Superior Electrocatalytic Activity of Ag doped MnWO_4 Microflowers towards Glucose molecules

Manisha Rajput

IISER Pune: Indian Institute of Science Education Research Pune

KUSHA KUMAR NAIK (✉ kkn10@iitbbs.ac.in)

Berhampur University <https://orcid.org/0000-0002-7304-7112>

Research Article

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Abstract

Herein we report the synthesis of Ag doped MnWO_4 material carried out by facile hydrothermal method and its catalytic property towards glucose molecules. The Ag- MnWO_4 material is characterized by XRD, SEM and EDX respectively. The morphology of the synthesized material is nanorod like structure and the nanorods are converged with each other constructing microflower structure. The microflowers are uniform and sparsely distributed in all direction. The fabricated Ag- MnWO_4 electrode performs huge sensitivity of $17.9 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ in the linear range 5-110 μM with response time 8 s. Further, excellent selectivity and acceptable stability of the material are achieved. It is predicted that Ag- MnWO_4 material would be a good glucose catalytic material for sensing applications.

1. Introduction

Exact and fast detection of glucose molecules present in the blood serum is very much important to avoid the diabetes complexity [1, 2]. According to international diabetes federation (IDF) report 2020, about 463 million people are living in diabetes worldwide and diabetes has been declared as pandemic which is affecting both mentality and economic prosperity of the nation's [3, 4]. Diabetes is a curable disease and in simple sense, it is just an elevated level of glucose molecules present prolong time in the blood. To measure the concentration of glucose molecules precisely, a lot of methods like mechanical, [5] optical, [6] electronic, electrochemical, [7] and gravimetric [8] are developed. Still, there are many curiosity and privilege challenges to fabricate reliable glucose sensors due to its wide applications in bioprocessing, biotechnology and food technology industries [7, 9].

Electrochemical method is simple, economic and reliable technique to enumerate the glucose molecules dissolve in the blood [10]. It deals with electrochemistry of both interacting material and glucose molecule. Glucose molecules interact and react with electrode material and generate an electrochemical stimulus which expose the molarity of glucose concentration existing in the blood [11, 12]. Electrochemistry of the material solemnly depend on the reactivity of ions manifesting in the material and it can be enhanced by engineering and adorning the morphology the materials [13]. Chemical reactivity of the material relies on the net electronic structure as well as crystal structure of the material. Although, chemical nature of the individual elements composing in the material offers significant contribution but integrated chemical environment and consolidated free electrons of the material communicate chemical response with the interacting molecules [14]. Thus, electro and biocatalytic properties of the material is by virtue of its electro-chemical essence which develop naturally inside the material during the synthesis period and it should resonate with the catalytic nature of the glucose molecule [15, 16].

Manganese and Tungsten are transition elements having d-orbitals are partially and half-filled and these two elements combined with oxygen in the stoichiometric ratio construct spinel structure of manganese tungsten oxide (MnWO_4). Spinel structure materials are very good materials for different technological applications like energy storage and memory devices [17, 18], field emitter [19], and sensor [20, 21]. By

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js es within its crystal structure and it can be filled

up by suitable reciprocal elements[22]. As we know, Silver is a highly noble and catalytic element and it can be resided in the vacancy and lattice sites of MnWO_4 crystal structure by doping process [23]. As a result, net electro and bio catalytic properties of the MnWO_4 material is expected to be enhanced by manifold. In this report, we have emphasized the synthesis of Ag doped MnWO_4 microflowers by hydrothermal method and its catalytic activity towards glucose molecules is analyzed precisely. The fabricated Ag- MnWO_4 electrode performs huge sensitivity of $17.9 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$ in the linear range 5-110 μM with response time 8 s. It is predicted that the Ag- MnWO_4 material would be good glucose catalytic material for the industrial applications.

2. Experimental Section

In a typical synthesis procedure, 10 mM of manganese chloride and 10 mM of sodium tungstate were dissolved in 20 ml DI water to make a clear solution. After complete dissolution of precursors, 1 mM of silver nitrate and 300 mM of Urea were mixed into the solution and ultra-sonicated for 30 minutes. The pH of the as-prepared solution was adjusted to 9 by adding NaOH solution. Then the solution was transferred into Teflon lined stainless steel autoclaves (25 ml capacity) and placed in the hot air oven at 200 °C for 18 hrs. The idea behind the addition of urea into the solution was to accelerate the hydrolysis process and to avail more OH^- inside the solutions. At the high temperature, the dissolved ions reacted with each other and nucleated to form MnWO_4 molecules. Since, the amount of "Ag" is very less, they take the lattice or vacancy position in the MnWO_4 crystal structure. The obtained product was washed in DI and ethanol several times separately and filtered to remove the unreacted impurities present in the sample. After that, the sample was dried at room temperature in the vacuum followed by annealing at 450 °C for 12 hours. Finally, the powder sample was collected for characterization and examined the catalytic nature of it towards glucose molecules.

2.1 Electrode preparation for Glucose sensing and measurement

Thin films of Ag- MnWO_4 material were deposited on cleaned Ni foam substrates by simple drop casting method. At first, 1 mg of Ag doped MnWO_4 material was dissolved in 100 μl of ethanol and sonicated for 20 min. to disperse properly. Then the dispersed solution was drop casted on Ni foam ($0.5 \times 0.6 \text{ cm}^2$) substrate dropwise and dried at room temperature. After drying, Ni foam strips were crimped at 100 MPa pressure to stick the material properly with substrate and applied as working electrode for electrochemical measurement. The electrochemical measurements were executed by three electrodes glass cell connected with an electrochemical workstation (PG262A, Techno science instruments, Bangalore, India) by taking Pt wire as counter electrode, Ag/AgCl as reference electrode and Ag- MnWO_4 /Ni foam as working electrode. The glucose sensing study was performed taking the 0.5 M of glucose concentration in the 0.1 M of NaOH electrolytic solution. For CV experiment 10 ml of NaOH solution was taken in the glass cell and its electrochemical response toward glucose molecules were recorded. Similarly, for CA

experiment 140 ml of NaOH aqueous solution was taken in the glass cell and then, different concentrations of glucose analytes were dropped into the rotating solution periodically to study the stepwise current response of the synthesized material.

3. Result And Discussion

Figure 1 specifies XRD pattern of the pristine MnWO_4 and Ag-MnWO_4 materials performed at wide ranges from 20 to 80 degree. The intensity of all peaks are distinct and well exposed from the materials confirming their crystallinity nature and the characteristic peaks are matched with pure phase of MnWO_4 material (JCPDS-74-1497). There are no separate peaks of pure silver or silver oxide materials characterising the purity of the material. The silver atoms are present in the lattice sites or the vacancy positions of the crystal structure. The synthesized materials possess monoclinic crystal structure with lattice parameters: $a = 4.820 \text{ \AA}$, $b = 5.760 \text{ \AA}$, and $c = 4.970 \text{ \AA}$ respectively.

Morphological feature and EDX spectrum of the Ag doped MnWO_4 material are depicted in Fig. 2. From the FESEM images, Ag-MnWO_4 material shows nanorod like morphology but individual nanorods are converted to form flower like structure. The width of the nanorods is 50–100 nm and the flower is some micrometers respectively. The nanorods are distinct in shape, size and closely packed with each other in different orientations forming charming microflowers. The microflowers are also homogeneous, uniform and spread in marked fashion. The atomic percentage of the constituent elements is Mn (14.74%), W (15.12%), O (69.76%) and Ag (0.39%) with well-defined stoichiometric ratio.

3.1 Cyclic Voltametric (CV) study of Ag-MnWO_4 material

To analyze the electrochemical activity of Ag doped MnWO_4 materials, CV experiment was executed in 10 mL NaOH solution taking the three electrodes; Pt wire as a counter, Ag/AgCl as a reference electrode and the crimped Ni foam as the working electrode. The measurements were performed in the potential range of 0 to 0.7 V at a sweep rate of 20 mVs^{-1} to observe the electrocatalytic as well as glucose catalytic activity of the synthesized materials. For Ag-MnWO_4 material, CV of bare electrode without the presence of glucose concentration was executed then CV of different concentrations of glucose was executed in the same potential range as shown in Fig. 3(a). The anodic oxidation peak (I_{ap}) at 0.58 V and cathodic reduction peak (I_{cp}) at 0.4 V respectively were observed precisely and assigned to the pure MnWO_4 material [24, 25]. The small oxidation hump at 0.4 V and reduction at 0.18 V is assigned to Ag atom [26–28].

The mechanism of glucose oxidation and sensing may be explained as follow; the catalytic metal ions associate with MnWO_4 material form into Mn-OOH [26–28] and W-OOH compounds in the aqueous solution as below

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When CV performs in the applied potential, Mn and W species hydrolyse to form MnOOH and WOOH compounds by releasing two electrons. Similarly, glucose molecule (GL) dissociates to design gluconolactone (GE) by giving up two electrons into the solution. The oxidation of metal ions and glucose molecules happen simultaneously and distinct peaks appear in the applied potential range. The oxidation of glucose molecule is incorporated by Mn and W ions but the rate of oxidation of metal ions determine the rate of detection of glucose molecules. Thus, the sensing of glucose molecule is by virtue of its electro and biocatalytic nature of the material. The rate of quantization and sensing performances can be modulated by switching morphology and substrate of the materials as well as other parameters like pH and molarity of aqueous solution.

The magnitude of redox peak current has increased at every addition of glucose molecules due interaction and participation more electrons as shown in Fig. 3(b). The linearity of oxidation peak current signifies the mutual coordination and cordial activity between material and glucose concentration. The CV of different scan rates were performed in the aforesaid potential and its result is depicted in Fig. 3 (c) demonstrating the uniformity and homogeneous nature of diffusion and kinetic coefficient of the interacting species [9, 29].

3.2 Chronoamperometric (CA) Study of Ag-MnWO₄ material

The amperometric response of Ag-MnWO₄ was analyzed taking 140 ml of NaOH solution and a potential of 0.47 V was applied to the three electrodes to notice the staircase like current response of the synthesized material. When 5 μM of glucose analyte was piped into the solution, the originating current increased instantly and saturated horizontally giving its response time of 8 s as shown in Fig. 5(b). After that, different amount of glucose concentrations were added successively at an interval of 70 s as shown in Fig. 4(a) to distinguish the electrocatalytic reprocation of the material with increasing glucose concentrations. Figure 4(b) shows the calibration curve of the material which performs linear activity with enhancing glucose molecules. The sensitivity of the Ag-MnWO₄ of the material is calculated as 17.9 μA μM⁻¹ cm⁻² in the linear range 5-110 μM and 6.12 μA μM⁻¹ cm⁻² in linear range of 110–450 μM respectively. Table 1 represents the glucose sensing performance of the synthesized material with similar kind of materials and confirmed its good sensing properties.

Table 1
glucose sensing performance of the synthesized material with similar kind of materials

Electrode	Sensitivity ($\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$)	Linear range (μM)	Response time (s)	Reference
NiMoO ₄	0.193	0.01-8 mM	2	[30]
CuFe ₂ O ₄	0.637	0.6–5.6 mM	–	[31]
NiMn ₂ O ₄	1.31	2 μM -20 mM	3.5	[32]
MnWO ₄	6.7	5-110	12	[25]
Ag-MnWO ₄	17.9	5-110	8	Present Work

3.3 Interference Study of Ag-MnWO₄ material

Interference study or selectivity towards glucose analytes is important for glucose sensor and it is executed at 0.47 V potential in the presence of matrix of other chemical and biomolecules. At first 0.05 M of different glucose correlating species like ascorbic acid (AA), uric acid(UA), dopamine (DA), lactic acid (LA) and maltose (M) were dissolved in 10 ml of NaOH solution separately then 10 μM of each interfering species were pipped into the solution continuously at an interval of 70 s as shown in Fig. 4(c). The Ag doped MnWO₄ material showed high selectivity toward glucose molecules and very low catalytic to other molecules. Similarly, interference effect was studied taking the similar kind of glucose species like Maltose(MA), Sucrose (SA),Lactose(LA), D-Galactose (D-GL) and its result is depicted in Fig. 5(a) The stability of the sensitivity performance is confirmed by testing three independent electrodes and the error of $\pm 3\%$ was recorded as shown in Fig. 5(c). It is predicted that the Ag-MnWO₄ material is a good glucose catalytic materials for the industrial applications.

4. Conclusion

Manganese tungstate doped with Ag metal is synthesized by a facile hydrothermal method and its electrocatalytic properties is investigated precisely. The synthesized material possesses highly crystalline with pure phase of monoclinic crystal structure. The morphology of the synthesized material is microflower like structure composing of numerous nanorods. The microflowers are well populated and homogeneous in nature. The electrocatalytic and biocatalytic properties of the material towards glucose molecule is executed intensely which show sensitivities of $17.94 \mu\text{A} \mu\text{M}^{-1}\text{cm}^{-2}$ in linear range of 5-110 μM . The as-prepared materials has good interference with increasing glucose molecules. It is expected that the synthesized material is good catalytic material for glucose sensing application and industrial production of it can be recommended.

Declarations

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Figures

Figure 1

represents the XRD spectrum of MnWO₄ and Ag-MnWO₄ materials

Figure 2

(a) and (b) Low and high magnification image of Ag-MnWO₄ material, (c) EDX spectrum with elemental composition.

Figure 3

(a) CVs of Ag-MnWO₄ material at different concentrations of glucose (b) Current Vs Concentration graph at different concentrations and (c) Current Vs Concentration graph at different scan rates.

Figure 4

(a) IT graph performed at 0.47 V, (b) Calibration graph and (c) Interference graph of the Ag-MnWO₄ materials.

Figure 5

(a) Interference graph performed taking associate glucose molecules (b) response time and (c) stability of the Ag-MnWO₄ materials.

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