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ONE-POT ELECTROCHEMICAL FABRICATION OF SnO-REDUCED GRAPHENE OXIDE ELECTRODES FOR AMPEROMETRIC SENSING OF DOPAMINE

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In this study, the preparation of tin(II) oxide/reduced graphene oxide (SnO/rGO) hybrid electrodes was simultaneously performed by a one-pot electrodeposition process for the first time by using a single cell. The morphological and structural characterizations of SnO/rGO were performed by scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Additionally, the electrocatalytic activities of the electrode materials for the determination of DA were tested by the linear sweep voltammetry technique. Furthermore, the amperometric sensing of DA was carried out with a detection limit of 0.32 µM. The results suggest that our fabricated biosensor exhibited an ultrahigh sensitivity, low detection limit, and excellent selectivity.

Keywords: dopamine; graphene; reduced graphene oxide; tin oxide

ЕЛЕКТРОХЕМИСКО ДИЗАЈНИРАЊЕ НА ЕДНА ЕЛЕКТРОХЕМИСКА ЌЕЛИЈА НА ЕЛЕКТРОДИ ИЗРАБОТЕНИ ОД SnO И РЕДУЦИРАН ГРАФЕН ОКСИД ЗА АМПЕРОМЕТРИСКО ОПРЕДЕЛУВАЊЕ НА ДОПАМИН

Во оваа студија е претставен метод за изработка на хибридни електроди добиени од калај(II) оксид и редуциран графен оксид (SnO/rGO) со симултана електродепозиција во еден чекор со употреба на само една електрохемиска ќелија. Морфолошката и структурната карактеризација на SnO/rGO беше извршена со примена на скенирачката електронска микроскопија (SEM), енергетската дисперзивна рендгенска спектрометрија (EDS), рендгенската фотоелектронска спектроскопија (XPS) и рендгенската дифракција (XRD). Притоа, електрокаталитичката активност на електродниот материјал беше тестирана за определување на допамин со употреба на линеарна волтаметрија. Амперометриското определување на допамин се карактеризираше со лимит на детекција од 0,32 µM. Резултатите од оваа студија сугерираат дека дизајнираниот биосензор покажува висока осетливост, ниска граница на детекција и одлична селективност.

Клучни борови: допамин; графен; редуциран графен оксид; калај(II) оксид

1. INTRODUCTION

Dopamine (DA) plays an important role in the central nervous, kidney, and hormonal systems [1, 2]. Besides, DA is one of the major catecholamines found in the central nervous system that regulates our feelings and thoughts in our body [3, 4]. The deficiency of this substance in the body can lead to symptoms of many bad diseases such as cancer, Parkinson's disease, and cardiovascular diseases [5, 6]. Until now, various techniques such as high-performance liquid chromatography

(HPLC) [7], spectrophotometry [8], and electrochemical methods [9] have been used for the determination of DA in the presence of AA. However, electrochemical methods are much simpler, cheaper, highly sensitive, and much more environmentally friendly than other traditional methods [10–12]. Moreover, the finding of electrochemical activities of AA and DA has increased the interest in electroanalysis methods in determining AA and DA [13]. However, the co-existence of AA and DA in the metabolic system and the proximity of oxidation potentials in electrochemical fixation make it difficult to separate them potentiometrically [14–16]. To overcome this problem, modified electrodes have been prepared using conductive polymers, metals, or metal oxides with various carbon-based materials, including carbon nanotubes, carbon nanofibers, and graphene (G) used to separate oxidation potentials [13, 17, 18].

G is a promising nanomaterial for the formation of nanocomposites with metal oxide due to its economy, ease of functionality with other molecules, and easy synthesis approaches [19–27]. For the synthesis of G, the reduction of graphene oxide (GO) using various techniques such as chemical, electrochemical, hydrothermal, or photochemical is often used [28, 29]. Recently, G-based electrochemical sensors have been widely used for the electrocatalytic oxidation of DA [30–36].

Metal oxides such as Fe_3O_4, CuO, TiO_2, SnO_2, and ZnO can interact with graphene oxide via carboxylic acid functional groups [37, 38]. On the other hand, tin(II) oxide (SnO) has been studied less extensively and has gained attention due to its natural p-type conductivity, large hole mobility, and high theoretical specific capacity [39]. The SnO is a semiconductor with a tetragonal crystal structure and has a wide bandgap that has been used as an anode material in lithium batteries, gas sensors, and transparent conductors in solar cells [40]. Besides, SnO nanoparticles have attracted considerable attention, especially due to their high electrocatalytic activity in dye removal, as well as their selectivity in determining many biological analytes.

In this study, we aimed to synthesize SnO/reduced graphene oxide (SnO/rGO) nanocomposites with a single-step co-electrodeposition method, which is easier and less time-consuming than other methods reported in the literature. Moreover, this technique does not require any complexing agents, binders, and/or toxic reagents. The as-prepared composite electrode was used for the amperometric determination of DA. To the best of our knowledge, the use of the SnO/rGO composite electrode prepared by electrochemical co-deposition method for electrochemical determination of DA has not been reported in the literature. This work presents a good candidate for developing next-generation bio-sensing applications.

2. EXPERIMENTAL SECTION

For the experiments, graphene oxide (GO), tin(II) chloride ($SnCl_2$), dopamine (DA), ascorbic acid (AA), uric acid (UA), hydrogen peroxide (H_2O_2), sodium dihydrogen phosphate (NaH_2PO_4), and disodium hydrogen phosphate (Na_2HPO_4) were purchased from Sigma-Aldrich (U.S.A). Electrochemical synthesis of SnO/rGO nanocomposites was carried out using BAS 100i potentiostat. In the three-electrode cell system, Au, Pt wire, and Ag/AgCl (3 M KCl) electrodes were used as the working, counter, and reference electrodes, respectively. SnO/rGO nanocomposites were prepared by depositing at −600 mV for 6 minutes. A schematic illustration of the experimental procedure is given in Fig.1. Thanks to electrochemical co-deposition, Sn^{2+} ions and GO can be deposited simultaneously on the Au electrode surface. While GO is reduced to rGO, Sn^{2+} ions and the oxygen groups of GO combine to form SnO. The prepared SnO/rGO electrode was used for amperometric detection of DA.

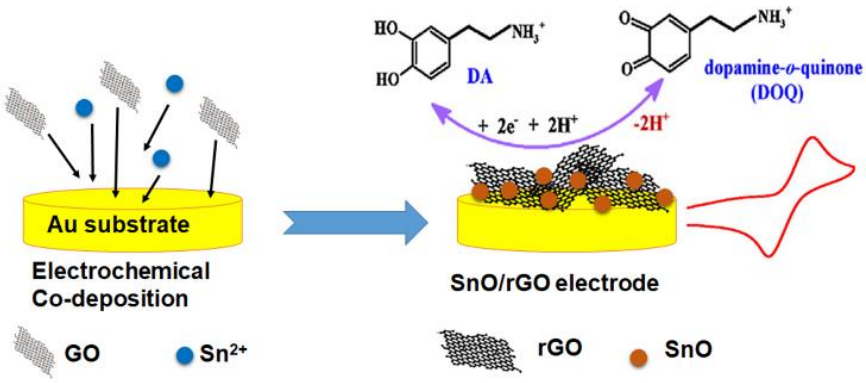

Fig. 1. Schematic illustration of the experimental procedure

The morphological and analytical characterizations of SnO/rGO nanocomposites were performed using scanning electron microscopy (SEM, FEI Quanta), energy dispersion spectroscopy (EDS, combined with FEI Quanta), X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe), and X-ray diffraction spectroscopy (XRD, Rigaku Advance) techniques. The voltammetric detection of DA was performed using linear sweep voltammetry (LSV) and cyclic voltammetry (CV) techniques in phosphate buffer solution (PBS, 0.1 M, pH 7.0).

3. RESULTS AND DISCUSSION

3.1. *One-pot electrochemical synthesis of SnO/rGO nanocomposites*

For the one-pot electrochemical synthesis of SnO/rGO nanostructures on the Au electrode surface, 5 mM Sn^{2+} and 0.1mg/ml GO/0.1 M KNO_3 solutions were mixed, and the CV of the Au electrode was recorded in the mixture solution (Fig. 2). The CV was recorded at 0 mV−(-1000 mV) potential region with a scan rate of 100 mV s^{-1}.

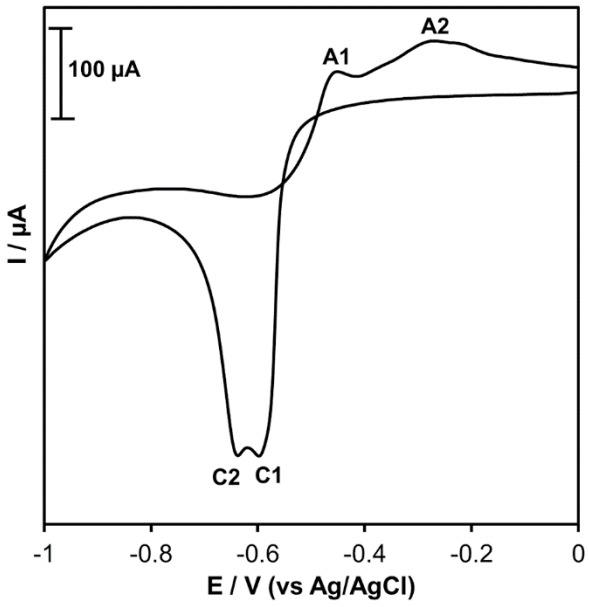

Fig. 2. The CV of Au electrode in the mixed solution of Sn^{2+} and GO

As can be seen in Figure 2, two reduction peaks (labelled C_1 and C_2) were present in the CV that corresponded to the reduction of GO to rGO (at approximately −630 mV) and Sn^{2+} to Sn (at approximately −580 mV). Both SnO and rGO can be simultaneously deposited on the electrode surface at a single potential of about −600 mV.

3.2. *The morphological and analytical characterization of Au-SnO/rGO electrode*

X-ray diffraction (XRD) analysis was performed to determine the crystal orientation of SnO/rGO nanostructures. In the XRD pattern of Fig. 3a, the diffraction peaks at $2\theta = 33.2^{o}$ and 50.7^{o} correspond to the SnO (110) and SnO (211) structures, respectively. The diffraction peaks occurring at $2\theta = 38$, 43.7, 63.9, and 76.9^{o} correspond to (111), (200), (220), and (311) crystal structures of the Au electrode, respectively. In addition to these peaks XRD diffraction of the (211) crystal structure of $Sn_6O_4(OH)_4$, formed as an intermediate product, was also determined. Moreover, the XRD diffraction peak of rGO at approximately 25° could not be observed since the rGO structures diverged from each other when metal particles are deposited on the G surface in G-metal composites.

XPS analysis generally provides information about the qualitative, quantitative, and chemical structure of the synthesized materials. The XPS spectrum shows both the binding energies (eV) of the X-ray photoelectrons of the elements that make up the synthesized material and the oxidation step with the presence of that element. Moreover, these measurements allow understanding of chemical differences such as metal/metal oxide or carbon/carbonyl. The presence of C, O, and Sn elements in the survey XPS spectrum recorded for the SnO/rGO composite was detected (Fig. 3b). The carbon peak in the survey XPS spectra supported that the electrochemical reduction of GO was successfully achieved. In the XPS spectrum in Figure 3c, the positions of the binding energies of the Sn3d peaks (486 eV for $Sn3d_{5/2}$ and 494.4 eV for $Sn3d_{3/2}$) exactly match the standard data of SnO [41]. The XPS spectrum of Sn3d confirmed that tin in nanostructures has the Sn^{2+} oxidation step. On the other hand, the broad peak observed at 530.4 eV in the XPS spectrum obtained for O1s in Figure 3d corresponds to the various bindings of oxygen.

The morphology of as-prepared SnO/rGO nanostructures was determined by the SEM technique. The typical morphology of SnO/rGO nanostructures electrodeposited from an oxygen saturated solution at a constant potential of −600 mV on the Au electrode surface for 6 minutes is shown in Figure 4a. In this SEM image, it is seen that a few squares and rectangular particles of the SnO structure and a curled structure originating from the graphene structure were formed on the electrode surface. The EDS spectrum of the SnO/rGO composite (Fig. 4b) included C atoms from rGO and Sn and O atoms from SnO. Besides,

the peak of the Au electrode, which was used as a substrate, is present in the EDS spectra. The EDS spectrum confirmed that an elemental impurity-free SnO/rGO composite was synthesized.

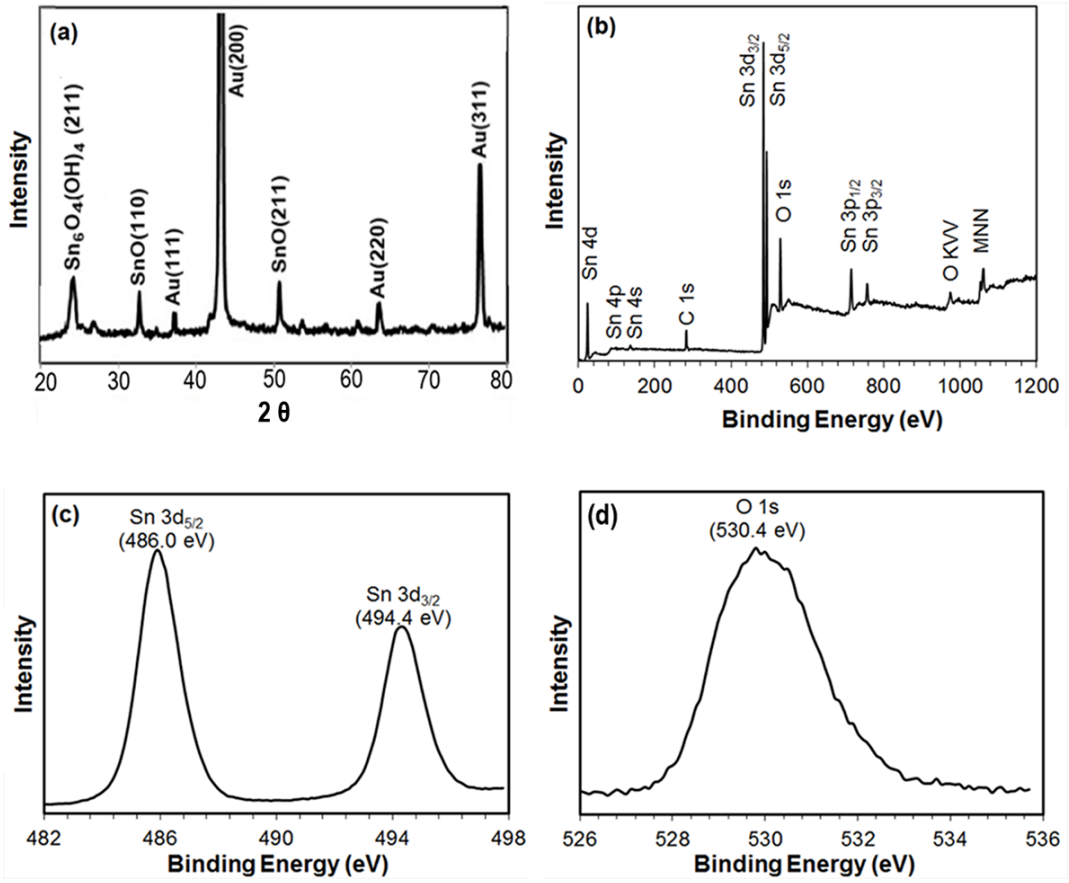

Fig. 3. XRD spectrum (a) and XPS spectra (b-d) of SnO/rGO

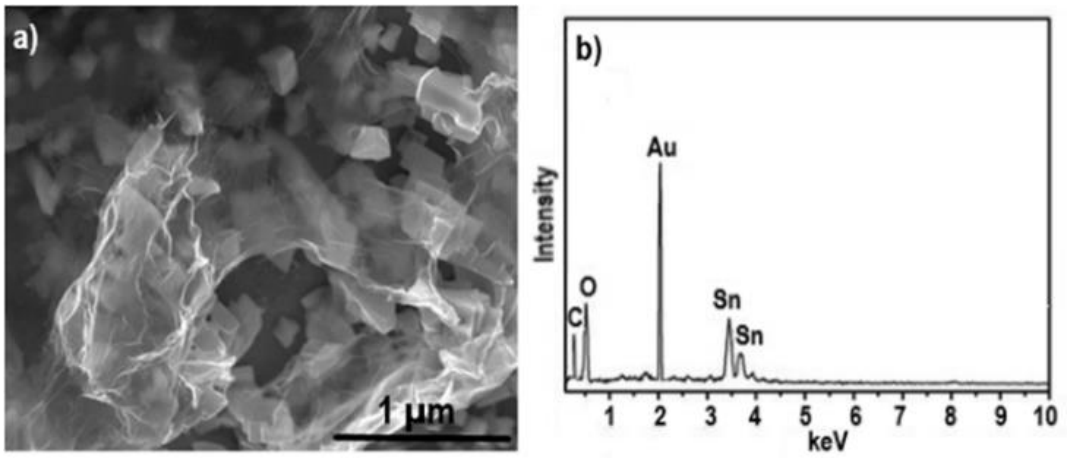

Fig. 4. SEM image (a) and EDS spectrum (b) of SnO/rGO

3.3. *The amperometric sensing of DA on Au-SnO/rGO electrode*

Firstly, the oxidation potential of DA on the SnO/rGO electrode was determined by a voltammetric study. The concentration of DA was chosen as 10.0 mM in all measurements. To determine the electrocatalytic properties of the composite modified Au electrode, the linear sweep voltammograms (LSVs) for Au, SnO, and SnO/rGO electrodes in 10.0 mM DA solution are shown together in Figure 5a. In these LSVs, a wide oxidation peak

resulting from the oxidation of DA at a potential value of approximately 300 mV is observed. Also, the composite material exhibited the highest current value and the lowest oxidation potential in the LSVs. The negative shift in peak potential originates from the electrocatalytic effect of SnO/rGO. In other words, it perceives more sensitive DA with higher current and with less energy.

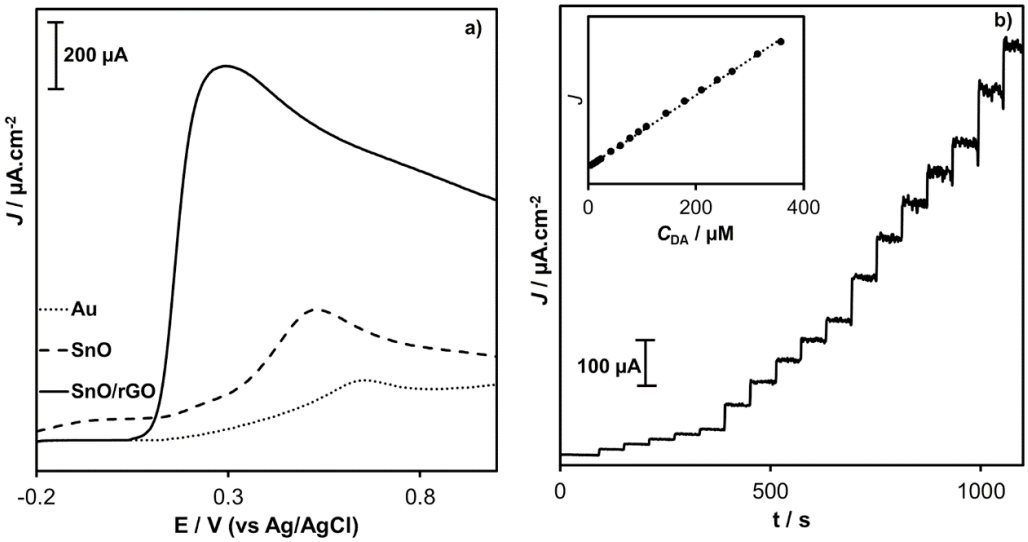

Fig. 5. a. LSVs in 10 mM DA solution on SnO/rGO, SnO, and Au electrodes, v = 50 mV s^{-1}.
b. Current density-time graphic of SnO/rGO electrode for different concentrations of DA at 0.3 V.

The graph of current-time (i-t) resulting from the sequential addition of different concentrations of DA to the stirring 0.1 M PBS solution is given in Figure 5b. After DA was added to the pH 7 solution, the anodic current densities increased gradually to reach a constant value by applying the potential of 0.3 V. As proof that the electrocatalytic response at the nanocomposite electrode is fast, the almost constant current was obtained in less than 3 seconds. When the typical amperometric response of SnO/rGO electrode at different concentrations of DA was examined, a fast amperometric response (with a steady-state current of 98 %) was observed, especially in the low concentration range (Fig. 5.b inset graph). For the amperometric detection of DA, it was determined that the SnO/rGO electrode has a high sensitivity of 2.55 µA cm^{-2} mM^{-1} and shows a linear relationship (R = 0.9991) in a concentration range of 0.5 µM to 400 µM. Besides, the limit of detection (LOD) was calculated to be about 0.32 µM when the signal-to-noise ratio was 3. The detection limit calculated in the literature for different electrodes is compared in Table 1. Compared with the electrodes of Table 1, SnO/rGO electrode can be used successfully in the amperometric detection of DA due to its relatively lower detection limit.

Detection of DA in biological systems becomes difficult in the presence of AA. Due to the higher amount of AA in the body system, it has become necessary to develop biosensors sensitive to DA. For this purpose, the interference test of the SnO/rGO electrode was examined by the sequential addition of biomaterials such as DA, AA, UA, H_2O_2, etc. (Fig. 6a). The concentrations of DA, AA, UA, and H_2O_2 were selected as 1 mM, 50 mM, 2 mM, and 2 mM, respectively. Remarkably, when the DA was added in the PBS, the amperometric current of DA was increased while the current of the interference species was not detected in Fig. 6a. This result showed that SnO/rGO electrode had excellent catalytic activity and selective sensing towards DA. Five modified electrodes prepared in the same experimental conditions in the DA solution, recorded LSV measurements to verify the reproducibility of the SnO/rGO electrode. The recovery of current densities of the modified electrodes are shown in Figure 6b. The different SnO/rGO electrodes exhibited similar recovery values. To investigate the stability of the electrode, the LSV experiments were conducted for 20 days on the modified electrode. The modified electrode had an initial recovery of the current value of 100 %, while this value decreased to 72 % after 20 days (Fig. 6c). Thus, the good stability and reproducibility of the SnO/rGO electrode were proved by the obtained results.

T a b l e 1

Comparison of different electrodes for detection of DA

Electrode	Technique	pH	LOD (μM)	Linear range (μM)	Ref
G/SnO_2	DPV	6.8	1	1–20	[42]
GCE/G/SnO_2	DPV	6.5	1	5–50	[43]
Nanostructured gold	DPV	7.4	5	10–100	[44]
G-Au NPs	DPV	6.0	1.86	5–1000	[45]
rGO	CA	7.0	2	5–200	[16]
Au-SnO/rGO	CA	7.0	0.32	0.5–400	This work

DPV – Differential pulse voltammetry, CA – Chronoamperometry, G – Graphene, NPs – Nanoparticles, GCE – Glassy carbon electrode, rGO – reduced graphene oxide

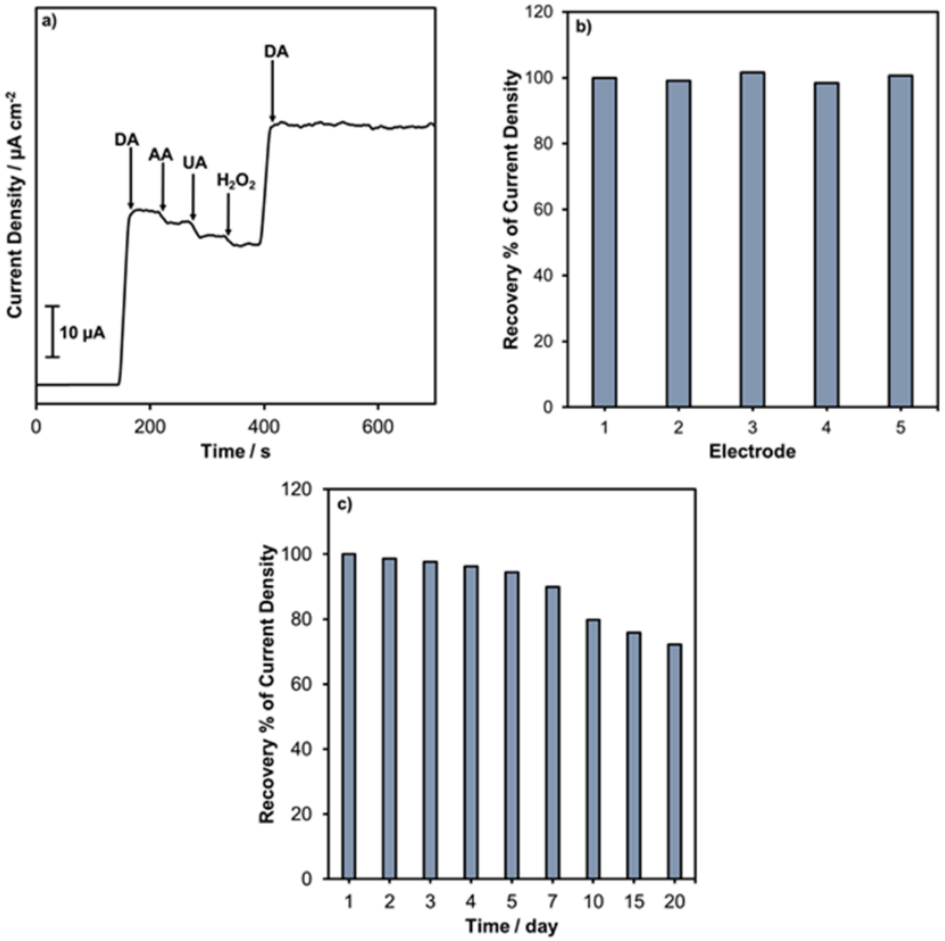

Fig. 6. a. Interference test, **b.** reproducibility, and **c.** stability of SnO/rGO electrode for DA sensing

The real sample analysis was carried out by measuring the concentration of DA in human serum by the standard addition method. The serum samples were diluted 50 times with PBS buffer before measurement, followed by the addition of known concentrations of DA to the samples, and the recovery rates were calculated. For 1, 5, and 10 mM, the recovery rates were 98.6, 99.4, and 100.1 % with an average of 4 measurements, respectively, implying a hopeful biosensor application of the SnO/rGO electrode in amperometric sensing of DA in real samples.

4. CONCLUSION

The Au electrode was successfully modified with SnO/rGO composite by applying a one-pot constant potential from the solution mixture containing Sn^{2+} and GO. The SnO and rGO structures in the nanocomposite were supported by analytical

and morphological characterizations. Compared to Au and SnO electrodes, the lower oxidation potential and high current density of DA on the SnO/rGO electrode were confirmed by LSV results. In addition, the SnO/rGO modified electrode was used for the amperometric determination of DA. Amperometric studies revealed that DA can be detected by the large linearity (with 0.5–400 μM) and low LOD (with 0.32 μM). Moreover, the SnO/rGO electrode exhibited high selectivity for DA in the presence of interference species, good reproducibility, and relatively long-term stability. This study shows that the as-prepared SnO/rGO nanocomposite electrode has great potential for the sensitive detection of dopamine in real sample analysis.

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