



Carbon paste electrodes modified with SnO₂/CuS, SnO₂/SnS and Cu@SnO₂/SnS nanocomposites as voltammetric sensors for paracetamol and hydroquinone

Ebrahim Naghian¹ · Mostafa Najafi²

Received: 13 July 2018 / Accepted: 2 August 2018 / Published online: 9 August 2018
© Springer-Verlag GmbH Austria, part of Springer Nature 2018

Abstract

Several nanocomposites of tin oxide with CuS, SnS or Cu@SnS were prepared and used to modify carbon paste electrodes (CPEs). The structure and morphology of the materials were studied by XRD and SEM techniques. Cyclic voltammetry and electrochemical impedance spectroscopy were applied to investigate their electrochemical properties. The modified CPEs exhibit superior voltammetric response to paracetamol (PAT) and hydroquinone (HQ) (when compared to a bare CPE) in terms of onset oxidation potential and current density. The CPE modified with SnO₂/SnS was applied to voltammetric determination of PAT (at a working potential of 0.55 V versus Ag/AgCl and with a 0.06 μM detection limit), and of HQ (at 0.39 V versus Ag/AgCl with a 0.2 μM detection limit). The voltammetric responses were linear in the range from 1.0 to 36 μM for PAT and from 1.0 to 85 μM for HQ.

Keywords Tin oxide · Differential pulse voltammetry · Cyclic voltammetry · Nanoparticles · Pharmaceutical analysis · Nanomaterial · Electrode modification · Microstructural analysis · Electrocatalytic oxidation

Introduction

Tin oxide nanostructures have been the most important n-type semiconductor with a lot of properties and characteristics that may justify their potential applications within various fields. A large band gap of 3.6 eV [1], catalytic activity, good compatibility and biocompatibility, non-toxic, inexpensive, green material, good chemical stability and medium conductivity [2, 3] are some of these properties. Different types of tin oxides structures have been introduced for application in electrochemical sensor and biosensor such as nanotubes [1], nanospheres [2], core shell [4], nanowires [5], hollow spheres [6]

and nanosheets [7]. Additionally, the composite of SnO₂ with some materials such as Ni [8], Cu [9], graphene [10], reduced graphene oxide [11] and Co₃O₄ [12] have been reported in literature. These structures are used in optical materials [13], gas sensor [14], electrochemical sensors and biosensor [15, 16] and secondary batteries [17].

This study describes synthesis and characterization of some novel nanocomposites of tin oxide such as SnO₂/CuS, SnO₂/SnS and Cu@SnS/SnO₂. These new nanoparticles are used as modifier for preparation of carbon paste modified electrodes and their electrocatalytic behaviors have been investigated by cyclic voltammetry in the presence of some important chemical compounds. The carbon paste modified electrode with SnO₂/SnS has been utilized for determination PAT and HQ in real samples.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00604-018-2948-6>) contains supplementary material, which is available to authorized users.

✉ Mostafa Najafi
mnajafi@ihu.ac.ir

¹ Department of Chemistry, South Tehran Branch Islamic Azad University, Tehran 1777613651, Iran

² Department of Chemistry, Faculty of Science, Imam Hossein University, Tehran 16597, Iran

Experimental

Chemicals and apparatus

Tin(II) chloride dihydrate (SnCl₂ · 2H₂O), tin(IV) chloride (SnCl₄), thiourea (NH₂CSNH₂), thioacetamide (CH₃CSNH₂) and ammonium acetate (NH₄CH₃COO) were bought from

Scharlau (<http://www.scharlab.com>). Sodium hydrogen phosphate salt and all other solvents and reagents were obtained from Merck (<https://www.merck.com>). All the chemicals were ultrapure or reagent grade and were used without further purification.

Cyclic voltammetry measurements were performed by PalmSens EmStat³⁺ and **PSTrace software for Windows**. Electrochemical impedance spectroscopy experiments were performed using μ Autolab type III/FRA2 potentiostat/galvanostat with NOVA software. A three electrode system: Ag|AgCl|KCl (3 M) as reference electrode a platinum wire as auxiliary electrode and homemade carbon paste modified electrode as working electrode with a diameter of 2 mm was used. All experiments were carried out at room temperature (25 ± 1 °C).

Preparation of SnO₂/SnS nanocomposite

First, 8.0 mL of 0.5 M SnCl₂ aqueous solution was mixed under stirring with 8.0 mL of 1.0 M NH₄CH₃COO solution. In the next step, 10.0 mL of SnCl₄ 8% (V/V) aqueous solution and 10.0 mL of 0.4 mol L⁻¹ CH₃CSNH₂ solution was added to the initial mixed solution and stirred for 30 min. Then, de-ionized water was added to the prepared mixed solution to make a total volume of 50 mL. Next, the prepared reaction solution was transferred into an autoclave and heated with temperature of 80 °C for 24 h. After that, the mixture was centrifuged at 8000 rpm and isolated nanoparticles were washed several times with de-ionized water. Next the nanoparticles were filtered through filter paper (0.45 μ m porosity) and dried at 50 °C for 24 h.

Preparation of CuS@SnO₂ nanoparticles

The procedure was same as in the previous section except that the dried precipitate dispersed in 150 mL of de-ionized water in an Erlenmeyer flask to form a suspension. Then, 1.0 mL of copper acetate solution 0.002 M was added to 25 mL of the above suspension drop by drop to obtain the CuS@SnO₂ nanoparticles. The homogenous precipitation of CuS@SnO₂ nanoparticles was filtered through filter paper (0.45 μ m porosity) washed several times by de-ionized water and dried at 50 °C for 24 h.

Preparation of Cu@SnS/SnO₂ nanoparticles

The Cu@SnS/SnO₂ nanoparticles were synthesized according to the procedure explained in the literature with some modification [18]. The procedure is presented in the Electronic Supporting Material in detail.

Electrochemical analysis procedure

The experiments were carried out in 0.1 M phosphate buffer (pH 4.0). Differential pulse voltammograms from 0.2 to 0.8 V were recorded by adjusting the following parameters: amplitude of 0.08 V, pulse width of 0.05 s, pulse period of 0.5 s and time of equilibrating for 4 s. The impedance analysis was performed under the oscillation potential 0.005 V from 200,000 Hz to 0.1 Hz at open circuit potential.

Sample preparation and procedures

The urine sample of a healthy man was stored 2 h in refrigerator (at 4 °C). Then, it was centrifuged for 30 min at 5000 rpm and filtered using filter paper and diluted 100 times with phosphate buffer pH = 4. PAT tablet from Aria Iranian Company was examined for estimation of its acetaminophen content. Five tablets of PAT (500 mg of PAT in each tablet) were accurately weighed and powdered in a mortar. An adequate amount of the powders was weighed and transferred to a 100 mL volumetric flask and then dissolved in distilled water. The standard addition method was used for analyzing PAT and HQ-spiked samples for validation of the CPE modified with SnO₂/SnS.

Characterization methods

The structure and surface morphology of nanomaterials was investigated by scanning electron microscopy (FE-SEM-EDX MIRA3 TESCAN). The crystallization degree and the size of nanoparticles were specified by X-ray powder diffractometer (XRD PHILIPS - PW1730).

Preparation of working electrodes

To investigate the electrochemical properties of nanomaterials, the carbon paste electrodes were prepared by hand-mixing of 0.9 g graphite fine powder 30 mg mineral oil and 70 mg from each of the synthesized nanomaterials with a mortar and pestle in 30 min for total uniformity. The resulting carbon paste was packed at the bottom of a polypropylene tube (internal diameter of 2.1 mm). The electrical connection was performed by a copper wire.

Results and discussion

Choice of materials

Electrodes modified with carbon nanomaterials [19–21], nanostructured metal oxides [22, 23], conductive polymers [24–26], various metal nanoparticles [27–29] and other nanostructured [30–33] have been demonstrated to enhance the

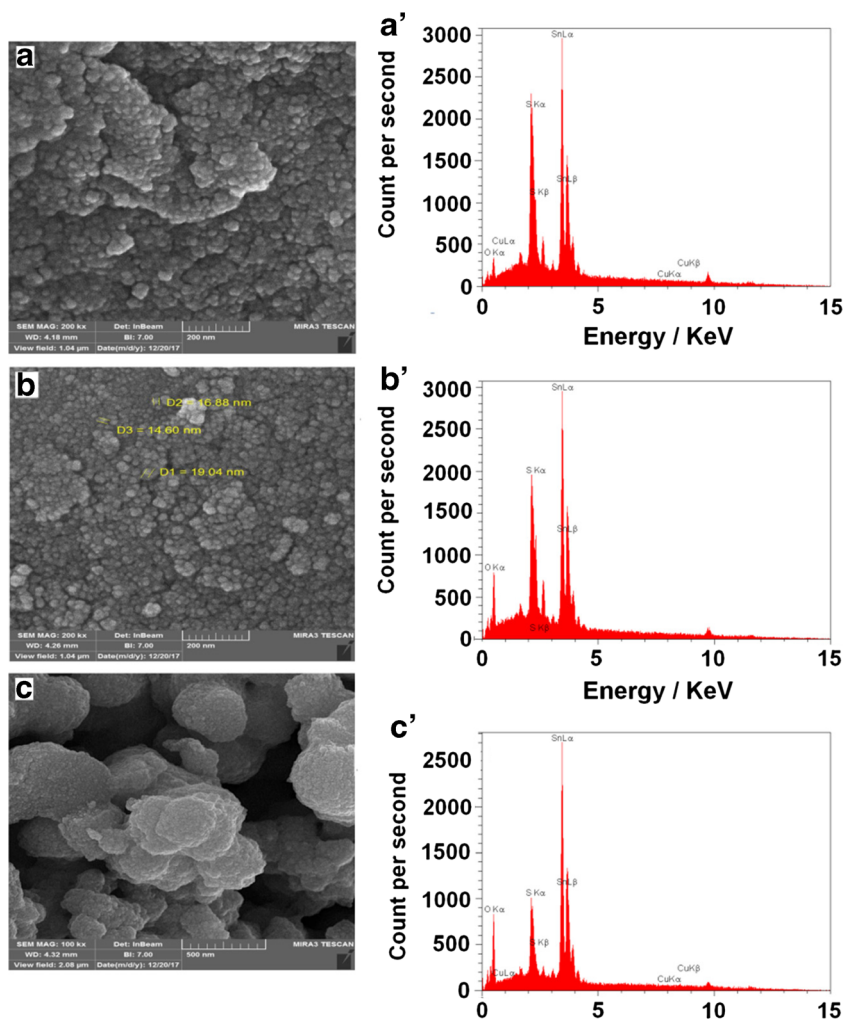
electroanalysis efficiency of PAT and HQ. Composite or hybrid materials containing two or more constituents are of great interest. They can exhibit combination of individual properties of the components or unique new physical and chemical properties for various applications. Among these, composite of SnO_2 nanoparticles attract considerable attention due to their fascinating physical and chemical properties. Metal sulfide nanocrystals have been studied the most due to their great number of applications in different technological areas including biological labeling and diagnostics, photovoltaic devices, sensors and electroluminescent devices. CuS was found to show interesting properties including metal-like electrical conductivity which may have potential application in electrochemical sensors [34, 35]. SnS is a p-type semiconductor with a band gap of 1.3 eV. The most significant aspect of SnS is being cheap and nontoxic [36]. Additionally, the preparation of their hybrid materials is convenient. Based on the above-mentioned notes, the investigation of sensing properties of new composites of SnO_2 and CuS, SnS and their utilization in constructing electrochemical sensors are worthy of studying.

Microstructural analysis of the electrocatalysts

Characterizations of the SnO_2/CuS , SnO_2/SnS and $\text{Cu}@ \text{SnS}/\text{SnO}_2$ nanoparticles were investigated by SEM and XRD techniques. The microstructural characterization of modified electrode surface have significant role in the response of electrochemical sensor. Figure 1 shows FE-SEM micrographs of surface morphologies of SnO_2/CuS , SnO_2/SnS and $\text{Cu}@ \text{SnS}/\text{SnO}_2$ nanoparticles respectively. As seen, the homogenous dispensation of the very fine spherical shape particles with a diameter of approximately 10–30 nm is observed. Figure 2d shows the EDX analysis of SnO_2/SnS nanoparticles which indicates the existence of Sn, O, S, and Cu elements in the chemical composition.

Powder X-ray diffraction (XRD) is carried out to investigate the crystal structure analysis of the prepared nanocomposites (Fig. 2). As seen, XRD pattern of SnO_2 in Fig. 2a–c shows the peaks at 266° , 340° and 518° which are assigned to (110), (101), and (211) indicating the rutile structure of SnO_2 (JCPDS card: 41–1445).

Fig. 1 SEM images of SnO_2/CuS (a), SnO_2/SnS (b) and $\text{Cu}@ \text{SnS}/\text{SnO}_2$ (c). (a'–c') are EDX analysis of SnO_2/CuS , SnO_2/SnS and $\text{Cu}@ \text{SnS}/\text{SnO}_2$ respectively



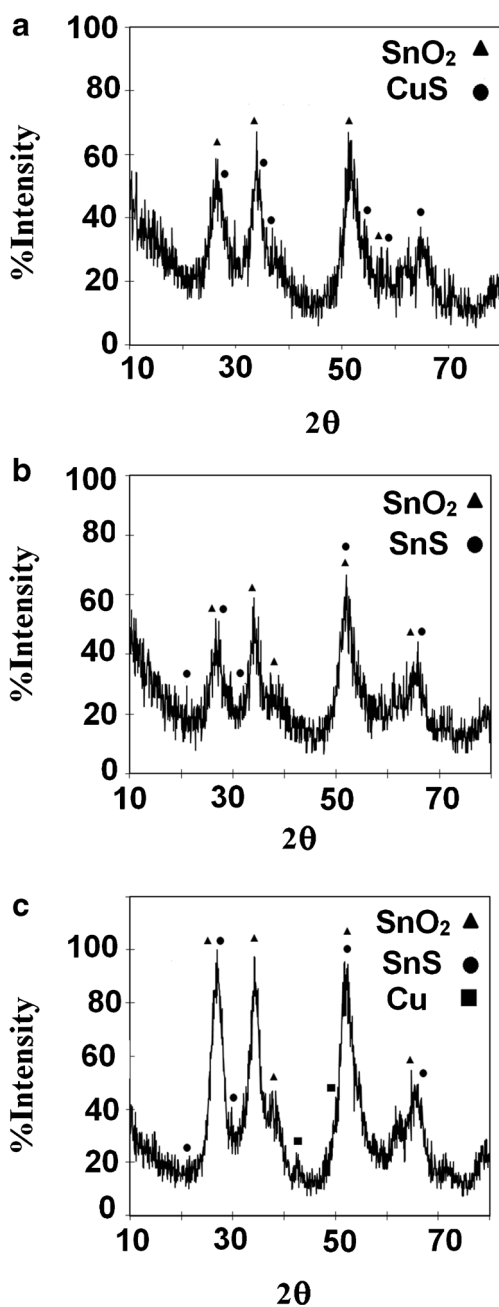


Fig. 2 Powder XRD patterns of (a) SnO_2/CuS (b) SnO_2/SnS and (c) $\text{Cu@SnS}/\text{SnO}_2$ composites

Figure 2a shows the peaks at 273° , 281° , 342° , 541° and 588° . These can be attributed to the hexagonal covellite crystalline phase of CuS with characteristic (101), (102), (006), (110) and (116) planes. This is in good agreement with the standard data for CuS (JCPDS Card No 06–0464).” Fig. 2b shows the XRD pattern of SnO_2/SnS composite. As seen, in addition to the peaks observed for SnO_2 , the peaks around 220° , 271° , 315° , 519.5° and 658° are observed. These are related to lattice planes of (110), (120), (111), (151) and (251), SnS (JCPDS Card No 39–0354). Concerning $\text{Cu@SnS}/\text{SnO}_2$ nanocomposite, the XRD pattern (Fig. 2c) contains the peaks

around 430° and 501° . These are assigned to (110) and (200) planes of copper and agree with the standard diffraction card of JCPDS No 04–0836.

The crystallite size of the nanocomposites powders are calculated according to Scherrer equation. The value of 17.7 nm for SnO_2/CuS , 15.0 nm for SnO_2/SnS and 16.6 nm for $\text{Cu@SnS}/\text{SnO}_2$ are obtained respectively.

Electrochemical characterization

Electrochemical properties of carbon paste modified electrodes are evaluated by cyclic voltammetry and electrochemical impedance spectroscopy. Figure 3a, b show the cyclic voltammograms and the Nyquist plots for unmodified carbon paste electrode (a) SnO_2/CuS (b) SnO_2/SnS (c) and $\text{Cu@SnS}/\text{SnO}_2$ (d) in phosphate buffer containing 1 mmol L^{-1} $[\text{Fe}(\text{CN})_6]^{3-}$ and 1 mmol L^{-1} $[\text{Fe}(\text{CN})_6]^{4-}$. As can be seen in Fig. 3a, a well-defined redox peaks is observed for all modified electrodes. However, partial differences are observed for peak to peak potential separation (ΔE_p). The ΔE_p value for SnO_2/CuS , SnO_2/SnS , $\text{Cu@SnS}/\text{SnO}_2$ modified CPEs and bare CPE are calculated as 145, 130, 140 and 260 mV versus Ag/AgCl respectively. These show increasing electron transfer rate for the modified electrodes.

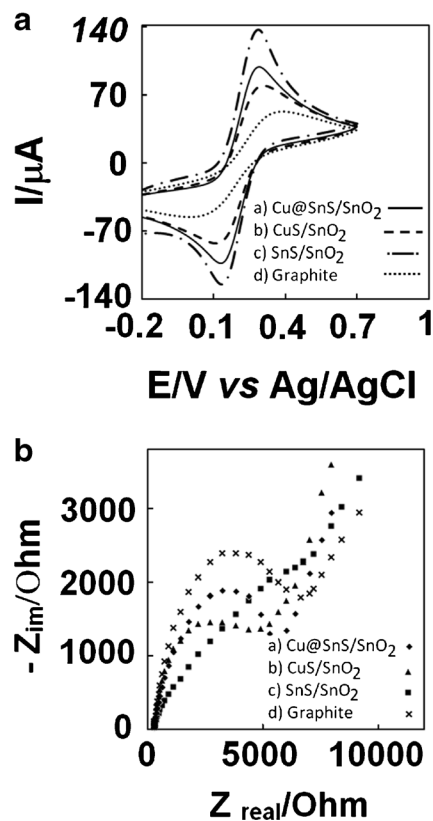


Fig. 3 a Cyclic voltammograms (b) Nyquist plots for $1 \text{ mM } [\text{Fe}(\text{CN})_6]^{3-}$ in a solution of $0.1 \text{ M } \text{KH}_2\text{PO}_4$ at the surface of modified CPEs. Scan rate: 50 mV s^{-1} , EIS condition: frequency range: $200 \text{ KHz} - 0.1 \text{ Hz}$, perturbation amplitude: 5 mV

The effective surface area of the electrodes was examined by recording CVs of $1 \text{ mmol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ at various scan rates for a reversible process by the Randles–Sevcik equation:

$$I_p = 269 \times 105AD^{1/2}n^{3/3}C\nu^{1/2} \quad (1)$$

where I_p refers to the peak current (A), n is the electron transfer number, A is the effective surface area (cm^2), D is the diffusion coefficient of $\text{K}_3[\text{Fe}(\text{CN})_6]$ in the solution ($7.66 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at $0.1 \text{ mol L}^{-1} \text{ KCl}$ [37], C is the concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (mol cm^{-3}) and ν is the scan rate (V/s). The calculated effective surface areas (A) for bare CPE, SnO_2/CuS , SnO_2/SnS and $\text{Cu@SnS}/\text{SnO}_2$ modified CPEs are calculated as 0.257, 0.597, 0.773 and 0.457 cm^2 respectively. As a result, current responses for the redox couple of $[\text{Fe}(\text{CN})_6]^{3-4-}$ increase with rise in the effective surface area of the modified electrodes. Accordingly, the highest current is observed for CPE modified with SnO_2/SnS (Fig. 3a).

The EIS can provide information about the electron transfer rate of reaction. The Fig. 3b represents the EIS curve obtained from the modified and unmodified electrodes. The Nyquist-shaped EIS curves contain a semicircular part and a linear part. The semicircle in the Nyquist plot is related to the charge-transfer limiting processes at high frequencies. Moreover, the semicircle's diameter corresponds to the charge transfer resistance (R_{ct}) of the redox probe at the interfacial surface while the linear portion represents the diffusion process. However R_{ct} is small, the system is kinetically facile. As can be seen in Fig. 3b, the R_{ct} values are much lower for the

modified electrodes compared with the R_{ct} of the bare carbon paste electrodes which indicate increased electron transfer at their surface.

Electrocatalytic oxidation of some important species

The electrocatalytic properties of the carbon paste modified electrodes are studied toward some important drugs, biological and environmental species such as ascorbic acid (AC), uric acid (UA), salicylic acid (SA), paracetamol (PAT), carbidopa (CA), methyl paraben (MP), hydroquinone (HQ) and hydrazine (HZ). The CVs responses are shown in Fig. 4. As seen, good responses are observed at the carbon paste modified electrodes for all those redox systems. For example, the overpotential for oxidation of HQ and hydrazine are significantly decreased to 335 and 680 mV at the surface of CPE modified with SnO_2/CuS compared to 455 and 880 mV at bare carbon paste electrode respectively. On the other hand, the onset potentials for all tested compounds are dramatically decreased as shown in Fig. 4. Moreover, considerable increases in peak currents are also observed due to the enhancement in reversibility of the electron transfer processes. These suggest an efficient electrocatalytic reaction for HQ and hydrazine at the carbon paste modified electrodes.

In spite of observed electrocatalytic behavior, it should be noted that oxidation potentials are still high for some tested compounds. This may cause fouling of the electrode surface and selectivity reduction in determining the analyte in the real samples.

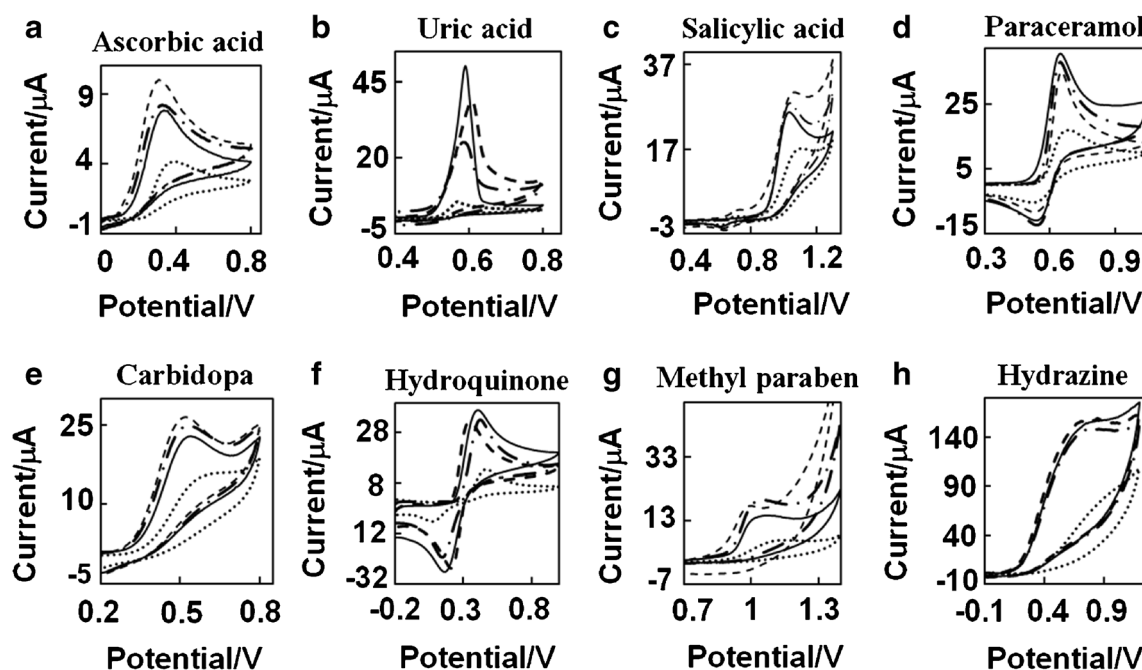


Fig. 4 Cyclic voltammograms of 0.5 mmol L^{-1} (a) ascorbic acid (b) uric acid (c) Salicylic acid (d) PAT (e) carbidopa (f) HQ (g) methyl paraben and (h) hydrazine, recorded at the surface of bare and modified CPEs.

Scan rate: 50 mV s^{-1} , $\text{pH} = 4.0$. Graphite (bare electrode) (.....), SnO_2/CuS (— — —), $\text{Cu@SnS}/\text{SnO}_2$ (————) and SnO_2/SnS (— • — •)

Differential pulse voltammetric determinations

Case study evaluation of linear concentration range, sensitivity and detection limit using the differential pulse voltammetry (DPV) method has been used for PAT and HQ at surface of modified electrodes. The results of these initial studies are shown in Fig. S1. Figure 5 shows differential pulse voltammetry responses of PAT and HQ in different concentrations at surface of CPE modified with SnS/SnO₂. The experiments were performed under the optimal conditions by keeping concentration of one component constant at 20.0 μmol L⁻¹. A working voltage of 0.390 V (vs. Ag/AgCl) for PAT and 0.550 V (vs. Ag/AgCl) for HQ were used for obtaining current data. Detection limits were calculated using 3σ/s definition, where σ is the standard deviation of the blank signals (*n* = 5) and *s* is the slope of the calibration curve. As seen, the peak currents increase linearly with the increase in the concentration of the target molecules. In both, two linear dynamic ranges are observed. The relationship between peak currents PAT and concentration is in the range of 1–36 μmol L⁻¹, and the linear

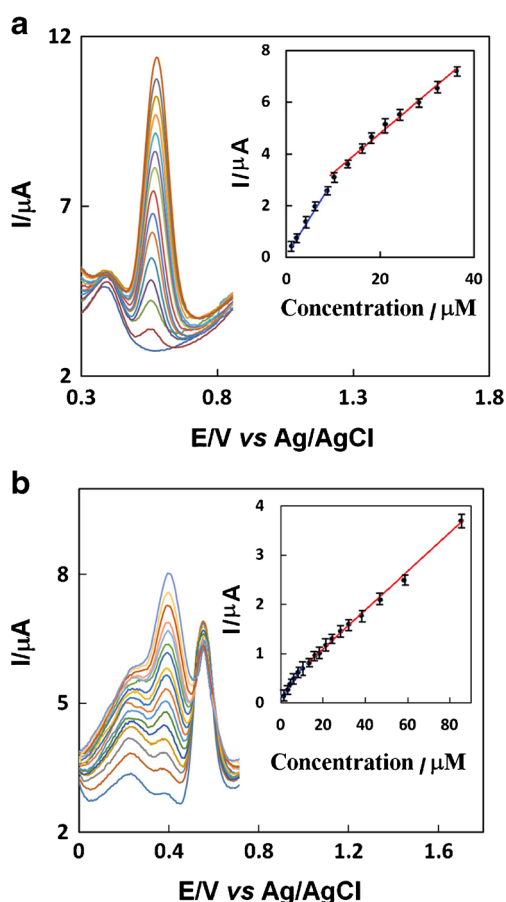


Fig. 5 a Differential pulse voltammograms at surface CPME with SnS/SnO₂ in phosphate buffer (pH 4.0) a for a binary mixture of 20.0 μmol L⁻¹ HQ and different concentrations of PAT (1–36 μmol L⁻¹). b For a binary mixture of 20.0 μmol L⁻¹ PAT and different concentrations of HQ (1–85 μmol L⁻¹). The inserts are the relationships between the anodic peak currents and concentrations

equations of PAT are $I_{pa} (\mu\text{A}) = 0.290 C (\mu\text{mol L}^{-1}) + 0.190$ (1–8.5 μmol L⁻¹, *R* = 0.9973) and $I_{pa} (\mu\text{A}) = 0.154 C (\mu\text{mol L}^{-1}) + 1.758$ (8.5–36 μmol L⁻¹, *R* = 0.9912). The limit of detection (LOD) was calculated to be 0.06 μmol L⁻¹. Similarly, the anodic peak current for HQ is proportional to its concentration from 1.0 to 85 μmol L⁻¹. The linear equations are $I_{pa} (\mu\text{A}) = 0.0756 C (\mu\text{mol L}^{-1}) + 0.060$ (1.0–10 μmol L⁻¹, *R* = 0.9919) and $I_{pa} (\mu\text{A}) = 0.038 C (\mu\text{mol L}^{-1}) + 0.340$ (10–85 μmol L⁻¹, *R* = 0.9968) with a LOD of 0.2 μmol L⁻¹. The sensitivities are 7.07 μA μM⁻¹ cm⁻² for PAT and 1.8 μA μM⁻¹ cm⁻² for HQ, respectively. The sensitivity and detection limit are comparable with or sometimes better than previously reported electrochemical methods for PAT and HQ in Table S1.

The relative standard deviations for the determination of 10 μmol L⁻¹ of PAT and HQ were obtained 3.9 and 2.5% by successive 5 measurements, respectively. These indicate that the CPMEs have excellent repeatability. The stability of all modified electrodes is also evaluated by measuring the anodic peak currents responses at a fixed 15 μM of the some substances under study over a period of 5 months. The peak potentials are unchanged and the current signals are decreased by less than 2%. These results show that the modified electrodes have a long-term stability.

Interference study

The potential interference of some inorganic and organic species was investigated accurately to detect PAT and HQ in the real sample. The results indicate that the 300 fold Na⁺, Ca²⁺, Mg⁺² and K⁺, 300 fold of NO₂⁻, NO₃⁻, H₂PO₄⁻, HPO₄²⁻, SO₄²⁻, Cl⁻, 50 fold of glucose, ascorbic acid, quercetin, allura red, 80 fold of codeine sulphate and ibuprofen (as PAT ingredients) and 100 fold of benserazide and bisoprolol (as PAT similar structure) have no notable interference with PAT and HQ determination (the peak current response change <5%). This suggests that CPE modified with SnO₂/SnS has a great selectivity for PAT and HQ determination without sensible problem in presence of usual interfering species.

Table 1 Determination of PAT and HQ with modified carbon past electrode in Tablet, urine and tap water

Sample	Added (μM)		Detected (μM)		Recovery (%)	
	PAT	HQ	PAT	HQ	PAT	HQ
PAT Tablets (Aria, Iran)	–	50	–	48.3	–	96.9
	–	10	–	10.4	–	103.8
Urine	–	15	–	15.3	–	101.7
	–	20	–	19.4	–	97.1
Tap water	10	–	10.9	–	100.9	–
	20	–	19.5	–	97.5	–

Real sample analysis

To evaluate the efficiency of the CPME with SnS/SnO₂, the standard addition method was used. For this purpose, known quantities of PAT and HQ within the linear range of PAT and HQ were added to tablet, urine and tap water samples. The analyses of their concentrations were performed by DPV method in the optimal conditions. The results have been shown in Table 1. As seen, the PAT and HQ concentrations determined using this sensor is in good agreement with the spiked value.

Conclusions

Electrocatalytic properties of the novel SnO₂/CuS, SnO₂/SnS and Cu@SnS/SnO₂ nanocomposites toward several important molecules were investigated. The results indicate that the novel tin oxide nanocomposites can be used in construction of electrochemical sensors and biosensors as an effective electrocatalyst. Differential pulse voltammetric determinations of PAT and HQ were accomplished at CPE modified with SnO₂/SnS. Additionally, the novel nanocomposites can also offer a high electrocatalytic activity towards other electroactive species such as ascorbic acid, uric acid, salicylic acid, carbidopa and methyl paraben. The oxidation potentials of the tested species are relatively high and this can limit selectivity. However, this new modified electrodes show good sensitivity, repeatability and reproducibility.

Acknowledgements We are grateful to the financial support of the South Tehran Branch Islamic Azad University.

Compliance with ethical standards The author(s) declare that they have no competing interests.

References

- Miao Y-E, He S, Zhong Y, Yang Z, Tjiu WW, Liu T (2013) A novel hydrogen peroxide sensor based on Ag/SnO₂ composite nanotubes by electrospinning. *Electrochim Acta* 99:117–123
- Gan T, Sun J, Yu M, Wang K, Lv Z, Liu Y (2017) Amplified electrochemical determination of maltol in food based on graphene oxide-wrapped tin oxide@carbon nanospheres. *Food Chem* 214: 82–89
- Wang T, Sun Z, Li F, Xu L (2014) Nanostructured polyoxometalate-modified SnO₂ photoanode with improved photoelectrochemical performance. *Electrochem Commun* 47:45–48
- Li Q et al (2017) Tuning Sn-catalysis for electrochemical reduction of CO₂ to CO via the Core/Shell cu/SnO₂ structure. *J Am Chem Soc* 139:4290–4293
- Yang M, Jiang T-J, Guo Z, Liu J-H, Sun Y-F, Chen X, Huang X-J (2017) Sensitivity and selectivity sensing cadmium(II) using amination functionalized porous SnO₂ nanowire bundles-room temperature ionic liquid nanocomposite: combined efficient cation capture with control experimental conditions. *Sens Actuators B-Chem* 240:887–894
- Cho YH, Liang X, Kang YC, Lee J-H (2015) Ultrasensitive detection of trimethylamine using Rh-doped SnO₂ hollow spheres prepared by ultrasonic spray pyrolysis. *Sensors Actuators B Chem* 207:330–337
- Tao T, He L, Li J, Zhang Y (2015) A new way for synthesizing SnO₂ nanosheets. *Mater Lett* 138:45–47
- Lavanya N, Radhakrishnan S, Sekar C (2012) Fabrication of hydrogen peroxide biosensor based on Ni doped SnO₂ nanoparticles. *Biosens Bioelectron* 36:41–47
- Xu W, Canfield NL, Wang D, Xiao J, Nie Z, Zhang J-G (2010) A three-dimensional macroporous cu/SnO₂ composite anode sheet prepared via a novel method. *J Power Sources* 195:7403–7408
- Sun W, Wang X, Wang Y, Ju X, Xu L, Li G, Sun Z (2013) Application of graphene–SnO₂ nanocomposite modified electrode for the sensitive electrochemical detection of dopamine. *Electrochim Acta* 87:317–322
- Wei Y, Gao C, Meng F-L, Li H-H, Wang L, Liu J-H, Huang X-J (2011) SnO₂/reduced graphene oxide nanocomposite for the simultaneous electrochemical detection of cadmium(II), lead(II), copper(II), and mercury(II): an interesting favorable mutual interference. *J Phys Chem C* 116:1034–1041
- Zeinali H, Bagheri H, Monsef-Khoshshesab Z, Khoshshafar H, Hajian A (2017) Nanomolar simultaneous determination of tryptophan and melatonin by a new ionic liquid carbon paste electrode modified with SnO₂-Co₃O₄@rGO nanocomposite. *Mater Sci Eng C Mater Biol Appl* 71:386–394
- Ghalkhani M, Hosseini nia B, Beheshtian J, Anaraki Firooz A (2017) Synthesis of undoped and Fe nanoparticles doped SnO₂ nanostructure: study of structural, optical and electrocatalytic properties. *J Mater Sci Mater El* 28:7568–7574
- Borah S et al (2017) Enhanced catalytic activity and near room temperature gas sensing properties of SnO₂ nanoclusters@mesoporous Sn(IV) organophosphonate composite. *Dalton Trans* 46:8664–8672
- Zhou Q, Yang L, Wang G, Yang Y (2013) Acetylcholinesterase biosensor based on SnO₂ nanoparticles-carboxylic graphene-nafion modified electrode for detection of pesticides. *Biosens Bioelectron* 49:25–31
- Lavanya N, Sekar C (2017) Electrochemical sensor for simultaneous determination of epinephrine and norepinephrine based on cetyltrimethylammonium bromide assisted SnO₂ nanoparticles. *J Electroanal Chem* 801:503–510
- Liang J, Yu XY, Zhou H, Wu HB, Ding S, Lou XW (2014) Bowl-like SnO₂@carbon hollow particles as an advanced anode material for lithium-ion batteries. *Angew Chem Int Ed Eng* 53:12803–12807
- Dastkhooon M, Ghaedi M, Asfaram A, Arabi M, Ostovan A, Goudarzi A (2017) Cu@SnS/SnO₂ nanoparticles as novel sorbent for dispersive micro solid phase extraction of atorvastatin in human plasma and urine samples by high-performance liquid chromatography with UV detection: application of central composite design (CCD). *Ultrason Sonochem* 36:42–49
- Fu L, Wang A, Lai G, Lin CT, Yu J, Yu A, Su W (2018) A glassy carbon electrode modified with N-doped carbon dots for improved detection of hydrogen peroxide and paracetamol. *Microchim Acta* 185(2):87–93
- Ruiyi L, Haiyan Z, Zaijun L, Junkang L (2018) Electrochemical determination of acetaminophen using a glassy carbon electrode modified with a hybrid material consisting of graphene aerogel and octadecylamine-functionalized carbon quantum dots. *Microchim Acta* 185(2):145–153
- Huang H, Zhang J, Cheng M, Liu K, Wang X (2017) Amperometric sensing of hydroquinone using a glassy carbon electrode modified with a composite consisting of graphene and molybdenum disulfide. *Microchim Acta* 184(12):4803–4808

22. Eroglu S, Bas SZ, Ozmen M, Yildiz S (2015) A new electrochemical sensor based on Fe₃O₄ functionalized graphene oxide-gold nanoparticle composite film for simultaneous determination of catechol and hydroquinone. *Electrochim Acta* 186:302–313
23. Ghanbari K, Bonyadi S (2018) An electrochemical sensor based on reduced graphene oxide decorated with polypyrrole nanofibers and zinc oxide–copper oxide p–n junction heterostructures for the simultaneous voltammetric determination of ascorbic acid, dopamine, paracetamol, and tryptophan. *New J Chem* 42:8512–8523
24. Liu J, Xie Y, Wang K, Zeng Q, Liu R, Liu X (2017) A nanocomposite consisting of carbon nanotubes and gold nanoparticles in an amphiphilic copolymer for voltammetric determination of dopamine, paracetamol and uric acid. *Microchim Acta* 184(6):1739–1745
25. Li M, Jing L (2007) Electrochemical behavior of acetaminophen and its detection on the PANI–MWCNTs composite modified electrode. *Electrochim Acta* 52:3250–3257
26. Liu R, Zeng X, Liu J, Luo J, Zheng Y, Liu X (2016) A glassy carbon electrode modified with an amphiphilic, electroactive and photosensitive polymer and with multi-walled carbon nanotubes for simultaneous determination of dopamine and paracetamol. *Microchim Acta* 183(5):1543–1551
27. Li Z, Yue Y, Hao Y, Feng S, Zhou X (2018) A glassy carbon electrode modified with cerium phosphate nanotubes for the simultaneous determination of hydroquinone, catechol and resorcinol. *Microchim Acta* 185(4):215–223
28. Goulart LA, Gonçalves R, Correa AA, Pereira EC, Mascaro LH (2018) Synergic effect of silver nanoparticles and carbon nanotubes on the simultaneous voltammetric determination of hydroquinone, catechol, bisphenol a and phenol. *Microchim Acta* 185(1):12–20
29. Shen Y, Rao D, Sheng Q, Zheng J (2017) Simultaneous voltammetric determination of hydroquinone and catechol by using a glassy carbon electrode modified with carboxy-functionalized carbon nanotubes in a chitosan matrix and decorated with gold nanoparticles. *Microchim Acta* 184(9):3591–3601
30. Movlaee K, Beitollahi H, Ganjali MR, Norouzi P (2017) Electrochemical platform for simultaneous determination of levodopa, acetaminophen and tyrosine using a graphene and ferrocene modified carbon paste electrode. *Microchim Acta* 184(9):3281–3289
31. Kalaiyarasi J, Meenakshi S, Gopinath SC, Pandian K (2017) Mediator-free simultaneous determination of acetaminophen and caffeine using a glassy carbon electrode modified with a nanotubular clay. *Microchim Acta* 184(11):4485–4494
32. Kemmegne-Mbougouen JC, Toma HE, Araki K, Constantino VRL, Ngameni E, Angnes L (2016) Simultaneous determination of acetaminophen and tyrosine using a glassy carbon electrode modified with a tetraethenated cobalt(II) porphyrin intercalated into a smectite clay. *Microchim Acta* 183(12):3243–3253
33. Huang W, Zhang T, Hu X, Wang Y, Wang J (2018) Amperometric determination of hydroquinone and catechol using a glassy carbon electrode modified with a porous carbon material doped with an iron species. *Microchim Acta* 185(1):37–42
34. Mane R, Lokhande C (2000) Chemical deposition method for metal chalcogenide thin films. *Mater Chem Phys* 65:1–31
35. Zhang X, Wang G, Gu A, Wei Y, Fang B (2008) CuS nanotubes for ultrasensitive nonenzymatic glucose sensors. *Chem Commun* 0: 5945–5947
36. Hasan BA, Shallal IH (2014) Structural and optical properties of SnS thin films. *J Nanotech Adv Mater* 2:43–49
37. Bard AJ, Faulkner LR (2001) *Electrochemical methods fundamentals and applications*. Wiley, New York