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Supplementary Information

Highly Efficient CeO_2–$CuCrO_2$ Composites Nanofibers Used for Electrochemical Detection of Dopamine in Biomedical Applications

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1. Materials and Methods

1.1. Preparation of CeO_2 Precursor

(PVP, ACROS, purity: 85–95%), cerium nitrate hexahydrate (Alfa Aesar, Ward Hill, MA, United States, purity: 99.5%), Cu(NO3)2·3H2O (Showa, Am-sterdam, The Netherlands, purity: 99.0%), $Cr(NO_3)_3$·9H2O (ACROS, Geel, Belgium, purity: 98.5%), and dimethylformamide (DMF, Showa, purity: 99.8%).

1.2. Preparation of CeO_2 Precursor

First the CeO_2 precursor was prepared by using 0.6g, 0.3g and 0.36g cerium nitrate with 2 g polyvinylpyrrolidone (PVP) added to 10 mL dimethylformamide (DMF) solution. And obtain precursor 0.2 M,0.1 M and 0.12 M concentration respectively. The mixture was stirred using magnetic stirrer at room temperature for 6 h to obtain a light-yellow gel-like solution of CeO_2.

1.3. Preparation of $CuCrO_2$ Precursor

Second, the 10 mL of $CuCrO_2$ precursor solution was prepared with different concentration (0.1:0.1, and 0.2:0.2 M) of chromium nitrate and copper nitrate with 0.75 g of PVP, were dissolved into N,N-dimethylformamide (DMF). The mixture was stirred at room temperature for 6 h to obtain the homogenous green gel-like solution of $CuCrO_2$ (se main Figure 1).

1.4. Ratio Modulation for Electrospinning

The pre-mixed precursor solution will be divided into three sets of parameters with different concentration ratios: (CCC2:1) 0.2 M CeO_2-0.1 M $CuCrO_2$, (CCC1:2) 0.1 M CeO_2-0.2 M $CuCrO_2$, and (CCC1.2:2) 0.12 M CeO_2-0.2 M $CuCrO_2$, and these will be used for electrospinning The effect of different concentration ratios will be compared in X-ray diffraction (XRD) analysis.

1.5. Characterization

The SEM and TEM (FESEM/EDX, JEOL, JSM-7610F, and Hitachi Regulus 8100) observations revealed that the nanofibers have a tubular structure with CeO_2 as the outer layer and $CuCrO_2$ as the inner layer. The changes in fiber morphology at different voltages (22, 24, and 26 kV) were observed. XRD (D2 Phaser, Bruker, Cu Kα = 1.540 Å) analysis was applied to studied the crystalline nature of the prepared nanofibers. The porous

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nature and surface area have observed by BET (Micromeritics TriStar II, USA) analysis. The chemical composition or distribution of the prepared nanofibers were analyzed by XPS (Thermo Scientific Multilab 2000 XPS) techniques. Raman (ACRON, UniNanoTech Co., Ltd.) analysis was utilized to examined the vibrational bonds of this nanofibers.

1.6. Electrochemical Process

The prepared nanofibers electrochemical characteristics were studied by cyclic voltammetry and differential pulse voltammetry techniques towards the detection of dopamine. Before the experiment, the 1 mg of prepared nanofibers has dissolved in 1 mL of water and sonicated for 30 min to make homogenous solution. Then, 6 µL of catalyst solution was decorated on the disposable SPCE electrodes surface, which was used as a working electrode. Furthermore, the platinum wire and Ag/AgCl was utilized as a counter and reference electrodes. The sodium phosphate monobasic and di-sodium phosphate was used prepared the phosphate buffer solution (PBS) electrolyte solution.

2. Results and Discussions

2.1. Electrochemical Active Surface Area Study

The proposed materials decorated electrodes active surface area (EASA) was measured by using electrochemical CV studies. This process was carried out by using 5 mM of $[Fe(CN)6]^{3-/4-}$ with 0.1 mM KCl at room temperature with fixed scan rate of 50 mV/s. The Figure S1 clearly indicate that the CeCr decorated electrodes have higher current values of ~247 µA compared to bare SPCE (Figure S1a,b). In addition, the materials decorated electrodes exhibit the pair of peaks in redox. Whereas, this electrodes have low peak separation and higher current response, which is revealted that it has better electrons transfer. Therefore, the EASA was obtained by using Randles-Sevick equation of

$$Ip = 2.69 \times 10^5 (\Pi^{3/2}) AD^{1/2} v^{1/2} C \quad (1)$$

The calculates EASA of the prepared materials is 0.106 cm^2.

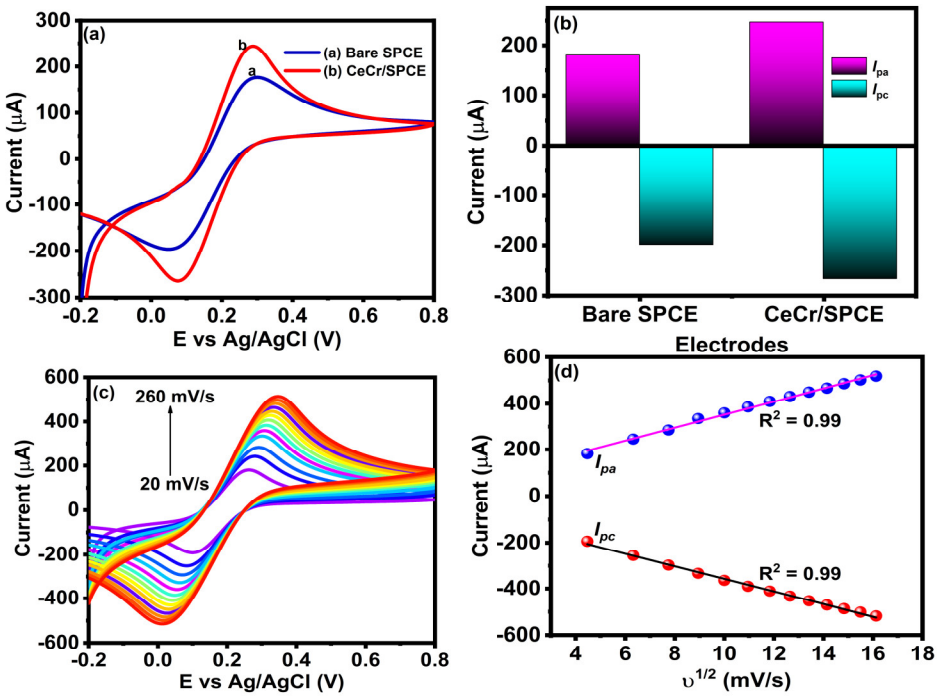

Figure S1. (**a**) CV curve for ferricyanide system for bare SPCE and CeCr decorated SPCE with scan rate of 50 mV/s, (**b**) Related current values bar diagram, (**c**) different scan rates (20–260 mV/s), and (**d**) related current values for square root of scan rates.

2.2. BET Analysis

Nanofibers porous nature and surface area was measured by using BET analysis. The CeO_2-$CuCrO_2$ have better surface area of 25.03 m^2/g. Compared with pure $CuCrO_2$, CeO_2, and CeO_2-$CuCrO_2$ prepared by electrospinning and glycine combustion method, the specific surface area of the composite nanofibers obtained in this experiment is higher than that of $CuCrO_2$ but much lower than that of porous structured powders obtained by CeO_2 and glycine combustion method. However, this also proves that the combination of CeO_2 and $CuCrO_2$ improve the specific surface area.

2.3. Real-Samples Analysis

The real-time potential applications of the proposed sensor electrodes for DA detection was examined in human urine samples after spiking the known concentration of DA. Initially, the human samples were collected and diluted to 0.05 M of PBS solution and observed the electrochemical behaviors with different additions of DA. Then sample found and recovery could be obtained via comparing the known concentrations of standard solution. The real-samples analysis data were reported in Table S1 The results indicating that the proposed nanofibers decorated electrodes have high reliability, higher conductivity towards detection of DA in biological samples for bio-medical applications. The prepared materials decorated electrodes stability, repeatability and reproducibility studies were studied. These results indicated that the proposed materials have excellent stability, repeatability and reproducibility.

Table S1. DA detection in human urine samples.

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Human Urine-1	5	4.51	90.2	1.47
	10	9.54	95.4	1.15
	20	19.74	98.7	1.23
Human Urine-2	5	4.52	90.4	1.49
	10	9.31	93.1	1.14
	20	19.13	95.6	1.24

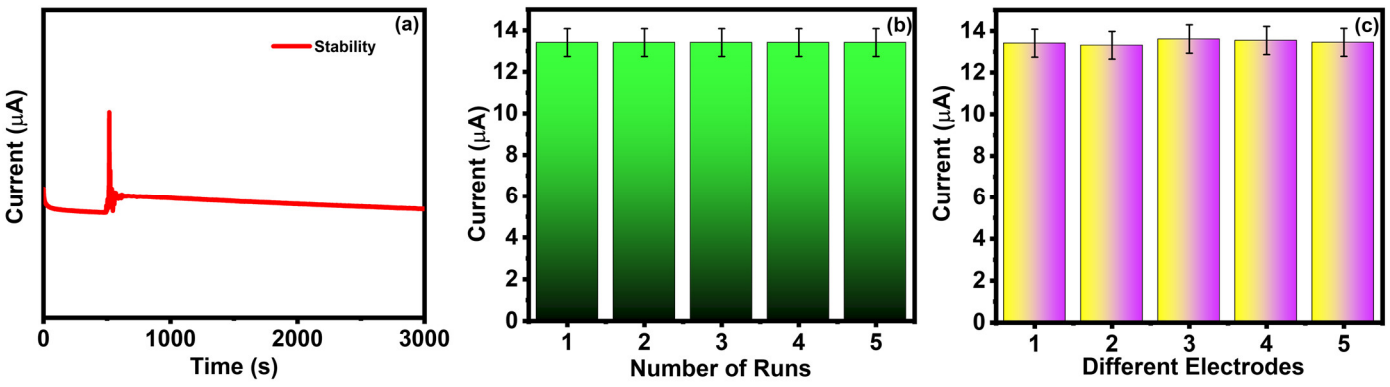

Figure S2. CeCr/SPCE (**a**) stability, (**b**) repeatability and (**c**) reproducibility