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Electrodeposition of Metallic Nanostructures for Biosensing Applications in Health Care

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Abstract: **Biosensors are rapidly gaining prominence as the first line of diagnostic approaches in home as well as in clinical settings owing to their excellent sensitivity and quick response time. To achieve better stability, sensitivity, and anti-fouling effects nanomaterials are incorporated in the biosensors development. Metallic nanostructures, a type of nanomaterial is widely used in the biosensors due to its excellent conductivity, electrocatalysis, and optoelectronic property. Among many methods of metallic nanomaterial synthesis, controlled electrodeposition is a simple approach that allows to develop metallic nanostructures with unique shape, size, and catalytic property. There are many factors like pH, temperature, potential, and electrolysis time that influence the growth as well as the kinetics of the nanostructures formation. In this article, we have discussed the mechanism behind the synthesis of nanostructures via electrodeposition, its importance over conventional wet chemistry synthesis protocols, and fabrication procedures of different dimensional (0D, 1D, 2D, and 3D) nanomaterials in view of their uses in various biosensing applications.**

Index Terms: **Biosensors, electrodeposition, nanostructures, electrocatalysis, nanorods, dendrites.**

I. INTRODUCTION

Detection of the diseases at the earliest phase is very crucial, as it enhances the possibilities of survival and recovery of the diseased individuals, especially in case of chronic disease like cancer and cardiac disorders (Etzioni et al., 2003). However, the currently used traditional diagnostic approaches are heavily dependent on the bulky and sophisticated instruments that lack the robustness and portability to reach a wider population. Among all the diagnostic approaches, biosensors are being widely used for its robustness, miniaturized form, portability, quick detection and user friendliness (Mahato et al., 2018a; 2018b). Biosensors are analytical devices that consist of biologically active molecules (i.e. enzymes, proteins, peptides, DNA, aptamer, cells etc.) that recognize a particular molecule of interest and convert the biochemical signals into a form of measureable signal (Kumar et al., 2019a; Purohit et al., 2019a). The performance of a biosensor is evaluated on the basis of its sensitivity towards a particular analyte, the quickest time it can generate a quantifiable signal, its stability in a varied physical conditions, and the lowest amount of an analyte it can detect in a system (Kumar et al., 2018). To achieve better sensitivity, selectivity and avoiding biofouling effects in the presence of biological molecules, nanostructures (NS) are being widely used to develop novel engineered surfaces and unique biochemical catalyst (Kumar et a., 2019c). The NS are used in biosensor fabrication to achieve fast movement of charged ions between electrode and target, better electro-catalytic activities, fast diffusion, pre-concentration of analyte molecules in the vicinity of active electrode surface, and anti-fouling effect (Sharma et al., 2018). Nanomaterials of different size, property, shape, and structures are now used to achieve better biosensing activity. Among all the NS, metallic NS are commonly used for their size dependent optical, electromagnetic, and chemical properties. The chemical structure, active surface area, surface charge, arrangement of atoms in crystal structure of these structures cumulatively effect its electrochemical behavior. The noble metals NS (i.e. Au, Ag, and Pt) have been most commonly used for their exceptional opto-electronic properties, ease of conjugation with biological entities, and greater bio-compatibility (Kumar et al., 2019c; Purohit et al., 2019b), whereas metallic oxide NS (especially of d- and f-block elements i.e. Cu, Co, Hf, Gd, Sn, Mn, and Fe) are used for their direct electron transfer activity, adsorption capacity, and unique catalytic activity (Mandal et al., 2018).

Electrodeposition is a simple technique of deposition of metals Unlike wet-chemical methods of NS synthesis, electrodeposition is very fast, does not require any chemical reductant or oxidants, low energy as well as low raw material consumption, cost-effective and devoid of formation of any undesirable by-products (Scavetta et al., 2014). As the NS are directly deposited over the electrode surface, it strongly binds to the surface and avoid the errors in signal generation caused due to the faulty transfer of materials on to the electrode surface. In addition to its robustness, size of NS by electrodeposition can be tuned by

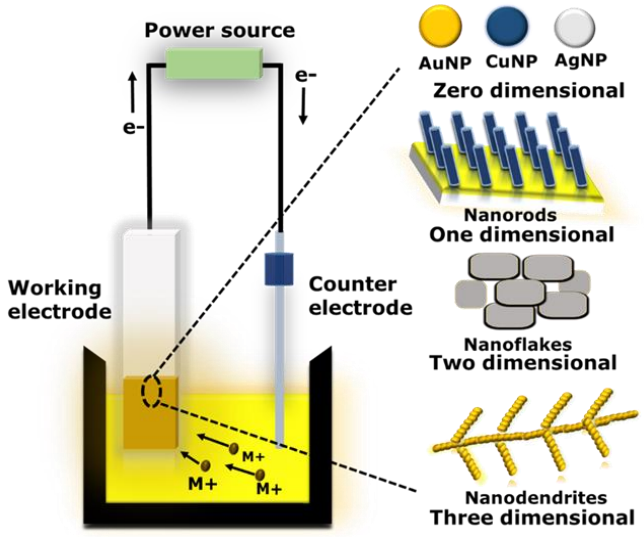
optimizing the current density, applied potential, salt concentration, and electrolysis time. Some more complex NS require various templates viz. mesoporous silica film to synthesize a number of 3D structures (Zhu et al., 2015). Electrochemical techniques such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry, and sonoelectrodeposition are generally used to get a uniform layer of these NS (Natter et al., 1998; 2000; Wang et al., 2004). In addition, multi-layers of mono or multi metals NS can be achieved by electrodeposition easily.

II. ELECTRODEPOSITION OF NANOSTRUCTURES

The electrodeposition of NS is generally performed in a three electrode system containing a metal ion of particular concentration. The working electrode (cathode) and counter electrode (anode) are connected to a battery or power source to complete the circuit (as shown in fig. 1). When a particular potential is applied, charged metal ions from the electrolyte solutions move towards the cathode, resulting in a film of metal sheet on the electrode. The theoretical basis of electrodeposition can be explained by Faraday's law (Al-Bat'hi, 2015). With the increase in the electrolysis time, there is an increase in the amount of material deposited over the electrode surface.

An optimum parameter of various factors ensures the deposition of desired NS (Kumar et al., 2015). The nature of the metals plays the most crucial role in the electrodeposition leading to differential nucleation of NS, growth kinetics, NS size, and number of NS per unit area. pH of the electrolyte solution influences the precipitation, decomposition of the salts, and thus determines the uniformity of the NS deposition over the electrode surface.

Fig 1. Schematic representation of electrodeposition of NS of different dimensions on the electrode.



An increase in the electrolyte temperature increases the solubility of the salts, thereby increase the conductivity of the solution and leads to higher electrodeposition. The higher precursor salt concentration leads to higher concentration of metal ions in the electrolyte solution, which leads to higher deposition as well as fast rate of deposition. Also, longer electrolysis time leads to higher deposition of the materials.

III. BIOSENSING APPLICATIONS OF NANOSTRUCTURES

A. ZERO DIMENSIONAL NANOSTRUCTURES

Nanoparticles of various metals are directly electrodeposited over the electrode surface by using various electrochemical methods. Among them, gold nanoparticles (AuNP) are the most commonly used NS for biosensing applications due to their superior optoelectronic property. Kumar et al. (2019b) reported an optimized AuNP synthesis protocol by simple electrodeposition method, where AuNP was electrodeposited by performing multiple cycles of LSV in an acidic solution of (0.6 M H_2SO_4) with 0.003% $HAuCl_4$. The formation of AuNP was also confirmed by the appearance of a reduction peak at 0.95 V. The reducing current increased with each cycle of LSV until the 4^{th} cycle. After the 4th cycle, the LSV current response of electrodeposition became saturated. The AuNP NS was further incorporated with reduced graphene oxide (rGO) to develop a sinapic acid sensor. The sensor was found to detect the sinapic acid in the range of 20-200 μM with a lower limit of detection (LOD) of 33.4 nM. Dai & Compton (2006) designed electrodeposited AuNP over ITO surface by applying -0.6 V for 60 s in a 0.5 M H_2SO_4 solution containing 0.1 mM $HAuCl_4$. The fabricated probe was able to detect arsenic with a LOD of 5 ± 0.2 ppb. Chandra et al. (2013) electrodeposited AuNP over a glassy carbon electrode (GCE) for cancer cell detection, where the deposited AuNP act as a scaffold for further deposition of monomers. Salimi et al. (2007) reported the development of an electrodeposited cobalt nanoparticle biosensor to detect H_2O_2. Phosphate buffer containing 1 mMCoCl was used for the electrodeposition by repetitive potential cycling (30 cycles at 100 mV s^{-1} at potential range between 1.1 V and −1.1 V). The CoNPmodified GCE surface shows excellent peroxidase activity to detect H_2O_2 with a LOD of 0.4 nM and a response time of < 2 sec. Various bimetallic/multi-metallic nanoparticles are also developed using the same electrodeposition methods. Tao (2014) reported the development of a sensor by electrodepositing Ag–AuNPs on the activated ITO surface to monitor hazardous effects of mercury. The surface was developed by cyclic voltammetry in the potential range of 0 to (-0.9) V, with scan rate of 0.05 V/s for 30 cycles, where the initial precursor concentration was 0.14 mM $AgNO_3$, 0.06 mM $HAuCl_4$ in PBS solution. Naik & Rout (2015) developed a $ZnCo_2O_4$ nanoparticle by co-deposition by applying 1.3 V for 180 s in a 3 mM KCl stirring solution containing 3 mM of $Zn(NO_3)_2$ and 6 mM of $Co(NO_3)$. Here, they reported that the solution was heated to 70 ˚C for better nucleation of the nanoparticle during the electrodeposition process. The sensor was reported to detect the

glucose concentration in the range of 10-290 µM and a LOD of 36 µM. This signifies that in the electrodeposition of nanoparticles, several factors like the concentration of precursor salt in electrolyte, the method of electrodeposition, nature of the material, temperature play an important role as well as varies from one another.

B. ONE DIMENSIONAL NANOSTRUCTURES

Metallic nano arrays structures are a cable like one-dimensional NS, that works as an excellent charge collector for various biosensing applications. Unlike other NS electrodeposition, nanowire arrays synthesis usually needs a template (like anodic alumina membrane, anodic alumina membrane on silicon substrate, polycarbonate template) for aligned nucleation and growth of the NS in one direction only (Banerjee et al., 2002). The conductivity of a nanowire largely depends on the diameter, composition and crystallinity of the wire, which can be tuned by optimising the electrodeposition parameters (Yogeswaran & Chen, 2008). Zhang et al. (2009) reported an Au nanowire based enzymatic glucose biosensor by electrodepositing the Au nanowires on ananodised aluminum foil. A suitable nanochannel alumina (NCA) template with proper pore size was prepared in oxalic acid by two-step anodization and chemical etching methods. Then Au nanowire was deposited using the NCA template in an electrolyte solution, and the rest of the alumina after electrodeposition was removed by etching to get the nanowire. Sensor fabricated using the Au nanowire and glucose oxidase (GOx) achieved a LOD of 4.6 x 10^{-5} M for glucose biosensing. Kurowska (2013) developed an electrodeposited Ag nanowire with 50 nm diameter using anodic aluminium oxide for the selective detection of H_2O_2. The sensor was able to detect H_2O_2 in the concentration range from 0.1 to 3.1 mM with a LOD of 29.2 µM. Dong et al. (2015) developed a vertically aligned bimetallic Cu@CuO nanowire for glucose sensing by electrodepositing a Cu nanowire wrapped in CuO particles. The Cu@CuO nanowire can non-enzymatically detect glucose with a LOD of 6.9 x 10^{-7} M.

C. TWO DIMENSIONAL NANOSTRUCTURES

2D NS show better electron transfer efficiency because of fewer grain boundaries, greater mechanical stability, and higher active surface area. The material properties of 2D materials can be tuned to achieve by the electrodeposition methods to achieve better sensitivity to detect various analytes efficiently. Nanoflakes that resemble the structure of a cabbage leaf are a 2D NS are being widely used due to its higher catalytic and conducting nature. Schiavi et al. (2016) developed a porous network of interconnected cobalt nanoflakes of thickness of 10 nm for higher catalytic and electrochemical activity. They reported two different methods of depositing the nanoflakes i.e. by applying a constant voltage and a mixed mode pulsed electrodeposition at different potentials. They concluded that under potentiostat condition, the average size of the NS is limiting to the overall transferred charge. A change in the cobalt ion concentration to 0.2 M led to deposition of round shaped nanoparticles over the nanoflakes in the constant potential mode, whereas in the mixed pulsed electrodeposition, both nanoflakes and NS were clearly visible in 0.1 M salt concentration. Lo et al. (2016) reported the electrodeposition of nickel hydroxide $Ni(OH)_2$ nanoflakes on to a Zn nanowire surface by cathodic electrodeposition. Cai et al. (2018) synthesized an aligned α-Fe_2O_3 nanoflakes structure over FTO surface for hydrogen peroxide sensing. After electrodeposition, however they performed calcination of the structure at 500 ˚C for 2 h, which led to some change in the mesoporous structure of nanoflakes due to the shrinkage and evaporation of water from the structure. The sensor achieved a LOD of 22 µM of H_2O_2. Premlatha et al. (2017) designed a Co-CeO_2 nanoflakes arrays by using 100 g/L cobalt acetate and 6 g/L CeO_2 salt in a 40 g/L boric acid solution with a current density of 4 A/dm^2 for 15 min. It is interesting to note that both the chemicals were stirred for 8 h before the electrodeposition process to obtain a homogenous distribution. The sensor was able to detect hydrazine in the range of 0.005 - 0.37 mM with a LOD of 6 nM. Premlatha & Bapu (2018) developed another Co-ITO nanoflakes structure by similar electrodeposition method. The sensor was able to detect catechol in the range of 1-200 µM and with a LOD of 1 µM

D. THREE DIMENSIONAL NANOSTRUCTURES

Three dimensional NS with active sites all over the surface provides an exceptional sensing matrix for various biosensing applications. Li & Lan (2007) designed a three dimensional Au nanocluster modified probe for simultaneous detection of epinephrine and uric in the presence of ascorbic acid. The Au nanocluster was electrodeposited by scanning the potential from (+0.2) to (−1.0) V for 15 cycles in a 0.5 M H_2SO_4 solution with 0.25 mM of $HAuCl_4$ over a PPY/GCE electrode. The sensor exhibited an LOD of 30 nM and 12 nM for epinephrine and uric acid, respectively. Abdelwahab & Shim (2015) developed an Au nanocluster modified probe to detect ascorbic acid, dopamine, uric acid and folic acid in biological samples. The Au nanocluster was electrochemically deposited over an activated GO/MWCNT composite for better bioelectronics properties following the same protocol as mentioned above. The sensor surface was able to detect ascorbic acid, dopamine, uric acid and folic acid with LOD of 0.27 µM, 0.08 µM, 0.10 µM, and 0.09 µM, respectively shows its excellent sensing activity.

Metallic dendrites, another class of three dimensional NS, are electrodeposited hierarchical arrangements of nanoparticles resembling fern like morphology. In the metallic dendrites, the primary branch formed first, followed by secondary and tertiary branches, with pointed tips and edges all over the structure. All the tips and edges all over the structures contributed to the superior active surface area. Such a large active area leads to the higher catalytic activity than other nanoparticles. The excellent catalytic activity is a result of the geometric orientation of the active sites and the inherent property for the nanoparticles,

which is enhanced in a structure with larger active surface area. The applied potential, electrolysis time, and salt concentrations are optimized for the synthesis of a superior dendritic biosensing matrix. Au nanodendritic structures are well characterized for its peroxidase activity and to detect glucose. Shu (2014) reported the development of Au dendrite by applying (-0.3) V for different time in a 0.1 M KCl solution with the 10 mM of HAuCl4 salt concentration. They reported that with more electrolysis time, the size of Au dendrites increased along with its catalytic activity. The NS was able to detect glucose in the range of 0.1 - 25 mM, and with a LOD of 0.05 mM. Purohit et al. (2019b) reported that the peroxidase activity was enhanced by sputtering of metallic nanoparticles over the electrodeposited Au dendrites. The electrode was able to detect hydrogen peroxide in the range of 10^{-12} and 10^{-5} M and LOD of 9.3 x 10^{-13} M. The result shows that two or more electrodeposition methods can be combined to achieve higher catalysis. Das et al. (2015) reported a NAD mediated method of Au dendrite synthesis using a solution containing 2 mM $HAuCl_4$ in a 0.5 M H_2SO_4 electrolyte with 150 mM NAD^+ by using square wave techniques with lower potentials of (-0.8) V and higher potential of 0.2 V, respectively at a frequency of 40 Hz for 2000 s. The developed electrode was capable of detecting glucose in the range of 1-10 mM with LOD of 7.29 mM. Ye (2010) reported another electrodeposition method of Au dendrite by applying a potential of (-0.6) V in a Na_2SO_4 solution. They evaluated that the nanodendritic structure exhibited super hydrophobic as well as oleophobicity nature, highly desirable for biosensing applications. Qui et al. (2009) developed a Cu dendritic structure by electrodeposition of 0.1 M $CuCl_2$ in a solution containing 0.1 Na_2SO_4 by applying a potential of (-1.0) V for 600 s. The electrode was able to detect H_2O_2 as well as NO_3. They also reported that the growth of the dendritic structure was driven by the sequential arrangements of cubic Cu structures. Bimetallic and multi metallic nanodendrites are being synthesized using a different concentration of the contributing salts. The applied potential for electrodeposition is generally different than their individual monometallic dendrite synthesis. Noh (2012) developed a CuCo bimetallic dendrite by applying a constant potential of (-0.8) V in a solution containing 0.01 M $CuCl_2$ and 0.01 M CoCl in an electrolyte solution containing 0.1 M Na_2SO_4 with electrolysis time of 600 s. The bimetallic dendrite shows excellent catalytic activity due to the synergistic activity of both Cu and Co unit. The electrode was able to detect glucose and H_2O_2 in the range of (0.5 μM to 14.0 mM) and (1.0 μM to 11.0 mM), respectively. Chang & Chun (2016) developed a trimetallic Au-Ag-Cu dendritic structure by sequential deposition of different layer of dendrite. First, the Cu dendrite was synthesized by applying (-0.8) V in a 10 mM $CuSO_4$ solution for 12 min, then it was dipped in 10 mM of $AgNO_3$ solution for 15 minutes. Next, Au dendrite was synthesized over the bimetallic structures by dipping in 10 mM of $HAuCl_4$ solution. It is interesting to note that the concentration of individual ions and the applied potential may vary to electrodeposit different metal.

IV. CONCLUSION

The biggest advantage of utilizing electrodeposition of metallic NS is that the shape, size and nature of the structures can be tuned by simple optimization of some parameters. Recent research on electrodeposition for biosensing applications focuses more on the sensing surface development to attend better sensitivity and catalysis. Advanced synthesis protocols and fabrication strategies of multi-metallic NS hold more promises for biosensing of bigger and more complex biological molecules.

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