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Electrochemical Sensing of Dopamine using Polyaniline/Copper Nano Composite

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ABSTRACT

Herein, the fabrication of a cheaper modified electrode based on polyaniline and Cu composite (PANI-Cu) for the sensitive determination of Dopamine (DA) is reported. The composite formation was characterized by SEM, FT-IR, XRD and Electrochemical methods. The PANI-Cu composite was used to modify Glassy carbon Electrode (GCE) and the resulting modified electrode (GCE/PANI-Cu) was used to develop a sensor for DA. The modified electrode has shown excellent electro catalytic activity to the oxidation of DA. The electrode was highly selective for DA detection. Besides, the electrode has good repeatability and reproducibility.

1. Introduction

Dopamine (DA) is an important neurotransmitter belonging to catecholamine family and plays a major role in the brain as well as outside of the nervous system. DA controls and regulates many fundamental processes in human physiology, including release of hormones, motor control, and the regulation of the cardiovascular system [1, 2]. Deficiency or excess of DA may result in serious diseases related to neurological disorders, including Parkinson's disease and schizophrenia [3]. In addition, DA is administered externally as a medication to DA deficient patients, but its excess dosage causes neurological side effects [4]. Therefore sensitive determination of DA is important in clinical analysis [5-7].

The concentration of DA (in micro molar level) is comparatively lower than that of AA (in millimolar level) in body fluids and hence the determination of UA usually encounters interference from AA rather than DA [8, 9]. Although traditional analytical methods can be used for the determination of DA, electrochemical methods are most preferable due to their simplicity, low-cost, easy-handling, rapid response time, portability and low power consumption [10]. All these three (Ascorbic acid, Dopamine and Uric acid) metabolites are electrochemically active and hence they are suitable for electro analytical determination. At conventional electrodes, all the three biomarkers are oxidized at similar oxidation potential and the voltammetry peaks usually overlap and hence difficult to determine them selectively [11].

Different electrode materials and modifications with various nanoparticles were employed to increase the sensitivity and the selectivity of dopamine detection nowadays. Using metal- (e.g. platinum) [12], metal oxide- (e.g. iron oxide) [13] and semiconductor- (e.g. zinc oxide) [14] nanoparticles for the electrode modification lead not only to an increase in the effective electrode area but also to better electron transfer kinetics due to their catalytic properties. On the other hand, the carbon-based electrodes such as graphene [15–18], carbon nanotubes (CNT) [19,20], carbon fiber electrode (CFE) [21], carbon-paste electrode (CPE) [22], glassy carbon electrode [23,24].

Polyaniline (PANI) is the most popularly used conducting polymer in electrochemical sensors, attributed to its excellent electro catalytic ability, conductivity, easy synthesis, high environmental stability and thermal stability [25]. The composites of PANI with carbon materials such as activated carbon, graphene and carbon nanotubes have shown improved electronic and mechanical properties compared with pure PANI, making

the composite more suitable for electronic/electrochemical applications [26].

Herein, the preparation of cluster like copper particles decorated polyaniline composite (PANI/Cu) for the sensitive determination of DA is reported. The composite is prepared through a straightforward solution-assisted method using cheaper precursors. The composite is demonstrated as a suitable electrode material for the determination of DA.

2. Experimental Methods

2.1 Chemicals and Apparatus

Aniline and Copper Sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were purchased from Merck. All the other reagents were purchased from Sigma-Aldrich and used as received. All the reagents used were of analytical grade and used without any further purification. Double distilled water was used for all the experiments. 0.1 M phosphate buffer (pH 7.0) was prepared from sodium dihydrogen phosphate and disodium hydrogen phosphate and used as supporting electrolyte.

Electrochemical studies were performed in a conventional three electrode cell using modified glassy carbon electrode (Bioanalytical Systems, Inc., USA) as a working electrode (area 0.071 cm^2), Ag|AgCl (saturated KCl) as a reference electrode and Pt wire as a counter electrode. All the electrochemical measurements were carried out using CHI 1205a electrochemical work station (CH Instruments, Inc., U.S.A) at ambient temperature. Prior to each electrochemical experiment, the electrolyte solutions were de-oxygenated with pre-purified nitrogen for 15 min. unless and otherwise specified. Surface morphological studies were carried out using Hitachi S-3000 H Scanning Electron Microscope (SEM).

2.2 Preparation of PANI/Cu/GCE

A 5 mM CTAB solution was prepared in 0.5 M H_2SO_4 . 40 mM aniline solution was added to the CTAB solution and the mixture was stirred using magnetic stirrer for 30 min. 50 mL of 0.05 M CuSO_4 solution was added drop-wise to the previous solution, stirring was continued for 30 min and the temperature was maintained below 0°C . Afterwards, a pre-cooled solution of 50 mM PDS was added drop wise to aniline solution with stirring over a period of 30 min. A dark green precipitate was formed, which was filtered and washed several times with water and acetone, respectively. The purified PANI/Cu composite was dried and redispersed in ethanol (1 mg mL^{-1}). Further, GCE surface was polished with $0.05 \mu\text{m}$ alumina slurry using a Buehler polishing kit, then washed with water and dried. $5 \mu\text{L}$ dispersion of PANI/Cu was dropped at the pre-cleaned GCE and dried at ambient conditions.

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3. Results and Discussion

3.1 FT-IR Spectral Studies

In PANI/Cu spectrum (Fig. 1), the absorption in the range 3343 cm^{-1} is attributed to the typical O-H stretching frequency. The band at 1562 cm^{-1} and 1482 cm^{-1} are attributed to the C=C stretching of phenyl ring [28]. The absorption band at 1297 cm^{-1} corresponds to C-N stretching. The band at 3200 cm^{-1} indicates the stretching of the N-H bond of the aromatic ring in PANI/Cu composite. The spectrum of PANI/Cu reveals the characteristic M-polymer bond around 610 cm^{-1} and 500 cm^{-1} . In the case of PANI/Cu, the bands are well matched with the literature [29].

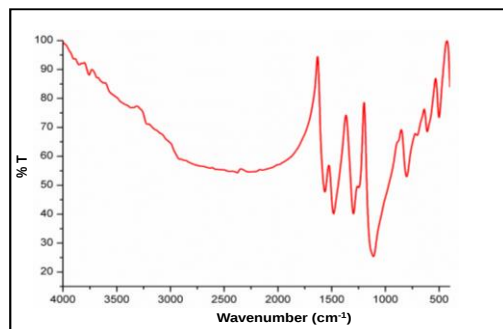


Fig. 1 FT-IR spectrum of PANI/Cu composite

3.2 XRD Analysis

X-ray diffraction has been used for structural determination of PANI/Cu nanocomposite. Fig. 2 shows the XRD pattern of PANI/Cu nano composite. The spectrum of PANI showed the typical broad peaks at $2\theta = 25.1^\circ$, suggested the amorphous structure of the PANI prepared by oxidative polymerization. As reported by Sanjeev Kumar et al, planar configuration of polyaniline due to the densely packed phenyl rings and thus an extensive interchain $\pi \rightarrow \pi$ orbital overlap has been indicated by the typical peaks $2\theta = 25.1^\circ$, for PANI [31]. Moreover it reveals that the sharp peak at 113° in PANI/Cu nanocomposite [30]. The crystal size of the PANI/Cu nanoparticles can be calculated using Debye-Scherrer formula, $D = 0.89\lambda/\beta\cos\theta$, where λ is $1.5418\text{ \AA}$ and β is the half maximum of the diffraction peak corresponding to the Bragg's angle θ . The calculated value of the PANI/Cu nano composite is in the range of 10-12 nm. The investigation of X-ray diffraction study confirms the presence of Cu nanoparticles in the PANI matrix.

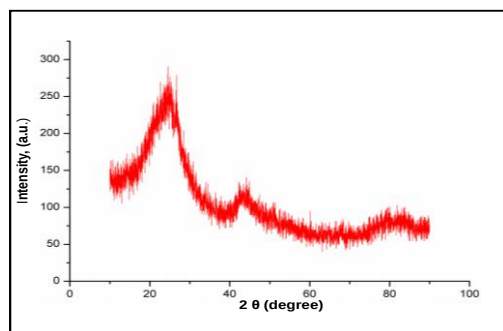


Fig. 2 XRD pattern of PANI/Cu nano composite

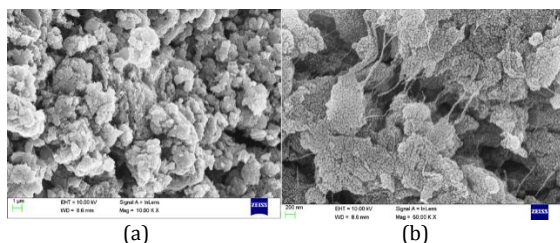


Fig. 3 FESEM image of PANI-Cu composite- (a) and (b)

3.3 Surface Morphological Characterization

The SEM image of PANI-Cu portrayed the presence of fiber of PANI and numerous Cu nano composite Figs. 3a and b. Besides, the composite is featured with several cavities and catalytic sites. It has a special porous morphology, which significantly improves the electrode surface and the mass transfer. The morphology indicates that the composite can have high surface area, which may be highly beneficial for electrochemical sensing applications.

3.4 Electro Catalysis of Dopamine

Fig. 4 shows the cyclic voltammogram (CV) obtained at bare GCE (a), PANI/GCE (b) and PANI-Fe/GCE (c) in phosphate buffer (pH 7.0) containing $3\text{ }\mu\text{M}$ DA. The scan rate is 50 mVs^{-1} . The unmodified GCE displays poor electro catalytic ability to oxidize DA. Compared with unmodified electrode, PANI/GCE has shown better electro catalysis for DA; however the oxidation peak is observed at higher over potential. On the other hand, PANI-Cu/GCE has shown excellent electro catalytic ability to oxidize DA at very low over potential and has displayed sharp peak with enhanced peak current. The oxidation peak of DA is observed at 0.22 V with PANI-Cu/GCE, which is about 100 mV and 160 mV lower potential than PANI/GCE and GCE, respectively. The CV results revealed that the PANI-Cu composite has synergistic catalytic ability over control electrodes. In addition, the composite possesses large surface area, high conductivity and abundant catalytic sites and these characteristics of the composite favored the high electro catalytic ability of the composite.

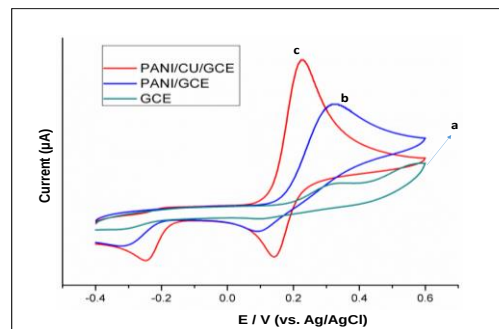


Fig. 4 CVs obtained at bare GCE (a), PANI/GCE (b) and PANI-Cu/GCE (c) in phosphate buffer (pH 7.0) containing $3\text{ }\mu\text{M}$ DA. Scan rate = 50 mVs^{-1}

3.5 Effect of Scan Rate

The influence of different scan rate towards the electro catalytic reaction of DA at PANI-Cu/GCE is investigated. The oxidation peak current of DA (Figs. 5a and b) linearly increased as the scan rate increases from 100 to 500 mVs^{-1} . The plot between oxidation peak current and scan rate displays good linearity, which indicates that the oxidation is surface confined diffusion process.

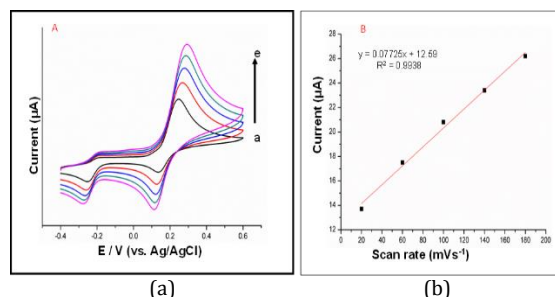


Fig. 5 (a) Effect of the scan rate: cyclic voltammogram obtained at PANI-Cu/GCE towards $3\text{ }\mu\text{M}$ DA at different applied scan rates from 100 to 500 mVs^{-1} , a=100, b=200, c=300, d=400 and e=500 mVs^{-1} ; (b) Plot between DA oxidation peak current (μA) and Scan rate (mVs^{-1})

3.6 Effect of Concentration of DA

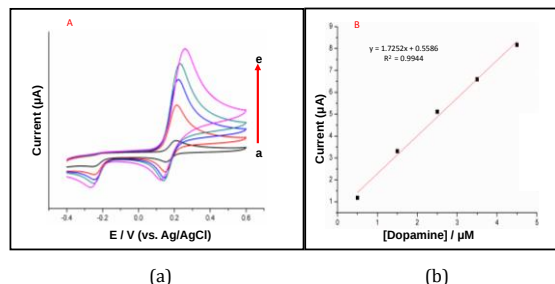


Fig. 6(a) CV obtained at PANI-Fe/GCE in phosphate buffer (pH 7.0) containing different concentrations of UA: $2.0, 4.0, 6.0, 8.0$, and $10.0\text{ }\mu\text{M}$; (b) Plot between response current (μA) vs. [DA], μM

Fig. 6(a) displays the CV curves obtained at PANI-Cu/GCE in phosphate buffer containing different concentration of DA. As represented in Fig. 6(b), the anodic peak current corresponding to the oxidation of DA is linearly increased as the concentration of DA increases. The plot between the concentration of DA and the corresponding response current exhibited good linearity with a slope of $1.7252\text{ }\mu\text{A}/\mu\text{M}$.

4. Conclusion

In summary, a sensitive and highly selective electrochemical DA detection platform was developed using PANI–Cu composite. The successful formation of the composite was revealed by FT-IR, XRD, and SEM. The electrochemical studies revealed that the composite has excellent electro catalytic ability towards oxidation of DA at very low over potential. The modified electrode has satisfactory stability, repeatability and reproducibility.

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