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ARTICLE

Sensing properties of Pt@SnO_2 core-shell nanocomposite detecting epinephrine

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Abstract

This proposed Pt@SnO_2 core-shell nanocomposite material based electrochemical sensor towards epinephrine detection showed high sensitivity, repeatability and high stability. It can play a significant role for precision determination of epinephrine in the drug sample and can also used for either simultaneous determination or others like acetaminophen (AC) and dopamine (DA) in samples.

KEYWORDS

cyclic voltammetry, epinephrine, nanocomposite, Pt@SnO_2

1 | INTRODUCTION

Epinephrine (EP) is a neurotransmitter (NT) necessary for human body functions, also referred to as adrenaline is another important catecholamine NT released from the adrenal glands. Normally, EP is designated for patients with anaphylaxis, cardiac arrest, asthma, and also used as a vasoconstrictor. The dosage of intravenous EP as a helpful inotrope is ranged from 0.01 to 1 μg kg^{-1} min^{-1}. The side effects of EP are including palpitation, tachycardia, cardiac arrhythmia, anxiety, headache, tremble, hypertension, and pulmonary edema. It is the reason to develop new low-cost, simple, and accurate quantitative methods to diagnose and to measure the concentrations of EP in the intravenous solution preparations for clinical practice.[1,2] A chemical structure of epinephrine is presented in Figure 1.

There is a demand to develop a method determining epinephrine concentrations precisely; the available instrumental techniques include high-performance liquid chromatography-mass spectrometer (HPLC-MS),[1] fluid fluorescence,[2] capillary electrophoresis (CE),[3] an electrochemical method,[4–6] and electrochemically using screen-printed electrodes.[7] These techniques, HPLC-MS, fluid fluorescence, and CE pose some drawbacks. For example, the cost of the instrument is very high and it could not be measured in time. Some studied for the analysis of dopamine and epinephrine in the presence of uric acid using boron-doped multiwalled carbon nanotubes as a sensing material.[8] Gold nanostructures on self-assembled monolayers were used for sensing epinephrine, noradrenaline, and dopamine.[9]

EP can be quantified in blood serum as a diagnostic aid. Usually, the endogenous plasma EP concentrations are less than 10 ng/L in resting adults, but it may increase by 10-fold during exercise and by 50-fold or more during times of stress. The patients suffering from pheochromocytoma exhibit EP levels of 1,000–10,000 ng/L in the serum and the acute-care cardiac patients may show plasma concentrations in the range 10,000–100,000 ng/L. The development of electrochemical technology to measure epinephrine seems to be low cost and at rapid speed seems an essential option.

The porous spongy Au-Ag electrode was used to modify the material on the glassy carbon electrode (GCE).[4] It can be used to detect epinephrine concentration, the linear range was measured from 25 to 700 μM and the detection limit was obtained to 5.05 μM.[4] An electrode was modified with an Au nanotube as the working electrode, and the electrochemical cyclic voltammetry (CV) was used to measure epinephrine concentration.[5] The linear concentration range was from 10 to 150 μM and the detection limit was detected as 2.8 μM.[5] A RuON sensing material was modified to a GCE and epinephrine was measured by using CV and differential pulse voltammetry.[6] The detecting result was found that the linear range of epinephrine was 2.0–758.6 mM and the detection limit was 0.46 μM.[6] Table 1 listed the sensing properties of the above various kinds' material on the working electrode.[4–6]

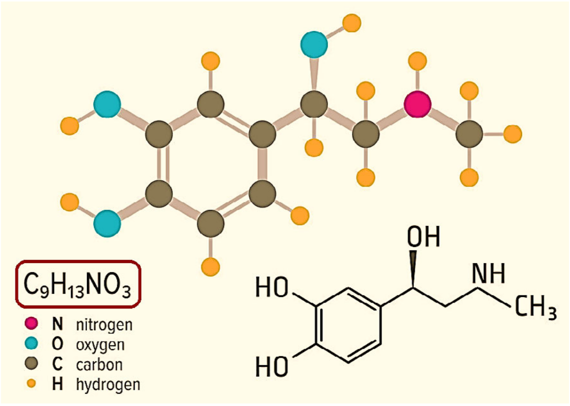

FIGURE 1 Chemical structure of Epinephrine

Recently, we have focused on semiconductor-based SnO_2 sensors, and the use of core-shell structure is a potential candidate for this purpose. Homemade Pt@SnO_2 core-shell nanoparticles were prepared the material and coated a GCE. In this study, we have used core-shell nanoparticles,[10] which regularly display enhanced catalytic properties due to the lattice strain created in these core-shell particles. Novel sensing core-shell material of Pt@SnO_2, which was successfully synthesized through a new modified sol–gel method have porous structures. In addition, platinum (Pt)-based nanomaterials are the most effective electrocatalysts[11]; here we discussed the performance evaluation of Pt@SnO_2 core-shell nanoparticles and SnO_2 nanoparticles and their EP sensing properties, seems to be a promising sensing material used for electrochemical detection of epinephrine.

2 | EXPERIMENT

2.1 | Materials

In this research, all the chemicals were of analytical reagent grade (AR) (Purity>99%) unless otherwise mentioned. Epinephrine (98%, Aladdin Industrial Corporation (Shanghai, China) was offered by Hualien Tzu-Chi Hospital (Buddhist Tzu Chi Medical Foundation, Chung Yang Rd., Hualien 970, Taiwan, ROC; http://hlm.tzuchi.com.tw/en/)) and was used without any further purification. Dihydrogen hexachloroplatinate (IV) Hexahydrate ($H_2PtCl_6 \bullet 6H_2O$, 99.95%), Polyvinylpyrrolidone, Sodium tin (IV) oxide hydrate (Na_2SnO_3), and Chitosan were purchased from Aldrich and other chemicals NaOH (UniRegion Bio-Tech) and Alcohol (J.T Backer) was procured. Water was distilled and de-ionized (DI) using a Milli-Q water purification system (Millipore Corp.).

TABLE 1 Comparison of various sensing materials for detection of epinephrine

S. no.	Authors	Sensing material	Range of detection	Detection limit (μM)	Reference
1	E. Wierzbicka et al. (2016)	Au–ag	25–700 μM	5.05	[4]
2	E. Wierzbicka et al. (2016)	Au nanotube	10–150 μM	2.80	[5]
3	H. R. Zare et al. (2013)	RuON	2.0–758.6 mM	0.46	[6]
4	H-N. Luk et al. (2019)	Pt@SnO_2	13.75–110 μM	0.35	This work

2.2 | Preparation of sensing materials

Platinum colloids were prepared using an alcohol reduction method. DI water (20 ml), C_2H_5OH (80 ml), and polyvinylpyrrolidone (0.429 g) were combined in a beaker, and $H_2PtCl_6{\cdot}6H_2O$ (0.05 g) was added to the solution. The mixture was then refluxed for 4 hr; the solution turned from yellow to black as Pt nanoparticles were formed. The nanoparticle solution was then adjusted to pH 7.0 by adding 0.01 M NaOH. Pt@SnO_2 core-shell nanoparticles were prepared by dropwise addition of Na_2SnO_3 (3.5 ml, 0.01 M) to the as-prepared solution. This solution was heated to 60°C for 10 min and then cooled to room temperature over 5 min. This cycle of adding Na_2SnO_3, followed by heating and cooling was repeated until the total volume was 15 ml. Pt@SnO_2 was dried at 100°C for 24 hr and calcined at 500°C for 1 hr. An appropriate amount of Na_2SnO_3 was added to 50 ml of DI water, and the solution was then boiled until it dried. Subsequently, this dry sample was calcined at 500°C for 2 hr, and SnO_2 was thus obtained.

2.3 | Preparation of Pt@SnO_2/GCE

Prior to modification, the GCE (3 mm dia.) was cleaned by polishing it with 0.01 mm α-Al_2O_3 powder and then carefully with a fine emery paper. Later using D.I. water, all the impurities on the GCE surface were washed off. The electrode surface was wiped with a filter paper. After washing with distilled water to remove Al_2O_3 and other substances, the electrode surface was cleaned with ethanol carefully. Then the electrode was sonicated for about 5 min with distilled water and then acetone. An appropriate ratio of Pt@SnO_2 with 5% chitosan and 5 ml acetone were mixed ultrasonically for more than 30 min., around 50–75 μl of this slurry was dropped onto the freshly polished GCE via a syringe. After the acetone evaporated completely, the prepared electrode (Pt@SnO_2/GCE) was used as the working electrode after drying in an oven.

2.4 | XRD and HR-TEM

The qualitative of SnO_2 and Pt@SnO_2 nanocomposite was characterized using XRD and TEM. Various samples were identified by the 2θ angles, and the crystal parameters were estimated by X-ray diffractometer (Shimadzu Scientific Instruments (SSI), Shimadzu Lab-X XRD-6000; X-ray tube: Cu Kα radiation (1.54060 Å), voltage: 40.0 keV and current: 30.0 mA). The XRD-6000 boasts an integrated design featuring high speed and a high precision vertical goniometer (compact design; 900 × 700 × 1,600 mm (w x d x h, in mm) suitable for diverse applications and data processing software supporting the Windows XP user interface. The 2θ scanning range was between 10 and 80°, at a scan rate of 4°/min. The morphology of the sensing materials was studied by high-resolution transmission electron microscope (JEOL 2010 TEM with accelerating voltage: 200 kV).

2.5 | Electrochemical detection system

The electrochemical behavior of SnO_2 and Pt@SnO_2 have been carried out using CV (ZIVE SP1 compact type Electrochemical Workstation, The Zive In this electrochemical system, the three-electrodes were used; GCE was used as a working electrode, a saturated Ag/AgCl electrode as a reference electrode and platinum wire as a counter electrode, as shown in Figure 2.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the Pt@SnO_2 nanocomposite

XRD patterns were recorded by a Shimadzu Lab-X-6000 X-ray diffractometer using Cu Kα radiation. The XRD spectra of Pt@SnO_2 and SnO_2 are revealed in Figure 3a,b. Various diffraction patterns were identified with the JPCDS database. Figure 3a,b, the diffraction peaks of SnO_2 with main lattice plane are (101), (110), (200), (211), (311), and (301) compared with JCPDS 41-1445.[12] The characteristic peaks proved the successful synthesis of SnO_2 shown in Figure 3b. Figure 3a shows the intense diffraction peaks of Pt with lattice planes (111), (200), and (220).[13] From Debye–Scherrer's equation in Figure 3a,b, it can calculate the crystalline grain size of

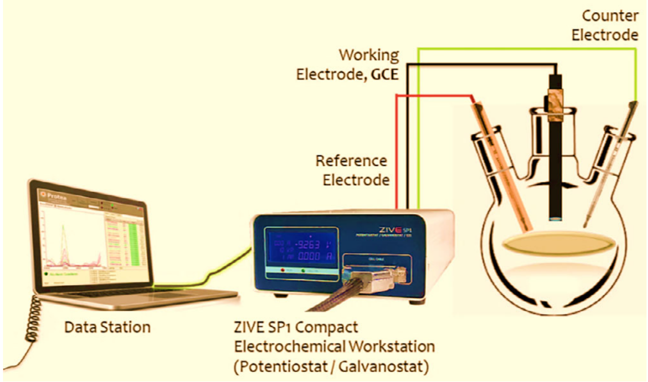

FIGURE 2 Setup for the electrochemical detection of epinephrine

SnO_2 (111) as 3.2 and 2.8 nm of SnO_2 and Pt@SnO_2, respectively. It was observed the diameter of the SnO_2 particle is decreased (figure 4) forming Pt@SnO_2. By the estimation of XRD spectra (Figure 3a), the crystalline grain size of Pt (111) was calculated to 5.6 nm of Pt@SnO_2.

HR-TEM images of Pt@SnO_2 at low magnification scale 500 nm and at higher magnification scale 20 nm are given in Figure 4a,b, respectively. Figure 4a shows a TEM image of some aggregation of Pt@SnO_2. Figure 4b shows the HRTEM image of Pt (111) and SnO_2 (101) lattice planes were about 0.22 and 0.26 nm lattice displace of Pt@SnO_2, respectively. In addition, the particle size of Pt is estimated as 5.3 nm of Pt@SnO_2, it is close to the result of XRD.

3.2 | Pt@SnO_2 electrochemical behavior

In Figure 5a–c, the measuring cyclic current (CV) during the potential scans were measured at the working electrode on bare, SnO_2 and Pt@SnO_2 to 45 μM epinephrine concentration. It can compare the current values of the three electrodes at the concentration of 45 μM EP, and the difference of oxidation peaks was obtained. The bare and SnO_2 electrodes have no obvious oxidation potential peak (Figure 5a,b). To Pt@SnO_2, the measured current value was higher than bare and SnO_2 and the oxidation potential appeared at about 0.41 V. It is clearly indicating the function of the modified electrode for the detection EP of Pt@SnO_2.

With the change of concentration, epinephrine was determined using CV in Figure 6a–f. The CV of Pt@SnO_2 profiled an oxidation peak at 0.41 V in the concentration of EP performed as (a) blank electrode, (b) 45 μM, (c) 55 μM, (d) 75 μM, 85 μM, and (f) 110 μM. It was at scan rate 50 mVs^{-1} in the potential range from −0.2 to 0.9 V. The linear calibration for oxidation peak current versus EP concentration is shown in Figure 7, revealed good linearity with R^2 value (0.9987) from 45 to 110 μM with at 0.41 V. CV calibration curves of the Pt@SnO_2 electrode obtained by changing the concentration of epinephrine at the voltages of 0.409 V; the regression

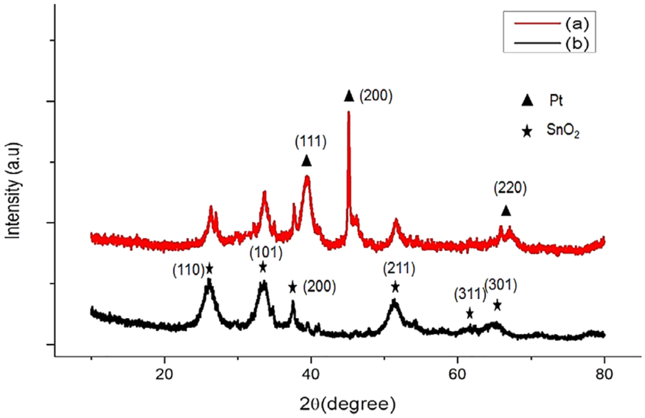

FIGURE 3 XRD spectra of (a) Pt@SnO_2 (b) SnO_2

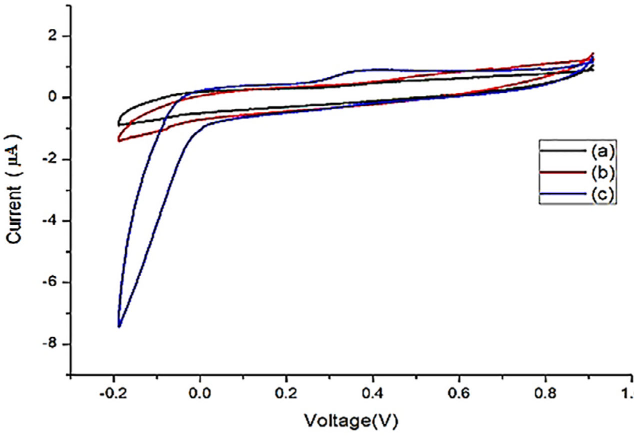

FIGURE 5 The measuring current during the potential scans at the working electrode on (a) bare (b) SnO_2 (c) Pt@SnO_2 to 45 μM epinephrine concentration

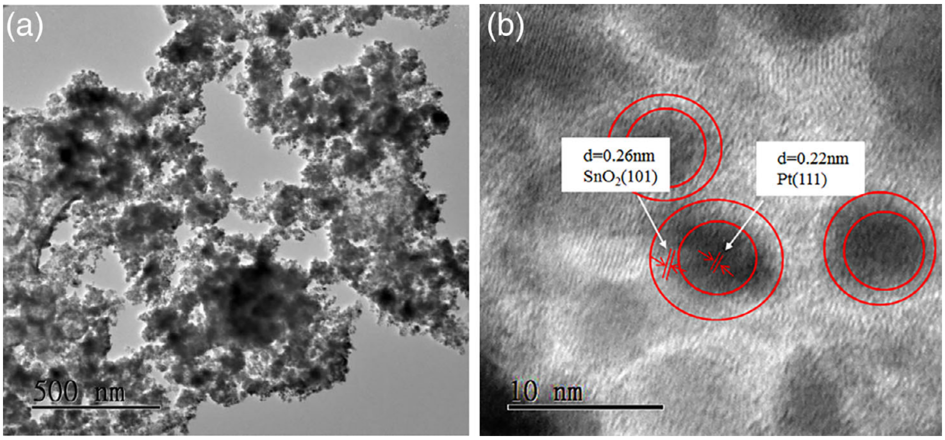

FIGURE 4 TEM images of Pt@SnO_2 scale bar of (a) 500 nm (b) 10 nm

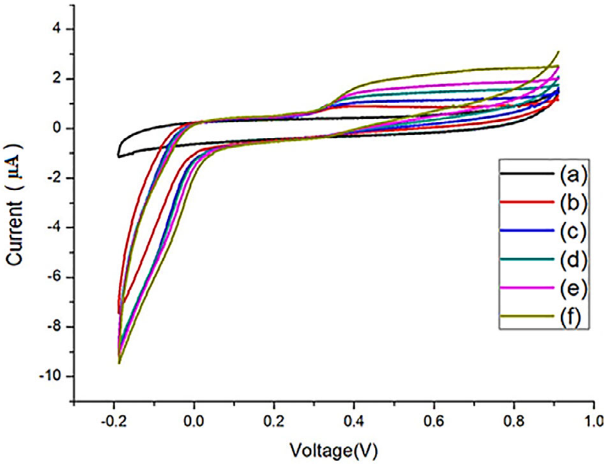

FIGURE 6 The measuring current at the working electrode on Pt@SnO_2 during the potential scans under various epinephrine concentrations of (a) blank (b) 45 μM (c) 55 μM (d) 75 μM (e) 85 μM (f) 110 μM

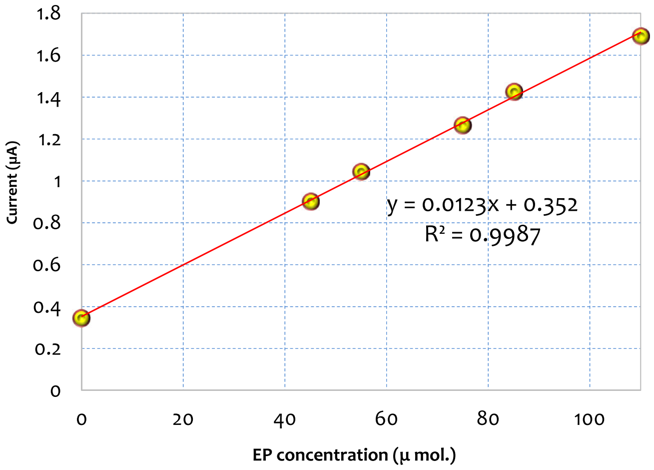

FIGURE 7 Detective current versus epinephrine concentration on Pt@SnO_2

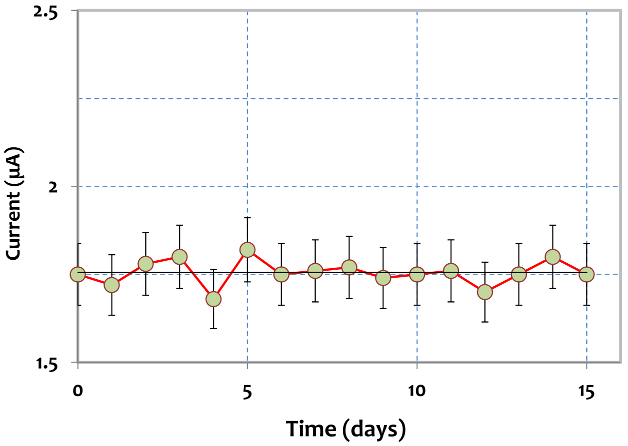

FIGURE 8 Stability test of detective current versus testing time on Pt@SnO_2

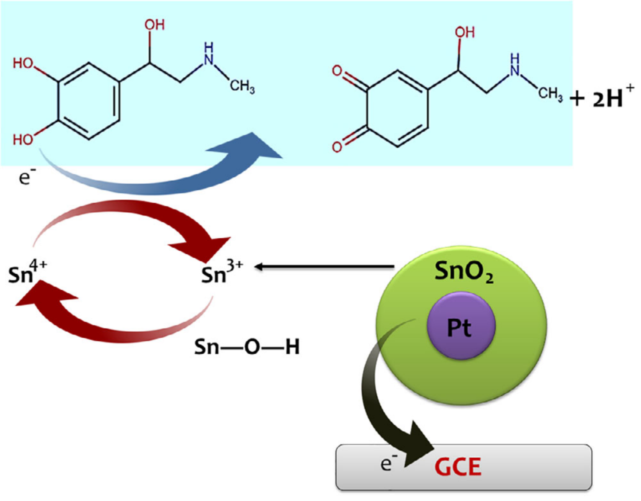

FIGURE 9 The sensing mechanism of epinephrine detection on Pt@SnO_2

coefficient, R^2 is 0.9987. CV calibration curves of the Pt@SnO_2 electrode obtained by changing the concentration of epinephrine at the voltages of 0.409 V. Voltages can be fixed at 0.409 V to get the current equivalent of epinephrine concentration in the electrochemical system.

3.3 | Stability test

In order to study the performance of the working electrode, it can be seen from the Pt@SnO_2 stability test (figure 8) measured continuously 110 μM EP for 15 days. It revealed the detection current value of 110 μM EP is continuously measured for 15 days. The current value is close to the stable average value of 1.75 μA for about half a month, which proves that the material can undergo long-term stability.

3.4 | Sensing mechanism

A major Pt@SnO_2 electrocatalytic oxidation mechanism is illustrated in Figure 9, and the synthesized Pt@SnO_2 nanocomposite was used for epinephrine detection. A proposed mechanism is electrocatalytic oxidation of epinephrine (removed two protons) in Figure 9.[4–6] In this work, the proposed EP electrocatalytic oxidation mechanism initiated by the electron transfer between SnO_2 and epinephrine followed by catalytic oxidation through SnO_2. On the SnO_2 surface of Pt@SnO_2, the variation in the charges of Sn^{+4} and Sn^{+3} is reversibly presented at Sn-OH on the surface to the redox reaction of the core-shell structure. In addition, Pt is located in the center of the core-shell nanostructure (Figure 9), it can improve the electron conduction properties.[14,15] It makes it possible for quicker electrochemical detection of epinephrine at the GCE electrode, which seems more feasible.

The grain size of SnO_2 on pristine SnO_2 (101, the grain size was 3.21 nm) was greater than on $Pt@SnO_2$ (2.75 nm). In general, the specific surface area of $Pt@SnO_2$ is higher than the pristine SnO_2. Pt is located in the center of the core-shell nanostructure, which improves the electron conduction properties aiding in sensing epinephrine detection.

4 | CONCLUSIONS

In this study, electrochemical sensor fabricated from hydrothermally synthesized $Pt@SnO_2$ core-shell nanocomposite material was investigated for epinephrine detection, which can play a significant role as an electrochemical sensor for precise detection of epinephrine. CV calibration curves of the $Pt@SnO_2$ electrode obtained by changing the concentration of epinephrine at the voltages of 0.409 V; the regression coefficient, R^2 is 0.9987. A sensing mechanism has also proposed a mechanism for the detection of epinephrine.

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