Li and co-workers designed a nonenzymatic glucose sensor based on mesoporous cobalt nitride nanosheets dispersed on pyrolytic carbon conductor ($Co_2N_{0.67}$ NS) modified GCE [371]. The $Co_2N_{0.67}$ nanomaterial is synthesized by hydrothermal method. The fabricated sensor showed excellent detection parameters such as wide linearity (0.01 to 8.0 mM), reasonable sensitivity 921.18 μA mM^{-1} cm^{-2} and fast response (< 3 s) with a low detection limit of 0.1 μM. A flexible nonenzymatic electrochemical glucose sensor was fabricated using AuNP/PANI/carbon cloth (CC) electrode [372]. The sensor responds linearly to glucose concentration from 10.26 μM to 10.0 mM with a sensitivity of 150 μA mM^{-1} cm^{-2}. Hedgehog-like NiO nanostructures decorated on hetero atom enriched activated carbon support (NiO-HAC) material has synthesized by two steps, eco-friendly

Table 5 Glucose sensor electrode material and their analytical performances

Sensor electrode	Potential (V)	Linear range (mM)	Response time (s)	Sensitivity $\mu AmM^{-1} cm^{-2}$	LOD (μM)	Ref.
NiO NF-rGO/GCE	+0.6	0.002–0.6	5	1100	0.77	[20]
CuO-graphene/GCE	+0.6	0.001–8		1065.21	1	[116]
Mn_3O_4 on 3D graphene	+0.4	0.1–8	5	360	10	[140]
CQD/octahedral Cu_2O	+0.6	0.02–4.3	10	298	8.4	[156]
NiO–Pt/rGO/GCE	+0.5	0.008–14.5	< 5	832.95	2.67	[186]
Co@Pt NP	−0.05	1–30	–	2.26	300	[228]
CuNiO–graphene/GCE	+0.6	0.05–6.9 6.9–16	–	225.75 32.44	16	[245]
Pt nanoclusters/graphene	+0.05	1–25	3	1.21	30	[302]
Pt NP/3D graphene hydrogel	+0.1	5–20	5	137.4	–	[303]
GO–thionine–Au nanostructure	−0.34	0.2–13.4	–	–	0.05	[304]
Nafion/graphene–Pd	+0.4	0.01–5	9	–	1	[305]
Pd NP/GO	+0.4	0.2–10	2	–	–	[306]
Pd_1Pt_3–graphene/GCE	+0.1	1–23	2	–	5	[307]
PtPd nanocubes/GN-nafion-GCE	+0.25	0.5–24.5	–	1.4	–	[308]
Pt-Au-graphene/GCE	−0.1	1–25	3	26.33	4	[309]
GNS/NiO/DNA-GCE	+0.6	0.001–8 0.001–0.2	< 8	9.0 14.3	2.5	[310]
CuO–G–GCE	+0.59	0.002–4	5	1360	0.7	[311]
Cu_2O/GN	+0.6	0.3–3.3	9	285.0	3.3	[312]
CuO/graphene	+0.6	0.00012–0.5	–	2367	0.034	[314]
CuO NP/S-doped graphene	+0.5	0.1–10.5	2	1298.6	0.08	[315]
Cu nanowires/GTE	+0.55	0.005–6.0	2	1100	1.6	[316]
Cu nanocubes-DLEG	+0.55	0.00025–4	< 3	4532.2	0.25	[317]
Graphene/Co_3O_4 hybrid	+0.6	0.05–0.3	–	–	10	[320]
Cu_2O/NiO*x*/GO/GCE	+0.6	0.002–0.87 0.87–2.95	–	285	0.4	[321]
Ni-Co/rGO/GCE	+0.5	0.01–2.65	2	1773.61	3.79	[323]
PtNi alloy NP/rGO	−0.35	up to 35	–	20.42	10	[324]
Hollow Pt–Ni–graphene	−0.35	0.5–20	2	30.3	2	[325]
NiO/Pt/E-rGO/GCE	+0.6	0.05–5.66	2.5	668.2	0.2	[72]
PdCu NP/3D graphene hydrogel	−0.4	1–18	< 10	48	20	[193]
MnCu/MWCNT/GO	−0.05	1–32	–	59.3	1	[326]
$Ni_{0.31}Co_{0.69}S_2$/rGO	+0.5	0.001–5 5–16	3	1753 954.7	0.078	[327]
Mn_3O_4 NP/N-GR/CPE	+0.9	Up to 0.5295	–	101.1	1	[328]
CuO/rGO	+0.5	0.0005–3.75	4	52.1	0.1	[329]
CuNW/rGO	+0.58	Up to 11	< 2	1625	0.2	[330]
NN-CuO/N-rGO	+0.6	0.0005–0.639	4	3.4	0.01	[331]
Pt_3Pd NP/rGO	+0.6	0.2–9	–	1.52	0.002	[332]
Pd-graphene wrapped CNT	+0.05	Up to 19.5	0.1	–	1	[333]
Cu NP/GO/SWCNT	+0.5	0.001–4.538	< 8	930.07	0.34	[334]
Cu_2O nanocubes/rGO	+0.6	0.005–2.095 2.595–9.595	< 3	37.55 23.06	1.0	[335]
Pt-CuO/rGO	+0.6	0.0005–12	< 3	3577	0.01	[336]
PVA/MnO_2@GO/CuO	+0.4	0.55–4.40	–	–	53	[337]
PtAu–MnO_2/graphene paper	0.0	0.1–30.0	3	58.54	20	[338]
CuO/rGO/GCE	+0.4	0.0004–3 3–12	–	2221 1004	0.1	[339]
Au-CuO/rGO	+0.6	0.001–12	< 3	2356	0.1	[340]

Table 5 (continued)

Sensor electrode	Potential (V)	Linear range (mM)	Response time (s)	Sensitivity $\mu AmM^{-1} cm^{-2}$	LOD (μM)	Ref.
Pd@NiO/Nile–rGO/CPE	−0.04	0.02–20	–	–	2.2	[341]
Pd-CuO/rGO/SPE	+0.6	0.006–22	3	3355	0.03	[342]
CuS/rGO/CuS/Cu foam	+0.65	0.001–0.65 0.655–1.05	< 5	22.67 10.54	0.5	[343]
Co nanostructures /rGO/PPy/GCE	+0.4	0.0005–2.67	< 1	297.73	0.029	[344]
Cu_2O/AlOOH/rGO	+0.55	0.005–14.47	–	155.1	2.6	[345]
Ni-PANI-rGO/GCE	+0.45	0.0001–1	2	6050	0.08	[346]
$Ni(OH)_2$-PEDOT-rGO	+0.55	0.002–7.1	< 1	346	0.6	[347]
$Ni(OH)_2$-graphene	+0.45	0.001–0.01 0.01–1.0	2	494 328	0.6	[348]
Graphene/NiO	+0.4	0.005–2.8	< 3	1571	1.0	[349]
NiO/chitosan/rGO	+0.6	0.2–9.0	–	318.4	4.4	[350]
Cobalt oxide NP/r-GO	+0.45	0.04–4	–	1.21	1.44	[351]
$Co(OH)_2$/3D–graphene foam	+0.6	0.1–10	–	3690	0.016	[352]
CuO_x-CoO_x/graphene	+0.5	0.005–0.57	< 3	507	0.5	[353]
CuO/rGO/Cu_2O/Cu foil	+0.65	0.0005–8.3	< 0.5	3401	0.1	[354]
$Ni(OH)_2$/N-rGO/GCE	+0.45	0.0005–0.0115; 0.0115–0.24	< 3	3214; 1879	0.12	[355]
Nafion/rGO-Au nanocubes@CuO	+0.31	0.0001–3	–	–	0.03	[356]
Co nanobeads/rGO	+0.55	0.15–6.25	2	39.32	47.5	[357]
NiO mesoporous nanowalls/rGO	+0.5	0.01–0.2	< 2	3230	10	[358]
$Ni(OH)_2$/CQD microspheres	+0.55	0.02–0.35 0.45–2.5	< 6	2760.05 1853.64	–	[359]
GQD/CoNiAl-layered double-hydroxides/CPE	+0.1	0.01–14.0	< 6	48.717	6	[360]
N-doped graphene aerogel/CuO	+0.4	0.01–6.75	–	223.1	2.7	[361]
Cu_2O hallow cubes /rGO	+0.6	0.01–9.0	–	813.713	0.44	[362]
N-doped graphene CuO/nafion/GCE	+0.6	0.003–1	5	2365.7	22	[363]
PDDA-graphene/CuO	+0.58	0.0004–4	2	4982.2	0.2	[364]
3D graphene/Ni	+0.47	0.015–6.45	< 2	207	4.8	[365]
Ag/NiO/rGO/GCE	+0.6	0.05–7.5 10–25	< 4	1869.4 115.8	2.44	[366]

CQD, Carbon quantum dots; *PVA,* Polyvinyl acetate; *GONR*, Graphene oxide nanorods; *GN*, Graphene nanosheets; *PPy*, Polypyrrole; *GQD*, Graphene quantum dots; *PDDA*, Poly- (dimethyl diallyl ammonium chloride)

chemical activation followed by hydrothermal process [373]. The NiO-HAC composite modified electrode was employed for the glucose detection in alkaline medium with a wide linear range (10 μM to 3.3 mM), fast response (5 s) and sensitivity of 199.86 $\mu A\ mM^{-1}\ cm^{-2}$. Glucose sensor based on hierarchical Cu@porous carbon electrode was fabricated by in-situ growth and subsequent pyrolysis of MOF on Cu foam [374]. The sensor displayed an ultrahigh sensitivity of 10.1 $mA\ mM^{-1}\ cm^{-2}$ with a lower limit of detection 0.6 μM. A nonenzymatic glucose sensor based on bis(acetylacetonato)oxovanadium(IV) complex, $[VO(acac)_2]$, fabricated on a self-assembled 4-(pyridine-4′-amido) thiophenol (PATP) monolayer modified gold electrode was developed by Barman and Jasimuddin [375]. The Oxovanadium complexes have good catalytic and pharmacological properties. The $[VO(acac)_2]$–PATP–Au sensor shows a linear response to glucose up to 5 mM in a neutral medium with a sensitivity of 120.24 $\mu A\ mM^{-1}\ cm^{-2}$. An ultrasensitive glucose sensor was developed by Ye et al. using C_{60}-fullerene functionalized with tetraoctylammonium bromide (C60-TOAB+) [376]. The sensor exhibited a very low detection limit of 3.3 nm with a linear range 10 to 10 mM.

Current challenges

Although many research works related to various nanomaterials based electrochemical glucose sensors has been reported. There are still many challenges to overcome, in the aspect of achieving its commercialization. One of the greatest

challenges is the lifetime of the glucose sensor. It is well known that enzymes are biomolecules, most of the biomolecules have an intrinsic nature in terms of instability, even if numerous materials have been used to comfort the enzyme environment, the shelf life of the biosensor is still within a few months. To solve this issue nanomaterials based sensors are developed. These nonenzymatic/enzymeless sensors showed remarkable sensor characteristics. As progression of nonenzymatic sensors, various materials have been tried to get the solution for the enzymatic sensors have been rising. But the nonenzymatic sensors still in the process of optimization. Some of the precious metal based sensors work in the neutral medium with a wide linear range of detection. Even though the sensors which works at simulate similar conditions as biological matrices cannot be directly substitute to clinical conditions. Once developed and tested at lab scale there is room for further improvements for nonenzymatic glucose sensors at the clinical level and their application to real biological samples. Other than that, these kinds of sensors have some key issues such as the chloride ion poisoning and high adsorption of other species on the active surface area that decreases the sensor performance.

Non-precious metal and metal oxides based sensors proven to be unaffected by chloride ion concentration and effect of the electrode fouling due to other interfering species is ignorable. But most of the non-precious metal or metal oxide sensors works in alkaline pH. In other words, these materials display specific electrocatalytic activity to the target only in the strong alkaline conditions. Their catalytic activity turns to be negligible in either acidic or neutral conditions. Hence, their use in glucose monitoring is very limited. Apart from that, other serious issues such as linear range of detection, specificity and reproducibility also hamper the nonenzymatic biosensor progression towards commercialization. Few of the important problems that needs to be concentrated to overcome the current challenges in nonenzymatic glucose biosensor to enter the market they are specificity, working potential, linearity, working pH values and sensitivity. Some of the sensors have good sensitivity and LOD, but those have a serious problem in terms of linearity. The low linear detection range sensors are not useful for the diabetes care. These sensors can be used in some other applications for example analyzing the glucose transport in adipose tissues and fabrication of glucose based fuel cells.

i. *Specificity, electrolyte pH and working potential:* Though some exogenous/endogenous species including AA, DA, UA, AP, chloride ion and other monosaccharides have been reported providing a very weak interference on the detection of glucose, the selectivity of this kind of sensors remain a huge problem. It has been found that the small organic molecules can be oxidized at the same potential, immediately after the formation of active sites. As a major oxidizable component, ethanol, is often present in many samples, the presence of even low alcohol levels will affect the glucose determination significantly. The transition metal based sensors are not affected by chloride ion concentration and electrode fouling problem is ignorable and this extends the long-term stability of these kinds of sensors. The transition metal based sensors works in highly alkaline conditions, and the underlying mechanism is still not clear. This type of sensors requires another separate mechanism to maintain the alkaline environment on the electrode surface. This increases the complexity during the device fabrication process. There are several reports on non-enzymatic glucose sensors with high sensitivity in alkaline medium. But the attainment of such a high pH is practically impossible in real time systems.
ii. *Sensitivity, stability and reproducibility:* By comparing the reported literature of nonenzymatic glucose sensors, it is found that the sensitivities of these sensors gradually improved by different strategies. However, these results are obtained by different research groups under their own optimized conditions. The sensitivity of the sensor has an important effect on the working potential, glucose oxidation kinetics and electrolyte. So far there has been no universal performance testing protocol, which is also hamper the progression of this filed. Nanomaterial based sensors easily suffer from the agglomeration, deformation/change of activity in an extended period, thus results the decrease in durability of performance. Although many nanomaterials based sensors shown the excellent analytical properties for the nonenzymatic detection of glucose, the reproducible synthesis of these nanostructures on a large scale is challenging issue.

However, several advanced approaches have been introduced to successfully improve the detection properties of nonenzymatic glucose sensors, it must be recognized that the real application of these fabricated devices is still a great challenge. In our opinion, many efforts soon will be focused on mentioned key challenges to minimize the intrinsic drawbacks that hinder the commercialization of nonenzymatic glucose sensors.

Conclusions and outlook

This review discussed the selective reports on the developments and critical drawbacks of enzymatic glucose sensors and way forward toward fabrication of various nonenzymatic electrochemical glucose sensors. In the enzymatic sensors, only glucose oxidase (GOD) was discussed as it has been the most used and beneficial enzyme so far. On the other hand, different nonenzymatic approaches representing the

fabrication techniques, working potential, linear detection ranges, LOD, sensitivity and analytical performances were discussed in detail. The rapidly growing number of publications are the strong evident that the research in this field is extremely active. Researchers are working to exploit every possible nanostructure as catalyst to achieve higher sensitivity, linearity, and selectivity. However, several possibilities and significant advances are expected in the future. For example, commercialization of sensors is the foremost requirement. The sensors need to be disposable, cost effective, easy to fabricate and possibly recyclable if costly metals or nanomaterials are used. One of the key issues is to fabricate disposable/reusable glucometers with high accuracy and high shelf-life which can possibly lead to combining all the characteristics into simple microfluidic chips. It is worth mentioning that there exist the associated health risks in disposing large amount of used sensing substrates, however, nanostructured glucose sensors offer several beneficial characteristics which are important enough for the further development of glucose and other biochemical sensing platform for use in large volume.

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