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# A Review on Glucose and Hydrogen Peroxide Biosensor Based on Modified Electrode Included Silver Nanoparticles

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To modification of electrochemical biosensors greatly approaches have been done based on Ag nanoparticles (AgNPs) included electrode. In this review we will focus on production, classification and application of AgNPs toward glucose and hydrogen peroxide biosensors. It is well known that Ag is the best conductor among metals and so AgNPs may assist more efficient electron transfer than other nanoparticles in biosensors. The exclusive properties of AgNPs (e.g. improved mass transport, high surface area, enhanced signal-to-noise ratio) can frequently be useful in electrochemical biosensors. The goal of this paper is to provide an updated summary of the works in this field and the works have been done summarized together with the outcome of electrochemical analysis.

**Keywords:** AgNP, electrochemical, cyclic voltammetry, glucose, hydrogen peroxide

## 1. INTRODUCTION

The study of nano materials in recent years has been widespread with regarding to metallic or nonmetallic nanoparticles [1-2]. Electrochemical sensing is an easy way of determining species in solution both quantitatively and qualitatively. The benefit of electroanalytical techniques over other detection methods such as luminescence, spectroscopy and chromatography is the cheap cost associated with them, and the ease of use, accuracy and consistency. Analytical techniques employed such as cyclic voltammetry (CV), differential pulse voltammetry (DPV), chronoamperometry, stripping voltammetry and linear sweep voltammetry, all of which are successful electroanalytical techniques provided they are optimized to obtain the best electrochemical response. These processes can be affected by many factors, including the nature of the analyte, the type of electrode and the selection of electrolyte. Particularly, the size and morphology of the electrode and the fabrication method used can be very influential on the voltammetric response of the system.

Among all metal nanoparticle, silver nanoparticles (AgNPs) keep on to be of enormous current research attention because of their catalytic properties [3]. AgNP traditionally been explored to employ as catalysts in various reactions and also Ag exhibits the highest electrical and thermal conductivity among all the metals. Additionally it is also known for its antibacterial properties and its ability to promote surface enhanced optical phenomena [4].Campbell et al. [5] studied H2O2 reduction at an AgNP array, which has shown that the voltammetric trace for H2O2 reduction will vary with both NP size and the extent of surface coverage. A decrease in NP size causes a negative shift in the peak potential, whereas increasing coverage causes a positive shift. Additionally, NP size effects have been simulated by Ward Jones et al. [6] for the anodic stripping voltammetry of various sizes of AgNPs and have been compared with experimental data.

The review by Welch et al. [7] has provided a complete overview of synthesis and application of metallic NPs and covers the most recent advances in both the preparation of NPs and their subsequent use in electroanalytical systems.

However, so far, there has been no comprehensive review article concentrated on the use of AgNPs for constructing electrochemical biosensors toward H2O2 and glucose analysis. This review will summarize the use of AgNP to improve the electrochemical sensing capability of H2O2 and glucose biosensors.

## 2. METHOD OF PRODUCING AgNPs FOR SENSING PURPOSE.

The most distinctive method of AgNP preparation in recent years is by reduction of an Ag salt in the presence of a protecting/stabilizing agent. This is usually performed in an aqueous surfactant polymer solution as the composition of the reaction mixture can be very easily altered to utilize different reducing and capping agents to obtain AgNPs. Stabilizing agents such as cetyl trimethylammonium bromide (CTAB), humic acid, citrate, surfactin and oleate are classically used [8-10].

An Ag salt (AgNO3) can be reduced by NaBH4, in the presence of stabilizing agent, representative a renewable and environmentally compatible synthesis. The obtained AgNPs will be uniform in both size and shape and were shown to vary in size with both pH and reaction temperature.

In other similar method sodium citrate will be used acting as a reducing agent with heating. Charged citrate ions adsorb onto the NP surface to stabilize AgNPs and prevent aggregation.

mainly spherical AgNPs were synthesized.

AgNPs can also be very easily deposited via electrochemical methods, typically by potentiometric techniques, such as pulsed or constant potential application. Furthermore, stripping of a film can result in NPs of various sizes depending on the duration of the stripping potential applied.

## 3. FABRICATION OF AgNPs ON THE ELECTRODE SURFACE

There are plentiful approaches to manufacture nanomaterials on the electrode surface, through chemical reduction from the aqueous solution of halo-metallate anions [11], electrochemical

deposition [12–15] and metal-vapor synthesis [16]. Electrochemical-metal deposition is a suitable, fast method for organize metal nanoparticles on large areas of conductive substrates. Fig. 1 demonstrates the modification of the surface of electrode with AgNP modified matrices. This method of surface modification with nanoparticles has been applied in numerous reports [15].

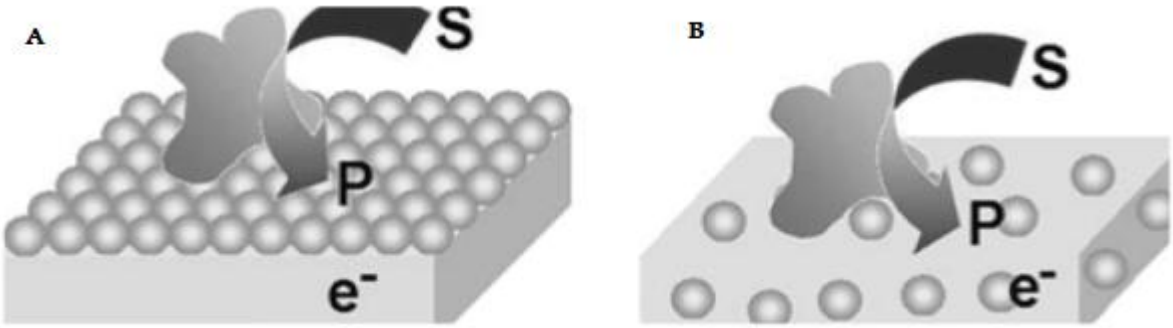



**Figure 1.** Modification of electrode surface by AgNP (A) directly on the electrode surface and. (B) embedded inside the matrix on the electrode surface.

## 4. IMMOBILIZATION OF THE ENZYMES

Nanoparticles have dimensions similar to those of biomolecules such as enzymes. Therefore, the combination of biomolecules with nanostructures produces functional nanostructured bio interfaces with synergistic functions and properties [17].

There are various techniques of immobilization of biomolecules, such as enzymes on inorganic substrate materials in literatures [18]. The most established method is the "cross-linking", in which enzyme molecules are bound to each other by a cross-linking agent. With regarding to this method, the manufacture of stable biosensors is feasible, but most of the cross-linking agents are known to reduce the enzymes activity significantly.

Another suitable method is to employ physical adsorption for the enzymes/ biomolecules immobilization [19-20], which increase a surface bio-layer without loss of the enzyme activity. It is necessary to use a variety of mechanical entrapments to keep biomolecules on the surface. However, weak bond between the solid surface and the enzyme, resulting in fast leakage and the sensitive components still presents the major problem of the short lifetime for this kind of biosensors. Also using nano-porous surface as the novel support matrix will increase the effectiveness of enzymes adsorption.

Proposed approach to developing the nano-structured biosensor substrate suggests that the modified surface should be fabricated by depositing the bioactive components, e.g. enzymes or antibodies, onto it. The immobilization of the biosensing materials on the surface is the vital step in biosensors, production, particularly when dealing with enzymes and antibodies.

The sol–gel process, a method for the production of ceramic materials is gaining renewed interest because it provides a suitable method to embed active proteins to prepare the biosensor [21].

Some new methods and new composite sol-gel were studied to improve the character. The sol–gel film modified with nanoparticles has been proved that it has new properties .

## 5. APPLICATION OF BIOSENSORS INCLUDED AgNPs TOWARD GLUCOSE AND H2O2 ANALYSIS

### *5.1. Glucose Biosensors*

Fast quantitative determination of glucose is important in the field of clinical chemistry, and food analysis [22]. Glucose biosensors have long been developed. Up until now, three generations of glucose biosensors using (i) natural oxygen co-substrate and generation and detection of hydrogen peroxide, (ii) synthetic electron mediators, and (iii) direct electron transfer between GOx and the electrode, have been reported [23]. Due to good sensitivity and low detection limit amperometry is recommended for detection method toward glucose. To improving the performance of glucose biosensors, different nanomaterials such as carbon nanotube (CNT) and metal nanoparticles have been incorporated into electrode surface. Recently, metal nanoparticles such as gold and AgNPs have been used as nanomaterial labels or "markers" in electrochemical biosensors and immunosensors [24–26].

The oxidation of glucose to hydrogen peroxide (H2O2) can be catalyze by glucose oxidase (GOx) and gluconolactone in the presence of dissolved oxygen. So, classical determinations of glucose were based on monitoring either the production of H2O2 or the amount of used oxygen [27]. Unfortunately, the amperometric determination of H2O2 requires high anodic potential [28-29], which resulted in the interferences from ascorbic acid, uric acid and acetaminophen, and so on. So to reduce the interference introducing novel nanometer materials is recommended to understand the direct electrochemistry of H2O2 at a low potential [30–38]. There are high sensitivity glucose biosensors based on immobilization of enzyme in AgNPs. The enzyme electrode included AgNPs considerably enhances the response current compared with the bare electrodes so the responding speed of the biosensors will be improved.

The possibility of an amperometric glucose biosensor based on immobilization of glucose oxidase (GOx) in Ag sol was investigated by Xiangling et al [39]. They used AgNP to enhance the sensitivity of the glucose biosensors.

They mixed GOx with AgNP and coated onto a platinum electrode with polyvinyl butyral (PVB) and glutaraldehyde by sol–gel process. To study the effect of the AgNP on the sensitivities of the glucose biosensor, enzyme electrodes coated with either hydrophobic or hydrophilic AgNP were tested. They figure out the current response curves of GOx electrodes without and with AgNP (Fig. 2). This result indicates that the current response of the electrode containing AgNPs increases dramatically. In particular, the current response of the GOx electrode containing hydrophobic AgNP is much larger than that of the enzyme electrode containing hydrophilic ones and than that of electrode d, which contains 10 times more GOx than that of electrode a, but without Ag particles involved.

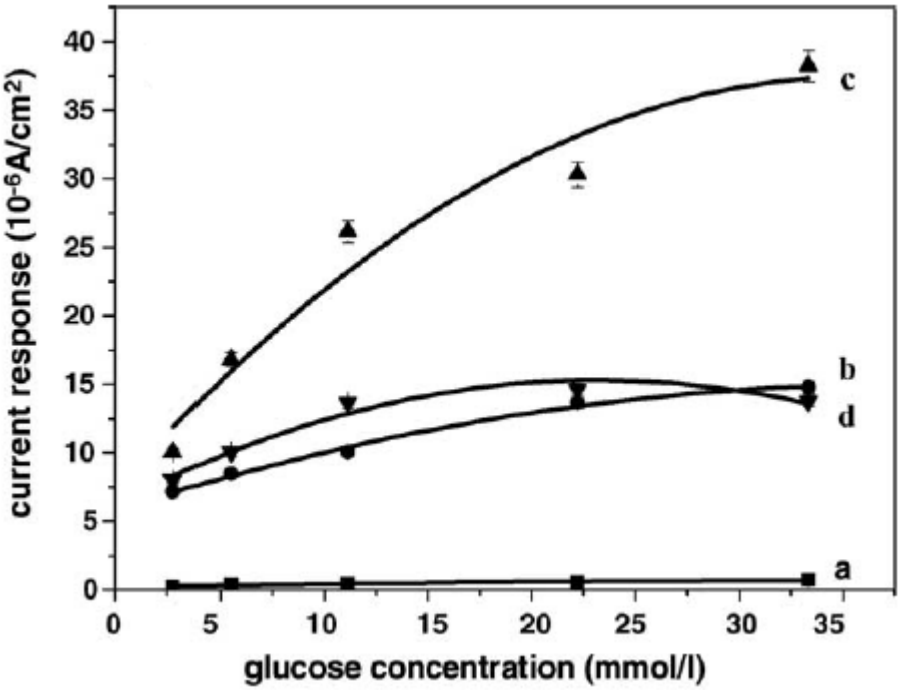



**Figure 2.** Calibration curves of the electrodes: electrode a, containing no AgNP; electrode b, containing hydrophilic AgNP; electrode c, containing hydrophobic AgNP; and electrode d, containing no AgNP, but 10 times more GOx than that of electrode a [39].

In other work Xiangling et al. [40] made a Glucose biosensors using glucose oxidase (GOx) immobilized in Ag–Au sol. They used Ag–Au nanoparticle because silver is the best conductor among metals and gold has good biocompatibility.

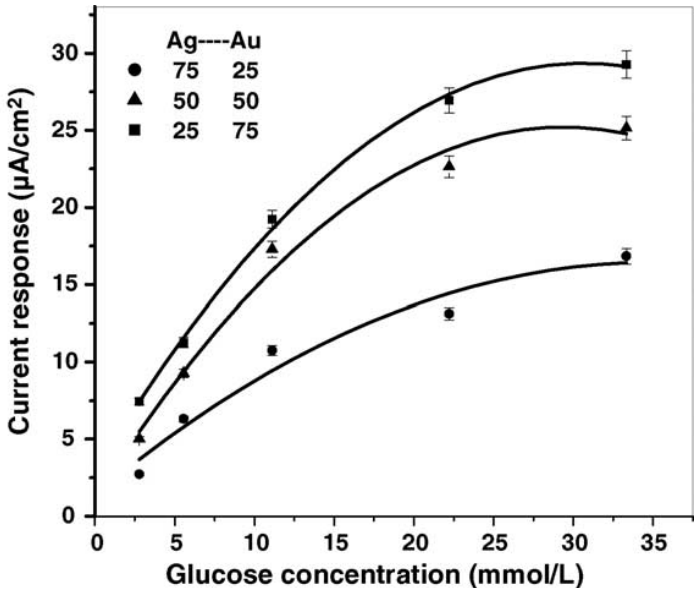



**Figure 3.** Calibration curves of the electrodes containing various molar ratios of Ag–Au composite particles [40].

Their experiments show that these Ag–Au particles can significantly enhance the current sensitivity of GOx enzyme electrodes. They studied the effects of the various molar ratios of Ag–Au particles with respect to the current response and the stability of the GOx electrodes. The current response curves of GOx electrodes with various molar ratios of Ag–Au composite particles shown in Fig. 3. From Fig. 3 it can be seen that the current response of Ag will be increase by increasing the ratio of Au/ AgNPs.

Jiehua et al. [41] reported a sensitive glucose biosensor based on the one-step synthesis of AgNPs /CNTs/chitosan film (Ag/CNT/Ch) hybrid film as a new alternative for the immobilization of GOx and horseradish peroxides (HRP) based on layer by layer technique. *o*-Phenylenediamine (OPD) was chosen as the electronic mediator, and also co-immobilized in the Ag/CNT/Ch film with HRP. By combining the profit of Ag/CNT hybrid and chitosan film, the projected Ag/CNT/Ch matrix by simple one-step synthesis offered an excellent amperometric response for HRP and GOx with high sensitivity and quick response. Fig. 4 shows a current–time plot for the bienzymatic biosensor on successive step changes of glucose concentration at a working potential of −0.51 V. The biosensor exhibited a rapid and sensitive response to the changes in glucose concentration, and the reducing current increased to reach a relatively stable value after 10 s. they determined glucose in a linear range from 0.5 to 50μM with a correlation coefficient of 0.9990 ($n$ = 24) and a detection limit of 0.1μM at 3 S/N.

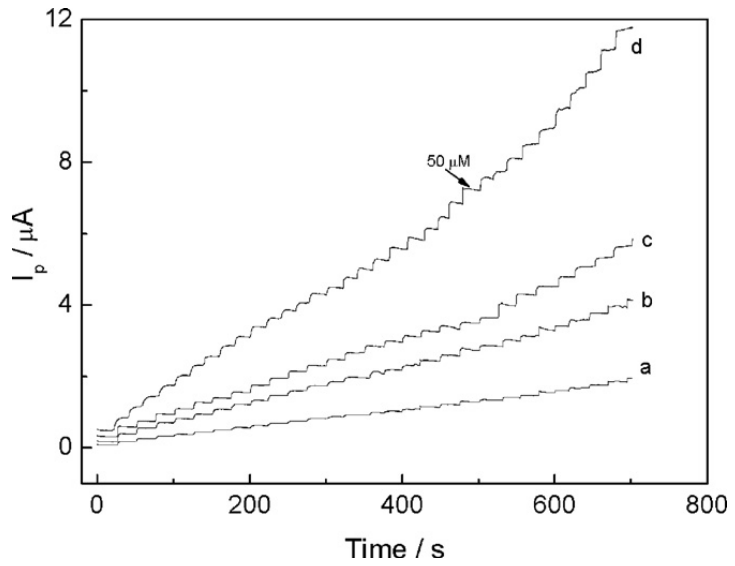
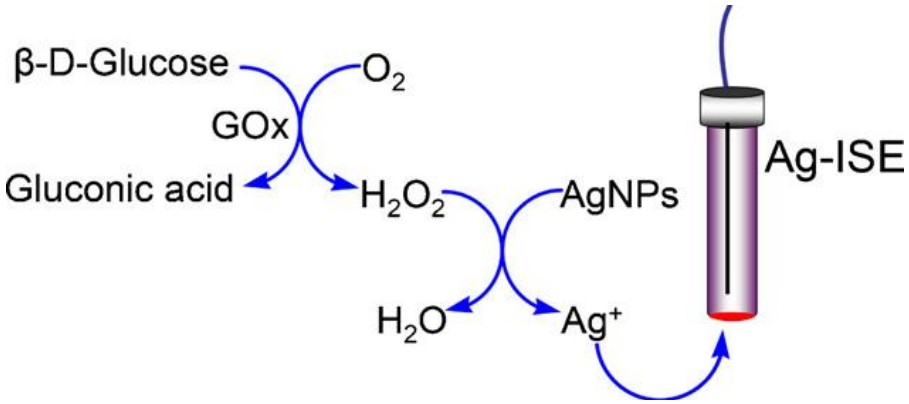



**Figure 4.** Current–time responses of the different glucose biosensor obtained based on (a) pure chitosan, (b) Ag/Ch, (c) CNT/Ch and (d) Ag/CNT/Ch films by successive additions of glucose at an applied potential of −0.51V.

Wittaya et al.[42] reported A new approach in glucose biosensor based on polymeric, membrane Ag-ISE fabricated from benzothiazole calix[4] arene. They synthesized AgNPs to be used as a potentiometric redox marker in a glucose biosensor. They obtained linear relationship between logarithmic of H2O2 concentration and activity of free Ag+ releasing from AgNP by direct potentiometry. The enzyme–substrate reaction between β-D-glucose and GOx produced H2O2 as a

product as shown in scheme 1. The generated H2O2 was able to oxidize AgNPs to free Ag+ ions. The amount of Ag+ ions corresponded to the concentration of glucose could be directly monitored using the Ag-ISE. The proposed sensor provided a double selective function and could be used to determine glucose in beverages with good accuracy and precision. They earned the detection limit of 1.0×10−5 M. The sensors exhibited very good repeatability with %R.S.D. < 7




**Scheme 1.** The Use of AgNPs as a newpotentiometric redoxmarker in a glucose biosensor [42].

*5.2. Hydrogen Peroxide Biosensor*

Sensitive determination of H2O2 is of great significance in biological, clinical and environmental and many other fields. Many analytical methods have been developed for this reason, such as electrochemistry, photometry and titrimetry. Among these methods, amperometric enzyme-based biosensors have received significant concentration due to its expediency, high selectivity and sensitivity [43-44]. As mentioned before a significant confront to development of sensitive and stable sensors comes from the effective immobilization of enzyme to solid electrode surface [45]. There are many materials have been used to immobilize enzyme on the electrode surface toward $H_2O_2$ sensing, such as quantum dots [46], polymers [47-48], mesoporous materials [49] and nanomaterials [50–52]. Among these, nanomaterials have attracted great research interest in biosensor because of their flexibility of the physical and chemical properties [53]. Also in order to retain the electrocatalytic activity and further modification onto the electrode surface, various methods have been used to enhance the electron transfer, such as electropolymerization [54], sol–gel [55], layer by layer assembly [56], covalent bonded immobilization [57] and direct embedded biocompatible membrane [58].

Yanxia et al. [59] fabricated a H2O2 biosensor based on the direct electrochemistry of hemoglobin (Hb) in Hb–Ag sol on GC electrode. They used Hb acts as a pattern to manufacture the Hb–Ag sol. In role of Hb is showing a pair of distinct redox peaks on GC electrode. This biosensor showed a good reduction response for H2O2 and exhibited high sensibility, good reproducibility, and long-term stability. They gained the detection limit of $1\times10^{-7}$M at $3\sigma$ linearly in the concentration range of $1\times10^{-6}$ to $2.5\times10^{-2}$M toward H2O2 .

They compared the cyclic voltammograms of the bare GC electrode, Ag/GC electrode and the Hb–Ag/GC electrode. The results are shown in fig.5. It can be seen nearly reversible redox peaks on Hb–Ag/GC electrode (curve a), while no peak is observed at bare GC electrode (curve c) and Ag/GC electrode (curve b). Clearly, the redox peaks observed on Hb–Ag/GC are accredited to the redox of the electroactive center of Hb in Hb–Ag sol. There were not any peaks observed for Hb in the sol film in the absence of AgNPs. While, AgNPs are the main factor that enhance the direct electron transfer of Hb.

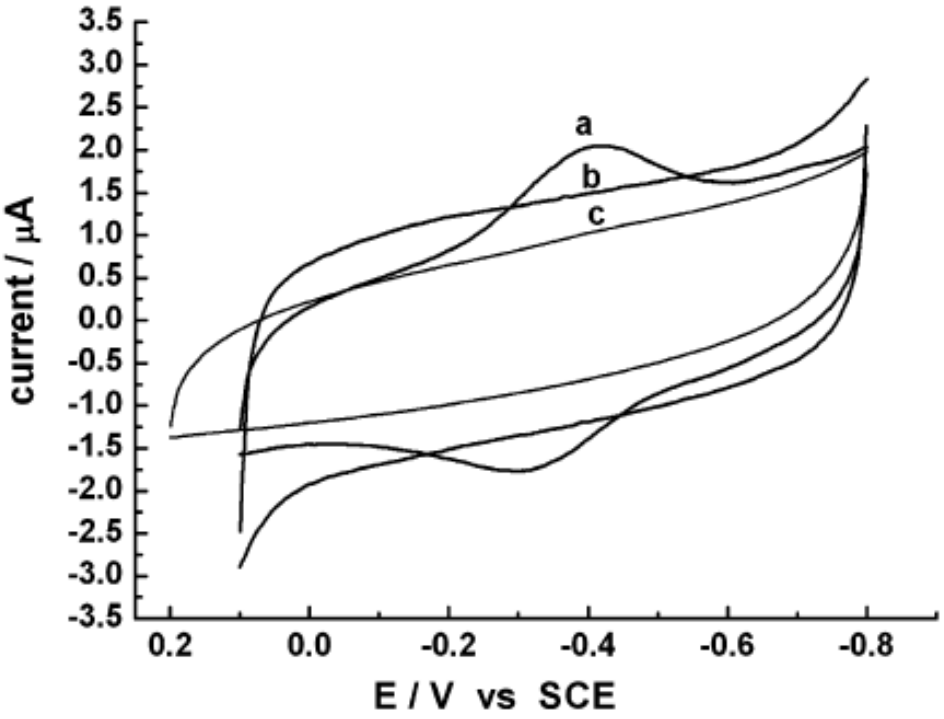
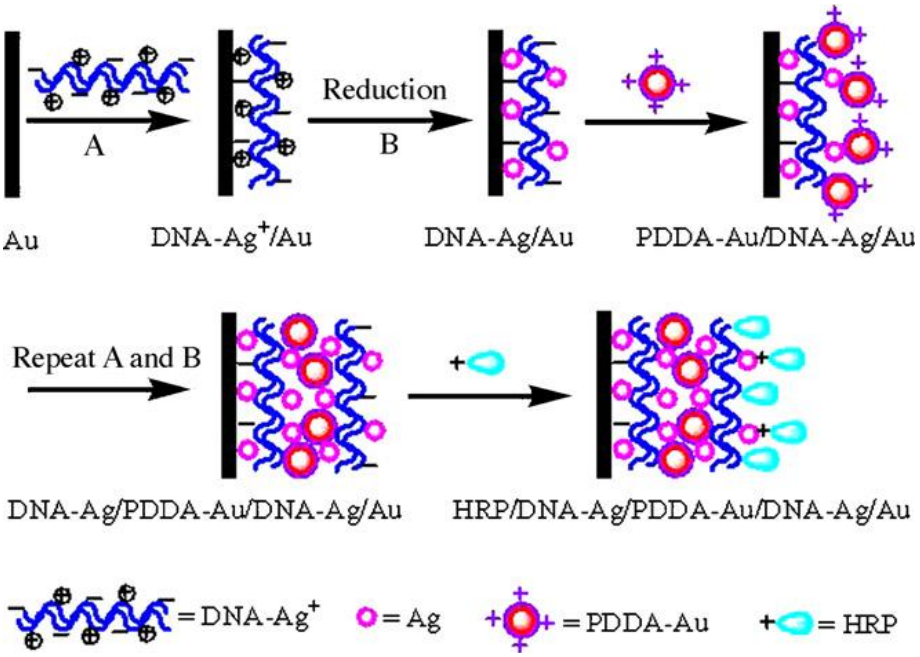



**Figure 5.** Cyclic voltammograms of (a) Hb–Ag/GC; (b) Ag/GC; (c) bare GC in 0.1M pH 7.0 PBS. Scan rate: 300 mV/s [59].

A new amperometric H2O2 biosensor reported by Liping et al. [60] based on the immobilization of HRP on DNA–Ag nanohybrids (DNA–Ag).

They fabricated a H2O2 biosensor formed with DNA–Ag and PDDA–Au to entrap HRP. First, they electrochemically reduced the DNA–Ag+ complex to obtain negatively charged immobilization matrix (DNA–Ag) to immobilize poly (diallyldimethylammonium chloride) (PDDA)–Au. Here, immobilization of PDDA–Au was attributed to the two forces. The one is electrostatic force between positively charged PDDA–Au and the negatively charged DNA. The other is the adsorption of the nano-Ag to the PDDA–Au. Then, the second layer of DNA–Ag was assembled onto the modified electrode based on the electrostatic force and outstanding film-forming ability of DNA. Lastly, the positively charged HRP was adsorbed firmly onto the DNA–Ag layer just as the adsorption of PDDA–Au to obtain H2O2 biosensor without losing their biological activity. The mechanism are shown in Scheme 2.




**Scheme 2.** design of the preparation process of modified electrode [60].

This approach has the next advantages. First, Au and AgNPs not only possess larger specific surface area, good biocompatibility, but also possess good conductivity. They can make possible conducting channels to make easy charge transfer between the prosthetic groups and the electrode surface [61]. Secondly, PDDA can act as the reducing and stabilizing agents to fabricate the PDDA-protected Au nanoparticles simultaneously [62]. In addition, PDDA is a positively charged ionic polymer, and the PDDA-protected Au nanoparticles can be effectively self-assembled onto the negatively charged DNA–Ag membrane by electrostatic interaction. The resulting biosensor showed a linear response to H2O2 over a concentration range from 7.0μM to 7.8mM with a detection limit of 2.0μM (S/N = 3) under optimized conditions.

Chuan et al. [63] used a novel H2O2 biosensor based on the direct electrochemistry and electrocatalysis of myoglobin (Mb) immobilized on AgNPs doped carbon nanotubes film with hybrid sol–gel techniques. AgNPs have been electrodeposited and modified onto CNTs. In their work, the nanocomposite was used to modify the electrode surface to construct active layers, and then Mb-hybrid silica sol–gel (HSG) was coated onto the active layers. Due to the biocompatibility and synergistic electrocatalysis of SN-CNTs and ideal micro-circumstance of HSG, the direct electrochemistry of Mb was achieved; the strong electrocatalysis towards H2O2 has been evaluated by cyclic voltammetry and amperometry. They mentioned excellent sensitivity, wide linear range, favorable stability and reproducibility, low detection limit and low Michealis–Menten constant for proposed biosensor.

Balamurugan [64] and coworker reported Ag nanograins incorporated PEDOT modified electrode by electrochemically without using any reducing agent or stabilizer. They utilized this modified electrode for electrocatalytic reduction of H2O2. Fig. 6 shows the cyclic voltammograms recorded in the presence of certain concentration of hydrogen peroxide. They gained the detection limit of 7 mM at the optimum condition.

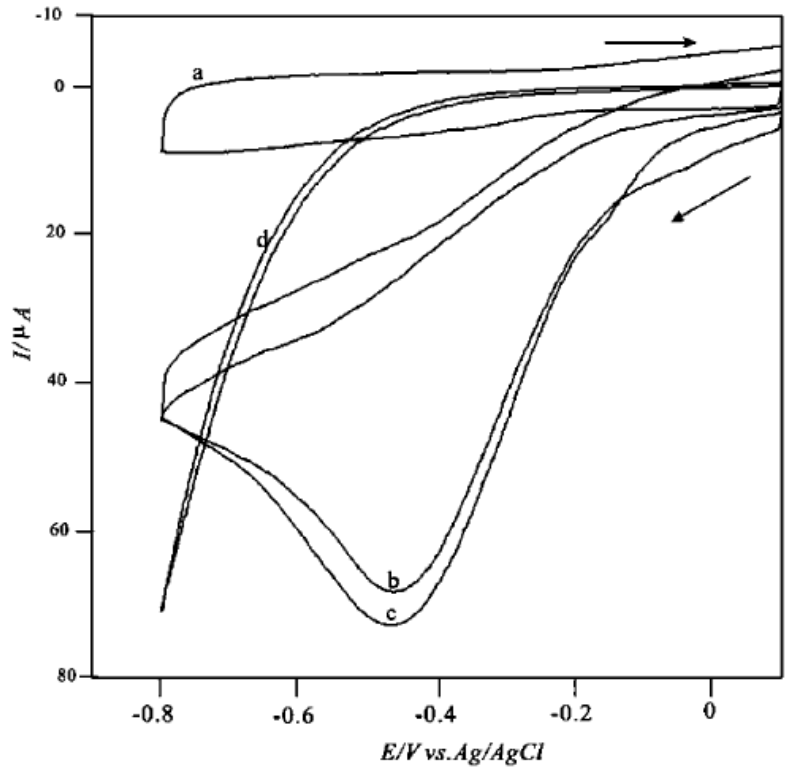
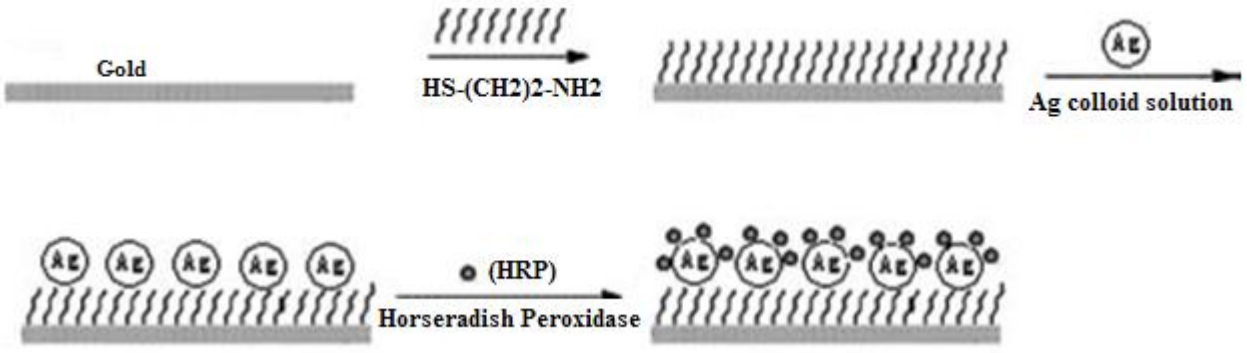



**Figure 6.** CVs of different electrodes a) Ag nanograins unmodified electrode b) AgNPs modified electrode; c) Ag nanograins incorporated PEDOT modified electrode and d) bare GC electrode [64].

Ren et al. [65] immobilized HRP on AgNPs adsorbed on a cysteamine monolayer-modified gold electrode, and detected its electrocatalytic response to the reduction of H2O2 via cyclic voltammetry and amperometry. The preparation process of the electrode is shown in Scheme 3.




**Scheme 3.** Preparation process for the HRP/AgNPs/cysteamine/ gold electrode

After the immobilization of cysteamine on the gold surface, the amino terminals of the cysteamine monolayer were protonated in order to load positive charges. So, the AgNPs, which were stabilized by negative ions, could attach to the cysteamine monolayer through electrostatic adsorption also between similar charges the electrostatic repulsion caused AgNPs to be dispersed on the cysteamine monolayer homogeneously. HRP was either absorbed on the surface of a AgNPs or buried in the interstices between AgNPs, due to the interaction between the cysteine or NH4 + -lysine residues of HRP and the Ag surface. One AgNP was able of linking a number of HRP molecules means the two dimensional electrode surface was modified to be three dimensional, so that more binding sites were provided by the AgNPs for the immobilization of HRP . They reported the linear range of the biosensor was 3.3 l M to 9.4 mM, and the detection limit of 0.78 μM.

## 6. CONCLUSIONS

Due to their great specific surface area and high surface free energy of Nanoparticles, they can play a significant function in adsorption of biomolecules. The combination of nanometer materials and biomolecules is of considerable interest in the fields of biotechnology and bioanalytical chemistry. From consideration of the work discussed in this review, we can conclude that AgNP have been applied as catalyst in various sensor and biosensor applications, due to their superior stability and complete recovery in chemical and biochemical redox processes.

It is well known that Ag is the best conductor among other metals, and so AgNPs may make easy well-organized electron transfer than other nanoparticles in biosensors. Biosensors are currently the focus of extensive research for the development of a wide variety of applications in clinical diagnosis, biomedical, industrial and environmental monitoring . Two aspects, which are the most problematic in developing enzyme-based biosensors, are the inclusion of sensing molecules in suitable matrix and monitoring the interactions between the analytes and those molecules. So the expansion of active layers or suitable matrix to immobilize redox proteins for biosensors is an important task. In the field of electrochemical biosensors, efforts have been made in designing well-organized bio-immobilization matrices as well as improving transduction processes.

The goal of this paper was to provide an updated summary of the works using AgNPs toward glucose and hydrogen peroxide sensing. For this purpose the synthesis, classification and practical function of AgNPs are discussed.

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