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Experimental Investigation and Analysis of Glucose Sensing Properties of ZnO Rods

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Abstract-*In this study it made an attempt to ZnO rods using simple wet chemical route method. The structure and morphology of ZnO nanostructures like ZnO rods are characterized by XRD and SEM. It focused to find electro catalytic properties of rods for glucose sensing. The electro catalytic activity of ZnO rods/CHIT/GOD/GCE electrodes are studied using cyclic voltammetry. It infers that ZnO rod modified electrode shows good electro catalytic efficiency.*

1. INTRODUCTION

Nanomaterials are the building blocks of nanotechnology. A material having particle size less than 100 nm is called Nanomaterials. When the particle size is reduced, most of the physical properties of the Nanomaterials get changed [(1)]. Due to the change in physical properties of nanomaterials, they have various applications different from those of bulk materials. Nanomaterials are classified into categories such of carbon based materials, metal based materials and composites. Carbon based nanomaterials are made of carbon and it takes the form of hollow spheres, ellipsoids or tubes. Metal based nanomaterials include quantum dots, Nano gold, and Nanosilver and metal oxides such as TiO_2, MnO_2. Composites combine nanoparticles with other nanoparticles or with larger, bulk type materials. The individual particles in the nanomaterials are called nanoparticles. Nanoparticles form the bridge between the bulk materials and atomic or molecular structures Nano powders forms the bridge between the bulk materials and atomic or molecular structures. Nano powders are the agglomerates of ultrafine particles, nanoparticles, or Nanoclusters and nanometer sized single crystals are called Nano crystals. Nano materials are used for hard cutting harder and tougher tools, to eliminate pollutants, to produce low cost flat panel electro chromic displays, high power magnets, high energy density batteries and high sensitivity sensors.

Zinc Oxide:

Zinc oxide is an inorganic compound with the formula ZnO. It appears as white powder that is insoluble in water. Synthetic ZnO appears naturally as the mineral Zincite[(2)]. ZnO has a large excitation binding energy so that excitation emission processes can persist at or even above room temperature[(3)]. It is relatively soft material with approximate hardness of 4.5 on the Mohs scale. Its elastic constants are smaller than those of relevant III – V semiconductors, such as GaN. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnO are beneficial for manufacturing ceramics. ZnO has a relatively large direct band gap of ~3.3eV at room temperature. This semiconductor has several favourable properties, including good transparency, high electron mobility, wide band gap and strong room temperature luminescence, Piezo electricity, chemical stability, visible optical transparency, high voltage-current non linearity[(3)]. ZnO is a versatile functional material. ID ZnO nanostructures such as nanotubes, nanowires, nanorods, nanobelts, tetrapod, nanocombs and nanoribbons stimulate considerable interests for scientific research due to their importance in fundamental physics studies and their potential applications in nanoelctronics, nanomechanics and flat panel displays. Among this rod like nanostructures of ZnO produced via aqueous methods, has wide advantages because of the following reasons: They are low cost, less hazardous and thus capable of easy scaling up: the growth occurs at a relatively low temperature, compatible with flexible organic substrates: there is no need for the use of metal catalysts, and thus it can be integrated with well-developed silicon technologies [(4)].

Biosensor:

A biosensor can be defined as a device incorporating a biological sensing element connected to a transducer to convert and observed response into a measurable signal, whose magnitude is proportional to the concentration of a specific chemical species. Transducers in biosensors may be optical (optical fibers, wave guides, interferometers, fiber gratings, ring resonators, and photonic crystals), electrochemical (pH, polarographic, capacitive, potentiometric or conductor metric probes, Amperometric etc.), micromechanical, piezoelectric, magnetic or thermometric[(5)]. Biosensors can be applied to a large variety of samples including body fluids, food samples and cell cultures may be used to analyse environmental samples. The recognition elements used in biosensors are: enzymes, nucleic acids, antibodies, whose cells, and receptors. According to the receptor type, biosensors can be classified as enzymatic biosensors, genosensors, immune sensors, etc[(6)]. Among these various kinds of biosensors, electrochemical biosensors are a class of the most wide spread, numerous and successfully commercialized devices of biomolecular electronics.

Electrochemical Biosensor

It is an attractive means to analyse the contents of a biological sample due to direct conversion of a biological event to an electric signal. Electrochemical biosensors convert proportionally the chemical information obtained by the enzymes into a measurable electrical variable such as electrical current, voltage or resistance. This type of biosensors have very attractive advantages respect to other types of biosensors such as portability, rapid measurement, repeatability, robustness, compactness, excellent selectivity, high sensitivity, wider linear range, and reduction of the volume of sample to realize the recognition. This type of biosensors uses four different sensing modes potentiometry or voltammetry, amperometry, surface charge using field-effect transistors (FETs), and conductometry. Electrochemical sensing usually requires a reference electrode, a counter or auxiliary electrode and a working electrode, also known as the sensing or redox electrode.

Counter Electrode:

It is an electrode used to close the current circuit in the electrochemical cell it is made up inert material (pt, Au, graphite, glassy carbon) and it does not participate in the chemical reactions. Current is flowing between working electrode and counter electrode. The total surface are of counter electrode must be higher than the area of working electrode so that it will not be a limiting factor in the kinetics of the electrochemical process. This electrode is also known as auxiliary electrode.

Reference Electrode:

This electrode has a stable and well known electrode potential. In other words, potential of an electrode will remain upon the passage of small current. It is used as a point of reference in the electrochemical cell for the potential control and measurement. The high stability of the reference electrode potential is usually reached by employing a redox system with constant (buffered or saturated) concentrations of each participants of the redox reaction. The current flowing through the reference electrode is kept zero.

The reference electrode used for study is Ag/AgCl in saturated KCl. This electrode consists of Ag wire in contact with AgCl in a saturated KCl solution. This results in an electrode potential of 0.197 volt vs SHE at 25^{o}C. Although most electrode of this type uses KCl as electrolyte, 3M KCl and 1M KCl solutions are used as well. Electrodesof this type can be used upto fairly high temperatures (80-100^{o}C). The reference solution is separated from electrochemical cell by a ceramic frit or by a glass sleeve.

Glucose Electrochemical Biosensor

Enzymatic Biosensor

Enzyme-based electrochemical biosensors have been used widely in our life, such as health care, food safety and environmental monitoring. Health care is the main are in biosensor applications, such as monitoring blood glucose levels and diabetics by glucose biosensors. The electrochemical glucose enzymatic sensor possesses high selectivity and high sensitivity due to the specificity of enzyme[7].There is four regular methods for enzymes immobilization such as Adsorption, Entrapment, Covalent Bonding, Cross-linking. Among this adsorption is the simplest and fastest way to prepare immobilized enzymes[7].

Non-Enzymatic Sensor

These are the sensors which do not make use of the mediators. The direct electrochemical oxidation of glucose without enzyme are said to be non-enzymatic sensor. The sensor is not involved in enzymatic bioactivity and very stable but need to overcome high over potential of glucose oxidation.

Role of ZnO in Biosensing:

In the area of Bioscience, ZnO has attracted much attention due to wide range of applications. Nano ZnO acts as a promising candidate in the field of Biosensors because of itsexcellent bio capability, high surface area, non-toxicity, chemical stability and fast electron transfer between the enzyme's active sites and the electrode and this made thematerial to be favour for functioning as the biomimic membrane to immobize enzymes. Since ZnO act as a biocompatible material, it has a high isoelectric point (IEP)of about 9.5 which provide a positively charged substrate for immobilization of low IEPs of protein or enzymes such as glucose oxidises(IEP~4.5) by electro static adsorption.

Various ZnO nano structures such as nanorods, nanowires, nanobelts, nanoring, nanosheet, tetrapod, nanoflower, nanocombs, nanosprings, nano cages, hexagonal pyramid and cylinder and radial nano wire array have been used for fabrication of biosensor. Thin films of ZnOnanorods and nanocombs have been used for the fabrication of glucose biosensor. Electrodeposited nanoporous ZnO film has been used for the interfacing with myoglobin for biosensing applications. A mediator free phenol biosensor has been fabricated based on immobilizing tyrosinase to ZnO nanoparticles. Uric acid has immobilized on ZnO nanorods for the fabrication of urea biosensor[8]. Among this ZnO nanorod, possess unique optical and electrical properties such as high energy band gap and high excitation binding energy.

II. EXPERIMENTAL PROCEDURE

Synthesis of ZnO Nano Rod Structure

The ZnO nanorod structure was prepared by wet chemical route method. Where nanorod structures Zinc nitrate hexahydrate ($ZnN_2O_6.6H_2O$) and hexamine (HMTA) ($C_6H_{12}N_4$) was used as the precusors. An equal mole of Zinc nitrate hexahydrate ($ZnN_2O_6.6H_2O$) and HMTA was dissolved in the double distilled water having the quantity of 150ml in

different containers. Then both the solutions are stirred well separately for 2 min. After stirring the HMTA solution was added drop wise into the Zn pecursors. In order to maintain the acidic condition, Conc.HNO_3 is added drop wise in the precursor solution until the pH is set to 3.5. Then the precursor is vigorously stirred for 10min. This acidic condition is maintained for the growth of rod like structure. Then the beaker containing the precursor solution was kept in the temperature bath ZnO for 3 hours maintained at 97°C. To remove the unwanted particles or ions, prepared ZnO particles are cleaned by ethanol and distilled water. The precipitate was collected and cleaned three to four times repeatedly. The final product was dried at 200°Cfor 2 hours.

Cleaning of Electrodes:

The glassy carbon electrode was used as working electrode. The alumina slurry of 0.05µm, 0.3 µm size was dropped on alumina polishing pad and diamond polishing pad. The Glassy carbon electrode was sequentially polished to a mirror like surface for 10 min. the GCE was rinsed thoroughly with distilled water after each polishing step to remove the unwanted particles. Then it is ultrasonicated in ethanol, double distilled water for 10 min and then allowed to dry for room temperature.

ZnO Rods/CHIT/GOD Electrode Preparation:

3 mg of ZnO rods powder was dispersed in 5ml of ethanol solution and sonicated for 15 min to obtain the ZnO rods/ethanol suspension. 50 mg of chitosan powder was dissolved in 100 ml of acetate buffer solution (pH=5.4) to obtain chitosan solution. Then 3mg of ZnO rod powder was dissolved in 1 ml of chitosan solution and ultrasonicated for 15min to obtain ZnO rod suspension. 2mg of GOD (glucose oxidase) was dissolved in 1ml of 0.1 M PBS. 2µl of ZnO rods/chitosan suspension was initially deposited on the surface of freshly polished GCE. It is allowed to dry at room temperature in air. After drying, then ZnO rods/CHIT/GOD/GCE electrode were obtained by dropping 2µl of GOD on the top of ZnO rods/CHIT suspension to cover it. Then it is dried for 30min. After drying, the electrode was stored in refrigerator for 4°C, when not in use. The prepared ZnO rods/CHIT/GOD/GCE electrode was immersed into 20ml of 0.1M PBS solution. Then various concentration of glucose solution was added into 0.1M PBS solution.

X-Ray Diffraction Analysis of ZnO Rods:

The absorbed XRD peaks were indexed for hexagonal structure of Zinc Oxide[9] and compared with the JCPDS card number (361451) of ZnO. The diffraction peaks located at diffraction angles of 2Θ=31.92°, 34.62° and 36.42° are most pronounced. These 3 peaks corresponds to (100), (002), (101) directions of wurtzite ZnO rods, i.e., the growth along the directions of a and c axis of wurtzite hexagonal structure respectively. From the XRD pattern along the (100), (002), (101) planes, the grain size are determined to be 80.02 nm, 76.36 nm, 78.16 nm respectively. The calculated lattice constants of the ZnO microstructures re a=b=3.1682nm and c=5.101 nm. The calculated lattice constants matches well with the standard JCPDS card (361451) of hexagonal lattice value a=b=3.249nm and c=5.206nm.

III. RESULTS AND DISCUSSION

Scanning Electron Microscope Analysis:

The morphology of as prepared ZnO rods was studied by scanning electron microscope. It is observed that sample shows rods like structure with average diameter of 0.5 to 1 µm. The length of as prepared ZnO rods was estimated to be 6 to 10 µm. From this image, it is observed that the grown rod is straight with faceted structure[10]. This SEM image also reveals that ZnO rods are grown along c-axis.

Electrochemical Analysis of ZnORods- Cyclic VoltammetricAnalysis of ZnORods/CHIT/GCE Electrode:

The electrochemical responseof the prepared ZnO rods/CHIT/GCE was investigated by cyclic voltammetry. The figure 1 demonstrates the cyclic voltammograms of ZnO rods/CHIT/GCE electrode in 0.1 M phosphate buffer solution measured at various scan rates in the potential range from -1.5 V to 1.5 V. The anodic and cathodic peak currents increases linearly with increase in the scan rate[11]. The anodic and

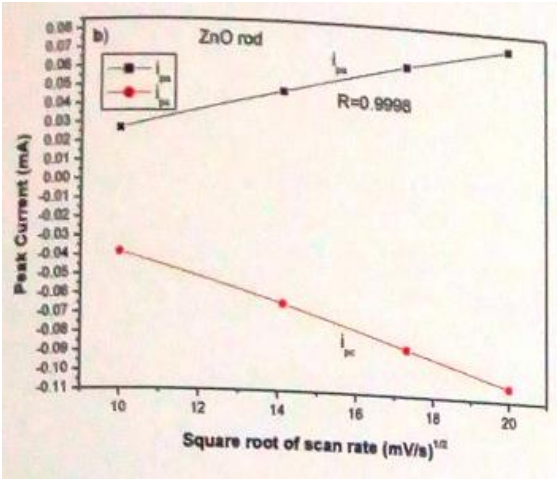

Fig. 1 Cyclic Voltammograms

cathodic peak potential also shows a small shift towards positive and negative direction. Moreover, the oxidation and reduction peak separation also increased slightly with increase in the scan rate. The incorporation of ZnO particles into CHIT films causing the increase in oxidation current as a function of scan rate.

Cyclic VoltammetricAnalysis Curve for Immobilization of Glucose Oxidase on ZnORods/CHIT/GOD Electrode:

The effect of scan of the glucose oxidase (GOD) molecule immobilized on GCE modified electrode was studied by cyclic voltammetry. The results of cyclic

voltammograms studies of ZnO rods/CHIT/GOD/GCE electrode at different scan rate of 200, 300, 400 mV/s was carried out in PBS (0.1M PH=7.0) in the potential range form -1.5V to 1.5 V. From the CV curves, it is observed that after the absorption of GOD molecules on modified electrode shows the increase in the oxidation and reduction peak current on increasing the scan rate. This significant increase in the redox current signal is due to the electron transfer that occurs between the active sites of GOD and ZnO rods/CHIT/GCE electrodes. This anodic and cathodic peak potential of both enzyme modified electrodes shows shifts in the positive and negative direction respectively. This results confirmed that the negatively charged GOD molecules is immobilized on positively charged ZnO rods/ CHIT matrix through electrostatic interactions[12].

IV. CONCLUSION

In summary, a wet chemical route method was adopted to synthesis ZnO rods. From the scanning electron microscopy analysis, the rods have length of 6 to 10µm, diameter of 0.5 to 12 µm. For cyclic voltammetric analysis glucose oxidase (GOD) enzyme was immobilized on as prepared ZnO rods. Therefore, it is concluded from Cyclic Voltammetry analysis that ZnO nanorod/CHIT/GOD/GCE electrode shows higher electro catalytic activity towards glucose oxidation.

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