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MWCNTs/MoS_2 Decorated Cobalt Oxide Polyhedrons Composite Film Modified Electrode for Electrochemical Determination of Dopamine in Rat Brain and Human Blood Serum Samples

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MWCNTs/MoS_2 decorated Cobalt oxide polyhedrons (MWCNTs/MoS_2/Co_3O_4 PHs) were synthesized via facile hydrothermal route. The morphological study clearly revealed the MWCNTs/MoS_2 decorated on Co_3O_4 PHs and additionally elemental, and electrochemical studies were performed to verify the structure and shape. Owing to excellent synergy between MWCNTs/MoS_2 and Co_3O_4 PHs, the composite possesses good porosity, large electrochemical area, roughened surface, and excellent electrocatalytic ability. The development of highly sensitive sensor is essential for dopamine (DA) due to its great significance in physiological, biochemical, pharmaceutical and medicinal applications. A rapid, sensitive, selective, reproducible, and durable electrochemical non–enzymatic DA assay, by employing MWCNTs/MoS_2/Co_3O_4 PHs modified screen print carbon electrode (SPCE) was described. The sensor displayed outstanding sensitivity with nanomolar limit of detection of 13 nM, which is superior to those of previously reported Co_3O_4 based electrodes. A rapid, sensitive real–time analysis was demonstrated in rat brain and human blood serum samples.

Keywords: Co_3O_4 polyhedrons; Molybdenum disulfide; Multiwall Carbon Nanotubes; Analytical Chemistry; Non–enzymatic sensing; Biochemistry.

1. INTRODUCTION

Dopamine (3,4-dihydroxyphenethylamine) is an important neurotransmitter biomolecule, which is a key factor in the function of central nervous systems. Abnormal levels of DA may cause depression, drug addiction, schizophrenia, Alzheimer's and Parkinson's disease [1]. Unfortunately, the electrochemical signal of DA is often overlaps to that of ascorbic acid (AA) and suffers from interference basal DA concentration in the extra cellular fluid of the central nervous system is very low (0.01–1 μM) [2, 3]. The concentration of DA in patients with these diseases is lower than that in healthy humans. Although many approaches have been conducted to determine the amount of DA in the biological systems, electrochemical methods are preferred due to the low detection limit and low cost of electrode preparation [4, 5]. Different shapes of Co_3O_4 such as, nanoparticles [6], flowers [7], nano flakes [8], nanofibers [9], microspheres [10] , nanocubes [11], nanowall arrays [12], mesoporous hollow spheres [13], nanograin [14], nanorods [15], and etc, have been prepared on MoS_2 by altering preparation strategies and tuning experimental conditions and precursors. However, polyhedrons structured Co_3O_4 has never been reported in the literature. For the first time, we are reporting the synthesis of polyhedrons shaped Co_3O_4 via hydrothermal route and the synthesis is simple, fast, mass producible and green approach. MWCNTs are one of carbon based low cast material and it's have good electrocatalytic property [16-18]. MoS_2 nanosheets also new material for electrocatalytic active matal sulfide last few years [19]. In the present work, we have prepared MWCNTs/MoS_2-Co_3O_4 polyhedrons by hydrothermal method for electrochemical detection of dopamine at room temperature. The structural and morphological properties of the prepared MWCNTs/MoS_2-Co_3O_4 polyhedrons were observed by scanning electron microscopy (SEM). The as–synthesized MWCNTs/MoS_2-Co_3O_4 polyhedrons was coated as a thin film onto the SPCE for the evaluation of electrochemical performance towards the detection of dopamine. The easy–coating method for the construction of MWCNTs/MoS_2-Co_3O_4 polyhedrons thin–film of paper like film onto SPCE. cobalt oxides (Co_3O_4) attracted considerable attention in many fields because Co_3O_4 and MoS_2 materials are low–cost, earth abundant, highly stable, easy to prepare and holding excellent electrocatalytic property for several important reactions [20, 21]. Controlled synthesis processes of nanomaterials to implement desired structure, shape, and size have guided to many applications and the morphology has profound impact on the performance of MWCNTs/MoS_2-Co_3O_4 PHs.

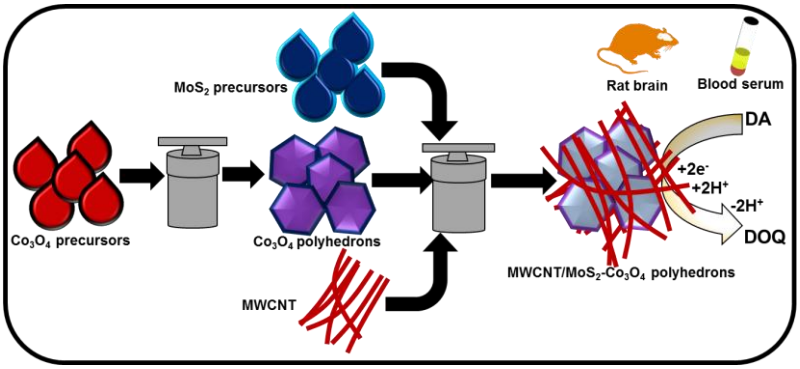

Figure 1. Schematic representation for selective detection of dopamine using MWCNTs/MoS_2-Co_3O_4 PHs

Here, highly sensitive, efficient and cost–effective enzymeless dopamine sensing was exploited using MWCNTs/MoS_2-Co_3O_4 PHs (Figure 1). The composite possess high porosity, roughed structure, large electrochemical active area, high defect density and superior electrocatalytic ability. An amperometric dopamine sensor was fabricated using MWCNTs/MoS_2-Co_3O_4 PHs modified electrode and its applicability was demonstrated in rat brain and human blood serum samples.

2. EXPERIMENTAL

2.1 Reagents

Sodium acetate, cobalt(II) chloride hexahydrate, tri sodium citrate di hydrate, glycerol, sodium hydroxide, sodium hypophosphite, $Na_2MoO_4.2H_2O$, thiourea, MWCNTs were purchased from sigma–Aldrich and used as received. The SPCEs were purchased from Zensor R&D Co., Ltd., Taipei, Taiwan. All the reagents used were of analytical grade and used without any further purification. The supporting electrolyte used for the electrochemical studies was 0.1 M Phosphate buffer solution (PB), prepared using Na_2HPO_4 and NaH_2PO_4 and the pH was adjusted either using H_2SO_4 or NaOH. Prior to each experiment, the electrolyte solutions were deoxygenated with pre–purified nitrogen gas for 15 min unless otherwise specified. The electrochemical measurements were performed using CHI 1205B work station. The electrochemical studies were carried out in a conventional three electrode cell using, saturated Ag/AgCl as a reference electrode and Pt wire as a counter electrode. Amperometric measurements were performed with analytical rotator AFMSRX (PINE instruments, USA) with a rotating disc electrode (RDE). Scanning electron microscopy (SEM) studies and Field emission–scanning electron microscopy (FE–SEM) have been performed with Hitachi S–3000 H scanning electron microscope and Hitachi H–7000 respectively. Energy–dispersive X–ray (EDX) spectra were recorded using HORIBA EMAX X–ACT (Sensor + 24V=16 W, resolution at 5.9 keV). EIM6ex Zahner (Kronach, Germany) was used for electrochemical impedance spectroscopy (EIS) studies. Rat brain sample and human serum were acquired from Chang Gung University, Taiwan and the experimental protocols were approved by the institutional Animal Ethic Committee.

2.2 Synthesis of MWCNTs/MoS_2-Co_3O_4 PHs and fabrication of MWCNTs/MoS_2-Co_3O_4 PHs modified SPCE

Firstly, sodium acetate (3.0 g), cobalt(II) chloride hexa hydrate (1.2 g), and tri sodium citrate di hydrate (0.2 g), were dissolved in the mixture of glycerol (30mL) and distilled water (10 mL) at room temperature. The homogeneous suspension was then transferred into a Teflon-lined stainless steel autoclave. Sodium hydroxide (1.6 g) and sodium hypophosphite (3.2 g) dissolved in 20 mL distilled water was slowly brought into the autoclave. After reacting at 140 °C for 15 h, the solution was cooled to room temperature. The resultant product deposited on the bottom of autoclave was then rinsed with distilled water and absolute ethanol, and finally dried under vacuum at 60 °C for 12 h. Then, 80 mg of cobalt oxide polyhedrons were ultrasonically dispersed in 55 mL of water, followed by addition of 5 mL of aqueous solution containing 155 mg of $Na_2MoO_4.2H_2O$, 243mg of thiourea and 40

mg of MWCNTs under sonication to form a homogeneous reaction mixture. Then, it was transferred into a Teflon-lined stainless autoclave with the capacity of 100 mL and sealed to heat at 200 C for 24 h. After this hydrothermal process, MoS_2 was grown on the cobalt oxide polyhedrons. Subsequently, they were washed with abundant water. As such, the final solid product of MWCNTs/MoS_2-Co_3O_4 PHs composite were simply synthesized, which was harvested by washing, centrifugation, and drying at 60 °C under vacuum for characterization.

3. RESULTS AND DISCUSSION

3.1 Surface morphological, and EDX

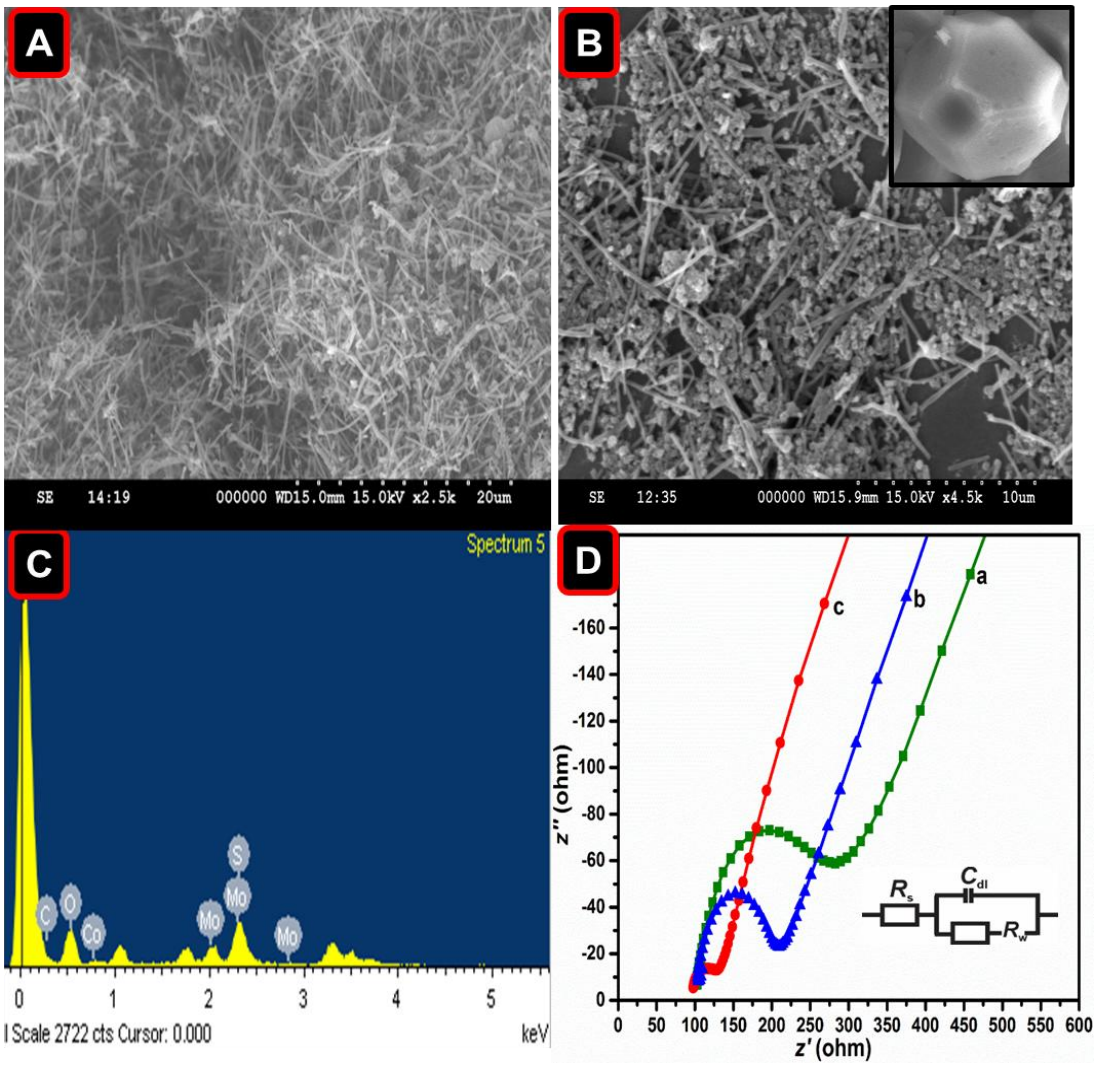

Figure 2. SEM image of MWCNTs (A), MWCNTs/MoS_2-Co_3O_4 PHs (B). Inset: FE-SEM image of Co_3O_4 PHs, EDX profile (C) and EIS spectra of (a) bare SPCE, (b) Co_3O_4 PHs/SPCE, (c) MWCNTs/MoS_2-Co_3O_4 PHs (D). Inset: Randles equivalent circuit model, R_s, R_{ct} C_{dl} and Z_w were electrolyte resistance, charge transfer resistance, double layer capacitance and Warburg impedance, respectively.

The morphology and structure of the MWCNTs Figure 2 (A), and MWCNTs/MoS_2-Co_3O_4 PHs composite (B) was examined by SEM. The FESEM images of Co_3O_4 PHs displayed polyhedron shaped micro particles figure 2B (inset). The magnified FESEM image of Co_3O_4 PHs showed high crystalline single polyhedron and the size was in micrometer range, which composed of polyhedrons architecture. The MWCNTs/MoS_2-Co_3O_4 PHs composite structure, roughed surface and high crystallinity jointly furnished large surface area, which is highly beneficial in electrochemical sensing. The EDX profile of MWCNTs/MoS_2-Co_3O_4 PHs composite featured with C, O, S, Co, and Mo elements.

3.2 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) has been used to monitor the electrochemical impedance changes of the different modified electrodes at the electrode and electrolyte interface. Figure. 2D shows the EIS plots of (a) bare SPCE, (b) MWCNTs/SPCE, (c) MWCNTs/MoS_2-Co_3O_4 PHs/SPCE in 5 mM $[Fe(CN)_6]^{-3/-4}$ with 0.1 M KCl as a supporting electrolyte. Figure. 2D inset shows the randles equivalent circuit model used to fit the EIS experimental data. The charge transfers resistance (R_{ct}) of the modified electrode is corresponds to the diameter of the semi-circle in the Nyquist plot. All the modified electrode exhibited semi circles of different diameters illustrate different R_{ct}. The higher R_{ct} value of about 197 Ω was obtained for the SPCE electrode. The MWCNTs/SPCE and MWCNTs/MoS_2-Co_3O_4 PHs/SPCE show the R_{ct} values of 112 Ω and 43.15 Ω, respectively. However, the R_{ct} value of the MWCNTs/MoS_2-Co_3O_4 PHs was about 43.15 Ω, which proposed that the charge transfer resistance of MoS_2 was decreased due to the non-covalent interaction with MWCNTs. Moreover, the MWCNTs enhance the electron conductivity properties at the electrode surface. The EIS results confirmed that the MWCNTs/MoS_2-Co_3O_4 PHs/SPCE have higher electron conductivity properties with low charge transfer resistance than that of the other modified electrodes.

3.3 Electrocatalysis of DA based on MWCNTs/MoS_2-Co_3O_4 PHs/SPCE

Figure 3A displayed the CVs recorded for unmodified SPCE (a), Co_3O_4 PHs/SPCE (b) and MWCNTs/MoS_2-Co_3O_4 PHs/SPCE (c), measured at a scan rate of 50 mV s^{-1} in the potential range of -0.2 to 0.6 V. The supporting electrolyte comprised 5 μM DA. The trend of electrocatalytic ability: MWCNTs/MoS_2-Co_3O_4 PHs/SPCE > Co_3O_4 PHs/SPCE >unmodified SPCE. The MWCNTs/MoS_2-Co_3O_4 PHs/SPCE offered great advantageous to DA oxidation as it exhibited highly enhanced electrocatalytic ability and fast electron transfer. In fact, the oxidation current obtained at MWCNTs/MoS_2-Co_3O_4 PHs/SPCE was 24.61 μA and 5.7, 3.5 folds higher than those obtained at Co_3O_4 PHs/SPCE and unmodified SPCE respectively. Moreover, the overpotential observed at MWCNTs/MoS_2-Co_3O_4 PHs/SPCE was 195 and 112 mV lower than those obtained at Co_3O_4 PHs/SPCE and unmodified SPCE. The improved electrocatalytic ability of the MWCNTs/MoS_2-Co_3O_4 PHs can be manifested to the great synergetic effect [1, 21-25]. Here great synergetic effect based on high surface area of MWCNTs and great catalytic activity of Co_3O_4 PHs. Figure 2B presented the CVs

obtained at MWCNTs/MoS_2-Co_3O_4 PHs/SPCE in 0.1 M PB (pH 7.0) containing various concentrations of DA. The anodic and cathodic peak current was linearly increased as the concentration of DA increased. The effect of scan rate towards the DA oxidation were studied by applying different scan rates from 10–250 mVs^{-1} (Figure 2C). The plot between anodic and cathodic peak current and square root of scan rate exhibited good linearity indicating diffusion controlled redox process (Figure 2D).

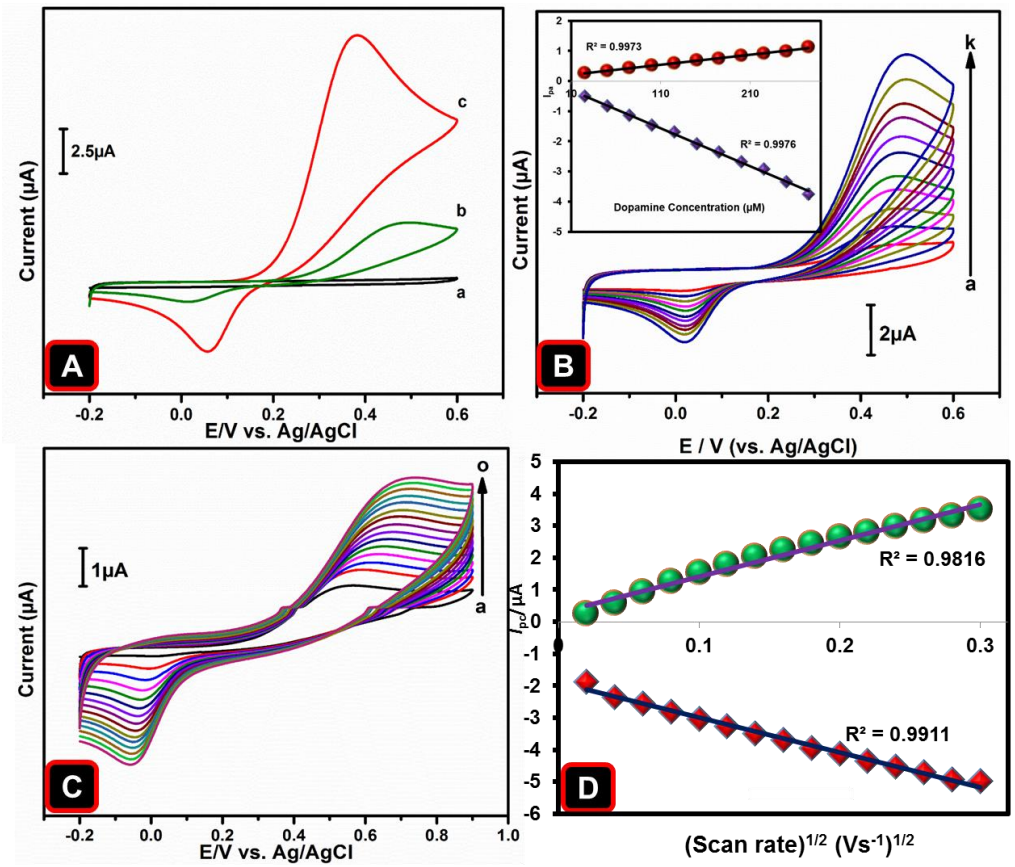

Figure 2. (A) CVs obtained at SPCE (a), Co_3O_4 PHs/SPCE (b), and MWCNTs/MoS_2-Co_3O_4 PHs/SPCE (c), in 0.1 M PB (pH 7) at a scan rate of 50 mV s^{-1}, (B) CVs of MWCNTs/MoS_2-Co_3O_4 PHs/SPCE in 0.1 M PB (pH 7.0) containing different concentrations of DA (a=25, b=50, c=750, d=100, e=125 μM, f= 150, g=175, h=200, i=225, j=250, k=275). Inset= current vs. [DA] (C) CVs of MWCNTs/MoS_2-Co_3O_4 PHs/SPCE in 0.1 M PB (pH 7.0) containing 5 μM DA at different scan rates (10 to 150 mVs^{-1}), Inset= $(\text{scan rate})^{1/2}/(Vs^{-1})^{1/2}$ vs. peak currents/μA (D) Effect of the scan rate: CVs of MWCNTs/MoS_2-Co_3O_4 PHs/SPCE in 0.1 M PB (pH 7) at different scan rates (10 to 150 mV s^{-1}).

3.4 Amperometric determination of dopamine

Figure 3A presented amperometric response of the MWCNTs/MoS_2-Co_3O_4 PHs modified electrode (rotation speed=1200 RPM) upon successive injections of DA into PB (pH 7) at a regular

intervals of 50 s (E_{app}= +0.34 V). Well–defined and quick responses were obtained and steady–state current was reached in less than 3s.

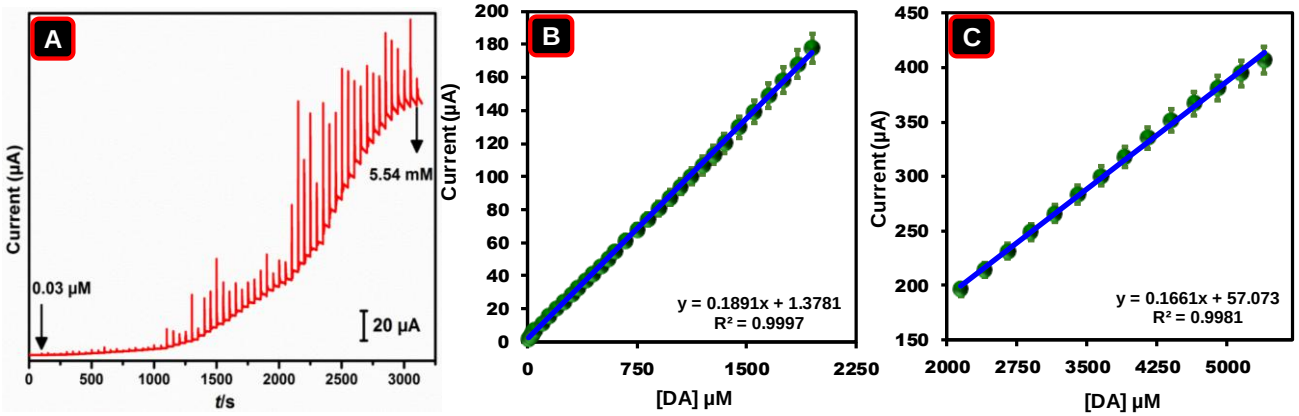

Figure 3. (A) **a**mperometric response of the MWCNTs/MoS_2-Co_3O_4 modified electrode (rotation speed=1200 RPM) upon successive injections of DA into PB (pH 7) at a regular intervals of 50 s (E_{app}= +0.34 V). Well–defined and quick responses were obtained and steady–state current was reached in less than 3s. (B) and (C) [DA]/μM vs. current (μA).

Table 1. Comparison of Analytical Parameters at MWCNTs/MoS_2-Co_3O_4 PHs modified electrode with previously reported dopamine sensors.

Electrode	LOD/ μM	Linear range /μM	Method	Ref.
[a]TiN-reduced graphene oxide	0.012	0.1–80	DPV	[26]
graphene	2.64	4–100	DPV	[27]
graphene/chitosan/[b]CPE	0.098	0.2–100	DPV	[28]
graphene/[c]nAu/[d]GCE	1.86	5–1000	DPV	[29]
[e]GNS/nAu/[f]PEI	0.2	2–48	DPV	[30]
[g]rGO/[h]MWCNT/nAu/GCE	0.067	0.20–70	ECL	[31]
GO/[i]C60/GCE	0.008	0.02–73.5	DPV	[32]
[j]HAu/graphene/GCE	0.05	0.08–600	AMP	[33]
[k]GNC/[l]CMG/GCE	0.028	0.1–80	AMP	[34]
MWCNTs/MoS_2-Co_3O_4 PHs/SPCE	0.013	0.03–1950.2 2150.2–5540	AMP	This work

[a]TiN= titanium nitride, [b]CPE= carbon paste electrode, [c]nAu= gold nanoparticles, [d]GCE= glassy carbon electrode, [e]GNS= graphene nanosheets, [f]PEI= polyethyleneimine, [g]rGO= reduced graphene oxide, [h]MWCNT= multiwall carbon nanotubes, [i]C60= fullerene, [j]HAu= hallow gold particles, [k]GNC= gold nanocages, and [l]CMG= chemically modified graphene oxide.

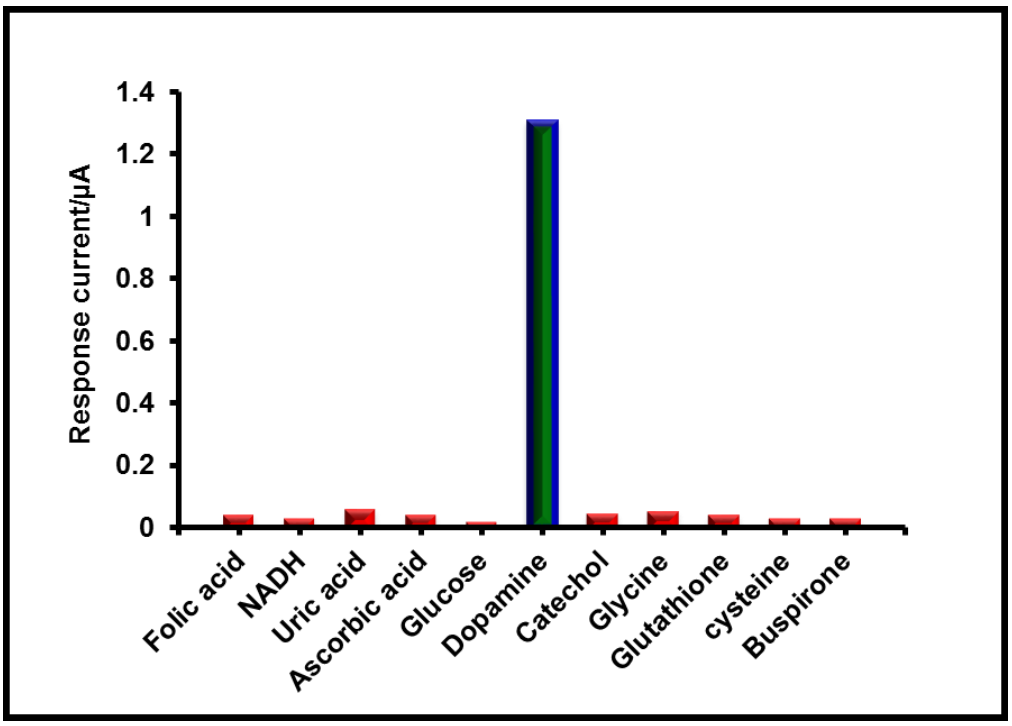

Figure 4. (A) Amperometric response of MWCNTs/MoS_2-Co_3O_4 PHs film modified electrode towards 2 μM of 4–NP (a), and 0.5 mM of 0.5 mM of folic acid, NADH, uric acid, ascorbic acid, glucose, catechol, glycine, glutathione, cysteine, and buspirone into 0.1 M PB (pH 7.0) electrode rotation speed = 1200 RPM and applied potential = +0.34 V.

The linear range was 0.03–1950.2 μA and 2150.2–5540 μM with limit of detection (LOD) was 13.45 nM, then sensitivity was calculated to 2.197 and 3.486 μA μM^{-1} cm^{-2} respectively. Such a low detection limit at nanomolar level illustrated the outstanding sensing performance of the electrode. The sensor parameters were superior over existing MWCNTs/MoS_2-Co_3O_4 PHs incorporated electrodes. The selectivity of the sensor was evaluated by performing the interference experiments in presence of likely interfering agents. Figure 4 showed the amperometric response of the electrode towards 5 μM of DA (a), and 0.5 mM of folic acid, NADH, uric acid, ascorbic acid, glucose, catechol, glycine, glutathione, cysteine, and buspirone. The electrode quickly responded to DA; however, it was insensitive with the other species, thus, the electrode specifically recognizes and sensed DA in the pool of other biological analytes.

3.5 Durability, Reproducibility and Repeatability

In order to evaluate durability of the sensor, to find out the storage stability of the electrode. The sensor performance of the MWCNTs/MoS_2-Co_3O_4 PHs modified electrode was monitored every week, while the electrode was stored at 5°C when not in use. The electrode retained 97.35% of its initial current even after 30 weeks of its continuous use, which endorsed excellent durability.

3.6 Real sample analysis

The practical feasibility of the fabricated sensor was demonstrated in rat brain and human blood serum. These solutions already contained inherent DA and hence directly spiked into the supporting electrode and amperometry experiments were performed by following the optimized experimental conditions of lab samples. Similar to lab samples, both the real samples showed quick and sensitive signals within 5s. Notably, the real samples have not undergone any pre–sampling procedures. The obtained amperometric results are consistent with lab sample results. The obtained results of the rat brain and human blood serum samples given in table 2. From the results, the MWCNTs/MoS_2-Co_3O_4 PHs modified electrode revealed the excellent practicality for the determination of DA in rat brain and human blood serum samples.

Table 2. Real-time determination of ATP in rat brain serum and human blood samples using MWCNTs/MoS_2-Co_3O_4 PHs /SPCE film modified electrode

Samples	Added/μM	Found/μM	Recovery/%	*RSD/%
Rat brain serum	20 μM	20.31 μM	103.1	3.73
Human blood serum	30 μM	30.32 μM	103.6	3.58

* Relative Standard Deviation of 3 individual measurements

4. CONCLUSIONS

A facile two step hydrothermal route was described to prepare polyhedrons shaped Co_3O_4 PHs metal oxide and the MWCNTs/MoS_2-Co_3O_4 PHs composite. The structure and shape of the materials were confirmed by morphological, elemental, spectral and electrochemical methods. The MWCNTs/MoS_2-Co_3O_4 PHs film modified electrode shown excellent electrochemical performances and a sensitive dopamine amperometric sensing platform was demonstrated which showed wide working range 0.03–1950.2 μA and 2150.2–5540 μM with low detection limit 0.013 μM. The other advantages of the sensor are its selectivity, repeatability, reproducibility, durability and practical feasibility. The future work will be focused on the fabrication of MWCNTs/MoS_2-Co_3O_4 PHs incorporated stretchable sensor devices for DA tracking and quantification in biological samples.

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