Selective detection of ascorbic acid with wet-chemically prepared CdO/SnO₂/V₂O₅ micro-sheets by electrochemical approach

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Received: 13 June 2020 / Accepted: 13 October 2020 / Published online: 6 November 2020
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Abstract

Generally, ascorbic acid (AA) is a potent reducing and antioxidant agent that regulates in fighting against bacterial infections as well as detoxifying reactions, which is functioned in the formation of collagen in fibrous tissue, teeth, bones, connective tissue, skin, and capillaries. Up to date, electrochemical enzymatic sensor are significantly used for enzymatic AA detection that exhibits an excellent selectivity, high reliability and handled under physiological conditions. However, considering some intrinsic dis-advantages of using enzymes, such as high fabrication cost and poor stability, non-enzymatic AA sensors have attracted increasing research interest in recent years owing to their low cost, high stability, fast response, and low detection limit. Moreover, the development of nanotechnology has also offered new opportunities to develop the nanostructured sensor probes for enzyme-less AA sensing applications. With beneficial advantages, ternary-doped metal oxides have gathered an extensive effort in the development of cost-effective sensors with high stability, sensitivity and quick response for the determination of selective AA by enzyme-free detection. In this approach, the mixed metal oxides of CdO/SnO₂/V₂O₅ micro-sheets (MSs) were prepared by facile wet-chemical method in alkaline phase at low temperature. Later, it was subjected to detail characterize by using various methods such as XPS, FESEM, EDS, and XRD. The slurry of prepared MSs in ethanol was deposited initially onto the surface of glassy carbon electrode (GCE) to make a thin film with conducting nafion (5% suspension in ethanol) adhesive to result the working electrode of proposed AA sensor probe. The sensor sensitivity ($21.3354 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$) is calculated by using the slope ($0.6742 \mu\text{A } \mu\text{M}^{-1}$) of the calibration curve by considering the active surface area of GCE (0.0316 cm^2) in the linear dynamic range (LDR; 0.1 nM to 0.01 mM). The limit of detection (LOD) ($98.64 \pm 4.98 \text{ pM}$) is obtained from the calibration curve. The proposed AA electrochemical sensor exhibits short response time, good reproducibility and successive outcome during the investigation of the real biological samples. The development of enzyme-free AA sensor by using CdO/SnO₂/V₂O₅ MSs onto GCE is simple as well as reliable and practically able to detect the biological stuffs for the safety of human health in the field of biomedical and sensor technology.

Keywords Mixed metal oxides CdO/SnO₂/V₂O₅ micro-sheets · Ascorbic acid sensor · Wet-chemical synthesis · Sensitivity · Glassy carbon electrode · Health care

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1 Introduction

Here, the role of AA in human body is to produce the collagen through bio-synthesis, which is essential for nervous system. The researches have commanded that the higher concentration of AA is able to change the brain response to neural signals rapidly [1–4]. Besides this, it has reported that AA is preserved in cardiac tissue and it inhabits the oxidative stress after ischemia and reperfusion [5, 6]. The ascorbic acid is also acted as angiogenesis inhibitors, which is responsible for the growth of tumor, chronic inflammatory, and metastasis syndromes [7]. Moreover, it is also well-known as a powerful antioxidant to effectively prevent gastric cancer [8, 9]. Thus, AA is an important for human metabolism and known as vitamin C, which is naturally obtained in food. To ensure the good physiological conditions, it is necessary to check its concentration level in human serum periodically. The normal level of AA in human serum is 11.4~28.4 μM [10].

Up to date, various analytical methodologies have been applied to determine the ascorbic acid such as High Performance Liquid Chromatography Coupled with Electrochemical Detection (HPLC-CED) [11], Ion-Pair HPLC with UV Detection [12], Colorimetric method [13], Flow injection method [14] and distinct electrochemical techniques [15]. Among these methods, electrochemical is found as reliable and potential to detect AA. Very recently, the graphene (GO) conjugated with metal and metal oxides such as 3D graphene foams decorated with CuO nano flowers [16], Cu-Ag bimetallic nanoparticles on reduced graphene oxide nano-sheets [17] and graphene/size-selected Pt nanocomposites [18] has been tested as the reliable ascorbic acid sensor applying electrochemical method. Besides this, the glassy carbon electrode modified with Poly(p-aminobenzene sulfonic acid) and MWCNT/GONR has claimed to detect the ascorbic acid in electrochemical approach [19, 20]. Moreover, the hybrids nanocomposites of $\text{MoS}_2/\text{f-MWCNTs}/\text{ZnO}$ and GNP/AgNR/poly (AY) decorated GCE have been shown high potentiality as electrochemical sensor to detect dopamine and ascorbic acid as reported previously [21, 22]. Another report has claimed that a voltammetric detection of ascorbic acid based on Plu/BNQDs/GCE as electrochemical sensor has been performed appreciably [23]. Furthermore, Gold nanoparticle-decorated MoS_2 nano-sheets [24], carbon-polyvinylchloride composite electrode [25] and molecularly imprinted polyaniline film [26] have been also reported as ascorbic acid sensor. Various doping of non-metal and metal part incorporated carbon material composites are used for chemical sensor development for the detection of anionic/cation, biochemical and chemicals using electrochemical approach. For doping-treated materials indeed

make doped nanomaterials more electro-catalytic than undoped material. Decorated materials exhibit much better electro-catalytic properties toward both oxygen reduction and hydrogen evolution. Doping transition materials into semiconductor, it produces more electro-catalytic materials than many complex multi-elemental doping procedures [27–32].

The cadmium oxide (CdO) is an n-type semiconductor with higher conductivity ($10^3/\Omega\text{ cm}$), lower optical band-gap energy (2.5 eV) and larger linear refractive index. Therefore, CdO is promising material as chemical sensor, catalyst, solar cells, transparent electrode, and photo transistors [33–37]. Particularly as electrochemical sensor, CdO has reported to detect melamine [38], ethanol [39], and bilirubin [40] in electrochemical approach. Besides this, the another important n-type semi-conductor SnO_2 with wider band gap (3.6 eV) energy has auspicious electrochemical properties and applied as catalytic materials, biochemical sensor, environmental monitoring, lithium rechargeable batteries, ultrasensitive gas-sensors and dye-sensitized solar cells [41–44]. The sensing properties of semiconductor can be increased/decreased by doping with various metal oxides. Therefore, the co-doped of CdO/ SnO_2 has been tested as gas sensor successively [45]. Moreover, the V_2O_5 is transition metal oxide having the band gap 2.52 eV and is found to apply as electrochromic devices [46–48], optical switching devices [49] and cathodic material in lithium batteries [50, 51]. Therefore, this study is performed using three promising metal oxides (CdO, SnO_2 and V_2O_5) in together to construct a sensor for the reliable recognition of biochemical. The proposed electrochemical method has potential advantages including trustworthy sensitivity, wider range for the detection, quick response time, appreciable lower limit of detection and above all, suitable to detect in-situ. As a result, the various researches activities based on the transition metal oxides with single, binary or ternary combination have reported in detection of numerous bio-chemicals and chemicals as reported previously [52].

Doped and un-doped metal oxide nanostructure materials have concentered the way for a novel and advanced chemical and bio-chemical sensing matrixes owing to their noble and unique physical, structural, morphological, electrical, and chemical properties for the detection of enzyme-less sensor. Generally, enzymatic selective AA sensor worked based on the electro-catalytic efficiency of enzymes and the non-enzymatic sensors exploit the electro-catalytic as well as electro-chemical properties of chemical components. Previously, the non-enzymatic sensor probes were developed by using the conventional sensor substrates such as silver electrode, glassy carbon electrode, platinum electrode and gold electrode. However, a high overvoltage for AA electro-oxidation on

traditional bare electrodes often results in fouling on the sensing interface owing to the absorbance of the oxidation product of AA at the surface of the fabricated electrodes, which would lead to low sensitivity, low selectivity, and poor reproducibility. To decrease the over-potential during selective AA electro-oxidation, several doped or un-doped nanostructure or composite materials (noble metals, polymer/metal composites, transition metal/metal oxides, hydroxides, carbon composites) and modified electrodes are anticipated with a wide linear range and low detection limit [53]. In this approach, the ternary mixture of CdO/SnO₂/V₂O₅ MSs were prepared by using wet-chemical (co-precipitation) method, which was deposited as thin film onto GCE with conductive nafion (5%) as binding agent. The proposed electro-chemical sensor showed the selectivity toward AA compared to other biological stuffs. Then, the analytical parameters of the sensor probe were assessed and validated in details with the real samples and found satisfactory. For the first time, CdO/SnO₂/V₂O₅ MSs fabricated GCE as a sensor probe is prepared and applied to selective AA sensor application by electrochemical method at room conditions. It is anticipated that the research methodology would be a turning point in the field of health care section (pathological diagnosis) to develop the selective and sensitive sensor probe with mixed metal oxide by non-enzymatic approach for the detection of AA.

2 Experimental

2.1 The methods and materials

As the sources of Cd, Sn, and V, the analytical grade chemicals such as cadmium sulfate (CdSO₄·H₂O), tin chloride (SnCl₂·H₂O) and vanadyl sulfate (VOSO₄(H₂O)₅) were used to prepare the micro-sheets (MSs) of CdO/SnO₂/V₂O₅ applying wet-chemical method (co-precipitation). As a part of this study, the bio-chemicals in analytical grade such as acetylcholine, bilirubin, ascorbic acid, D-fructose, cholesterol, D-glucose, L-cysteine, L-leucine, L-glutathione, and L-tyrosine were obtained from Sigma-Aldrich (USA). Besides that, the concentrated ammonia, mono- & disodium phosphate and nafion (5% suspension in ethanol) adhesive were used to execute this study. To evaluate the binding energy and ionization states of existing atoms in synthesized co-doped CdO/SnO₂/V₂O₅ MSs, X-ray Photoelectron Spectrometer (Thermo Scientific K-Alpha KA1066 spectrometer) with Al-Kα x-ray excitation radiation source containing the beam-spot size of 300.0 μm was implemented. The powder X-ray Diffraction (XRD) analysis was performed on synthesized MSs to investigate the

phase crystallinity and average grain size. Field-emission Scanning Electron Microscope (FESEM; JSM-7600F, Japan) equipped with EDS (JEOL, Japan) were subjected to assess the structural morphology of the prepare sample. The Keithley Electrometer (USA) was performed for electrochemical characterizations of the synthesized co-doped CdO/SnO₂/V₂O₅ MSs onto GCE. Informed consent was obtained from the volunteers who gave their serum for real sample analysis. The serum samples were collected from the local medical stores. The procedures were carried out in accordance with relevant laws (including WHO's standard operational guidance for ethics review of health research with human participants, 2011) and local guidelines (Ethics guidelines approved by King Abdulaziz University, Medical Centre, Saudi Arabia).

2.2 Synthesis of CdO/SnO₂/V₂O₅ MSs

Here, to prepare MSs, CdSO₄·H₂O, SnCl₂·H₂O and VOSO₄·5H₂O obtained from Sigma-Aldrich in the analytical grade were used applying the wet-chemical method. In this procedure, 0.1 M solution of each chemicals in deionized water were prepared in the three individual 100.0 mL volumetric flasks. Afterward, 50.0 mL recently prepared solution from each volumetric flask was taken into 250.0 mL beaker and kept on a heating plate with magnetic stirring at 80.0 °C. Subsequently, 0.1 M solution of NH₄OH was added into the beaker dropwise to rise the pH up to 10.5. At this high alkaline phase, the co-precipitate of metal ions in the form of metal hydroxides were obtained. The reaction scheme is as following.

Then, the resultant precipitate was filtered and washed using deionized water successively. Then, the drying of the wet metal hydroxides precipitates were executed by keeping overnight at 120.0 °C in an oven. After that, the dried Cd(OH)₂·Sn(OH)₂·V(OH)₅ was subjected to the calcination in a furnace around 6 h at 500.0 °C in presence of pure oxygen flow. In the furnace, the metal hydroxides were

transformed to the respective metal oxides and the corresponding reactions are supposed as

2.3 Modification of GCE with active CdO/SnO₂/V₂O₅ MSs

The expected sensor was fabricated using GCE coated with CdO/SnO₂/V₂O₅ MSs as the layer of thin film. In this electrode fabrication process, the CdO/SnO₂/V₂O₅ MSs was thinned in ethanol to form slurry and it was deposited on GCE as thin film. Then, the modified GCE was dried at keeping the ambient conditions of laboratory. As the essential requirement, the stability of MSs layer on GCE is important. Therefore, few drops of nafion adhesive was added on the MSs layer of GCE and again subjected to dry at 35.0 °C keeping inside an oven for an hour. After that, the expected sensor was assembled using Keithley Electrometer, where, the resulted working electrode (CdO/SnO₂/V₂O₅ MSs decorated GCE) and Pt-wire (counter electrode)

were connected through it as series manner respectively. The ascorbic acid solutions (0.1 mM to 0.1 nM) were prepared in deionized water to apply as analyte for the execution I-V characteristics of sensor. The proposed AA sensor is calibrated using a straight-line relationship as current verses conc. of AA denoted as calibration curve (calibration-curve). The sensitivity (AA biosensor) is calculated using the slope of calibration-curve and the cross-section of GCE (0.0316 cm²). Recognizing the highest expanded linear section on the calibration-curve applying regression co-efficient (R²) for linearity, the dynamic range (LDR) was indicated and the lower limit of the detection limit (DL) was estimated from 3 as signal-to-noise ratio. The buffer solution was prepared using mono- and di-sodium phosphate at equimolar mixture in deionized water and for sensing experiments, the buffer phase as 10.0 mL as constant throughout experiment is taken in examined beaker.

Fig. 1 The XPS analysis to estimation of binding energy of atoms and corresponding oxidation. **(a)** High resulted XPS spectra of Cd3d orbit, **(b)** O1s, **(c)** core level spin orbitals of Sn3d level and **(d)** Sn3d spin orbits in CdO/SnO₂/V₂O₅ MSs

3 Results and discussions

3.1 XPS analysis

To study the binding energy and oxidation of existing elements in CdO/SnO₂/V₂O₅ MSs, the XPS (X-ray photoelectron spectroscopy) analysis was experimented and the resulted spectrum is illustrated in the Fig. 1. As appearing in Fig. 1a, the core level of Cd3d shows two spin obvious peaks located at 405.4 and 412.2 eV respective to Cd3d_{5/2} and Cd3d_{3/2} spin orbits with 6.8 eV separation, which are well defined with consistent value for Cd²⁺ as described by previous authors [54, 55]. A well-defined and sharp distinct XPS peak of O1s is presented in Fig. 1b with binding energy located at 531.0 eV, a characteristic value for the lattice oxygen of O²⁻ ionization [56, 57]. The appearing symmetric XPS spectra for Sn3d spin orbits as in Fig. 1c are centered at 486.9 and 495.4 eV for Sn3d_{5/2} and Sn3d_{3/2}, which are representing to Sn⁴⁺ in synthesized CdO/SnO₂/V₂O₅ MSs [58, 59]. Furthermore, V2p orbitals are explored in Fig. 1d and witnessed that V2p_{3/2} and V2p_{1/2} spin orbitals are located at 516.9 and 524.2 eV separately. The spin distance between this two orbitals is around 7.3 eV, this respective value is corresponding with V⁵⁺ oxidation state as described elsewhere [60, 61].

3.2 The morphology and compositional analysis by FESEM

To survey the structural and elemental atomic analysis of synthesized CdO/SnO₂/V₂O₅ nanocomposites, the FESEM equipped EDS analysis were executed as illustrated in Fig. 2. The magnified images of FESEM analysis are epitomized in Fig. 2a, b and clearly perceived that the prepared CdO/SnO₂/V₂O₅ composites are morphologically micro-sheets with irregular shape and size. According to X-ray energy dispersive spectroscopy (EDS), the similar reflection is observed as explored in Fig. 2c and the resulted

Fig. 3 The powder X-ray diffraction spectrum of the synthesized CdO/SnO₂/V₂O₅ MSs

Fig. 2 The structural morphology and atomic analysis of mixed metal oxides. (a and b) FESEM analysis is representing the low and high magnified images, (c) The image of EDS, and (d) The atomic composition is existed in prepared CdO/SnO₂/V₂O₅ MSs

elemental analysis is conformed that the synthesized micro-sheets (MSs) of $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ are consist of Cd, Sn, O and V only as displayed in Fig. 2d. From Fig. 2d, the weight percentages of consisting atoms are O 22.22%, V 29.2%, Cd 44.59% and Sn 4.0% respectively.

3.3 Powder X-ray diffraction of $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs

The crystals morphology of the synthesized CdO , V_2O_5 , and $\text{SnO}_2/\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs were studied separately by applying the powder XRD investigation and presented in the Fig. 3. From the observation of Fig. 3, the XRD spectrum shows the well crystalline phases of CdO , SnO_2 , V_2O_5 , and $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs. As it is perceived in Fig. 3, the crystalline phases of CdO denoted as θ are (111), (200), (220), (311), and (222) plans, which are confirmed from the JCPDS card no. 05-0640, which is aligned with the reported results [36, 62]. Besides this, the crystalline phases of SnO_2 identified by μ are (110), (101), (200), (211), (002), (310), (301), (202), and (321) plans analogous with the JCPDS card no. 0041-1445 and matched with the published reports [63, 64]. Furthermore, the maximum number of crystalline phases of V_2O_5 such as (001), (011), (110), (040), (101), (130), (002), (012), (141), (060), (102), (200), and (240) symbolized by β are comparable with the previously reported articles [65, 66].

3.4 Optical analyses of $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs

In this examination, the optical property of synthesized $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs is measured which is an important characteristic features for evaluation the binding energy of each metal oxides [67–69]. Here, $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs and their oxide form were investigated by the UV-visible spectroscopy. As it is illustrated in Fig. 4a–d, the peaks are appeared at 305, 270, 315, and 385 nm for V_2O_5 , SnO_2 , $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$, and CdO respectively. The UV-vis spectrum is used to calculate the optical band-gap energy (E_{bg}) according to Eq. (6). The E_{bg} values are found as 4.066, 4.593, 3.937, and 3.221 eV for V_2O_5 , SnO_2 , $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs and CdO respectively. Band-gap energy of doped nanomaterial has been compared with un-doped counterpart and presented here in the Fig. 4a–d. By doping of metal oxide into the ternary materials, the resultant band gap-energy is reduced slightly. In the Fig. 4, the band-gap energy is calculated for $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs as 3.937 eV, which is smaller than the only SnO_2 (B.E.=4.593 eV) and V_2O_5 (B.E.=4.066 eV). Due to the reduction of band-gap, the conductivity is increased of this prepared ternary $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs [70–72]. In this approach, it was studied the electrochemical detection of chemicals for developing the enzyme-less sensor by electrochemical approach,

Fig. 4 Optical analyses of $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs by UV/visible spectroscopy. UV/visible spectrum of (a) V_2O_5 , (b) SnO_2 , (c) $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs, and (d) CdO . The corresponding band-gap energy is calculated and provided as an energy diagram

which can detect the selective chemical with CdO/SnO₂/V₂O₅ MSs modified working GCE electrode.

$$E_{bg} = 1240/\lambda_{max} \quad (7)$$

Here, E_{bg} (band-gap energy), λ_{max} (maximum absorbed wave length).

3.5 Electrochemical sensing performances of sensor with CdO/SnO₂/V₂O₅ MSs

As the part of this study, the working electrode of desire sensor was fabricated by the deposition of a thin layer of CdO/SnO₂/V₂O₅ MSs on GCE. As necessity of this study, the stability of MSs layer on GCE is important. To fulfil the requirement of the sensor, few drops of nafion adhesive was added on MSs layer on GCE to enhance the stability of working electrode. As, it is known that the nafion is a conductive co-polymer, so the application of its on modified GCE advances the binding strength of MSs layer on GCE and enhances the electron transfer rate and conductance of the fabricated working electrode as observed in our previous articles [73, 74]. In the electrochemical approach, the current density records on the surface of CdO/SnO₂/V₂O₅

MSs film on GCE during analysis of bio-chemicals. As it is known to the authors, the synthesized CdO/SnO₂/V₂O₅ MSs onto GCE is first time to the reliable detection of AA. During electrochemical analysis of AA, the holding time on Keithley electrometer was set as 1.0 s as constant.

Firstly, the electrochemical responsive activity of the sensor with CdO/SnO₂/V₂O₅ MSs/GCE is measured to define the selective biochemical. As a result, a number of biochemical such as acetylcholine, bilirubin, ascorbic acid, cholesterol, D-glucose, D-fructose, L-cysteine, L-leucine, L-glutathione and L-tyrosine were subjected to electrochemical analysis by the fabricated sensor based on CdO/SnO₂/V₂O₅ MSs/GCE. These experiments were performed at 0.1 μ M of each biochemical and potential range of 0~+1.5 V in buffer phase of pH 7.0 as the resulted data are presented in Fig. 5a. As illustrated in the Fig. 5a, the ascorbic acid (AA) displays the supreme electrochemical response at the experimental conditions. Therefore, considering this supreme electrochemical response of AA, it is chosen as the selective biochemical for CdO/SnO₂/V₂O₅ MSs/GCE sensor. It cannot be assumed that the fabricated sensor will show the same electrochemical responses at analysis of AA in buffer system with distinct pH value. Thus, the effective pH of buffer in analysis of AA should

Fig. 5 The electrochemical characterization of sensor created using CdO/SnO₂/V₂O₅ MSs/GCE. (a) The electrochemical analysis of various bio-chemicals at 0.1 μ M and potential of 0~+1.5 V, (b) Electrochemical responses of AA for various pH of buffer phase, (c) The electrochemical responses of AA at various concentration ranging lower to higher, and (d) The calibration of AA sensor [inset current vs. log (conc.)]

be examined. To execute this task, the sensor was applied to analyze AA at $0.1 \mu\text{M}$ concentration and potential $0 \sim +1.5 \text{ V}$ in the range of pH of buffer from 5.7 to 8.0 as shown in Fig. 5b. From the observation of the Fig. 5b, it is stated that the sensor with $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs/GCE shows the maximum electrochemical activity to AA at pH 7.0. After that, the electrochemical responses of AA were investigated with the variation of concentration ranging as $0.1 \text{ nM} \sim 0.1 \text{ mM}$ in a sequence from lower to higher at potential $0 \sim +1.5 \text{ V}$ in pH 7.0 buffer as presented in Fig. 5c. As apparent in Fig. 5c, the electrochemical responses are distinct and possible to separate one other in the lower order to higher base on the concentration of AA. So, it is noted that the electrochemical responses of AA are related directly with its concentrations. This reflections have described in the preceding articles to the sensing several chemicals and bio-chemicals in electrochemical approach [73–75]. The resulted data as in Fig. 5c were analyzed to establish the calibration of AA biosensor as illustrated in Fig. 5d. The current responses at potential $+1.5 \text{ V}$ were isolated from the Fig. 5c to execute current versus concentration of AA plot as in Fig. 5d denoted as calibration-curve.

As it is demonstrated in Fig. 5d, the current data are consistently explored on a line from 0.1 nM to 0.01 mM of

AA and this range is defined as dynamic range (LDR) for detection of AA. To examine LDR linearity, a plot current vs. $\log(\text{conc. of AA})$ is established from 0.1 nM to 0.01 mM of AA and it is found that this exploration of LDR is fitted with $R^2 = 0.9988$ (regression co-efficient), delivers the indication of linearity of LDR. The AA sensor sensitivity is calculated applying the calibration-curve slope and GCE cross-section (0.0316 cm^2) and the resulted sensitivity is $21.3354 \mu\text{A} \mu\text{M}^{-1} \text{ cm}^{-2}$, a value of high satisfactory. The lowest limit of detection (DL) of AA sensor is assessed using 3 as signal-to-noise ratio and obtained a value around $98.64 \pm 4.93 \text{ pM}$, might be considerable lower limit of detection.

For the reliability of this study, a number of experiments were performed as in the Fig. 6. The response time of a sensor is recognized as time essential for the sensor to the execute I-V response completely during analysis of an analyte and it proves the evidence of efficiency of sensor. The response time of the AA sensor with $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs/GCE was investigated at $0.1 \mu\text{M}$ of AA in buffer medium as demonstrated in Fig. 6a. As it shows in Fig. 6a, the AA sensor is able to complete an electrochemical analysis around 20 s, the value provides the information about the high efficiency of AA

Fig. 6 The tests for the reliability of the AA sensor based on $\text{CdO}/\text{SnO}_2/\text{V}_2\text{O}_5$ MSs/GCE. (a) Response time estimation at $0.1 \mu\text{M}$ AA, (b) Check for the interferences effect of AA sensor in the presence of common electrolytes, (c) Repeatability test, and (d) Long time performances test

sensor. The interference effect of the proposed AA sensor due to presence of common electrolytes is another criteria and confirmed the selectivity of a sensor. This performances was tested for analysis of AA co-existing with K^+ , Na^+ , Fe^{2+} and Ca^{2+} as presented in Fig. 6b. It is clearly explored in Fig. 6b, I-V responses of AA are not deviated due to presence of common electrolytes and the interference effect is not perceived. Therefore, it can be predicted that proposed sensor with $CdO/SnO_2/V_2O_5$ MSs/GCE is selective to AA only. The repeatability of a sensor is another measurable parameter and is measured as the ability to achieve repeatable electrochemical responses at identical conditions. This repeatability test of AA sensor based on $CdO/SnO_2/V_2O_5$ MSs/GCE was performed at 0.1 μM of AA and potential ranging as 0~+1.5 V in buffer phase as shown in Fig. 6c. As in Fig. 6c, the seven consecutive I-V responses are unique and undistinguished. The deviation in I-V responses are

not observed even the washing of electrode after each run. Thus, this experiment informs us that the projected AA sensor is able to perform with constant outcome in an identical conditions.

The precision of the current data at potential +1.5 V of repeatability test in term of relative standard deviation (RSD) is measured and found as 1.70%, provides the evidence of high precision. As it is known that the projected AA sensor is worked in phosphate buffer medium, so the necessary stability of it is required. To evaluate the long time performance capability of AA sensor, the similar repeatability tests were executed for long time around seven successive days as illustrated in Fig. 6g. The analogous observations are perceived as in repeatability test. As it is perceived in Fig. 7a, the ascorbic acid, dopamine and uric acid is exhibited the distinct electrochemical response at 0.1 μM in buffer phase and among these, the highest electrochemical response is found in analyzing of ascorbic

Fig. 7 Optimization of sensor probe. (a) The electrochemical responses of ascorbic acid, dopamine, and uric acid, (b) the investigation of interference effects of AA sensor in co-existence of uric acid and dopamine with ascorbic acid at 0.1 μM in buffer phase

Scheme 1 Proposed electrochemical oxidation mechanism of AA electrochemical approach with assembled $CdO/SnO_2/V_2O_5$ MSs/GCE sensor probe

acid. On the other hand as in Fig. 7b, the identical electrochemical responses of AA are obtained in presence of uric acid and dopamine. Therefore, it is clearly stated that electrochemical sensor based on CdO/SnO₂/V₂O₅ MSs/GCE is selective to AA and it has not any interference effect in co-existence with other biochemical such as dopamine and uric acid.

The fabricated AA sensor based on CdO/SnO₂/V₂O₅ MSs/GCE was subjected to electrochemical analyze of AA in the phosphate buffer medium. At the beginning of analysis, the AA molecules are adsorbed on the surface of AA sensor and the influence of applied potential (V), AA is started to oxidize and forms dehydroascorbic acid, two protons and two free electrons as represented in the Scheme 1. The generated free electrons are improved the conductance of the sensing medium as well as the electrochemical response. The similar electrochemical oxidation process of AA acid as in Scheme 1 has been reported by previous authors [76, 77]. At the beginning of the oxidation process, the small surface coverage on the surface of working electrode due to adsorption of few molecules of AA is perceived and the corresponding reaction is progressed. With time, more number of AA is adsorbed and the rate of reaction is enhanced. Further additional time, the rate of oxidation of AA is increased and approached to its equilibrium conditions. As it is perceived in Fig. 6a, the proposed AA sensor shows the response time around 20.0 s and that means, to execute a steady state equilibrium electrochemical response, the AA sensor needs 20 s.

In short, the proposed AA sensor with CdO/SnO₂/V₂O₅ MSs/GCE is showed the outstanding performances in term

of sensitivity, LDR, DL, response time, repeatability and longtime stability. For the reliability of this study, the necessary comparisons of the fabricated sensor with similar researches in term of sensor sensitivity, LDR and DL are illustrated in Table 1 [78–81] and the analytical parameters of this study are found as more appreciable.

Non-enzymatic chemical sensor applications are generally developed elsewhere based on various composite materials such as iron oxide nanoparticle decorated graphene sheets, chitosan grafted graphite composite, biocompatible pectin stabilized graphene nano-sheets hydrogel as well as modified of nanomaterials to attain the trace level, selective and sensitive detection of various bio-chemicals by using electrochemical methods [91–94]. Finally, ternary metal oxide doped nanostructure materials have employed a great deal of consideration owing to their chemical, structural, physical, and optical properties in terms of large-active surface area, high-stability, high porosity, and permeability, which is directly dependent on the structural as well as morphological properties. Here, the ternary CdO/SnO₂/V₂O₅ MSs were synthesized by a facile wet-chemical method using reactant precursors at ambient conditions at low temperature. This technique has several advantages including facile preparation, accurate control of the reactant temperature, one-step reaction, easy to handle, one-pot synthesis, and one-step reaction. Hence, optical, morphological, elemental, electrical, and chemical properties of ternary mixed doped MSs are of huge significance from the scientific aspect as well as potential applications compared to other undoped nanomaterials. Non-stoichiometry, mostly oxygen

Table 1 Comparison of the sensor performance with similar work based on the modified electrode by electrochemical approaches

Modified GCE	DL	LDR	Sensitivity (μA μM ⁻¹ cm ⁻²)	Ref.
PEDOT-SWCNT/GCE	0.7 μM	1 μM~18 mM	2.85 * 10 ⁻⁸	[78]
GO-Au NCs/GCE	50 nM	0.1 nM~1.0 mM	17.28	[79]
ZnO@SiO ₂ NSs/GCE	64.5 μM	0.1 nM~1.5 mM	0.2232	[80]
Co ₃ O ₄ /Fe ₂ O ₃ NSs/GCE	96.02 pM	0.1 nM~0.01 mM	15.4367	[81]
ZnO-CuO NLs/Nafion/GCE	12.0 pM	100.0 pM~100.0 mM	0.09494	[82]
βCD-oxCNF	0.9 μM	100–400 mM	0.1	[83]
SPGNE	–	4–4500 μM	0.03	[84]
MCPGE	–	0.5–2000 μM	0.08	[85]
Ni-G/GCE	–	100–400 μM	0.007	[86]
Graphene/Pt-GCE	–	0.15–34.4 μM	0.3	[18]
Ni/Ag@rGO	0.16 μM	4.89–90.09 μM	23.3818	[87]
N-rGO	9.6 μM	0.1–4 mM	–	[88]
Ag-Fe ₃ O ₄	74 nM	0.2–60 μM	1146.8	[89]
CeO ₂ -CNTs/GCE	3.1 nM	0.01–900.0 μM	0.0179	[90]
CdO/SnO ₂ /V ₂ O ₅ MSs/GCE	98.64 pM	0.1 nM~0.1 mM	21.3354	This work

*DL detection limit, LDR linear dynamic range

vacancies, makes it conducting nature in the doped ternary nanostructure materials. The formation energy of oxygen vacancies and metal interstitials in semiconductor is very low and thus these defects form eagerly, resulting in the experimentally elevated conductivity of CdO/

SnO₂/V₂O₅ MSs compared to other un-doped. CdO/SnO₂/V₂O₅ MSs have also attracted considerable interest due to their potential applications in fabricating opto-electronics, electro-analytical, selective detection of assays, sensor devices, hybrid-composites, electron-field emission

Fig. 8 Analyses of real biological samples with CdO/SnO₂/V₂O₅ MSs/GCE probe by recovery system. **(a)** Human serum, **(b)** Rabbit serum, and **(c)** Mouse serum

Table 2 The analysis of collected bio-samples using CdO/SnO₂/V₂O₅ MSs/GCE sensor in recovery system

Samples	Added AA conc. (μM)	Measured AA conc. ^a by CdO/SnO ₂ /V ₂ O ₅ MSs/GCE (μM)			Average recovery ^b (%)	RSD ^c (%) (n = 3)
		R1	R2	R3		
Human Serum	0.01000	0.01139	0.01134	0.01124	113.24	0.67
Rabbit Serum	0.01000	0.01002	0.01019	0.01034	101.83	1.57
Mouse Serum	0.01000	0.01006	0.01047	0.01022	102.50	2.02

^aMean of three repeated determination (signal to noise ratio 3) CdO/SnO₂/V₂O₅ MSs/GCE

^bConc. of AA determined/Concentration taken (Unit: nM)

^cRelative standard deviation value indicates precision among three repeated measurements (R1,R2,R3)

sources for emission exhibits, biochemical detections, and surface-enhanced Raman properties etc. Therefore, CdO/SnO₂/V₂O₅ MS offers improved performances due to the large-active surface area, which increased of conductivity and current responses of CdO/SnO₂/V₂O₅ MSs/GCE assembly during electrochemical investigation.

3.6 Analysis of collected bio-samples

Finally, the fabricated ternary metal oxides CdO/SnO₂/V₂O₅ MSs/GCE was applied to analyze the presence of AA in the real bio-samples, which were collected from animals and human serums. The real samples were diluted ten times in phosphate buffer solution. The electrochemical measurements were performed for three real samples, such as human serum, rabbit serum and mouse serum, which are presented in the Fig. 8a–c. The calculated results are illustrated in Table 2 by using recovery method. As it is illustrated in Table 2, the outcome of electrochemical responses are quite satisfactory and acceptable.

4 Conclusions

Applying co-precipitation process in alkaline medium, the micro-sheets of CdO/SnO₂/V₂O₅ were prepared and followed by calcination at 500.0 °C in the muffle furnace. To obtain the detail characterization of synthesized CdO/SnO₂/V₂O₅ MSs, it was subjected to analyses by using XPS, EDS, XRD, and FESEM. A thin layer of MSs was prepared onto the top of GCE to result the proposed AA sensor. From detail electrochemical analysis of AA sensor probe, the analytical parameters such as sensitivity, reproducibility, LDR, linearity, DL of AA sensor based on with CdO/SnO₂/V₂O₅ MSs/NaF/GCE were calculated. Besides this, the fabricated AA sensor was used to analyze the real biological samples, which are collected from animals and human serums. Finally, it was found the good and acceptable results to detect the enzyme-free AA with MSs/NaF/GCE sensor probe by electrochemical method. To ensure the available technology, this enzyme-free method is used to develop of sensor which might be very effective in the field of healthcare and biomedical sectors.

Acknowledgements Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Saudi Arabia is highly acknowledged for the technical supports and instrumental facilities such as XPS, FESEM, EDS, UV/vis., XRD and Keithley Electrometer.

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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