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Review Article

Cobalt oxide-based nanomaterial for electrochemical sensor applications

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Abstract

Amongst the extended list of metal oxides, Co_3O_4 has gained envisioned attention in various technological fields. It has a proven record of promising material in optical, optoelectronics, sciences, engineering, medicines, and biological studies. Co_3O_4 is a promising candidate due to its large surface-to-volume ratio, sample preparation methods, higher well-defined electrochemical redox activity, high theoretical capacity, low cost, and stable chemical states. Co_3O_4 has been used in various applications such as fuel cells, photoelectrochemical water splitting, solar cells, supercapacitors, batteries and electrochemical sensors due to its applicability in various fields. Furthermore, it has shown promising outcomes as an electrochemical sensor in multiple areas such as detecting water contamination, as physiological molecule detectors, etc. This mini-review summarizes the fields of contaminated water, as fuel and in the physiological system.

***Keywords*:** Cobalt oxide-based nanomaterial; electrochemical sensor; 4-Nitrophenol & Hydrazine sensor; Hydrogen peroxide; Physiological molecules

1. Introduction

Electrochemical sensors are extensively used tools in daily life such as in industries, monitoring of environmental changes, medicine, biological control processes and analysis of physiological molecule concentrations. The electrochemical sensing method is a powerful tool to get real-time measurements of a process without sampling by using in-situ measurements. The electrochemical sensors can be employed for a real-time analysis at a temperature range from -30^{o}C to 1600^{o}C depending upon the electrolyte used [1]. The conventional electrochemical sensor based on aqueous electrolytes or solution phased electrochemical sensor can be used at maximum temperature up to 140^{o}C. on the other hand, a solid electrolyte-based electrochemical sensor has an operating temperature range > 500^{o}C. Both these sensors work by following the electrochemical measuring principles as potentiometric amperometric, or impedimetric. An efficient sensor should have the feature such that it should be sensitive, selective, and stable (in terms of reliability and durability), which depends upon the measuring condition, temperature, pressure and chemical setting, etc. electrochemical sensors operating at low temperature are usually used to measure the pH-values, impedance and concentration of the target molecules dissolved in the electrolyte in the form of ions or gas [1]

The simplicity of electrochemical sensors in their setup and electronics equipment for data acquisition and operation make them ideal for detecting target molecules. They are simple in operation when compared to spectrometric (FTIR, UV–VIS), mass spectrometric (MS) and chromatographic (GC, HPLC), techniques. There is less effort involved in maintenance and calibration in electrochemical sensors. In electrochemical sensors, the sensor signal is obtained in-situ that offers real-time information of the target molecules. Hence, electrochemical sensors are preferred in industrial use as well as in field applications. Although electrochemical sensors are simple in their operation, one should have improved knowledge of measuring conditions such as temperature, pressure, behavior of sensor signals, and their influence on the determination of application limits in electrochemical sensors.

Until now many materials either unaided or in the form of composite have been investigated as sensors. These materials include the conduction polymers [2, 3], mixed metal oxides [4], carbon-based nanocomposite materials [5, 6]. Among the list of all these materials, semiconductor-based metal oxides sensor is the most used sensor material due to their simple preparation method [7], cost-effectiveness [8], stability [9], and simple measurement techniques. The most commonly used material as the electrochemical sensor are n-type oxides such as TiO_2 [10], ZnO [11], WO_3 [12], Fe_2O_3 [13], and SnO_2 [14] and p-type includes Co_3O_4 [7], CuO [15], Mn_3O_4 [16], NiO [17], and Cr_3O_4 [18], etc. p-type metal oxides are the extensively used catalysts for the detection of target molecules owing to the feature of selective oxidation of a variety of volatile organic compounds [19, 20]. This is the reason that p-type oxides material is the potential candidate for the development of new chemiresistors

Amongst the p-type oxides catalyst spinal Co_3O_4 a mix valence oxide of CoO and Co_2O_3 with high oxygen contents have also been used extensively. Co_3O_4 has been investigated intensively in many studies such as energy storage and conversion applications [21], sensors [7], electrochemistry [22], and magnetism [23] as a potential catalyst. The spinal Co_3O_4 has proved itself as an attractive material for sensing application due to its higher theoretical surface area (2630 m^2g^{-1}) [24], charming optical, magnetic and transport properties [25], high surface to volume ratio [6] and higher theoretical capacity (890 $mAhg^{-1}$) [26]. Recent studies proved that cobalt oxides' morphological tuning can further enhance their electrochemical properties [21]. Co_3O_4, magnetic p-type semiconductors, have direct and indirect band gaps of 2.10 eV and 1.60 eV, respectively [27]. Due to the diverse feature and simple preparation method, cobalt oxide has been synthesized by applying various synthesis procedures such as hydrothermal, sol-gel, and so on [28-30]. Pure Co_3O_4 has long been considered in diverse fields by researchers due to its promising properties. Therefore, Co_3O_4 has been synthesized in the form of various morphologies such as nanotubes, nanowires, nanobundles, nanoplates, and nanoflowers etc. [7]. This mini-review focuses on the use of unaided Co_3O_4 synthesized by various methods for detecting target molecules in different research areas such as in contaminated water, as fuel, and in the physiological system. The block diagram in figure 1 shows few electrochemical applications of Co_3O_4.

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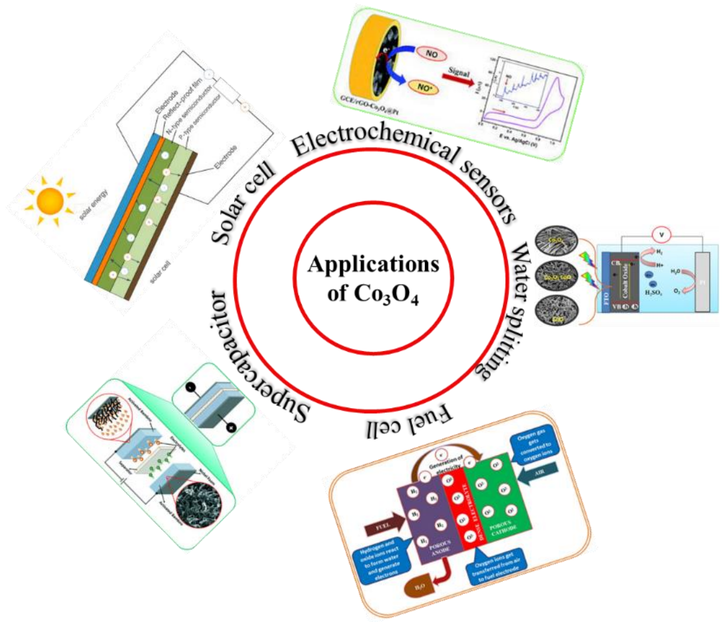

Figure 1: Block diagram of various applications of Co_3O_4

2. Co_3O_4 as an electrochemical sensor

The electrochemical sensing of various molecules such as 4-Nitrophenol (para-nitrophenol), Hydrazine, Hydrogen peroxide (H_2O_2), and Dopamine are discussed in this review. This mini-review paper aims to give the reader an overview of the electrochemical detection of different molecules present in different systems. The electrochemical studies are usually taken by setting up three-electrode cell systems. Where three electrodes consist of working electrodes, commonly Glassy carbon electrode is used, Pt wire or Graphite rod are served as counter electrode and Ag/AgCl or Saturated calomel electrode SCE is used as a reference electrode. Figure 2 shows an ideal picture of an electrochemical setup for clear understanding. The electrochemical studies are carried out in the suitable electrolyte at the desired pH in the presence of target analyte/molecules. Analysis techniques such as Cyclic voltammetry CV, linear sweep voltammetry LSV, chronoamperometry CA, Electrochemical impedance spectroscopy EIS and so on are used normally to study the different parameters of a sensor. The limit of detection of a sensor is calculated from CA. This most important parameter shows the lowest limit of a sensor that can be detected by employing the sensor.

Similarly, long-term stability is also an important parameter determining that the sensor is still responding after multiple times of its usage. The stability test can be done in different ways such as the sensor can be stored for a specific number of days and then tested again, another way to run the sensor is by using a CV or CA for a long duration and analyses the degradation in the performance of the sensor. another most crucial parameter of electrochemical sensing is selectivity since it is known that in every system such as physiological, contaminated water, foods and so on there exist other molecules also called co-existing molecules which interfere with the adequate detection of the desired molecule, therefore, a sensor must be so efficient and sensitive towards the target molecule/analyte that it should not be interfered by other co-existing molecules. Here in the following sections, few important studies were carried out to understate electrochemical sensing further.

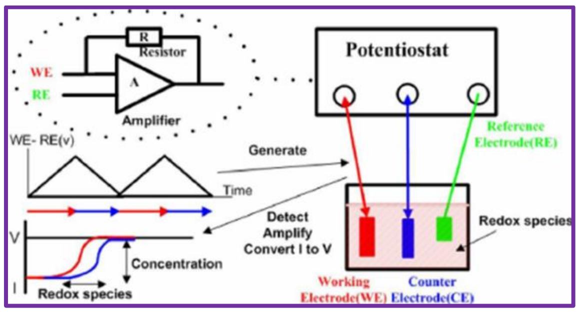

Figure 2: The schematic diagram of the electrochemical setup

3. 4-NP sensor

It is known that contaminated water causes severe health issues to all living organisms and plants, even a low concentration of contaminated water can cause serious health issues to human beings [31]. Nitro-compounds are one of the contaminations extensively used in chemical and pharmaceutical industries. 4-NP is a class of phenol-based nitro compounds, a toxic compound found in wastewater released by chemical and pharmaceutical industries. 4-NP is a common intermediate used in the production of leather products, dyes, pharmaceuticals and analgesics. Acute exposure to 4-NP can cause severe headaches, breathing issues, fever, and a high level of exposure can even cause death. 4-NP can be further found in crops, vegetables, fruits and water sources due to its use as an ingredient in fertilizers and pesticides [32]. 4-NP is highly stable in water and has low biodegradability since it is highly toxic and persistent therefore is on the priority list of the environment protection agency (EPA) US [33]. Leading from the abovementioned facts, the realistic trace amount of 4-NP in water sources and the environment is highly important. Of the available techniques used for the detection of target molecules, electrochemical techniques are the potential detection method, as discussed earlier. In our previous report [7], we have synthesized different structures (nanocubes, nanowires, nanobundles, nanoplates, and nanoflowers) of Co_3O_4

as shown in figure 3 and employed for the reduction of 4-NP and its detection in a neutral environment (pH=7.2).

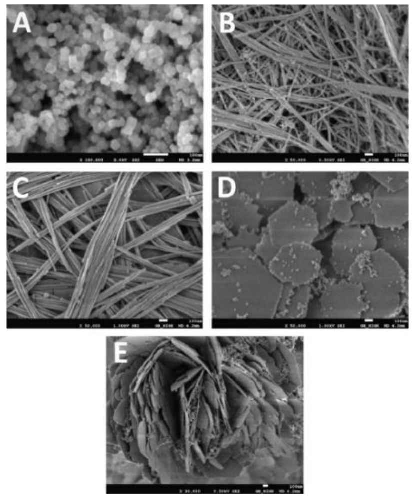

Figure 3: FESEM images of the various structure of Co_3O_4 (nanocubes, nanowires, nanobundles, nanoplates, and nanoflowers) [7].

Co_3O_4 with cubical structure has shown promising results for detecting 4-NP with a limit of 0.93 μM by using the square wave voltammetric technique. The reduction of 4-NP (figure 4A) by CV was carried out in an environment starting from acidic to basic medium. The highest performance was shown by the Co_3O_4 nanocubes at neutral pH values as can be seen through figure 4B respectively.

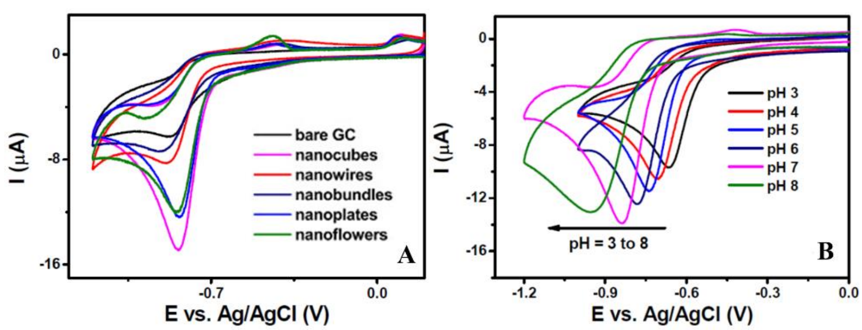

Figure 4: A) Reduction of 4-NP by different morphologies of 4-NP and B). pH-dependent studies of 4-NP [7].

4. Hydrazine sensor

Hydrazine is a toxic molecule, it is flammable and has no color [34]. The EPA has classified it as carcinogenic and kept it in group B2. Exposure to hydrazine can cause injury in the lungs, liver, faintness, kidney problem, and damage to the nervous system [35, 36]. Severe contact with hydrazine can result in death. Hydrazine and its derivatives are highly toxic pollutants, they are widely used as rocket fuel, in fuel cells, as textile dyes, weedkillers, insecticides, photograph developing chemicals in various pharmaceuticals. Chemical and agriculture industries [6, 37-42]. Due to all these facts, the detection of hydrazine in the physiological system is highly needed, thus detection of hydrazine in the physiological system attracted much attention in recent decades [43]. The electrochemical method is used for the oxidation of hydrazine on carbon-based electrodes, the other species produced by the oxidation of hydrazine are nitrogen and water, which do not harm the environment and do not cause any pollution. Zhang et al. [39] fabricated a highly sensitive, reproducible and reliable electrochemical sensor consisting of porous Co_3O_4 nanowires synthesized by hydrothermal method to detect hydrazine (Figure 5).

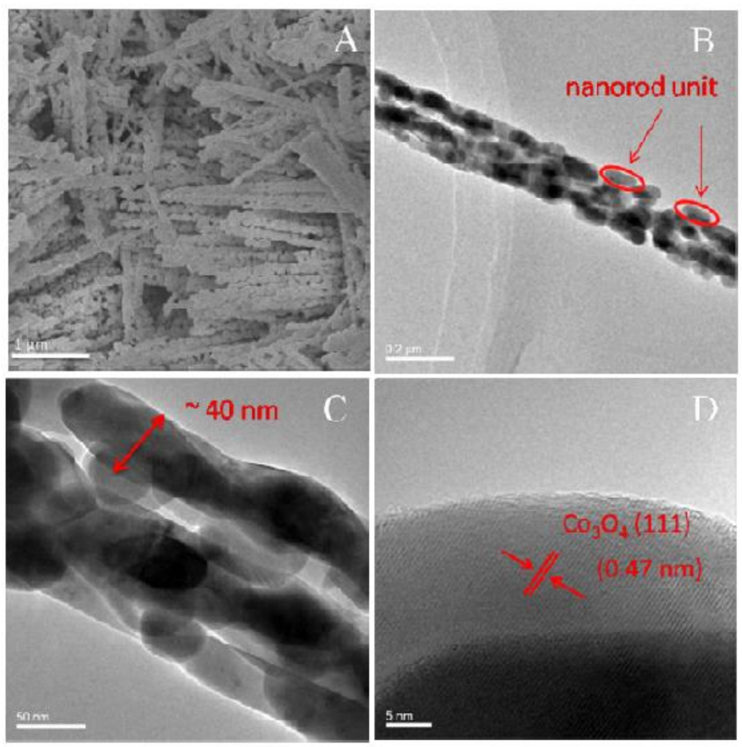

Figure 5: SEM image (A), TEM images (B, low magnification; C, high magnification) and HR-TEM image (D) of Co_3O_4 NWs [39].

The sensor constructed by porous Co_3O_4 nanowires has shown high sensitivity (28.63 µA mM-1) with a lower detection limit (0.5 µM). The porous network of Co_3O_4 NW assisted the fast electron transfer hence catalyzed the electrooxidation of hydrazine. The nanowires are constructed by a porous network of 3D nanorods connected by each other as indicated by the TEM image in figure 4B, facilitating mass transportation. The following figure 5 shows the detection of hydrazine by using a chronoamperometric method, it can be seen through the image that the sensor consists of Co_3O_4 nanowires had shown the sophisticated detection as of hydrazine as compare to other controlled electrodes, when hydrazine with a concentration of 20 mM was injected after a specific interval of time.

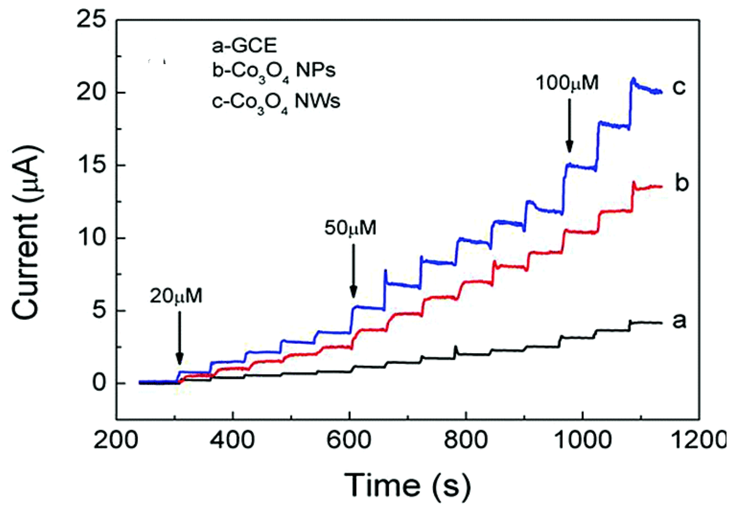

Figure 6. Amperometric responses of GCE, Co_3O_4 NPs, and Co_3O_4 NWs towards hydrazine sensing [39].

5. H_2O_2 sensor

H_2O_2 is used in food, clinical, and pharmaceutical in the form of essential mediators. The by-products of H_2O_2 are used in many oxidase catalyzed reactions [44]. It has a wide application range in biomedical and environmental studies also. H_2O_2 is a by-product of enzymatic reactions. Due to its oxidizing competence, excess exposure to H_2O_2 can cause damage to lipids, carbohydrates and proteins in the body [45]. The accumulated H_2O_2 in the body can cause oxidation for metabolic products, which results in necrosis and can cause cancer [46].

Furthermore, the accidental absorption of H_2O_2 can lead to cancer, asthma, diabetes, and high consumption of it can cause death as well. Therefore the accurate detection of even the lowest concentration of H_2O_2 is of utmost importance. Different techniques are available for the detection of H_2O_2; these techniques include chemiluminescence [47], fluorescence [48], and spectrophotometry [49]. The disadvantage of these techniques is time-consuming, and it takes a high cost. H_2O_2 is an electroactive material, so detection of H_2O_2 via electrochemical method has drawn much interest by the researchers due to its low cost, ease of operation and higher selectivity [44, 50]. CAO and co-workers [51] have developed Co_3O_4 nanocubes by using H_2O_2 as an oxidant and employed it to reduce H_2O_2, as shown in figure 7.

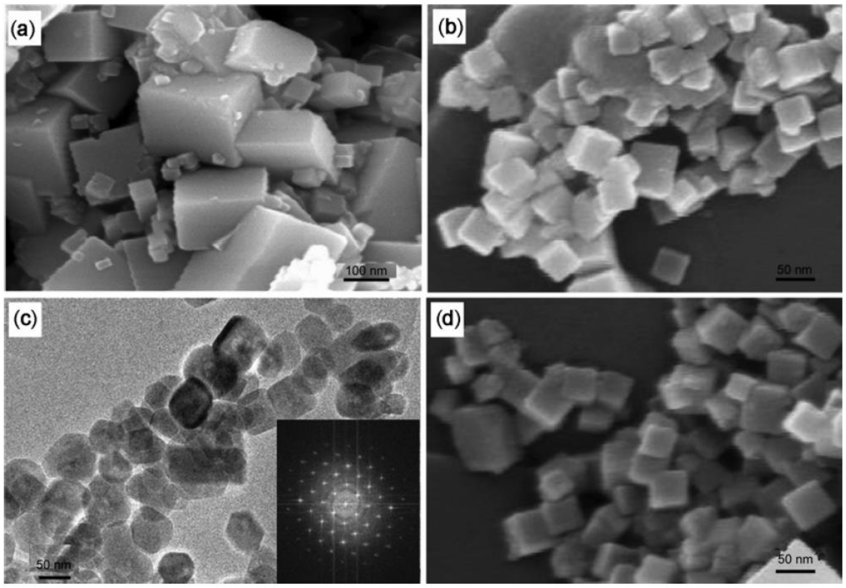

Figure 7: SEM images of products synthesized with different amounts of H_2O_2: (a) 0·5 mL, (b) 0·8 mL and (d) 1·2 mL. (c) TEM images of products synthesized with 0·8 mL of H_2O_2 [51].

The hydrothermally synthesized Co_3O_4 nanocubes have exhibited extraordinary electrocatalytic activity in the catalysis of H_2O_2. The sensor further has shown promising results for the detection of H_2O_2. The amperometric response shown by the current vs. time curve shows the rapid detection of H_2O_2 in phosphate buffer solution at neutral pH=7. It was observed that the Co_3O_4 based sensor responded sensitively within 2 seconds after the injection of H_2O_2 into an electrolyte solution, and the current reached steady-state values (figure 8a). The sensitivity values of 13·6175 μA mM–1 were calculated from the linear curve of current vs time as shown in figure 8b.

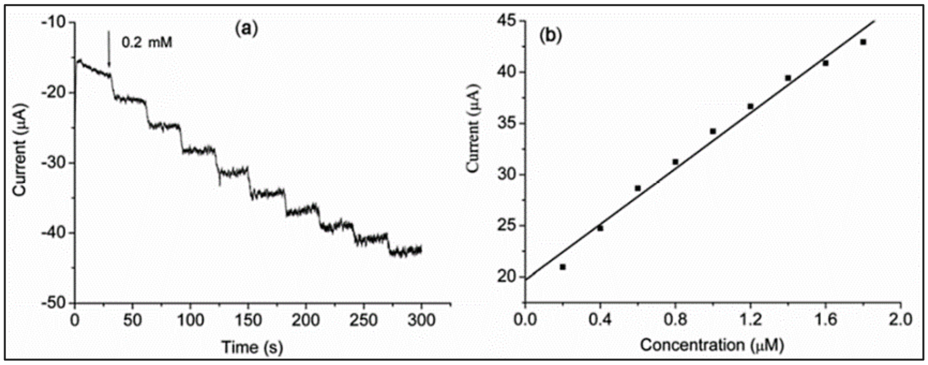

Figure 8: (**a**) Amperometric response of H_2O_2 utilizing Co_3O_4 nanocubes sensors with successive additions into 0·01 M phosphate buffer at an applied potential of –1 V (vs Ag/AgCl) and (**b**) its corresponding calibration plot [51].

6. Dopamine sensor

Dopamine is present in the central nervous system of mammals and it is an important neurotransmitter. It participates in the renal, hormonal, and cardiovascular systems along with the central nervous system, significantly [52]. DA is responsible for many functions in the human body, such as communicates the electrical signals between the brain tissues and substantia nigra. It helps control hormonal balance, attention span, neuroplasticity, and emotion, etc. [53]. The abnormality in dopamine concentration can cause neurological diseases that include Parkinson's disease [54], Human immunodeficiency virus infection [55], and Huntington disease [56]. Considering all these facts, it is important to develop a sensor material with higher sensitivity that can detect the concentration of DA quantitatively by ex-vivo testing of disease symptoms. The electrochemical detection of DA is highly preferred due to its discussed features. Elhag et al. [57] have grown Co_3O_4 nanowires with a low thickness on a gold-coated glass substrate. The SEM images in figure 9 show the growth of Co_3O_4 in nanowires shapes by the hydrothermal chemical deposition method. The synthesized material was employed for the comprehensive range detection of DA utilizing potentiostatic method of determination.

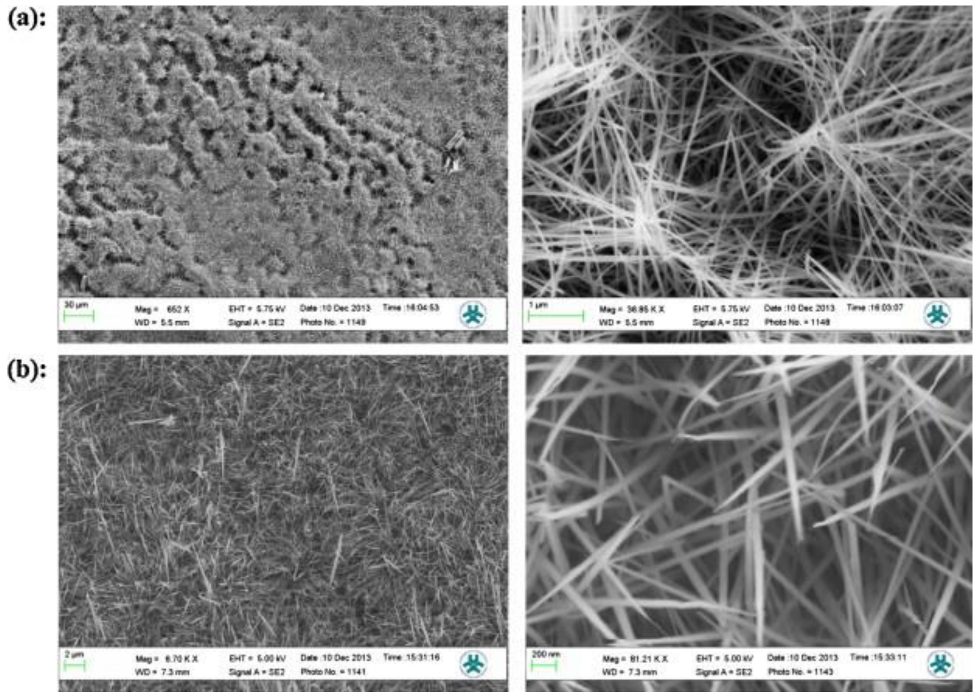

Figure 9: The morphology of the Co_3O_4 nanowires grown with high and low magnifications and both of them are dense with a high aspect ratio [57].

The growth of Co_3O_4 nanowires on a gold-coated glass substrate is shown by the schematic diagram in figure 10. They have used chemically modified electrodes (CMEs) for the potentiometric detection of DA. They have achieved A wide range of detection ranging from 10^{-9} M and up to 10^{-2} M. Furthermore, the sensor has a quick response time of about 10 s with an additional high range of selectivity as 52 mV/decade.

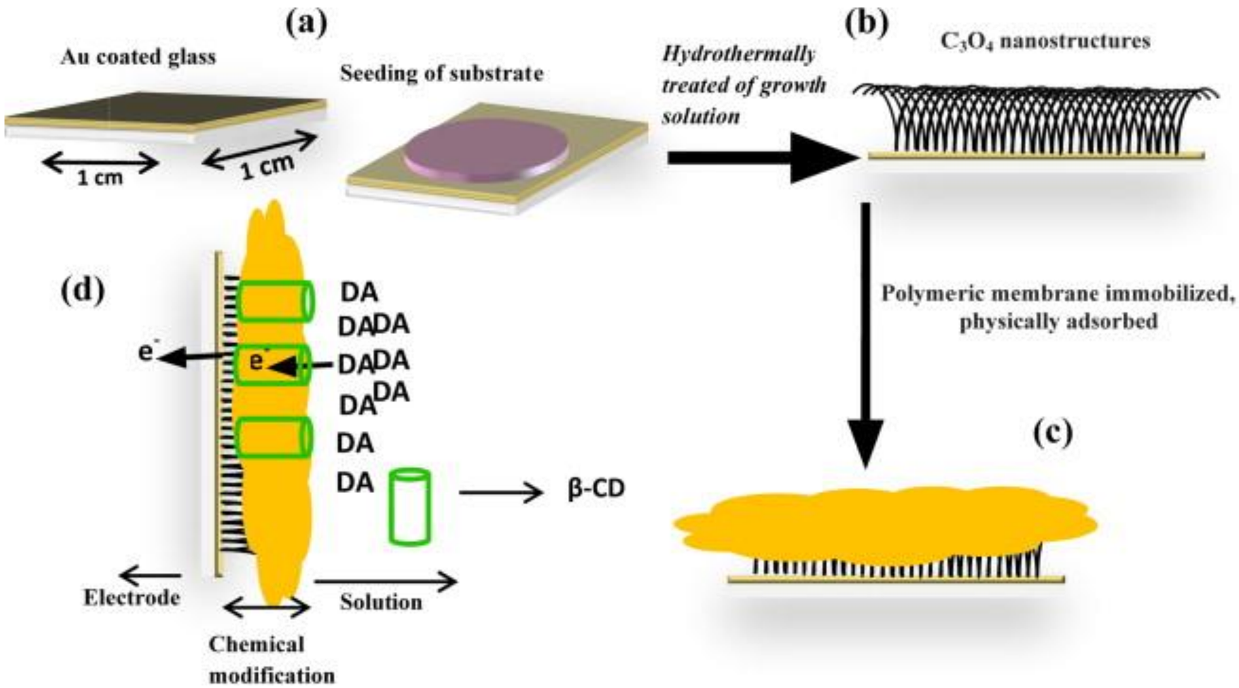

Figure 10: Illustrate the fabrication of electrode modifications (a) spin coating of cobalt acetate on Au coated glass, (b) growth of Co_3O_4 nanostructures, (c) immobilization of polymeric membrane by deep coating and (d) proposed mechanism of CME where a DA accumulated and β-CD controlled that selections [57].

7. Summary and Future Perspective

The current mini-review paper discussed the use of purely Co_3O_4 and its applications in various electrochemical fields. This review paper aims to give an overview to the readers about the potential metal oxide material in this field. Further, this review paper has touched on the electrochemical sensors used in different research areas such as detection of water pollutants, determination of analytes used as fuel in different systems and textile and agricultural fields, and clinical application in the form of physiological sensors. Here the idea was given to the researcher interested in the field of electrochemical sensors field that one can use metal oxide as primary starting material. It can be further enhanced by making composites by using graphene, conducting polymers and carbon nanotubes, etc. similarly ternary nanocomposites can also be made by using metal nanoparticles to enhance the sensor's performance.

Conflicts of interest

Authors declared no conflict of interest.

Acknowledgments

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