Chapter VII

PREPARATION OF NiO/ZnO HYBRID NANOPARTICLES FOR ELECTROCHEMICAL SENSING OF DOPAMINE AND URIC ACID

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Chapter VII

7.1. Introduction

The NiO/ZnO hybrid nanoparticles were synthesized using sodium dodecyl sulfate (SDS) in a micro-emulsion method. The NiO/ZnO nanoparticles were characterized using X-ray diffraction, scanning electron microscopy, UV-visible absorption spectroscopy, infrared absorption spectroscopy and energy dispersive X-ray spectrum. The obtained NiO/ZnO hybrid nanoparticles were used for the preparation of modified carbon paste electrode (MCPE) for electrochemical detection of dopamine and uric acid at physiological pH 7.4. The MCPE exhibits enhanced electrochemical parameters such as peak current response, surface area of electrode, electrocatalytic activity, diffusion-coefficient, lower detection limit, sensitivity and higher linear range. The proposed method was successfully applied for the detection of dopamine and uric acid in real samples.

7.2. Chemistry and Biological Relevance of Dopamine and Uric acid

The chemistry and biological relevance of dopamine has been explained in details in chapter 2 section 2.2 to 2.2.3 and uric acid described in detail in chapter 5 section 5.3.

7.3. Review of NiO/ZnO hybrid nanoparticle, Dopamine and Uric acid

Dopamine (DA) is a well-known biogenic amine acting as a neurotransmitter in the brain. It has received considerable attention because of its suspected role in a variety of neuropsychiatric disorders such as Parkinson's disease and Schizophrenia [1, 2]. DA concentration is very low (0.01–1μM) in the extracellular fluid of the central nervous system [3]. Uric acid (2,6,8-trihydroxypurine, UA), a major nitrogenous compound in urine, is a product of purine metabolism in human body and its higher levels leads to many clinical disorders [4]. High levels of UA in the blood (hyper uricemia or Lesch-Nyhan syndrome) are linked with the body disorders like gout, kidney, and cardiac problems. Many epidemiological studies have suggested that elevated serum UA is also a risk factor for cardiovascular disease [5-10]. Hence, a simple, accurate and reliable method for the determination of dopamine and uric acid became an urgent need.
Electrochemical methods were commonly accepted as the fastest analytical assay (compared with traditional spectroscopic technique [11]), simple, sensitive and environmentally friendly detection method that is even suitable for the analysis of colored or turbid samples [12].

The literature reported on nanoparticles and organic compounds modifier electrode was used for investigation of dopamine and uric acid such as: CdO, CuO and MgFe2O4 nanoparticles modified electrode for detection of DA [13-15], gold-modified vertically aligned multi-walled carbon nanotubes (MWCNTs) electrode as a biosensor for uric acid detection [16]. Self-assembled gold nanoparticles onto the L-cysteine-modified glassy carbon electrode for simultaneous determination of uric acid and ascorbic acid were reported [17]. Cu-metal nano particles in over-oxidized poly pyrrole film modified GCE was utilized as the sensing matrix for the simultaneous determination of DA and UA [18].

It is a well-known fact that the electrochemical activation of carbon based electrodes will result in improved performance during electroanalysis [19]. In particular, their porous and large specific surface area, interfacial adsorption properties and enhanced electrocatalytic activity have opened doors for tailoring a variety of electrochemical sensors and biosensors [20]. Carbon, conducting polymers and transition metal oxides are the most widely used active electrode materials [21, 22]. The literature review of composite electrodes made from transition metal oxides and carbonaceous materials [23,24] showed very high surface area due to the increased electrical conductivity, electrochemical utilization of the metal oxide and ionic transport throughout the internal volume of the electrode.

A composite composed of ZnO and NiO nanoparticles can be of interest as a complex catalyst and a nanosized semiconductor with interesting transport and magnetic properties [25, 26]. The NiO/ZnO hetero structural nanomaterials attract much interest in particular because of NiO, as a p-type semiconductor (Eg = 3.5 eV), possesses high p-type concentration, high hole mobility, and low lattice mismatch with ZnO, which is beneficial for the formation of p-n heterojunction with ZnO [27-30].
7.4. Experimental

7.4.1. Reagents and Chemicals

The NiO/ZnO hybrid nanoparticles were characterized by various techniques. Powder XRD patterns was recorded on Philips XRD ‘X’ Pert Pro diffractometer, using Cu-Kα radiation (λ=1.5438 Å) as source. IR absorption spectra was recorded on the Perkin Elmer Spectrum 1000 FTIR spectrometer on thoroughly dried samples using KBr pellets as dilutants, UV-visible spectra was obtained on the a Perkin Elmer UV-VIS Spectrophotometer by dispersing and sonicated NiO/ZnO hybrid nanoparticles in the distilled water. The structural morphology of the NiO/ZnO hybrid nanoparticles the sample was studied using a JEOL JSM-848 scanning electron microscope (SEM). All the electrochemical experiments were performed using a single compartment, three-electrode cell with above the bare CPE, NiO/ZnO hybrid nanoparticles MCPE was used as a working electrode, an aqueous saturated calomel electrode (SCE) as reference electrode and a Pt wire as auxiliary electrode. All potentials were measured and reported vs the SCE. The cyclic voltammetric measurements (CV) and differential pulse voltammetry techniques (DPV) were performed on a Model 660c (CH Instruments) Potentialstat / Galvanostat.

7.4.2. Materials

Cyclohexane, n-butyl alcohols were purchased from Nice chemicals. Graphite powder, absolute ethanol, perchloric acid were from Merck chemicals, Nickel Chloride (NiCl₂.6H₂O), Zinc Chloride (ZnCl₂.6H₂O), liquid ammonia aqueous solution were from SD-Fine chemicals, sodium dodecyl sulfate (SDS), uric acid (UA), dopamine (DA), silicon oil, sodium dihydrogen phosphate and disodium hydrogen phosphate were from Himedia chemicals. All chemicals were analytical grade and used as received without further purification. Phosphate buffer was prepared and the pH was adjusted by the addition of 0.2 M NaH₂PO₄ and Na₂HPO₄ solutions. All the aqueous solutions were prepared with double distilled water.
7.4.3. Preparation of NiO/ZnO hybrid nanoparticles

The NiO/ZnO hybrid nanoparticle were synthesized according to the microemulsion method described elsewhere [31], with minor modifications. In this method cyclohexane is used as the oil phase, SDS is used as surfactant, n-butyl alcohol is used as co-surfactant. In order to determine the phase behaviour of four component system on a pseudo-ternary phase, the relative concentration of the two constituents must be fixed throughout the investigations. Here in a constant weight ratio of surfactant to co-surfactant was fixed. The microemulsion system was chosen because of enough stable space, high reaction efficiency and yield. In order to dissolve the water as much as possible, five different ratios of surfactant to co-surfactant was chosen and as shown in Table-7.1. From the table-7.1 which shows that the ratio of 2:3 is the appropriate.

The procedure was, titrating a series of SDS/n-butyl alcohol/cyclohexane mixtures with water. The formation of clear, homogenous and transparent solution after the mixture stirred vigorously was considered as microemulsion region. If the mixture became turbid, it was considered as the occurrence of phase separation and ME represents the microemulsion region. In this region the system formed clear and homogenous microemulsion. The typical microemulsion system employed in the study has a composition of 50% cyclohexane, 20% SDS and 30% n-butyl alcohol.

The oil phase, the surfactant and the co-surfactant were mixed with weight ratio 5:2:3 by magnetically stirring until it became transparent (ME). Three microemulsions were prepared as follows: ME 100g, 20g of 0.1 mol/L NiCl₂ aqueous solution was added (ME1). ME 100g, 20g of 0.1 mol/L ZnCl₂ aqueous solution was added (ME2). ME 200g, 40g of 0.2mol/l of NH₃·H₂O aqueous solution was added (ME3). All these experimental processes were under magnetically stirring, ME1 was added dropwise to the ME3 under stirring for another 30 min at room temperature. Then ME2 was added dropwise to the mixture of ME1 and ME3 under stirring for 30 min at room temperature. Thus the obtained precipitate was repeatedly washed using ethanol and followed by centrifuge for 15 minutes at 2000 rpm. The precursor powders were dried in an oven for 24hrs at 80°C until a constant weight of the particles is achieved. The NiO/ZnO hybrid nanoparticles was obtained after calcination at 500°C for 3 hours.
7.4.4. Preparation of bare carbon paste electrode and modified carbon paste electrode

The bare carbon paste electrode (bare CPE) was prepared by hand mixing of 80% graphite powder with 20% silicon oil in an agate mortar for about 30 minutes to produce a homogenous carbon paste. The paste was packed into the homemade cavity and smoothed on a weighing paper. The modified carbon paste electrode (MCPE) was prepared by adding 20 mg NiO/ZnO hybrid nanoparticles to above mentioned graphite powder and silicon oil mixture.

7.5. Results and Discussion

7.5.1. Characterization

The XRD pattern of the synthesized nanoparticles is shown in the Fig.7.1. The position and intensity of the characteristic peaks of the sample are well consistent with that of the standard JCPDS Card No.780429 and No. 891397. The sharp diffraction peak in the XRD pattern indicates the crystalline nature. No other metal oxide impurity peaks present in NiO/ZnO pattern were observed, indicating the high purity of the products and by using Debye Scherrer’s formula, the crystalline sizes of NiO/ZnO hybrid nanoparticles was calculated. The obtained average particle size is 28nm.

The IR transmittance spectrum for the NiO/ZnO hybrid nanoparticles synthesized by using SDS is displayed in Fig. 7. 2. The peaks at around 2931, 2854 and 1117 cm\(^{-1}\) are due to C–H stretching and bending. These band vibrations provide evidence for the incorporation of SDS into the NiO/ZnO hybrid. A broadening peak at around 3438 and 1624 cm\(^{-1}\) was proposed to be due to H–OH stretching and broad intense peak observed in the range 420 cm\(^{-1}\) and small peak in the range 601 cm\(^{-1}\) attributed to the frame work vibration of metal oxide nanoparticles [38, 39].

According to the SEM observations reveals that flake shaped structure were grown and each flake have thin \(\sim 40 -50\) nm, long 500 nm structures and some irregular shaped particles powder shows less than \(\sim 40\) nm size in Fig.7.3. The EDS indicates that the atomic ratio of Zn and Ni is about stoichiometry 1:2 exists in a sample shown in Fig.7.4.
7.5.2. The response of DA and UA at the bare CPE, and MCPE

The electrochemical responses of $1 \times 10^{-5}$ M DA in 0.2 M phosphate buffer solution of pH 7.4 at the bare carbon paste electrode (BCPE) and the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE) with scan rate 0.1 V/s is shown in Fig. 7.5a. At the BCPE, the difference between the anodic peak potential ($E_{pa}$) 0.157 V and the cathodic peak potential ($E_{pc}$) 0.096 V with $\Delta E_{p}$ 0.061 V, However a well-defined redox wave of DA was observed and the peak currents significantly increased at the MCPE with the anodic peak potential shifting negatively to 0.146 V and the corresponding cathodic peak potential is 0.097 V and $\Delta E_{p}$ is 0.049 V indicates the modified electrode shows fast electron transfer process.

Fig. 7.5b. shows the electrochemical responses of $1 \times 10^{-4}$ M UA in 0.2 M phosphate buffer solution of pH 7.4 at the bare CPE and the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE) with scan rate 0.1 V/s. At the bare CPE, the anodic peak potential ($E_{pa}$) 0.335 V and the MCPE with anodic peak potential ($E_{pa}$) 0.304 V. Compared with bare CPE the enhancement in the peak currents with reduction of oxidation peak potential showed catalytic effects of the NiO/ZnO hybrid nanoparticles.

7.5.3. The effect of scan rate

The effect of scan rate for $1 \times 10^{-5}$ M DA and $1 \times 10^{-4}$ M UA in 0.2 M phosphate buffer solution of pH 7.4 was studied by CV at the MCPE. It showed an increase in the peak current shown in the Fig. 7.6a and 7.6b respectively for scan rate (0.100 to 0.600 V/s) with the graph obtained was good linearity between the square root of the scan rate ($\sqrt{\nu}$) versus peak current for MCPE with correlation coefficients ($r^2=0.999$) as shown in the Fig. 7.7a and 7.7b for DA and UA which indicate the MCPE electron transfer reaction was diffusion-controlled process. The surface area available for the electron transfer to species in solution can be estimated by the Randles–Sevcik equation (1) for reversible electrode process and equation (2) for irreversible electrode process and assuming charge transfer coefficient for irreversible electrode process is 0.5 ($\alpha_n=0.5$) [32-34]. This equation relates the peak current for an electron transfer-controlled process with the square root of the scan rate, as follows:
where \( i_p \) is the peak current (A), A is the electroactive area (cm\(^2\)), C is the concentration of the electroactive species (mol cm\(^{-3}\)), n is the number of exchanged electrons, \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)) and \( v \) is the scan rate (V s\(^{-1}\)). The values of the diffusion coefficients were obtained from the slopes of \( i_{pa} \) vs \( v^{1/2} \) and by using equation (1), the surface area electrode for the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE) was calculated and the surface area of MCPE at 0.1 V s\(^{-1}\) were found to be 0.0673 cm\(^2\) for DA and 0.136 cm\(^2\) for UA. Compared with bare CPE the MCPE exhibits enhanced surface of electrode. Hence the probable mechanism may be NiO/ZnO hybrid nanoparticles combined with the hydrogen bond of the hydroxyl of DA which activated hydroxyl, weakened the bond energy of O–H and improved the electron transfer rate. At the same time, high surface area of the NiO/ZnO hybrid nanoparticles improved the electrode contact area of DA and UA.

### 7.5.4 The effect of concentration of DA and UA

The differential pulse voltammetric technique was used for the analysis of DA. DA concentration was varied from 1 to 600 \( \mu \)M and UA concentration was varied from 12.9 \( \mu \) to 0.0429 M is shown in Fig.7.8A and 7.8B respectively for the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE). By increasing the concentration of DA from \( 1\mu \)M to 600 \( \mu \)M and 0.129 \( \mu \) to 0.0429 M the graph of \( i_{pa} \) vs concentration of DA and UA shows an increase in anodic peak current as shows three linear ranges (Figure 7.9a and 7.9b). According into reported literatures [35, 36] state that it may be due to kinetic limitations decrease its sensitivity (slope of calibration of plot) and due to this, it shows different linear range in calibration plot. The obtained linear ranges equations for DA and UA concentration are shown in Table-7.2. The detection limit for DA and UA in the lower concentration linear range region was found to be 0.062 \( \mu \)M for DA is less than reports literatures [37-40] and 0.97 \( \mu \)M for UA is less than reports literatures [41-44] respectively for MCPE and was calculated according to the
recent reports [37] and calculated by using the same formula. The sensitivity is found to be 59.26 μA/μM.cm² for DA better than reported [45] and 1.18 μA/μM.cm² for UA better than reported [46].

7.5.5. Detection of DA, UA and AA mixture

AA and UA were present along with DA in mammalian brain and the concentrations of these were much higher than that of DA. Hence the NiO/ZnO hybrid nanoparticles MCPE is applied for electrochemical analysis of DA (1x10⁻⁵ M) in the presence of UA (0.5x10⁻⁴ M) and AA (1x10⁻⁴ M) in 0.2M phosphate buffer solution of pH 7.4. The obtained results show that voltammetric peak between DA and UA is 0.2V and AA oxidation peak is merged with DA oxidation peak as shown in Figure 7.10a and 7.11a. Therefore based on reported literature [14], the SDS/ polyglycine/ NiO/ZnO hybrid nanoparticle MCPE was prepared and applied for electrochemical analysis of DA (1x 10⁻⁵ M) in the presence of UA (0.5x10⁻⁴ M) and AA (1x10⁻⁴ M) in 0.2M phosphate buffer solution of pH 7.4. The obtained results exhibit enhanced peak currents response, separation and selectivity for analysis of DA, UA and AA. The oxidation peak potentials of DA, AA and UA were at 0.236, 0.019 and 0.348 V respectively. The peak to peak separation of DA-AA is 0.218 V and that of DA-UA is 0.112 V. This results were large sufficient to identify DA in the presence of AA and UA at SDS/ polyglycine/ NiO/ZnO hybrid nanoparticle MCPE as shown in Figure 7.10b and 7.11b.

7.5.6. Real Sample Analysis

Abnormal concentrations of DA and UA in body fluids influence the function of central nervous system; hence the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticle (MCPE) was applied to the determination of DA and UA content in healthy human blood serum samples applying the differential pulse voltammetric procedure. Using the proposed method, the uric acid and dopamine concentration was analyzed in healthy human blood serum from the results obtained are listed in Table 7.3. Procedure for real sample analysis is 1 ml of healthy human blood serum sample without any pretreatment were diluted to 100 ml with buffer respectively and diluted solutions were pipetted into each of series of 10 ml volumetric flasks and to
this, different known standard concentrations of DA and UA solutions were added and diluted to the mark with pH 7.4 phosphate buffer. The results are shown in Table.7.3 and the recovery and relative standard deviation (RSD) were acceptable, showing that the proposed methods could be efficiently used for the determination of DA and UA in real blood serum sample with recovery in the range ~97.00 to 99. % for both DA and UA analysis.

7.6. Conclusions

1. NiO/ZnO hybrid nanoparticles were synthesized using simple microemulsion method.

2. The average crystalline size is found to be 28 nm.

3. SEM observations reveals flake-like with typical length in the range of several micrometers with a tendency to form 40-50 nm thin NiO/ZnO hybrid nanoparticles.

4. The modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticle (MCPE) exhibits stable enhanced electrocatalytic activity, sensitivity, surface area of electrode, low detection limit and high linear range in 0.2M phosphate buffer solution at pH 7.4 compare with bare CPE and other previous reports.

5. The proposed methods can be applied to the detection of DA and UA in blood serum samples.

6. Therefore present method extended to many metal oxides, ferrites for synthesis and their modified electrode in the field of electroanalytical chemistry and biosensors.
Fig. 7.1. XRD patterns for NiO/ZnO hybrid nanoparticles sample

Fig. 7.2. IR Spectra of NiO/ZnO hybrid nanoparticles samples
Fig. 7.3. SEM images of NiO/ZnO hybrid nanoparticles samples

Fig. 7.4. EDS of NiO/ZnO hybrid nanoparticles samples
Fig. 7.5. Cyclic voltammograms of 1X10^-4 M DA (a) and 1X10^-4 M UA (b) at solid line for modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE) and at dotted line for bare CPE.

Fig. 7.6. Cyclic voltammograms of 1X10^-4 M DA (a) and 1X10^-4 M UA (b) for the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE) with different scan rates (0.1, 0.150, 0.200, 0.250, 0.300, 0.350, 0.400, 0.450, 0.500, 0.550, and 0.600 V/s) in pH 7.4 PBS.
Fig. 7.7. Graph of anodic peak current versus the square root of the scan rate for DA (a) and UA (b) for the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE)
Fig. 7.8A shows Differential pulse voltammograms of (a) $1 \times 10^{-6}$ M, (b) $2 \times 10^{-6}$ M, (c) $3 \times 10^{-6}$ M, (d) $4 \times 10^{-6}$ M, (e) $5 \times 10^{-6}$ M, (f) $6 \times 10^{-6}$ M, (g) $7 \times 10^{-6}$ M, (h) $8 \times 10^{-6}$ M, (i) $9 \times 10^{-6}$ M, (j) $1 \times 10^{-5}$ M, (k) $5 \times 10^{-5}$ M, (l) $1 \times 10^{-4}$ M, (m) $2 \times 10^{-4}$ M, (n) $3 \times 10^{-4}$ M, (o) $4 \times 10^{-4}$ M, (p) $5 \times 10^{-4}$ M, (q) $6 \times 10^{-4}$ M DA and Fig. 7.8B shows Differential pulse voltammograms of (a) $1.29 \times 10^{-5}$ M, (b) $2.29 \times 10^{-5}$ M, (c) $3.29 \times 10^{-5}$ M, (d) $4.29 \times 10^{-5}$ M, (e) $5.29 \times 10^{-5}$ M, (f) $6.29 \times 10^{-5}$ M, (g) $7.29 \times 10^{-5}$ M, (h) $8.29 \times 10^{-5}$ M, (i) $9.29 \times 10^{-5}$ M, (j) $1.29 \times 10^{-4}$ M, (k) $2.29 \times 10^{-4}$ M, (l) $3.29 \times 10^{-4}$ M, (m) $4.29 \times 10^{-4}$ M, (n) $5.29 \times 10^{-4}$ M, (o) $6.29 \times 10^{-4}$ M, (p) $7.29 \times 10^{-4}$ M, (q) $8.29 \times 10^{-4}$ M, (r) $1.29 \times 10^{-3}$ M, (s) $2.29 \times 10^{-3}$ M, (t) $4.29 \times 10^{-3}$ M, (u) $6.29 \times 10^{-3}$ M, (v) $9.29 \times 10^{-3}$ M, (w) $1.29 \times 10^{-2}$ M, (x) $4.29 \times 10^{-2}$ M, (y) $9.29 \times 10^{-2}$ M, (z) $0.142$ M and (z1) $0.192$ M UA in $0.2$M phosphate buffer solution of pH 7.4 at MCPE.
Fig. 7.9. Graph of peak current versus concentration of DA (A) and UA (B) shows three linear range (I, II and III).

Fig. 7.10 (a) Cyclic voltammogram for simultaneous determination of $1 \times 10^{-5}$ M DA, $1 \times 10^{-4}$ M AA and $0.5 \times 10^{-4}$ M UA at NiO/ZnO hybrid nanoparticles MCPE (dashed line) and (b) at SDS/polyglycine/ NiO/ZnO hybrid nanoparticle MCPE (solid line) with the scan rate of 0.1Vs$^{-1}$.
Fig. 7.11 (a) Differential voltammograms for simultaneous determination of $1 \times 10^{-5}$ M DA, $1 \times 10^{-4}$ M AA and $0.5 \times 10^{-4}$ M UA at NiO/ZnO hybrid nanoparticles MCPE and (b) at SDS/ polyglycine/ NiO/ZnO hybrid nanoparticle MCPE at 0.1Vs$^{-1}$.
Table 7.1: Water content affected by different ratio of surfactant to co-surfactant

<table>
<thead>
<tr>
<th>SDS: Hexanol (w)</th>
<th>Cyclo Hexane (g)</th>
<th>Water (ml)</th>
</tr>
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<tr>
<td>1:4</td>
<td>5</td>
<td>0.3</td>
</tr>
<tr>
<td>2:3</td>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>1:1</td>
<td>5</td>
<td>0.2</td>
</tr>
<tr>
<td>3:2</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>4:1</td>
<td>5</td>
<td>0.1</td>
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Table 7.2: Calibration curve parameters for the determination of DA and UA.

<table>
<thead>
<tr>
<th></th>
<th>Linear range</th>
<th>Concentration ranges</th>
<th>Regression equations (i_p vs C)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>DA</td>
<td>First</td>
<td>1 to 6 µM</td>
<td>i_p (µA) = 3.011×10^-6 + 1.778 C (µM/L)</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>Second</td>
<td>7 to 100 µM</td>
<td>i_p (µA) = 1.3033×10^-5 + 0.1442C(µM/L)</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>Third</td>
<td>150 to 700 µM</td>
<td>i_p (µA) = 2.738×10^-5 + 0.02368C(µM/L)</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>First</td>
<td>12.9 µ to 0.629 mM</td>
<td>i_p (µA) = 4.0075×10^-6 + 0.03549C(µM/L)</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>Second</td>
<td>0.729 to 6.29 mM</td>
<td>i_p (µA) = 3.172×10^-5 + 0.000898 C(µM/L)</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>Third</td>
<td>9.29 m to 0.142 M</td>
<td>i_p (µA) = 4.672×10^-5 + 0.00004423 C(µM/L)</td>
<td>0.990</td>
</tr>
<tr>
<td>UA</td>
<td>First</td>
<td>12.9 µ to 0.629 mM</td>
<td>i_p (µA) = 4.0075×10^-6 + 0.03549C(µM/L)</td>
<td>0.996</td>
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<tr>
<td></td>
<td>Second</td>
<td>0.729 to 6.29 mM</td>
<td>i_p (µA) = 3.172×10^-5 + 0.000898 C(µM/L)</td>
<td>0.985</td>
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<tr>
<td></td>
<td>Third</td>
<td>9.29 m to 0.142 M</td>
<td>i_p (µA) = 4.672×10^-5 + 0.00004423 C(µM/L)</td>
<td>0.990</td>
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Table 7.3: Determination of DA and UA in human blood serum sample

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<tr>
<th>Sample</th>
<th>DA added (µM)</th>
<th>UA added (µM)</th>
<th>DA</th>
<th></th>
<th></th>
<th>RSD (%)</th>
<th></th>
<th></th>
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<th>RSD (%)</th>
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<tbody>
<tr>
<td></td>
<td>Found (µM)</td>
<td>Recovery (%)</td>
<td></td>
<td>Found (µM)</td>
<td>Recovery (%)</td>
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<tr>
<td>1</td>
<td>19.6</td>
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<td>3</td>
<td>49.9</td>
<td>99.8</td>
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<td>49.8</td>
<td>99.17</td>
<td>1.98</td>
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7.7. References


CuO nanoparticle sensor for the electrochemical determination of dopamine

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Differential pulse voltammetry

**A B S T R A C T**

In the present work, different shaped CuO nanoparticles were synthesized using cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) in a co-precipitation method. The CuO nanoparticles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared absorption spectroscopy (IR) and UV-visible absorption spectroscopy (UV–vis). The prepared CuO nanoparticles were used for the preparation of modified carbon-paste electrodes (MCPE) for the electrochemical detection of dopamine (DA) at pH 6.0. The MCPE prepared from flake-shaped CuO nanoparticles exhibited an enhanced current response for DA. Electrochemical parameters, such as the surface area of the electrode, the heterogeneous rate constant ($k_h$) and the lower detection limit ($5.5 \times 10^{-8}$ M), were calculated and compared with those of the MCPE prepared from rod-shaped CuO nanoparticles. The MCPE prepared from SDS/polyglycine flake-shaped CuO nanoparticles exhibited a further improved current response for DA and a high selectivity ($E_{DA} - E_{AA} = 0.28 \text{V}$) for the simultaneous investigation of DA and ascorbic acid (AA) at pH 6.0. The modified carbon-paste electrochemical sensors were compared, and the MCPE prepared from SDS/polyglycine flake-shaped CuO nanoparticles exhibited better performance than the MCPE prepared from CTAB/polyglycine flake-shaped CuO nanoparticles.

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1. Introduction

Copper (II) oxide is a p-type metal oxide semiconductor with a narrow band-gap that exhibits a versatile range of properties. It has been effectively used in the fabrication of electrical, optical and photovoltaic devices, heterogeneous catalysis, magnetic storage media, gas sensing, field-emission (FE) emitters and lithium-ion electrode materials [1,2]. Recently, the synthesis of leaf-like CuO nanoparticles and a Nafion/GOD/CuO modified electrode for the detection of glucose [3] and the synthesis of shuttle-like CuO nanoparticles and a CuO nanoparticles/poly(thionine) glassy carbon electrode for determination of Hg(II) in water samples have been reported [4]. CuO nanoparticles and their modified gold electrode have been used to investigate rutin [5]. A CuO-nanoparticle-modified sol-gel-derived carbon ceramic prepared by microwave irradiation has been applied for the determination of adenine at very low potentials [6]. Additionally, a Au-nanoplates-modified ITO electrode for the oxidation of dopamine (DA) and ascorbic acid (AA) exhibits good electrocatalytic activity than spherical gold-nanoparticle-modified ITO electrode [7].

DA is a prevalent catecholamine neurotransmitter in the brain. Degeneration of dopaminergic neurons is the predominant cause of Parkinson’s disease (PD), with which approximately 500,000 people in the United States have been diagnosed [8], and causes reduced DA concentrations, even DA depletion, in the striatum and probably in other basal ganglia areas [9,10]. DA is electrochemically active (oxidizable), which allows electrochemical techniques to be employed for the detection of DA levels. Electrochemical detection is a simple, sensitive and environmentally friendly detection method that is even suitable for the analysis of colored or turbid samples. However, the electrochemical detection of DA in physiological samples is challenging because of the high concentrations of ascorbic acid (AA) (0.2–0.5 mM) that accompany the low concentrations of DA ($10^{-8}$ to $10^{-7}$ M) in physiological samples [9,11,12]. In addition, DA exists in cationic form, whereas AA is in an anionic form. AA is not only an electrochemically active (oxidizable) compound but is also electrochemically oxidized at a potential close to that of DA at conventional unmodified electrodes [9,13,14].

The literature contains several reports that claim to have solved this problem. The reported approaches include the use of an IL N-butylpyridinium hexafluorophosphate (BPPF$_6$) MCPE [15], a ZnO MCPE [16], a ZnO/redox mediator composite–film-coated GCE [17], a polyglycine film coated on CPE [18], a poly(calmagite) film coated on CPE [19] and a SDS MCPE [20]. In a solution if the concentration of SDS is greater than that of CMC, a separation between the peaks of...
AA and DA, $E_{AA} - E_{DA}$, of 0.238 V is possible using a CPE [21] A cytoc/trimethyl ammonium bromide (CTAB) solution has also enabled the separation of the oxidation peak potentials of AA and DA with a 1:1 hexacyanoferrate-modified CPE [22].

Rod-shaped CuO nanoparticles have been synthesized using a one-step annealing process in air with copper plates as the starting material [23], and flake-shaped CuO nanoparticles have been synthesized by a hydrothermal method [24]. In the present work, rod and flake-shaped CuO nanoparticles were synthesized with a simple co-precipitation process based on a modified version of the method reported in the literature [25,26]. The synthesized CuO nanoparticles were characterized by XRD, SEM, TEM, IR spectroscopy and UV–vis spectroscopy. The obtained CuO nanoparticles were used for the preparation of a modified carbon-paste electrode (MCPE) for the electrochemical investigation of dopamine in the pH range from 5.5 to 8.0. The MCPE showed a maximum redox peak current at pH 6.0, and the redox peak was pH-dependent with a slope of 0.038 V/pH. Various electrochemical parameters of the MCPEs were calculated and compared, including the surface areas of the electrodes, the heterogeneous rate constants ($k_h$), the diffusion coefficients ($D_0$) and the detection limits. The MCPE prepared with flake-shaped CuO nanoparticles exhibited enhanced electrochemical parameters compared with those of the MCPE prepared with rod-shaped CuO nanoparticles. However, the MCPE prepared with flake-shaped CuO nanoparticles exhibited a peak-separation potential, $E_{AA} - E_{DA}$, of 0.12 V, which was not sufficient for the analysis of DA in the presence of AA. To solve this problem, MCPEs were prepared using a variety of different films, such as polyglycine flake-shaped CuO nanoparticles, SDS/polyglycine flake-shaped CuO nanoparticles, and polyglycine/CTAB modified CuO nanoparticles. The obtained results were compared based on enhanced redox peak currents for DA and electrochemical oxidation peak potential separation between DA and AA. The MCPE prepared with SDS/polyglycine flake-shaped CuO nanoparticles exhibited excellent redox peak current enhancement and a higher selectivity (peak separation potential of $E_{AA} - E_{DA} = 0.28$ V) than that exhibited by the MCPE prepared with flake-shaped CuO nanoparticles. The MCPE prepared from SDS/polyglycine flake-shaped CuO nanoparticles exhibited a linear increase in anodic peak current with an increased concentration of DA. Therefore, the MCPE prepared with SDS/polyglycine flake-shaped CuO nanoparticles can be used as an electrochemical sensor for the analysis of DA in the presence of an excess amount of AA.

2. Experimental methods

2.1. Apparatus

The CuO nanoparticles were characterized by various techniques. Powder XRD patterns were recorded on a Philips XRD X'Pert Pro diffractometer equipped with a Cu Ka radiation ($\lambda = 1.5438$ Å) source. IR absorption spectra were recorded on a Perkin Elmer Spectrum 1000 FTIR spectrometer on thoroughly dried samples using KBr pellets as diluents. UV–vis spectra were obtained on a Perkin Elmer Lambda 950 spectrophotometer. The CuO nanoparticles were studied using a JEOL JSM-840 scanning electron microscope and a JEOL 2000FX II transmission electron microscope equipped with ultra-thin windows from Oxford Instruments. All of the electrochemical experiments were performed using a single-compartment, three-electrode cell with MCPEs prepared with CuO nanoparticles, polyglycine flake-shaped CuO nanoparticles, SDS/polyglycine flake-shaped CuO nanoparticles, and CTAB/polyglycine flake-shaped CuO nanoparticles as the working electrode. An aqueous saturated calomel electrode (SCE) was used as the reference electrode, and a Pt wire served as the auxiliary electrode. All potentials were measured and reported versus the SCE. The cyclic voltammetry (CV) measurements and differential pulse voltammetry (DPV) techniques were performed on a model 660C (CH Instruments) potentiostat/galvanostat.

2.2. Materials

CuSO$_4$ 6H$_2$O was purchased from S D Fine Chemicals. Absolute ethanol (99.9%), sodium hydroxide (NaOH), and graphite powder were from Merck Chemicals, and AA, CTAB, and SDS were purchased from Himedia Chemicals. DA stock solutions were prepared in 0.1 M perchloric acid. Phosphate buffer was prepared, and the pH was adjusted by the addition of 0.2 M NaH$_2$PO$_4$ and Na$_2$HPO$_4$ solutions. All the aqueous solutions were prepared with double-distilled water.

2.3. Preparation of CuO nanoparticles

The rod- and flake-shaped CuO nanoparticles were synthesized according to the co-precipitation method described elsewhere [25,26], with minor modifications. In a typical experiment, the first solution contained 0.01 M CuSO$_4$ 6H$_2$O and 0.02 M SDS, and the second solution contained 0.02 M NaOH. All the solutions were prepared using distilled water. The first solution was added to the second solution with continuous stirring. The resulting brown-colored precipitate was filtered through Whatman filter paper (grade 41) and dried at 80°C in a hot-air oven for approximately 1 h. The dried precipitate was transferred to a silica crucible and ignited at 400°C for approximately 3 h. The obtained powder was then washed with ethanol three or four times to remove impurities present in the CuO nanoparticles. The same procedure was followed for the preparation of CuO nanoparticles using CTAB as the surfactant.

2.4. Preparation of bare carbon-paste electrode and modified carbon-paste electrode

The bare carbon-paste electrode (bare CPE) was prepared by hand mixing 80% graphite powder with 20% silicon oil in an agate mortar for approximately 30 min to produce a homogenous carbon paste. The paste was packed into the homemade cavity and smoothed on a piece of weighing paper. The modified carbon-paste electrode (MCPE) was prepared by the addition of 30 mg of CuO nanoparticles to the previously prepared graphite powder/silicon oil mixture.

2.5. Preparation of polyglycine flake-shaped CuO nanoparticle modified carbon-paste electrode

The following procedure was used to pack the paste and apply a polyglycine film onto the MCPE prepared from flake-shaped CuO nanoparticles [18]. Electrochemical polymerization of glycine on the MCPE prepared from flake-shaped CuO nanoparticles was performed using a cyclic voltammetric method in an aqueous solution that contained 0.04 M glycine in 0.2 M acetate buffer solution at pH 5.0. Electrolysis was achieved by the formation of a film that grew between -0.5 V and 1.8 V at a scan rate of 0.100 V/s for five cycles using CV. After polymerization, the electrode was thoroughly washed with distilled water.
2.6. Preparation of SDS/polyglycine/flake-shaped CuO nanoparticle and CTAB/polyglycine/flake-shaped CuO nanoparticle modified carbon paste electrode

SDS solution (10 μL) was added to the surface of the MCPE prepared from polyglycine/flake-shaped CuO nanoparticles for 5 min. The electrode was later thoroughly rinsed with water to remove unabsorbed modifier and dried in air at room temperature. The same procedure was followed for the preparation of the MCPE prepared from CTAB/polyglycine/flake-shaped CuO nanoparticles using a CTAB solution (10 μL).

3. Results and discussion

3.1. Characterization

The XRD pattern of the obtained CuO nanoparticles is shown in Fig. 1. All peaks in figures (A (SDS)) and (B (CTAB)) can be well indexed to the monoclinic structure of copper oxide (ICPDS PDF, no. 05-0661) with high crystallinity. No impurity peaks of other copper oxides were observed, which indicates the high purity of the products. The crystalline sizes of the CuO nanoparticles were calculated using the Debye–Scherrer formula. The average crystalline size is tabulated in Table 1.

The IR transmittance spectrum for the CuO nanoparticles synthesized using SDS is displayed in Fig. 2(A). The peaks at approximately 2923, 2858, 1439 and 1113 cm⁻¹ are due to O–H stretching and bending. These band vibrations provide evidence for the incorporation of SDS into the copper oxide. Broad peaks at approximately 2100 cm⁻¹ are assigned to C=CH₂ asymmetric stretching and symmetric (2924 cm⁻¹) and asymmetric (2852 cm⁻¹) stretching vibrations of C–CH₃ in the methylene chains. The sharp bands in the region of 1439 cm⁻¹ are attributed to the deformation of –CH₂– and –CH₃ groups [30] in the incorporated surfactants. The weak bands detected in the region of 2924 and 2852 cm⁻¹ were assigned to C–CH₃ asymmetric stretching and N–CH₃ symmetric stretching vibrations of the solid and the surfactant, respectively. These band vibrations provide evidence for the incorporation of CTAB into the copper oxide. The broad band between 3200 and 3600 cm⁻¹ and the band centered at 1630 cm⁻¹ were observed for all samples and assigned to O–H stretching and deformation vibrations of weakly bound water. Furthermore, the presence of bands at 1113 cm⁻¹ clearly indicates the binding of CTAB molecules to the CuO [32,33]. The sharp peak at 509 cm⁻¹ is attributed to the framework vibrations of copper oxide [33].

The surface morphology of the samples obtained using SDS and CTAB was examined using SEM and TEM; the images are shown in Fig. 3(A)–(D). The SEM and TEM images clearly show different morphologies and sizes for CuO nanoparticles prepared in different surfactants. A rod-like morphology was observed for CuO nanoparticles (SDS) in the SEM image in Fig. 3(A) and in the corresponding TEM image for the same sample in Fig. 3(C). Upon close examination, the particles in the TEM image were observed to be rod-shaped with a width of approximately 100 nm and a length of 200 nm. Flake-like morphology was observed for the CuO nanoparticles (CTAB) in the SEM image in Fig. 3(B) and in the corresponding TEM image for the same sample in Fig. 3(D). The particles, upon close inspection in the TEM image, were observed to be round and flake-shaped with a size of approximately 25 nm.

The UV–visible absorption spectra of the prepared CuO nanoparticles dispersed in ethanol solution show broad absorption peaks centered at approximately 366 nm for the flake-shaped CuO nanoparticles and at 394 nm for the rod-shaped CuO nanoparticles, as shown in Fig. 4(A) and (B). The UV–visible absorption spectra for both types of CuO nanoparticles show clear evidence that the absorption wavelength of the flake-shaped CuO nanoparticles was assigned to asymmetric (2924 cm⁻¹) and symmetric (2852 cm⁻¹) stretching vibrations of C–CH₃ in the methylene chains. The sharp bands in the region of 1439 cm⁻¹ are attributed to the deformation of –CH₂– and –CH₃ groups [30] in the incorporated surfactants. The weak bands detected in the region of 2924 and 2852 cm⁻¹ were assigned to C–CH₃ asymmetric stretching and N–CH₃ symmetric stretching vibrations of the solid and the surfactant, respectively. These band vibrations provide evidence for the incorporation of CTAB into the copper oxide. The broad band between 3200 and 3600 cm⁻¹ and the band centered at 1630 cm⁻¹ were observed for all samples and assigned to O–H stretching and deformation vibrations of weakly bound water. Furthermore, the presence of bands at 1113 cm⁻¹ clearly indicates the binding of CTAB molecules to the CuO [32,33]. The sharp peak at 509 cm⁻¹ is attributed to the framework vibrations of copper oxide [33].

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### Table 1
Comparison between rod-shaped and flake-shaped CuO nanoparticles and their electrocatalytic performances.

<table>
<thead>
<tr>
<th>CuO nanoparticles</th>
<th>Average crystalline size (nm)</th>
<th>Size of CuO nanoparticles (nm) from TEM image</th>
<th>UV-visible maxima absorption (nm)</th>
<th>Surface area of MCPE (cm²)</th>
<th>Charge transfer coefficient at MCPE (μ)</th>
<th>Number of electrons at MCPE (n)</th>
<th>Electron transfer rate constant at MCPE (k,)(s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flake shaped</td>
<td>37.2</td>
<td>~25</td>
<td>366</td>
<td>0.08081</td>
<td>0.654</td>
<td>2.066</td>
<td>0.5496</td>
</tr>
<tr>
<td>Rod shaped</td>
<td>110</td>
<td>~100 width and 200 length</td>
<td>394</td>
<td>0.0767</td>
<td>0.644</td>
<td>1.88</td>
<td>0.4314</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns for CuO nanoparticle samples prepared using (A) SDS and (B) CTAB.

Fig. 2. IR spectra of CuO nanoparticle samples prepared using (A) SDS and (B) CTAB.
blue-shifted compared to that of the rod-shaped CuO nanoparticles. The obtained wavelengths of maximum absorption are tabulated in Table 1.

3.2. Mechanisms

According to Yin et al. [34], the mechanism of the effect of SDS on the formation of rod-shaped CuO nanoparticles may be explained as follows: first, in aqueous solution, the hydrophilic group will point to the outer surface of the capsule, while the hydrophobic end points inward due to the electrostatic interaction of the sulfonic groups and the Cu$^{2+}$ ions. The outer surface of the hydrophilic end is occupied by numerous Cu$^{2+}$ ions. When this solution is subsequently added dropwise to the 0.02 M NaOH solution, it then contains hydroxy! groups that react to form dodecyl sulfate copper hydroxide ion (DS Cu(OH)$_2$); these ion nuclei will form active sites to generate DS [Cu(OH)$_2$]$_n$ rod-like structures. After calcination, the water molecules are removed to form DS [CuO]$_n$ rod-like nanostructures.

The mechanism of the effect of CTAB on the formation of flake-shaped CuO nanoparticles may be explained as follows: first, in aqueous solution, the hydrophilic group will point to the outer surface of the capsule, while the hydrophobic end points inward. After the solutions of the cetyltrimethyl ammonium ion (CTA$^+$) group and Cu$^{2+}$ ions are added dropwise to 0.2 M NaOH solution, it contains hydroxyl groups that react to form Cu(OH)$_2$' ion nuclei, which surround the CTA$^+$ groups due to electrostatic interactions. These ion nuclei subsequently form active sites to generate [Cu(OH)$_2$]$_n$ flake-like structures with the surrounding CTA$^+$ groups. After calcination, the water molecules are removed to form the CTA [CuO]$_n$ flake-like nanostructures.

3.3. Effect of pH

The effect of pH on the determination of DA in PBS solution at the MCPE prepared with CuO nanoparticles was carefully investigated in the pH range of 5.5–8.0. Graphs of $i_{pa}$ (A) versus the pH of the solution and $E^{\circ}$ (V) versus the pH of the solution for MCPEs prepared with flake- and rod-shaped CuO nanoparticles are shown in Fig. 5(A) and (B), respectively. The anodic peak current of DA increases with increasing pH values until the pH reaches 6.0–6.5; the anodic peak current then decreases with further increases in the pH. The maximum anodic peak current occurred at pH 6.0. Therefore, PBS with a pH of 6.0 was selected for all subsequent electrochemical DA analyses. The formal potential ($E^{\circ}$) of DA decreased with an increase in the pH value. A linear regression equations
Fig. 5. Plot of DA oxidation peak current versus PBS solution pH (5.5-8.0) and formal potential versus PBS solution pH (5.5-8.0) at a scan rate 0.100 V s⁻¹ for (A) the MCPE prepared with flake-shaped CuO nanoparticles and (B) the MCPE prepared with rod-shaped CuO nanoparticles.

Scheme 1. Schematic illustration of the catalysis of DA.

obtained were $E^0 (V) = -0.03691 \text{ pH} + 0.3968$ ($n=6, \gamma = 0.986$) for the MCPE prepared with flake-shaped CuO nanoparticles and $E^0 (V) = -0.0390 \text{ pH} + 0.428$ ($n=6, \gamma = 0.996$) for the MCPE prepared with rod-shaped CuO nanoparticles. The slopes were 0.0369 and 0.039 V/pH, respectively, which were nearly half of the theoretical value of −0.0576 V/pH at 18 °C. The results indicate that two-electron transfer accompanied by two-proton transfer occurred, which was identical to the results reported by Sun et al. [15] and by Bath et al. [35]. According to the above results, the electrode process for DA on the MCPE prepared with CuO nanoparticles is shown in Scheme 1.

3.4. Electrochemical response of DA at the bare electrode and the MCPE

The electrochemical responses of $5 \times 10^{-5}$ M DA in 0.2 M phosphate buffer solution of pH 6.0 at the bare CPE and at the MCPE prepared with CuO nanoparticles were measured at a scan rate of 0.200 V s⁻¹. The corresponding peak-potential differences, $\Delta\Delta E_p$, of 0.159 V, 0.097 V and 0.084 V for the bare CPE and the MCPEs prepared from rod- and flake-shaped CuO nanoparticles, respectively, are shown in Fig. 6(A)-(C). The result indicates both CuO nanoparticles exhibit good electrocatalytic activity than bare CPE and among CuO nanoparticles a flake-shaped CuO nanoparticles exhibit enhanced current response with slight reduction of over potential than the rod-shaped CuO nanoparticles. This shows that the MCPEs prepared from flake-shaped CuO nanoparticles exhibit good electrocatalytic activity.

3.5. The effect of scan rate

The effect of scan rate for DA in phosphate buffer solution at pH 6.0 was studied by CV at MCPEs prepared from flake- and rod-shaped CuO nanoparticles. The results in Figs. 7(A) and (D) show an increase in the redox peak current at a scan rate of 0.01-0.800 V s⁻¹ for MCPEs prepared from flake- and rod-shaped CuO nanoparticles, respectively. The graph obtained exhibited good linearity between the square root of the scan rate ($v^{1/2}$) and the redox peak currents for the MCPE prepared with flake-shaped CuO nanoparticles, with correlation coefficients of $r^2 = 0.999$ and 0.999 as shown in Fig. 7(B). The MCPE prepared from rod-shaped CuO nanoparticles exhibited correlation coefficients of $r^2 = 0.996$ and 0.998, as shown in Figs. 7(E). These results indicate that the electron-transfer reaction of MCPEs prepared with both rod- and flake-shaped CuO nanoparticles was a diffusion-controlled process. The surface area available for the electron transfer to species in the solution can be estimated by the Randles–Sevcik equation (1) [36,37]. This equation relates the peak current for an electron-transfer-controlled process with the square root of the scan rate:

$$I_p = 2.69 \times 10^{5} n^{1/2} A D^{1/2} C V_{Cu}^{1/2}$$

(1)

where $I_p$ is the peak current (A), $A$ is the electroactive area (cm²), $C$ is the concentration of the electroactive species (mol cm⁻³), $n$ is the number of exchanged electrons, $D$ is the diffusion coefficient (cm² s⁻¹) and $v$ is the scan rate (V s⁻¹). The values of the diffusion coefficients were obtained from the slopes of the $I_p$ versus $v^{1/2}$ plots shown in Figs. 7(B) and (E). The surface area of both of the MCPE electrodes prepared from CuO nanoparticles were calculated using Eq. (1); the results are presented in Table 1.

The MCPE electrodes prepared from CuO nanoparticles shows diffusion-controlled process and the peak-to-peak separation ($\Delta E_p$) was 0.097, 0.084 V and the ratio of redox peak currents ($I_{pa}/I_{pc}$) was 1.36,1.44 which were the characteristics of a quasi-reversible electrode process. Sun et al. [15], was successfully applied the below equation for diffusion-controlled and...
The relationship of the peak potentials with the scan rate was observed. The redox peak potentials increase as the scan rate increases. $E_{pa} = E^0 + \frac{RT}{\alpha n F} \ln \nu$, (2) $E_{pc} = E^0 + \left( \frac{RT}{(1 - \alpha) n F} \right) \ln \nu$, (3) and

$$\log k_s = \alpha \log (1 - \alpha) + (1 - \alpha) \log \alpha - \log \left( \frac{RT}{n F \nu} \right) - \left( 1 - \alpha \right) \frac{\alpha F \Delta E_p}{2.3RT}$$

where $\alpha$ is the charge-transfer coefficient, $n$ is the number of electrons transferred, $k_s$ is the electron-transfer rate constant, $E^0$ is the formal potential, $F$ is the Faraday constant, $E_{pa}$ is the anodic peak potential and $E_{pc}$ is the cathodic peak potential. The redox peak potentials increase as the scan rate increases. The relationship of the peak potentials with the scan rate was constructed and could be used for the calculation of the electrochemical parameters. A linear relationship between $E_{pa}$ and $\ln \nu$ was established according to the Laviron equation [15,38], and two straight lines were obtained, as shown in Figs. 7(C) and (F) for the MCPEs prepared with flake- and rod-shaped CuO nanoparticles, respectively. The linear-regression equations calculated for the MCPEs prepared with flake- and rod-shaped CuO nanoparticles were $E_{pa} (V) = 0.01676 \times (V^{-1} \ln \nu + 0.2973) (V) (n = 10, \ T = 0.990)$, $E_{pc} (V) = 0.00982 \times (V^{-1} \ln \nu + 0.1355) (V) (n = 10, \ T = 0.993)$ and $E_{pa} (V) = 0.0176 \times (V^{-1} \ln \nu + 0.3036) (V) (n = 10, \ T = 0.990)$, $E_{pc} (V) = -0.00989 \times (V^{-1} \ln \nu + 0.12707) (V) (n = 10, \ T = 0.993)$, respectively. The charge-transfer coefficient ($\alpha$) and the number of electrons ($n$) were calculated according to Eqs. (2) and (3), and the electron-transfer rate constant ($k_s$) was calculated using Eq. (4). All of the calculation results are shown in Table 1.

The differential pulse voltammetry technique was used for the analysis of DA concentration, which was varied from 0.1 to 30 $\mu$M. The results for the MCPEs prepared from flake- and rod-shaped CuO nanoparticles are shown in Figs. 8(A) and (C), respectively. The corresponding graphs of anodic peak current versus concentration of DA shows two linear relationship ranges of $0.3$ to $1.4 \mu$M and $2$ to $20 \mu$M, with linear regression equations of $I_{pa} (\mu A) = 2.99 (C_{CuM/L}) + 0.56 \mu A$ and $I_{pa} (\mu A) = 3.03 (C_{CuM/L}) + 2.71 (\mu A)$, respectively. The correlation coefficient for the first linearity was 0.991, and that for the second was 0.998 for the MCPE prepared with flake-shaped CuO nanoparticles, as shown in Fig. 8(B). For DA concentrations of 0.6 to 1.4 $\mu$M and 2 to 20 $\mu$M, the linear-regression equations were $I_{pa} (\mu A) = 1.372 (C_{CuM/L}) + 0.853 (\mu A)$ and $I_{pa} (\mu A) = 0.193 (C_{CuM/L}) + 2.048 (\mu A)$, respectively. The correlation coefficient for the first linearity was 0.996, and that for the second was 0.997 for the MCPE prepared with rod-shaped CuO nanoparticles, as shown in Fig. 8(D). The decrease in the sensitivity (slope) in the second linear range was due to kinetic limitations [19,39]. The detection limits for DA in the lower concentration range was $5.52 \times 10^{-8} \mu$M for the MCPE prepared with flake-shaped CuO nanoparticles and $1.8 \times 10^{-7} \mu$M for the MCPE prepared with rod-shaped CuO nanoparticles. The limit of detection (LOD) was calculated according to the equation $LOD = 3S_0/K$, where $K$ is a constant related to the confidence level. In accordance with the suggestion of the IUPAC, the value of $K$ is 3 at the 99% confidence level, $S_0$ is the standard deviation of ten blank-solution measurements (no added DA), and $S$ is the slope of the calibration graph. The proposed electrode exhibited a relatively lower detection limit than those recently reported elsewhere [18,40–43](Table 2).

Table 1 shows a comparison between the rod-shaped CuO nanoparticles and flake-shaped CuO nanoparticles. The flake-shaped CuO nanoparticles exhibit a smaller average crystallite size and a smaller particle size with a significant blue shift. The MCPE prepared with the flake-shaped CuO nanoparticles exhibits a higher electrode surface area, a higher electron-transfer rate constant and a lower detection limit (shown in Table 2) compared with the MCPE prepared with the rod-shaped CuO nanoparticles. Therefore, the MCPE prepared with flake-shaped CuO nanoparticles may form hydrogen bonds with the hydroxyl groups of DA, which would activate the hydroxyl groups and weaken the bond energy of O–H to form dopaquinone [44]. The MCPE prepared from flake-shaped CuO nanoparticles can therefore be used as an electrochemical sensor for the investigation of DA in the presence of AA.

3.7. Simultaneous determination of DA and AA by DPV

According to recent reports [18,19,21,45,46], the separation of the oxidation peak potentials between DA and AA plays an important role for the analysis of DA in the presence of AA. Fig. 9(A)–(D) shows the separation of the oxidation peak potentials between DA and AA. The small separation of 0.12 V for the MCPE prepared with flake-shaped CuO nanoparticles may be due to a small amount of CTAB surfactants present on the CuO nanoparticles, as was clearly explained in recent reports [47,48]. The separations of the other
Fig. 8. Results for the MCPE prepared with CuO nanoparticles: (A) and (C) differential pulse voltammograms of (a) 6.0 x 10^{-6} M, (b) 8.0 x 10^{-6} M, (c) 10 x 10^{-6} M, (d) 2 x 10^{-5} M, (e) 3 x 10^{-5} M, (f) 5 x 10^{-5} M, (g) 10 x 10^{-5} M, (h) 2 x 10^{-4} M, (i) 3 x 10^{-4} M, (j) 5 x 10^{-4} M, (k) 2 x 10^{-2} M, (l) 3 x 10^{-2} M, and (m) 4 x 10^{-2} M in 0.2 M phosphate buffer solution at pH 6.0. (A) and (B) Graph of the peak current versus the concentration of dopamine for the flake-shaped (A and B) and rod-shaped (C and D) CuO nanoparticles.

Table 2
Comparison of the detection limits of different modified electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Detection limit (µM)</th>
<th>Techniques</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana/MWCNTs/MCPE</td>
<td>2.09</td>
<td>DPV</td>
<td>[41]</td>
</tr>
<tr>
<td>CCE/ferrocene carboxylic acid</td>
<td>0.45</td>
<td>SWV</td>
<td>[42]</td>
</tr>
<tr>
<td>Polyglycine/CPE</td>
<td>0.1</td>
<td>CV</td>
<td>[43]</td>
</tr>
<tr>
<td>MEI/SAM-Au electrode</td>
<td>1.1</td>
<td>CV</td>
<td>[43]</td>
</tr>
<tr>
<td>LDL/CEI</td>
<td>5.0</td>
<td>DPV</td>
<td>[40]</td>
</tr>
<tr>
<td>Rod shaped CuO nanoparticles/MCPE</td>
<td>0.18</td>
<td>DPV</td>
<td>Present work</td>
</tr>
<tr>
<td>Flake shaped CuO nanoparticles/MCPE</td>
<td>0.055</td>
<td>DPV</td>
<td>Present work</td>
</tr>
</tbody>
</table>

MCPEs were 0.16 V for the MCPE prepared with polyglycine/flake-shaped CuO nanoparticles, 0.26 V for MCPE prepared with CTAB/polyglycine/flake-shaped CuO nanoparticles and 0.28 V for MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles. The MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles shows a large peak-potential separation between DA and AA compared with both of other MCPEs in this study and recently reported results in the literature [15,19,21,45,46]. The DPV analysis of DA in the presence of AA exhibits a linear increase in the anodic peak current with an increase in the concentration of DA, as shown in Fig. 10(A). The graph of the peak current versus the concentration of DA also exhibited good linearity, as shown in Fig. 10(B). Therefore, SDS/polyglycine/flake-shaped CuO nanoparticles modification was prior to the selective detection of DA in the presence of AA. Our results suggested the possibility of a simultaneous multi-detection system based on the DPV method.

3.8. Electrochemical current response for DA at different MCPEs

Fig. 11 shows the electrochemical responses of 1 x 10^{-5} M DA in 0.2 M phosphate buffer solution at pH 6.0 at the MCPE prepared with flake-shaped CuO nanoparticles and at the MCPE prepared with different films of flake-shaped CuO nanoparticles at a scan rate of 0.05 V s^{-1}. The MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles exhibited an enhanced current response with sharp redox peak for DA compared with the MCPE prepared with CTAB/polyglycine/flake-shaped CuO nanoparticles, polyglycine/flake-shaped CuO nanoparticles and flake-shaped CuO nanoparticles. The current enhanced was found to be 18 µA compared with the MCPE prepared with flake-shaped CuO nanoparticles.

Fig. 9. Differential pulse voltammograms of 1 x 10^{-6} M DA in 0.2 M phosphate buffer solution of pH 6.0 in the presence of 2.0 x 10^{-4} M AA for peak separation between DA and AA at different MCPE: (A) MCPE prepared from flake-shaped CuO nanoparticles, (B) MCPE prepared with polyglycine/flake-shaped CuO nanoparticles, (C) MCPE prepared with CTAB/polyglycine/flake-shaped CuO nanoparticles and (D) MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles.

3.9. The effect of scan rate for DA at the MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles

The effect of the scan rate for DA was studied by CV at the MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles; the results show an increase in the redox peak current with an increase in the scan rate (0.01–0.800 V s^{-1}), as shown in Fig. 12(A). The peak current versus scan rate (ν) was
Fig. 10. (A) Differential pulse voltammograms of (a) 2.0 x 10^{-5} M, (b) 4.0 x 10^{-5} M, (c) 6.0 x 10^{-5} M, (d) 8.0 x 10^{-5} M, and (e) 1.0 x 10^{-4} M DA in 0.2 M phosphate buffer solution at pH 6.0 in the presence of 5.0 x 10^{-4} M AA at the MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles. (B) Graph of the anodic peak current versus the concentration of DA in the presence of AA.

Fig. 11. Cyclic voltammograms of 1 x 10^{-3} M DA at (A) the MCPE prepared with flake-shaped CuO nanoparticles, (B) the MCPE prepared with polyglycine/flake-shaped CuO nanoparticles, (C) the MCPE prepared with CTAB/polyglycine/flake-shaped CuO nanoparticles, and (D) the MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles at a scan rate of 0.050 V s^{-1}.

plotted. The graph obtained exhibited good linearity between the scan rates versus peak currents, as shown in Fig. 12(B). In the range from 0.01 to 0.800 V s^{-1}, both the anodic and cathodic peak currents were proportional to the scan rate (\(v\)). The correlation coefficient was 0.9994, which indicates the electrode reaction process was adsorption-controlled [49-51]. According to an equation previously reported [51] for determining the value of \(k^0\) from experimental \(\Delta E_p\) values, Eq. (5) was a valid approximation of such curves for \(\Delta E_p > 10\) mV. The values of \(k^0\) for the DA were determined from the experimental \(\Delta E_p\) values, the data in Table 3 and Eq. (5). The values of \(k^0\) indicate that strong adsorptions of reactants and products are involved. Here, the \(k^0\) is the heterogeneous rate constant, and \(\Delta E_p\) is the potential difference between the anodic and cathodic peak potentials. The heterogeneous rate constant (\(k^0\)) was estimated using Eq. (5). The value of \(k^0\) obtained at a scan rate of 0.100 V s^{-1} for the MCPE prepared with SDS/polyglycine/flake-shaped CuO nanoparticles exhibits a larger heterogeneous rate constant compared with those determined in other scan-rate-variation studies. The calculated data are tabulated in Table 3.

\[
\Delta E_p = 201.39 \log (\frac{\eta}{\mu}) - 301.78 \tag{5}
\]

4. Conclusions

The different shaped CuO nanoparticles were prepared by co-precipitation method and the electrochemical parameters are studied. The modified carbon paste shows effective sensor towards electrochemical investigation of DA in presence of AA. The prepared CuO nanoparticles MCPE shows low detection limit compared with the previous literatures. The SDS/polyglycine/flake shaped CuO nanoparticle MCPE shows significant effect of redox peak currents for DA and good electrochemical signal separation between DA and AA. Therefore, the present method could be extended to many metal oxides and ferrites for the synthesis of modified electrodes with good electrocatalytic activities for the simultaneous investigation of DA and AA and for bioactive molecules or neurotransmitters.

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Indian Institute of Science, Bangalore 560012, India for TEM, and to Dr. Michael Rajamathi of SL Joseph's College, 36 Lalbagh Road, Bangalore 560027, India for the IR spectra.

References

Synthesis of CdO Nanoparticles and their Modified Carbon Paste Electrode for Determination of Dopamine and Ascorbic acid by using Cyclic Voltammetry Technique

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Cadmium oxide (CdO) nanoparticles were prepared using cetyl trimethyl ammonium bromide (CTAB) as surfactant by co-precipitation method, in which cadmium sulphate (CdSO₄) was reacted with sodium hydroxide (NaOH) in the presence of acetic acid, ethanol, CTAB, at room temperature, then thermally treated at 400°C for 4 hours and the obtained product are analyzed by X-ray diffractometer (XRD), the average size of CdO nanoparticles found to be 47.8nm, UV-visible absorption spectra for CdO nanoparticles shows evidence of quantum size effect and compare with bare carbon paste electrode(BCPE), CdO nanoparticles modified carbon paste electrode(MCPE) shows enhanced peak current and exhibited excellent electrocatalytic activity towards oxidation of dopamine(DA) and ascorbic acid (AA) in acetate buffer solution at pH 6.5.

Keywords: Nanoparticles, CdO, XRD, UV-visible spectroscopy, modified carbon paste electrode, cyclic voltammetry.

1. INTRODUCTION

The science of nanomaterials has created great excitement and expectation in the last decade at the nanoscale fundamental properties changes for example a nanoscale wire or circuit component does not necessarily obey ohm’s law when we reach nanoscale everything will be change, including gold’s color, melting point and chemical properties [1]. Oxide nanomaterials used as catalysts and starting materials for preparing advanced structural ceramics [2-3]. CdO an important n-type semiconductor with a direct band gap of 2.5 eV and an indirect band gap of 1.98 eV [4], has promising applications in catalysts [5] sensors [6], nonlinear materials [7], solar cells [8], and other optoelectronic devices etc [9-
It has been reported that the physical and chemical properties of CdO are relative to its stoichiometry as well as particle shape and size, which, in turn, depend on its preparation methods and preparation conditions [9-14]. Recently, hollow nanostructures of inorganic materials have attracted great research attention [14-19] because they exhibit a lower density, higher surface area, and distinct optical property, and in most cases, have improved performances for applications in photonic crystals fillers, vehicle systems, catalysis, sensing devices. In nanoscience and nanotechnology synthesis forms an essential component. While nanomaterials have been generated by chemical methods have proved to be more effective, as they provide better control as well as enable different sizes shapes and functionalization than compare with the physical methods such as laser ablation, arc-discharge and evaporation chemical synthesis of nanomaterials has been reviewed by a few authors, (20-26) metal oxide nanoparticles can be produced by soft chemical methods, such as co-precipitation, sol-gel and hydrothermal synthesis [27]. Among these methods co-precipitation has chosen in the present work for synthesis of CdO nanoparticles by using CTAB as surfactant.

AA is one of the most important vitamins, due to its antioxidant and pH regulator properties, often being added to various food products and pharmaceuticals [29]. AA exists in mammalian brain in the presence of several other neurotransmitter amines including DA. DA is an important brain neurotransmitter molecule of catecholamine and its deficiency leads to brain disorders such as Parkinson's disease and Schizophrenia [29, 31]. Recently, their identification and determination of AA and DA with electrochemical procedures have attracted much attention.

In this paper, we report that synthesis of CdO nanoparticles using CTAB as surfactant by co-precipitation method and fabrication of carbon paste electrode with CdO nanoparticles. The modified electrodes are applied for determination of AA and DA by using cyclic voltammetric technique.

2. EXPERIMENTAL PART

2.1 Apparatus

Cyclic voltammetric experiments were performed with a model EA-201 Electro Analyzer (chemilink systems), equipped with a personal computer was used for electrochemical measurement and treating of data. A conventional three electrode cell was employed throughout the experiments, with bare or CdO nanoparticles modified carbon paste electrode (3.0 mm diameter) as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum electrode as a counter electrode.

2.2 Chemicals and Solutions

Cadmium sulphate, Sodium hydroxide, from S D fine chemicals, Graphite powder, Acetic acid (99.95%), Ethanol (99.5%), Hydrochloric acid, were from qualigens fine chemicals, CTAB was obtained from sigma, Ascorbic acid and Dopamine were purchased from Fluka. Acetate buffer was prepared by adjusted the pH with 0.2 M CH₃COONa and CH₃COOH solution 1X10⁻⁵ M stock solution.
of DA was prepared by dissolving in 0.1M perchloric acid solution. 1X10^-4M AA stock solution was prepared by dissolving in double distilled water.

2.3. Preparation of CdO nanoparticles

Ethanol was dried using type 3A molecular sieves before use. NaOH pallets were pulverized into fine powder under a dry use nitrogen flow. In a typical experiment first solution prepared using 0.03M CdSO₄, 0.06M CH₃COOH and 40 mg CTAB as surfactant in 1 dm³ of double distilled water. The second solution was prepared by 0.09 M NaOH pallets and 25ml 70% ethanol in 1 dm³ of double distilled water. Then first solution was added to second solution with continues stirring. The obtained precipitate was filtered by using Whatmann filter paper (grade-41) and dried at 80°C in hot air oven about 1hour. Then dried precipitate was transferred to silica crucible and ignited at 400°C for about 4hours. Then obtained powder was washed with ethanol three to four times to remove impurities present in the particles. Then these are characterized using XRD, UV-Visible absorption Spectroscopy, and applied for fabrication of carbon paste electrode for determination of DA and AA.

2.4. Characterization

The obtained above nanoparticles were then examined by a Brucker D/MAX 2500 X-ray diffractometer with Cu Ka radiation (λ =1.540 56 Å), and the operation voltage and current were maintained at 40 kV and 250 mA, respectively. Samples were measured and recorded using a TU-1901 double-beam UV-visible spectrophotometer were dispersed in toluene solution.

2.5. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of 70% graphite powder with 30% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the homemade cavity (3 mm in diameter) and then smoothed on a weighing paper. The electrical contact was provided by a copper wire connected to the paste in the end of the tube.

2.6. Preparation of CdO nanoparticles modified carbon paste electrode

The CdO nanoparticles modified carbon paste electrode was prepared by hand mixing of 70% graphite powder and 10 mg CdO nanoparticle with 30% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the homemade cavity (3 mm in diameter) and then smoothed on a weighing paper. The electrical contact was provided by a copper wire connected to the paste in the end of the tube.
3. RESULTS AND DISCUSSION

3.1. XRD pattern for CdO nanoparticles

The XRD pattern Fig. 1 for CdO nanoparticles, the diffraction peaks are absorbed at 2θ values. The prominent peaks have been utilized to estimate the grain size of sample with the help of Scherrer equation [32] \( D = \frac{K\lambda}{\beta \cos \theta} \) where \( K \) is constant(0.9), \( \lambda \) is the wavelength(\( \lambda = 1.5418 \) Å) (Cu Ka), \( \beta \) is the full width at the half-maximum of the line and \( \theta \) is the diffraction angle. The grain size estimated using the relative intensity peak (100) for CdO nanoparticles was found to be 47.8 nm and increase in sharpness of XRD peaks indicates that particles are in crystalline nature. The (111), (200), (220), (311) and (222) reflections are clearly seen and closely match the reference patterns for CdO (Joint Committee for Powder Diffraction Studies (JCPDS) File No. 05-0640).

![XRD pattern for CdO nanoparticles](image)

Figure 1. XRD pattern for CdO nanoparticles

3.2. UV-visible absorption spectra for CdO nanoparticles

The UV-visible absorption spectra of CdO nanoparticles are shown in Fig. 2 although the wavelength of our spectrometer is limited by the light source, the absorption band of the CdO nanoparticles have been shows a blue shift due to the quantum confinement of the excitons present in the sample compare with bulk CdO particles. This optical phenomenon indicates that these nanoparticles show the quantum size effect [33].

Here formation nanoparticle is depend on surfactant and organic solvent because surfactant CTAB helps to bind to the surface of the synthesized nanoparticles, thus acting as particle stabilizer and tuning the nucleation/growth of particles to achieve a higher degree of uniformity [34] and acetic
acid, ethanol solvent helps to disperse the particle in uniformly and it help to growth of particles slowly in restricted size and avoid the aggregation of particles [35].

**Figure 2.** UV-Absorption spectra for CdO nanoparticles

3.3. Electrochemical response of dopamine at CdO nanoparticles modified CPE

Electrochemical detection of DA and AA by using carbon paste electrode was studied by our group (36-39). Fig. 3 shows the CVs of 1X10^-5M DA at bare and CdO nanoparticles modified CPE at scan rate 100mV/s. The electrochemical response of DA shows increase in peak current at the CdO nanoparticles modified CPE. At the bare CPE the cyclic voltammogram of DA (dashed line) shows an oxidation peak potential at 249mV and reduction peak potential at 177 mV. The separation in peak potential (ΔEp) is 72mV which is the characteristic of a quasi-reversible electrode process. At CdO nanoparticles modified CPE pair of well defined redox waves of DA was obtained with an increase of the redox peak current (solid line). The oxidation peak potential occurs at 248mV and reduction peak potential at 172mV respectively, with the peak potential separation (ΔEp) 76mV. The negligible shift in the peak potential was observed which the characteristic of the quasi reversible nature. It was observed that the peak currents enhanced greatly at CdO nanoparticles modified CPE, which provides high surface area of the CdO nanoparticles improved the electrode contacting area of DA and its electrochemistry of reaction product, which increased.
Figure 3. Cyclic voltammogram of 1X10^-4 M DA at CdO nanoparticles modified CPE (solid line) and at bare CPE (dashed line).

3.4. Electrochemical response of Ascorbic acid at CdO nanoparticles modified CPE

Fig. 4 shows the CVs of 1X10^-4 M AA at bare and CdO nanoparticles modified CPE at scan rate 100mV/s. The electrochemical response of AA shows great increase in peak current at the CdO nanoparticles modified CPE. At the bare CPE the cyclic voltammogram of AA (dashed line) shows an oxidation peak potential at 227mV. At CdO nanoparticles modified CPE well defined oxidation wave of AA was obtained with an increase of the oxidation peak current (solid line). The oxidation peak potential occurs at 207mV. It was observed that the peak currents enhanced greatly at CdO nanoparticles modified CPE, which provides evidence for CdO nanoparticles having large surface area possessed highly electrochemical response towards the AA.

Thus, we suggest that the mechanism may be as follows: under the condition, CdO nanoparticles may be combined with the hydrogen bond of the hydroxyl of DA and AA, which activated hydroxyl, weakened the bond energy of O-H and improved the electron transfer rate.

3.5. The effect of scan rate and concentration of DA and AA on the peak current

The scan rate effect was studied at modified electrode in the range from 50 to 300 mVs^-1 showed linear response on peak currents with square root of scan rate. The result indicated that the
electron transfer reaction was controlled by diffusion and increases in the concentrations of DA and AA the corresponding peak currents were also increase linearly.

![Cyclic voltammogram of 1X10^-5M AA at CdO nanoparticles modified CPE (solid line) and at bare CPE (dashed line).]

\[ \text{Figure 4.} \]

4. CONCLUSIONS

This report has shown that synthesis of CdO nanoparticles using CTAB as surfactant by Co-precipitation method from XRD data obtained size was 47.8 nm. The absorption spectra shows evidence quantum confinement effect. Advantage of this method is convenient for synthesis of CdO nanoparticles in normal laboratory conditions, in low cost. The synthesized CdO nanoparticles modified CPE act as good electrode for determination of dopamine and ascorbic acid by using cyclic voltammetry. Hence this current synthetic method extended to many metaloxides, ferrites for synthesis and their modified electrode used as sensor application for determination of biological active compounds.

References


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Synthesis of MgFe$_2$O$_4$ nanoparticles and MgFe$_2$O$_4$ nanoparticles/CPE for electrochemical investigation of dopamine

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Magnesium ferrite nanoparticles (MgFe$_2$O$_4$ NPs) were prepared by a solution based method using magnesium sulphate (MgSO$_4$), ferrous sulphate (FeSO$_4$), dl serine and NaOH as a precipitant and the obtained precipitation was calcinated under 500 °C for 4 h. The resulting material was characterized by using X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The MgFe$_2$O$_4$ NPs were used for preparation of MgFe$_2$O$_4$ NPs/carbon paste electrode (MgFe$_2$O$_4$ NPs/CPE) and applied for electrochemical investigation of dopamine (DA) which exhibited good electrocatalytic activity for investigation of DA at physiological pH 7.4. The effect of pH range from 5.5 to 8.0 was studied and the result shows that the redox peak current was maxima at pH 7.5 and the redox peak was pH dependent with a slope of 0.061 V/pH. The scan rate effect was found to be an adsorption-controlling electrode process. The electrocatalytic currents increased linearly with an increase in DA concentration in the range 0.1-1.2 μM and the detection limit was found to be 7.7 x 10$^{-4}$ M. The proposed method was successfully applied to the determination of DA in injection samples.

1. Introduction

Magnesium ferrite, MgFe$_2$O$_4$, as a soft magnetic n-type semi-conducting material, is an important member of the spinel family. Apart from the applications of its magnetic properties, it can be used as a heterogeneous catalyst, adsorption and humidity sensor, oxygen sensor, sensor technology, and it has been demonstrated that this material can be used for thermal coagulation therapy, in which tumors are locally heated by an application of alternating magnetic fields.

It is well known that properties of ferrite materials strongly depend on the preparation conditions. At present, chemical methods, including coprecipitation method have been reported and recently the synthesis of leaf-like CuO nanoparticles and a Nafion/GOD/CuO modified electrode was used for detection of glucose, the synthesis of CuO nanoparticles and their modified gold electrode was used for investigation of rutin, NiFe$_2$O$_4$/MWCNTS/GCE was used for electrochemical investigation of hydrazine, silver pentacyanonitrosylferrate films modified electrode was used for investigation of L-cysteine, gold nanoparticles modified carbon paste electrode was used for determination of acetaminophen and atenolol.

Quantitative determination of dopamine (DA) in human physiological fluids is of considerable significance in both biochemical and clinical diagnosis. Methods for the detection of DA include chemiluminescence, fluorimetry, ultraviolet-visible spectrometry, capillary electrophoresis (CE-luminescence) and electrochemical methods. The electrochemical method detection is a simple, sensitive and environmentally friendly detection method that is even suitable for the analysis of colored or turbid samples. Particularly the development of voltammetric sensors for the determination of secretion neurotransmitters, such as dopamine (DA) and other catecholamine, that exist in the mammalian central nervous system has received a lot of interest. Among the catecholamines, DA has attracted much interest because the change in DA levels has proved to be a very effective route towards understanding brain functions, such as learning and memory formation, and the physiological and pathological process of Parkinson's disease.

Electrochemical detection of DA and AA by using LaFe$_2$O$_4$ nanoparticles, CdO nanoparticles, CuO nanoparticles, chemically modified carbon paste electrode, poly (Naphthol Green B) film graphite pencil electrode and gold nanoparticles modified ITO electrode has been reported. So in this work, a simple solution based method previously reported was used for the preparation of MgFe$_2$O$_4$ NPs with average crystalline size 15 nm and SEM morphology shows particle like small nanograins with average size 20-50 ± 1 nm. The MgFe$_2$O$_4$ NPs/CPE exhibits enhancement of current.
response for investigation of dopamine at pH 7.4 in 0.2 M phosphate buffer solution and the electrocatalytic current increases linearly with increase in concentration of DA and the detection limit was found to be $7.7 \times 10^{-8}$ M. The proposed method was successfully applied to the determination of DA concentration in injection samples.

2. Experimental

2.1. Apparatus

Cyclic voltammetric experiments were performed with a Model 660c (CH Instruments) Potentialstat/Galvanostat. A conventional three electrode cell is employed and the bare or MgFe$_2$O$_4$ NPs/CPE (3.0 mm diameter) as a working electrode, a saturated calomel electrode as a reference electrode and a platinum electrode as a counter electrode. XRD studies using a Phillips (with X'lerator detector) X-ray diffractometer. Structural morphology of the synthesis NPs was studied using a JEOL JSM-848 scanning electron microscope (SEM).

2.2. Chemicals and solutions

Magnesium sulphate (MgSO$_4$), ferrous sulphate (FeSO$_4$) and perchloric acid (HClO$_4$) were purchased from sd. fine chemicals. Dopamine hydrochloride, sodium dihydrogen ortho phosphate (NaH$_2$PO$_4$), disodium hydrogen phosphate (Na$_2$HPO$_4$) and silicon oil from Hi Media chemicals. dl-Serine, absolute ethanol (99.9%), sodium hydroxide (NaOH) and graphite powder was from Merck chemicals and all chemicals are of analytical grade quality. DA stock solutions (25 mM) were prepared by adding DA to 0.1 M perchloric acid. Phosphate buffer is prepared by adjusting the pH 7.4 with 0.2 M NaH$_2$PO$_4$ and Na$_2$HPO$_4$ solution. All the aqueous solution was prepared by using double distilled water.

2.3. Preparation of MgFe$_2$O$_4$ NPs

In a typical experiment, the first solution 0.2 M MgSO$_4$, 0.4 M FeSO$_4$ and 1.2 M dl serine was dissolved in 250 ml of deionized water and the second solution was prepared by 3 M NaOH pallets in 250 ml of deionized water and the first solution was added to second solution with continuous stirring. The obtained precipitate solution was taken in the condenser and boiled at 100 °C temperature for about 2 h then the hot solution was filtered by using whatmann filter paper (grade-41) and dried at 80 °C in a hot air oven for about 1 h. The dried precipitate was transferred to a silica crucible and ignited at 500 °C for about 4 h. Then the obtained powder was washed with ethanol three to four times to remove impurities present in MgFe$_2$O$_4$ NPs.

2.4. Preparation of bare CPE and modified CPE

The bare CPE (BCPE) was prepared by hand mixing of 70% graphite powder with 30% silicon oil in an agate mortar for about 30 min to produce a homogenous carbon paste. The paste was packed into the homemade cavity and smoothed on weighing paper. The MgFe$_2$O$_4$ NPs/CPE was prepared by adding 10, 20, 30 and 40 mg MgFe$_2$O$_4$ NPs to the above mentioned graphite powder and silicon oil mixture.

3. Results and discussion

3.1. Characterization

X-ray diffraction patterns were recorded using Cu-K$_\alpha$ ($\lambda = 1.5438$ Å) radiation sources for identification of the crystalline structure and average crystalline size of MgFe$_2$O$_4$ NPs. Fig. 1 shows that the obtained diffraction pattern reflects (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes belonging to a cubic spinel structure which are in good agreement with the standard pattern (JCPDS 17-0465). The average crystallite diameter can be determined from the full-width at half-maximum (FWHM) of the (311) diffraction peak by using the Scherrer formula.

$$D = \frac{0.89 \lambda}{p \cos \beta}$$

where $\lambda$ is the X-ray wavelength, $\beta$ is the Bragg diffraction angle, and $p$ is the full-width at half-maximum. The calculated value is 15 nm. SEM observations reveal that all the products consist of a large quantity of small nanograins with average size around 20–50 ± 1 nm, as shown in Fig. 2.

3.2. Effect of MgFe$_2$O$_4$ NPs in CPE for investigation of DA

The effect of MgFe$_2$O$_4$ NPs in the CPE on the peak current for the investigation of $1 \times 10^{-8}$ M DA in 0.2 M phosphate buffer
solution at pH 7.4 was studied by cyclic voltammetry technique. The modified CPE with 20 mg of MgFe$_2$O$_4$ NPs enhanced high anodic peak current as compared with the BCPE, 10, 30 and 40 mg of MgFe$_2$O$_4$ NPs as shown in Fig. 3.

3.3. The response of DA at the bare CPE, and MgFe$_2$O$_4$ NPs/ CPE

Fig. 4 shows the electrochemical responses of $1 \times 10^{-5}$ M DA in 0.2 M phosphate buffer solution of pH 7.4 at the BCPE and the MgFe$_2$O$_4$ NPs/CPE with scan rate 0.1 V s$^{-1}$. At the BCPE, the difference between the anodic peak potential ($E_{pa}$) 0.136 V and the cathodic peak potential ($E_{pc}$) 0.085V is reversible wave with $\Delta E_p$ 0.051 V. However, DA peak currents significantly increased at the MgFe$_2$O$_4$ NPs/CPE, with the anodic peak 0.124 V and the corresponding cathodic peak potential is 0.087 V and corresponding $\Delta E_p$ 0.037V.

Compared with BCPE the remarkable enhancement in the peak currents with reduction of over potential showed catalytic effects of the MgFe$_2$O$_4$ NPs. The mechanism may be MgFe$_2$O$_4$ NPs combined with the hydrogen bond of the hydroxyl of DA, which activated hydroxyl, weakened the bond energy of O-H and improved the electron transfer rate. At the same time, high surface area of the MgFe$_2$O$_4$ NPs improved the electrode contact area of DA.

3.4. Effect of pH value on the determination of DA at the MgFe$_2$O$_4$ NPs modified CPE

The pH of the supporting electrolyte has a significant influence on the DA electrocatalysis at the MgFe$_2$O$_4$ NPs/CPE by affecting both peak current and peak potential. The effect of pH value on the determination of DA in PBS solution at MgFe$_2$O$_4$ NPs/CPE was carefully investigated in a wider pH range of 5.3–7.7 of $1 \times 10^{-5}$ M DA in the different pH solutions. The cyclic voltammograms in Fig. 5 and Fig. 6, illustrate the dependency of the DA anodic peak current and formal potential ($E^0 (V)$) on the buffer solution pH. It can be seen that the peak current of DA increases with increasing pH value until it reaches 7.5 (shown with closed circles (●)). The formal potential of DA shifts negatively with the increase of the pH value of solution and depends linearly on the pH value in the range of 5.3–7.7 with a slope of 0.061 V/pH ($R^2 = 0.991$) (shown with line (–)). It demonstrates that the redox of DA undergoes a two-electron and two-proton process, which is consistent with that reported in literature.34–37

3.5. Effect of scan rate on the peak currents

The effect of scan rate for $1 \times 10^{-5}$ M DA in 0.2 M PBS at pH 7.4 was studied by cyclic voltammetry at MgFe$_2$O$_4$ NPs/CPE as shown in Fig. 7. MgFe$_2$O$_4$ NPs/CPE showed an increase in the redox peak current with increasing scan rate (0.05 to 0.45 V s$^{-1}$). The graph of redox peak current ($I_{pa}$) vs. scan rate ($v$) was plotted. The graph obtained has good linearity between the scan rate and redox peak current (Fig. 8). In the range from 0.05–0.45 V s$^{-1}$ the redox peak currents were proportional to $v$. The correlation coefficient ($R^2$) was 0.9993, which indicates the
Fig. 6  Shows the dependence of the DA oxidation peak current in closed circles (•) and with line ( - ) for formal redox potential versus pH with the scan rate of 0.1 V s⁻¹.

Fig. 7  Cyclic voltammograms of MgFe₂O₄ NPs/CPE in 0.2 M PBS solutions containing 1 × 10⁻⁹ M DA at different scan rates (0.05-0.45 V s⁻¹).

Fig. 8  Graph shows the linear relationship between the peak current and the scan rate.

Fig. 9  Differential pulse voltammogram of (a) 1.0 × 10⁻⁷ M, (b) 2 × 10⁻⁷ M, (c) 3 × 10⁻⁷ M, (d) 4 × 10⁻⁷ M, (e) 5 × 10⁻⁷ M, (f) 6 × 10⁻⁷ M, (g) 7 × 10⁻⁷ M, (h) 8 × 10⁻⁷ M, (i) 9 × 10⁻⁷ M, (j) 4 × 10⁻⁷ M, (k) 5 × 10⁻⁷ M, (l) 6 × 10⁻⁷ M, (m) 8 × 10⁻⁷ M, (n) 1.0 × 10⁻⁶ M and (o) 1.2 × 10⁻⁶ M DA in 0.2 M phosphate buffer solution of pH 7.4 at MgFe₂O₄ NPs/CPE.

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Fig. 10  Graph of iₚ/a vs. concentration of DA (0.1–1.2 µM).

3.6. Concentration effect of DA

The differential pulse voltammetric technique was used for analysis of DA concentration which was varied from 0.1 to 12 µM as shown in Fig. 9. For the MgFe₂O₄ NPs/CPE, the correspondence of anodic peak current versus concentration of DA shows two linear relationships ranges 0.1 to 0.6 µM and 0.8 to 12 µM with the linear regression equations as iₚ/a (A) = 15.28 CµM L⁻¹ + 4.628 × 10⁻³ and iₚ/a (A) = 4.776 CµM L⁻¹ + 5.696 × 10⁻³, respectively. The correlation coefficient for the first linearity was 0.987 and for the second linearity it was found to be 0.993 for the MgFe₂O₄ NPs/CPE shown in Fig. 10. The correlation coefficient for the first linearity was 0.987, the detection limit for DA in the linear range region was found to be 7.7 × 10⁻⁹ M for MgFe₂O₄ NPs/CPE which was calculated according to the equation of LOD = K S⁻¹, where K is a constant related to the confidence level. According to the
measurements (no added DA) and is the slope of the calibration graph. The proposed electrode showed relatively lower detection limits than recently reported and calculated by using the same formula.

3.7. Analytical application

The modified electrode was applied to the determination of dopamine hydrochloride injection. The DA injection sample purchased from Sterile Specialties India Private Ltd had a specified content of DA 40.0 mg mL⁻¹ and the sample was used after suitable dilution. The results are shown in Table 1 and the recovery and relative standard deviation (RSD) were acceptable, showing that the proposed methods could be efficiently used for the determination of DA in injections with recovery in the range 97.00 to 99.1%.

Conclusions

MgFe₂O₄ NPs with average crystalline size 15 nm have been synthesized by solution based method and MgFe₂O₄ NPs/CPE shows good sensor application for electrochemical investigation of DA with detection limit 7.7 × 10⁻⁹ M. The proposed methods shows good sensor application for electrochemical investigation of biological active compounds, injection sample and other neurotransmitters.

Acknowledgements

The authors are very thankful to the University Grant Commission, Government of India, New Delhi for the fellowship and funding given throughout project F.No 35-156 / 2008 (SR).

Notes and references


Table 1  Detection of DA in injection samples (n = 5)

<table>
<thead>
<tr>
<th>Tested Sample</th>
<th>Added (µg mL⁻¹)</th>
<th>Found (µg mL⁻¹)</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>19.44</td>
<td>2.87</td>
<td>97.2</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>29.58</td>
<td>2.66</td>
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<tr>
<td></td>
<td>40</td>
<td>39.64</td>
<td>2.48</td>
<td>99.1</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>19.36</td>
<td>2.57</td>
<td>96.8</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>29.66</td>
<td>2.72</td>
<td>98.6</td>
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<td></td>
<td>40</td>
<td>39.64</td>
<td>2.03</td>
<td>99.1</td>
</tr>
</tbody>
</table>

suggestion of IUPAC, the value of K is 3 at the 99% confidence level, S is the standard deviation of ten blank-solution measurements (no added DA) and S is the slope of the calibration graph, the proposed electrode showed relatively lower detection limits than recently reported and calculated by using the same formula.

ZnO and ZnO/polyglycine modified carbon paste electrode for electrochemical investigation of dopamine

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Present work describes the characterization of commercially available ZnO and its electrochemical investigation of dopamine in the presence of ascorbic acid. ZnO was characterized by powder XRD, UV-visible absorption, fluorescence, infrared spectroscopy and scanning electron microscopy. The carbon paste electrode was modified with ZnO and ZnO/polyglycine for further electrochemical investigation of dopamine. The modified electrode shows good electrocatalytic activity towards the detection of dopamine with a reduction in overpotential. The ZnO/polyglycine modified carbon paste electrode (CPE/ZnO/Pgl) shows excellent electrochemical enhancement of peak currents for both dopamine (DA) and ascorbic acid (AA) and for simultaneous detection of DA in the presence of high concentrations of AA with 0.214 V oxidation peak potential differences between them at pH 7.4. From the scan rate variation and concentration, the oxidation of DA and AA was found to be adsorption-controlled. The use of CPE/ZnO/Pgl is demonstrated for the detection of DA in blood serum and injection samples.

1. Introduction

Zinc oxide (ZnO) is a II-VI semiconductor with a wide band gap of 3.27 eV which has been intensively researched in areas such as transducers, actuators, photo-emitters, varistors, catalysis, sensors and piezoelectric devices. It has varied applications in pigments, rubber additives and so on. Quantitative determination of DA in human physiological fluids is very important in both biochemical and clinical diagnosis. Among the catecholamines, DA detection has attracted much interest because a change in DA levels in the body is a very effective route towards the understanding of brain functions, such as learning and memory formation, and the physiological and pathological process of Parkinson’s disease. Methods for the detection of DA include chemiluminescence, fluorometry, ultraviolet-visible spectrometry and capillary electrophoresis (CE-luminescence). Electrochemical detection of DA by fabricating ZnO as an electrode is also known. The advantages of electrochemical detection techniques are their fast speed, low cost, low detection limits and high accuracy. Particularly, the development of voltammetric sensors for the determination of DA and other catecholamines, that exist in the mammalian central nervous system, has received considerable attention. A major problem for the detection of DA is interference from AA which is also present in biological fluids at very high concentrations (10^{-4} to 10^{-7} mol L^{-1}), compared to DA (10^{-10} to 10^{-12} mol L^{-1}) levels. It is well known that direct electrochemical oxidation of DA and AA at bare electrodes is irreversible. Oxidation occurs in almost the same potential range and can have a pronounced fouling effect which results in poor selectivity and reproducibility. In order to increase the sensitivity and selectivity, various oxides nanoparticles modified electrodes have been studied such as ZnO, NiO, CdO, CuO and Mg_{2}Fe_{2}O_{4}. Among these ZnO based electrodes have been extensively studied. Here, a ZnO/redox mediator composite film coated GCE is used for the determination of DA in the presence of AA. ITO glass modified ZnO nanorods act as the electrode for the electrochemical investigation of DA and is better than a glassy carbon electrode. ZnO is used also in the detection of other organic molecules, e.g., thin toluidine blue (TBO) and zinc oxide (ZnO) hybrid films on glassy carbon electrode (GCE) and indium tin oxide coated (SnO_{2}) glass electrodes for the determination of nicotinamide adenine dinucleotide (NADH). Recently it has been found that the electropolymersation of many organic monomers on carbon paste electrodes show excellent results as sensors for the detection of DA.

Here we report an inexpensive commercially available highly pure ZnO and modified suitably for the detection of DA and AA. ZnO is characterized by powder XRD, UV-visible absorbance, fluorescence, IR-spectra, and SEM. A carbon paste electrode was modified ZnO and studied for electrochemical investigation of dopamine and ascorbic acid in phosphate buffer at pH 7.4. However, it could not be used for the simultaneous detection of...
dopamine and ascorbic acid at physiological pH 7.4. It was modified further with polyglycine\textsuperscript{11} and used for simultaneous electrochemical detection of DA and AA\textsuperscript{14}. The oxidation peak separation potential obtained between DA and AA was found to be 0.214 V and showed good selectivity compared to a polyglycine-modified carbon paste electrode\textsuperscript{12} without ZnO. Experiments carried out in the detection of DA in the presence of blood serum and injection samples showed excellent recovery characteristics, thus demonstrated capability as a sensor for pharmaceutical and clinical samples.

2. Experimental

2.1. Materials and stock solution

Analytical grade dopamine hydrochloride (DA), ascorbic acid (AA), sodium dihydrogen orthophosphate (Na\textsubscript{2}H\textsubscript{2}PO\textsubscript{4}), disodium hydrogen phosphate (Na\textsubscript{2}HPO\textsubscript{4}) and silicon oil were procured from Himedia Chemicals and ZnO (purity 99%), graphite powder (particle size μm) were supplied by Merck Chemicals. Chemicals were used as supplied without further purification.

Dopamine stock solution (25 mM) was prepared using a known quantity of dopamine in 0.1 M perchloric acid; 25 mM ascorbic acid was prepared in double distilled water. Phosphate buffer (pH 7.4) was prepared as per the literature with 0.2 M Na\textsubscript{2}H\textsubscript{2}PO\textsubscript{4} and Na\textsubscript{2}HPO\textsubscript{4} solution in double distilled water.

2.2. Characterization

ZnO powder was characterized by powder XRD using Cu-Kα radiation (λ = 1.5438 Å) in a Philips XRD 'X' PERT PRO diffractometer. IR absorption spectra was recorded on a FT-IR SPECTRUM 1000 Perkin Elmer spectrometer of thoroughly dried samples using KBr as diluant. UV-visible spectra was obtained using a Perkin Elmer UV-visible spectrophotometer and fluorescence spectra was obtained on a Perkin Elmer Luminescence Spectrometer (LS-55) using sonicated ZnO powder in millipore water. Morphological studies of ZnO powder was carried on a JEOL JSM-848 scanning electron microscope (SEM). All electrochemical experiments were carried out in a three-electrode cell with bare CPE, polyglycine-modified CPE, CPE/ZnO/polyglycine (Pgl) as the working electrode, aqueous saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the auxiliary electrode using an electrochemical workstation Model 660c (CH Instruments).

2.3. Modified carbon paste electrode

Carbon paste electrode (CPE) was modified by taking different weights of ZnO (24, 48, 72, 96, and 120 mg) in silicon oil (20%) and graphite powder (80%). This mixture was thoroughly mixed in an agate mortar for about 30 min and packed into a homemade Teflon cavity current collector and polished using soft paper.

2.4. ZnO/polyglycine-modified carbon paste electrode

Electrochemical coating of polyglycine film on ZnO/CPE by cyclic voltammetry and paste packing procedure was carried out as described by Ongera Gilbert et al.\textsuperscript{11} Typically, the polyglycine film was obtained in an aqueous solution containing 0.04 M glycine in 0.2 M acetate buffer (pH 5.0) by scanning between -0.5 V and 1.8 V at a scan rate of 100 mV s\textsuperscript{-1} for five cycles. The electrode was then thoroughly washed with distilled water. Similarly a polyglycine-modified carbon paste electrode without ZnO was prepared.

3. Results and discussion

3.1. Characterization of commercial ZnO

Fig. 1 shows a powder XRD pattern of commercial ZnO indexed to hexagonal wurtzite structure and matched with JCPDS 36-1451. The absence of impurity peaks and the presence of sharp reflection peaks of ZnO show that the sample is highly crystalline and X-ray pure.

Absorption and fluorescence spectroscopy are powerful non-destructive techniques to explore the optical properties of semiconducting nanoparticles. The UV-visible absorption spectra of ZnO dispersed in millipore water is presented in Fig. 2 with millipore water as reference. The sharp absorption peak around 398 nm corresponds to the band gap of 3.27 eV and is less than the bulk band gap of 3.27 eV reported for ZnO. When the sample was excited with light of λ = 415 nm, a broad fluorescence spectra was seen between 536 and 627 nm (inset Fig. 2). This is attributed to green emission due to oxygen vacancies. This green emission arises when a photo generated hole (O\textsuperscript{2+}) trapped at deep level above the valence band recombines with an electron trapped at a shallow level below the conduction band.\textsuperscript{38,39}

IR spectrum in the range 4000-400 cm\textsuperscript{-1} ZnO is shown in Fig. 3. The sharp band at 420 cm\textsuperscript{-1} is attributed to the vibrational frequency of the Zn-O bond. The broad and weak band around 3500 cm\textsuperscript{-1} may be attributed to adsorbed water. The clean IR spectrum shows the sample obtained is of high purity.

SEM micrograph of commercial ZnO reveals neatly cut rectangular cuboids of particles of ZnO of size varying between 0.5 and 0.2 μm (Fig. 4).

3.2. Electrochemical response of dopamine at ZnO/CPE electrode

In order to optimize the amount of ZnO in a carbon paste electrode, CV was run for different weights of ZnO prepared
3. Electrochemical response of dopamine at CPE/ZnO/Polyglycine electrode

The thickness of the polyglycine (Plg) film on ZnO/CPE can be adjusted by controlling the number of cycles in CV (1 to 13 cycles), while polymerizing the glycine monomer. Fig. 7 shows cyclic voltammograms of 0.1 mM DA in 0.2 M phosphate buffer at pH 7.4 for a different number of polymerization cycles. The peak current increases gradually and reaches a maximum at the
Fig. 7  Cyclic voltammograms of 2.5 × 10⁻⁴ M DA in 0.2 M phosphate buffer solution (pH 7.4) at different voltammetric scans and (inset) anodic peak current versus number of voltammetric scans.

Fig. 8  Shows cyclic voltammograms obtained for the electrochemical response of DA (2.5 × 10⁻⁴ M) at bare CPE (curve a) and at polyglycine/ZnO-modified CPE (curve b) in 0.2 M phosphate buffer solution (pH 7.4).

Fig. 9  Cyclic voltammograms for 2.5 × 10⁻⁴ M DA at the polyglycine/ZnO-modified CPE showing increased redox peak current with an increase in scan rate (50 to 170 mV s⁻¹) in 0.2 M phosphate buffer solution (pH 7.4) and (inset) anodic peak current versus scan rate (Iₚa vs. n).

Fig. 10  Cyclic voltammograms obtained for the electrochemical response of 2.0 × 10⁻⁴ M AA at bare CPE (curve a) and at polyglycine/ZnO-modified CPE (curve b) in 0.2 M phosphate buffer solution of (pH 7.4), scan rate 50 mV s⁻¹.

Fig. 11  Cyclic voltammogram for the solution containing 2.5 × 10⁻⁴ M DA and 2.0 × 10⁻⁴ M AA in 0.2 M phosphate buffer solution (pH 7.4) at the bare CPE electrode (a), ZnO-modified CPE (b), polyglycine-modified CPE (c) and polyglycine/ZnO-modified CPE (d) at the scan rate 50 mV s⁻¹.

5th cycle and thereafter the peak current response becomes almost constant (Fig. 7 inset). This may be due to an increase in the surface coverage of the electrode with polyglycine with increased scanning cycle. However, after 5 cycles, polyglycine covers the electrode surface completely and the active area does not change significantly. Hence, 5 cycles in CV was chosen as the optimum for glycine polymerization (Fig. 8).

At bare CPE the oxidation and reduction peak potentials occur at 0.14 V and 0.07 V, respectively, and for CPE/ZnO/Pgl at 0.13 V and 0.10 V, with a significant increase in peak currents. The enhancement of peak current and reduction in overpotential clearly indicates the higher electrocatalytic activity of polyglycine/ZnO-modified CPE.

The effect of scan rate for DA by CV at polyglycine/ZnO-modified CPE showed an increase in the redox peak current with increase in scan rate (50 to 160 mV s⁻¹) (Fig. 9). A linear plot of current (Iₚa) vs. scan rate (n) was obtained with good correlation.
Fig. 12: Differential pulse voltammogram for the solution containing $2.5 \times 10^{-4}$ M DA and $2.0 \times 10^{-1}$ M AA in 0.2 M phosphate buffer solution of pH 7.4.

Fig. 13: Differential pulse voltammograms at the polyglycine/ZnO modified CPE for AA and with different concentrations of DA in 0.2 M phosphate buffer solution of pH 7.4. The inset plot shows anodic peak current ($i_{pa}$) versus dopamine concentration.

The main objective of the work is the simultaneous detection of AA and DA in 0.2 M phosphate buffer solution at pH 7.4. Fig. 11 shows cyclic voltammograms obtained for the solution containing $2.5 \times 10^{-4}$ M DA and $2.0 \times 10^{-1}$ M AA in 0.2 M phosphate buffer solution (pH 7.4) at the bare CPE electrode solid line (Fig. 11a) and for CPE/ZnO (Fig. 11b) where the cyclic voltammogram exhibited one broad peak for both analytes, indicating that the oxidation potentials of DA and AA are merged and indistinguishable. The fouling effect of the electrode surface with the oxidized products of AA and DA is the reason for this broad peak in the AA and DA mixture. Similarly, cyclic voltammograms for the mixture on polyglycine-modified CPE and on CPE/ZnO/Pgl electrode shown in Fig. 11c and d, respectively. Polyglycine-modified CPE exhibited two well-defined oxidation peaks for AA and DA at 0.047 V and 0.137 V, respectively, with a potential difference 0.09 V. Whereas CPE/ZnO/Pgl electrode showed oxidation peaks at -0.081 V and 0.133 V with a significant difference of 0.214 V.

Fig. 12 shows differential pulse voltammogram (DPV) for AA and DA, with oxidation potentials -0.065 V and 0.184 V, respectively, and with a difference of 0.219 V for CPE/ZnO/Pgl. This is the largest peak potential separation reported between DA and AA, compared to the reported literature. Thus, polyglycine/ZnO-modified CPE exhibits excellent electrocatalytic activity, a considerable oxidation peak separation, enabling the simultaneous detection of both AA and DA in phosphate buffer (pH 7.4).

Fig. 13 shows the differential pulse voltammograms at CPE/ZnO/Pgl for a fixed concentration of AA ($2.5 \times 10^{-3}$ M) and DA with concentrations varying from $4.5 \times 10^{-4}$ to $21.5 \times 10^{-4}$ M, in 0.2 M phosphate buffer (pH 7.4) at the scan rate 50 mV s$^{-1}$. Obviously one can see the anodic current increases with increasing concentration of DA, while the anodic current of AA remains constant. A good linearity between $i_{pa}$ and the concentration of dopamine was obtained and is shown in the inset of Fig. 13. Furthermore, it was observed that in the presence of high concentrations of AA, the detection of low concentrations of DA is still possible. The polyglycine/ZnO modified CPE shows a good selectivity for electrochemical detection of DA in the presence of AA and sensitivity ($0.238 \mu A \mu M^{-1} cm^{-2}$) is found to be better than in earlier reports.

3.5. Application to real systems

Practical application of CPE/ZnO/Pgl was demonstrated by quantitative determination of DA in human blood serum.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Spiked DA sample (mM)</th>
<th>Found (mM)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drug injection</td>
<td>0.1</td>
<td>0.098</td>
<td>98.5</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.198</td>
<td>99</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.296</td>
<td>98.8</td>
<td>3.03</td>
</tr>
<tr>
<td>Blood serum</td>
<td>0.1</td>
<td>0.1</td>
<td>100</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.198</td>
<td>99.9</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.296</td>
<td>98.5</td>
<td>3.41</td>
</tr>
</tbody>
</table>

Table 1: Determination of DA in human blood serum and drug injection sample (number of trials = 5)
samples (obtained from the Health Centre, Kuvempu University, Shankaraghatta, India). The procedure was as follows: 2 mL of human serum sample without any pretreatment was diluted to 100 mL with pH 7.4 phosphate buffer. Different volumes of this solution were mixed with a known concentration of DA. Similarly, a drug injection capsule solution was mixed with a known volume concentration of DA samples (obtained from the Health Centre, Kuvempu University, containing 200 mg dopamine hydrochloride in 5 mL sterilized water (Sterile Specialities India Private Ltd) was suitably diluted to provide different known standard concentrations of DA which were analyzed by CV using the CPE/ZnO/Pgl electrode.

Each experiment was carried out at least 5 times and the results are presented in Table 1. The obtained recovery and relative standard deviation (RSD) is good, indicating a good performance of the glycine-modified ZnO electrode.

4. Conclusions

Electropolymerisation of glycine on ZnO/CPE produces a stable polymeric film. CPE/ZnO/Pgl exhibits remarkable electrocatalytic effects on oxidation of AA and DA. CPE/ZnO/Pgl clearly resolved mixed voltammetric signals of AA and DA. The modified electrode shows high electrocatalytic activity towards the oxidation of DA in the presence of AA and vice versa. The electrode is found to be very effective when applied to real systems. It is expected that CPE/ZnO/Pgl, with its high electrocatalytic behavior may find applications in the field of electroanalytical chemistry and as a biosensor.

Acknowledgements

The authors are very thankful to the University Grant Commission, Government of India, New Delhi for the fellowship and funding given through the project no. 35-156/2008 (SR).

Notes and references

Cationic Surfactants-Assisted Synthesis of ZnO Nanoparticles and Their Modified Carbon Paste Electrode for Electrochemical Investigation of Dopamine

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Abstract- ZnO nanoparticles were synthesized using zinc nitrate, cetyltrimethyl ammonium bromide and sodium hydroxide in co-precipitation method. The obtained particles were characterized using X-ray diffractometer (XRD), UV-Vis absorption spectroscopy (UV-Vis), Infrared absorption spectroscopy (IR) and Scanning electron microscopy (SEM). The ZnO nanoparticles are used for the preparation of modified carbon paste electrode (MCPE). The MCPE was applied for electrochemical investigation of dopamine (DA) which exhibits enhancement of current response with reduction of over potential for investigation of DA at pH 7.0. The effect of pH range from 5.5 to 8.0 was studied and the redox peak was pH dependent with a slope of 53 mV/pH. The effect of scan rate shows adsorption controlling process and the electrocatalytic currents increases linearly with increase in DA concentrations in the ranges of 0.1-20 μM. The detection limit was found to be 0.3×10⁻⁷ M.

Keywords- ZnO Nanoparticles, Carbon Paste Electrode, Dopamine Cyclic Voltammetry, Differential Pulse Voltammetry
1. INTRODUCTION

As a key semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO has been widely used in broad areas such as photo-emitters, transducers, actuators, varistors, sensors and catalysis [1,2,3].

Dopamine (DA) is one of the most important catecholamine neurotransmitters in mammals that play crucial roles in the functioning of cardiovascular, renal, hormonal and central nervous system [4]. Loss of DA is associated with neurological disorders such as Parkinson's disease [5]. DA acts like a brain chemical to transmit messages to parts of the brain for coordination of body movement. Thus monitoring the DA levels can be an important marker for biomedical diagnosis. Among other methods which are based on spectroscopy and chromatography [6,7], DA concentration is very low (0.01–1 μM) in the extracellular fluid of the central nervous system [8]. Electrochemical method is one of the most favorable techniques for the determination of dopamine because of its low cost, high sensitivity and easy operation [9] and nanometal oxide MCPE [3, 10-12] shows good sensors for detection of DA was studied.

In this work, very simple co-precipitation method was adopted for preparation of ZnO nanoparticles using CTAB as surfactant. The ZnO nanoparticles modified carbon paste electrode exhibits enhancement of current response with reduction of over potential for the investigation of dopamine at pH.7.0. in 0.2 M phosphate buffer solution and electrocatalytic currents increases linearly with increase of DA concentrations and the detection limit was found to be 0.3×10⁻⁷ M.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The ZnO nanoparticles were characterized by various techniques such as Powder XRD patterns are recorded for using Cu-Kα radiation (λ=1.5438 Å) as sources in Philips XRD ‘X’ PERT PRO diffractometer, IR absorption spectra are recorded in FT-IR SPECTRUM 1000 PERKIN ELMER spectrometer on thoroughly dried samples using KBr pellets as dilutants, UV-Vis spectra were obtained by using Perkin Elmer UV-Vis Spectrophotometer by dispersing and sonicated ZnO nanoparticles in the ethanol. Structural morphology of the synthesis nanoparticles is studied using a JEOL JSM-848 scanning electron microscope (SEM). All the electrochemical experiments were carried using a single compartment, three-electrode cell with above the bare CPE and ZnO nanoparticles MCPE was used as a working electrode, an aqueous saturated calomel electrode (SCE) as reference electrode, and a Pt wire as auxiliary electrode. All potentials were measured and reported vs. the SCE. The cyclic
voltammetric measurements (CV) and differential pulse voltammetry techniques (DPV) were performed on a Model 660c (CH Instruments) Potentialstat/Galvanostat.

2.2. Materials

Zinc nitrate [Zn(NO₃)₂⋅6H₂O] and perchloric acid (HClO₄) were purchased from sd. Fine chemicals. Dopamine hydrochloride, Sodium dihydrogen ortho phosphate (NaH₂P0₄), disodium hydrogen phosphate (Na₂HPO₄), silicon oil from Hi Media chemicals. Absolute ethanol (99.9%), sodium hydroxide (NaOH), and graphite powder were from Merck and all chemicals are of analytical grade quality. A dopamine stock solution (25 mM) was prepared by adding dopamine to 0.1 M perchloric acid. Phosphate buffer solution was prepared by adjusting the pH with 0.2 M NaH₂P0₄ and Na₂HPO₄ solution and all the aqueous solutions was prepared by using double distilled water.

2.3. Preparation of ZnO nanoparticles

In a typical experiment, the first solution contains 0.01 M Zn(NO₃)₂⋅6H₂O, 0.02 M CTAB and the second solution contains 0.02 M NaOH was prepared by using distilled water. The first solution is added to second solution with continues stirring. The obtained white precipitate was filtered by using Whatmann filter paper (grade-41) and dried at 80 °C in hot air oven about 1 h. The dried precipitate was transferred to silica crucible and ignited at 400 °C for about 3 h. Then obtained powder was washed with ethanol three to four times to remove impurities present in ZnO nanoparticles.

2.4. Preparation of bare carbon paste electrode and modified carbon paste electrode

The bare carbon paste electrode (BCPE) was prepared by hand mixing of 70% graphite powder with 30% silicon oil in an agate mortar for about 30 min to produce a homogenous carbon paste. The paste was packed into the homemade cavity and smoothed on a weighing paper. The modified carbon paste electrode (MCPE) was prepared by adding 10 mg, 20 mg, 30 mg and 40 mg ZnO nanoparticles to above mentioned graphite powder and silicon oil mixture.

3. RESULTS AND DISCUSSION

3.1. Characterization

The XRD pattern of the as-obtained ZnO nanoparticles was shown in Fig. 1. All the peaks can be well indexed to the Hexagonal structure of Zinc Oxide (JCPDS PDF, no. 89-0510) with high crystallinity. No impurity peaks present of other Zinc Oxide were observed, indicating the high purity of the products and by using Debye Scherrer's formula, the crystallite sizes of ZnO nanoparticles can be determined. The obtained average crystallite size of the particles was found to be 62 nm.
The IR transmittance spectrum for the ZnO nanoparticles synthesized by using CTAB was displayed in Fig. 2. (B) some bands are observed in the region 2800–3000 cm⁻¹ and attributed to CTAB surfactants [13-15]. CTAB IR spectra show two intense bands, assigned to asymmetric (2924 cm⁻¹) and symmetric (2852 cm⁻¹) stretching vibrations of C-CH₂ in the methylene chains. The sharp bands in the region of 1439 cm⁻¹ are attributed to the deformation of -CH₂- and -CH₃[14] of the incorporated surfactants. The weak band detected in the region of 2924 and 2852 cm⁻¹ was assigned to C-CH₃ asymmetric stretching and N-CH₃ symmetric stretching vibrations of solid and a surfactant. These band vibrations provide evidence for the incorporation of CTAB into the Zinc Oxide. The sharp peak 420 cm⁻¹ is attributed to the framework vibrations of zinc oxide [16].

UV–Vis absorption spectrum of the as-prepared ZnO nanoparticles dispersed in ethanol solution shows a broad absorption peak whose center was at about 355 nm shown in the Fig. 3A. The results of UV–Vis absorption spectra for ZnO nanoparticles shows good blue shift with enhanced band gap 3.49 eV.

The morphology of ZnO nanoparticles shows the flower-like with 4 to 5 petals were grown, each petals have tip ~50-60 nm, tapering width ~100 nm, width ~160 nm and length is ~200 nm structures and non-uniformly distributed is shown in Fig. 3B.
3.2. Effect of ZnO nanoparticles concentration in CPE on DA

The effect of ZnO nanoparticles concentration in the carbon paste electrode (CPE) on the peak current for the investigation of $1 \times 10^{-5}$ M DA in 0.2 M phosphate buffer solution of pH 7.0 was studied by CV method. The modified carbon paste electrode with 30 mg of ZnO
nanoparticles enhanced high anodic peak current as compared with the bare CPE, 10, 20, 30 and 40 mg of ZnO nanoparticles as shown in Fig. 4.

![Graph showing the relationship between anodic peak current (Ipa) and concentration of ZnO nanoparticles in CPE](image)

**Fig. 4.** Shows the graph between anodic peak current (Ipa) vs. different concentration of ZnO nanoparticles in CPE

3.3. The response of DA at the bare CPE, and ZnO nanoparticles MCPE

Fig. 5. shows the electrochemical responses of $1 \times 10^{-5}$ M DA in 0.2 M phosphate buffer solution of pH 7.0 at the bare CPE and the ZnO nanoparticles MCPE with scan rate 100 mV/s. Compared with the bare CPE the remarkable enhancement in the peak currents with reduction of over potential showed electrocatalytic effects of the ZnO nanoparticles. The mechanism could be as follows; under the condition, ZnO nanoparticles may be combined with the hydrogen bond of the hydroxyl of DA, which activated hydroxyl, weakened the bond energy of O-H and improved the electron transfer rate. At the same time, high surface area of the ZnO nanoparticles improved the electrode contacting area of DA.
3.4. Effect of pH

The pH of the supporting electrolyte has a significant influence on the DA electrocatalysis at the ZnO nanoparticles MCPE by affecting both peak currents and peak potentials. The effect of pH value on the determination of DA in PBS solution at ZnO nanoparticles MCPE was carefully investigated in a wider pH range of 5.5–7.5. Fig. 6. Illustrates the dependences of the DA anodic peak current and formal potential \( [E^0 (V)] \) on the buffer solution pH. It can be seen that the anodic peak current of DA increases with increasing pH value until it reaches 7.0, then decrease the peak current of DA until it reaches 7.5. The formal potential of DA shifts towards lower potential with the increase of the pH value of solution, and depends linearly on the pH value in the range of 5.5–7.5 with a slope of 53.3 mV/pH. It demonstrates that the redox of DA undergoes a two-electron and two-proton process, which was consistent with that reported in literature [3].

3.5. Effect of scan rate

The effect of scan rate for \( 1\times 10^{-5} \) M DA in 0.2 M PBS at pH 7.0 was studied by CV at ZnO nanoparticles MCPE. ZnO nanoparticles MCPE showed increase in the redox peak currents with increase in scan rate (10 to 800 mVs\(^{-1}\)). The graph of current (i) vs. scan rate (v) was plotted. The graph obtained was good linearity between scan rates and peak current shown in Fig. 7, in the range from 10–800 mVs\(^{-1}\). The correlation coefficient \( (r^2) \) was 0.99915, which indicate the electrode reaction was adsorption controlled process.
Fig. 6. Graph shows the dependences of the DA oxidation peak current (○) and for formal redox potential (●) on the PBS solution pH with a scanning rate of 100 mVs$^{-1}$.

Fig. 7. Graph the linear relationship between the peak current vs. the different scan rate (10–800 mVs$^{-1}$) in 0.2 M PBS solutions at pH 7.0.
3.6. Concentration effect of DA

The differential pulse voltammetric technique was used for the analysis DA concentration which varied from 0.1 to 20 µM shown in Fig. 8, for the ZnO nanoparticles MCPE. By increasing the concentration of DA from 0.1 to 20 µM. The graph of \( I_{pa} \) vs. concentration of DA showed increase in anodic peak current as shown in Fig. 9. The linear relationship ranges 0.3–22 µM with the linear regression equation as \( I_{pa} (\mu A) = 3.5396 C \mu M/L + 7.865 \times 10^{-7} \). The correlation coefficient for the linearity was 0.998 and the detection limit for DA in the linear range region was found to be \( 0.3 \times 10^{-7} \) M for ZnO nanoparticles MCPE and which was calculated according recent reported [17] and calculated by using same formula.

**Fig. 8.** Differential pulse voltammogram of (a) \( 1.0 \times 10^{-7} \) M, (b) \( 2 \times 10^{-7} \) M, (c) \( 4 \times 10^{-7} \) M, (d) \( 6 \times 10^{-7} \) M, (e) \( 8 \times 10^{-7} \) M, (f) \( 10.0 \times 10^{-7} \) M, (g) \( 12.0 \times 10^{-7} \) M, (h) \( 14.0 \times 10^{-7} \) M, (i) \( 16.0 \times 10^{-7} \) M, (j) \( 18.0 \times 10^{-7} \) M and (k) \( 20.0 \times 10^{-7} \) M DA in 0.2 M phosphate buffer solution of pH 7.0 at ZnO nanoparticles MCPE
4. CONCLUSIONS

ZnO nanoparticles with average crystalline size 62 nm with significant blue shift of band gap 3.49 eV having flower like morphology have been synthesized by coprecipitation method and their modified carbon paste electrode shows good electrocatalytic activity and enhanced current sensing with low detection limit (0.3×10^{-7}M).

Hence this present synthetic method extended too many metal oxides, ferrites for synthesis and their modified electrode used as sensor for application of determination of some biological active compounds and other neurotransmitters.

Acknowledgement

The authors are very thankful to the University Grant Commission, Government of India, and New Delhi for the fellowship and funding given through project F.No 35-156/2008 (SR).

REFERENCES

Preparation of NiO/ZnO hybrid nanoparticles for electrochemical sensing of dopamine and uric acid

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Abstract

The NiO/ZnO hybrid nanoparticles were synthesized using sodium dodecyl sulfate (SDS) in a micro-emulsion method. The NiO/ZnO hybrid nanoparticles were characterized using X-ray diffraction, scanning electron microscopy, UV-visible absorption spectroscopy, infrared absorption spectroscopy and energy dispersive X-ray spectrum. The obtained NiO/ZnO hybrid nanoparticles were used for the preparation of modified carbon paste electrode (MCPE) for electrochemical detection of dopamine and uric acid at physiological pH 7.4. The MCPE exhibits enhanced electrochemical parameters such as peak current response, surface area of electrode, electrocatalytic activity, diffusion-coefficient, lower detection limit, sensitivity and higher linear range. The proposed method was successfully applied for the detection of dopamine and uric acid in real samples.

Keywords: NiO/ZnO hybrid nanoparticle; Carbon paste electrode; Dopamine; Uric Acid; Cyclic Voltammetry; Differential pulse voltammetry

1. Introduction

Dopamine (DA) is a well-known biogenic amine acting as a neurotransmitter in the brain. It has received considerable attention because of its suspected role in a variety of neuropsychiatric disorders such as Parkinson’s disease and Schizophrenia [1, 2]. DA concentration is very low (0.01–1 μM) in the extracellular fluid of the central nervous system [3]. Uric acid (2,6,8-trihydroxypurine, UA), a major nitrogenous compound in urine, is a product of purine metabolism in human body and its higher levels lead to many clinical disorders [4]. High levels of UA in the blood (hyperuricemia or Lesch-Nyhan syndrome) are linked with the body disorders like gout, kidney, and cardiac problems. Many epidemiological studies have suggested that elevated serum UA is also a risk factor for cardiovascular disease [5-10]. Hence, a simple, accurate and reliable method for the determination of dopamine and uric acid is an urgent need. Electrochemical methods were commonly accepted as the fastest analytical assay (compared to traditional spectroscopic techniques [11]), simple, sensitive and environmental-friendly detection method that is even suitable for the analysis of colored or turbid samples [12].

The literature reported on nanoparticles and organic compounds modified electrode for investigation of dopamine and uric acid such as: CdO, CuO and MgFe₂O₄ nanoparticles modified electrode for detection of DA [13-15], gold-modified vertically aligned multi-walled carbon nanotubes (MWCNTs) electrode as a biosensor for uric acid detection [16]. Self-assembled gold nanoparticles onto the L-cysteine-modified glassy carbon electrode for simultaneous determination of uric acid and ascorbic acid were reported [17]. Cu-metal nanoparticles in over-oxidized polypyrrole film modified GCE was utilized as the sensing matrix for the simultaneous determination of DA and UA [18].

It is a well-known fact that the electrochemical activation of carbon based electrodes will result in improved performance during electroanalysis [19]. In particular, their porous and large specific surface area, interfacial adsorption properties and enhanced electrocatalytic activity have opened doors for tailoring a variety of electrochemical sensors and biosensors [20]. Carbon, conducting polymers and transition metal oxides are the most widely used active electrode materials [21, 22]. The literature review of composite electrodes made from transition metal oxides and carbonaceous materials [23,24] showed very high surface area due to the increased electrical conductivity, electrochemical utilization of the metal oxide and ionic transport throughout the internal volume of the electrode.

A composite composed of ZnO and NiO nanoparticles can be of interest as a complex catalyst and a nanosized semiconductor with interesting transport and magnetic properties [25, 26]. The NiO/ZnO heterostructural nanomaterials attract much interest in particular because NiO, as a p-type semiconductor (Eₜ 3.5 eV), possesses high p-type concentration, high hole mobility, and low lattice mismatch with ZnO, which is beneficial for the formation of p-n heterojunction with ZnO [27-30]. Hence in the present work, the NiO/ZnO hybrid nanoparticles were prepared using a simple microemulsion method based on modified version of the method reported in the literature [31] and NiO/ZnO hybrid nanoparticles modified carbon paste electrode is considered as a good electrochemical sensor for detection of dopamine and uric acid.
2. Experimental

2.1. Apparatus

The NiO/ZnO hybrid nanoparticles were characterized by various techniques. Powder XRD patterns were recorded on Phillips XRD X'Pert Pro diffractometer, using Cu-Kα radiation (λ=1.5438 Å) as source. IR absorption spectra were recorded on the Perkin Elmer Spectrum 1000 FTIR spectrometer on thoroughly dried samples using KBr pellets as diluents. UV-visible spectra were obtained on a Perkin Elmer UV-VIS Spectrophotometer by dispersing and sonicating NiO/ZnO hybrid nanoparticles in the distilled water. The structural morphology of the NiO/ZnO hybrid nanoparticles sample was studied using a JEOL JSM-848 scanning electron microscope (SEM). All the electrochemical experiments were performed using a three-electrode system with above bare CPE, NiO/ZnO hybrid nanoparticles MCPE as a working electrode, an aqueous saturated calomel electrode (SCE) as reference electrode and a Pt wire as auxiliary electrode. All the potentials were measured and reported vs the SCE. The cyclic voltammetric (CV) measurements and differential pulse voltammetry (DPV) measurements were performed on a Model 660c (CH Instruments) potentiostat /Galvanostat.

2.2. Materials

Cyclohexane and n-butyl alcohol were purchased from Nice chemicals. Graphite powder, absolute ethanol and perchloric acid were from Merek chemicals. Nickel chloride (NiCl2.6H2O), zinc chloride (ZnCl2.6H2O) and liquid ammonia aqueous solution were from SD-Fine chemicals. Sodium dodecyl sulfate (SDS), uric acid (UA), dopamine (DA), silicon oil, sodium dihydrogen phosphate and disodium hydrogen phosphate were from Himedia chemicals. All chemicals were of analytical grade and used without further purification. Phosphate buffer was prepared and the pH was adjusted by the addition of 0.2 M NaH2PO4 and Na2HPO4 solutions. All the aqueous solutions were prepared with double distilled water.

2.3. Preparation of NiO/ZnO hybrid nanoparticles

The NiO/ZnO hybrid nanoparticles were synthesized according to the microemulsion method described elsewhere [31], with minor modifications. In this method, cyclohexane is used as the oil phase, SDS is used as surfactant, n-butyl alcohol is used as co-surfactant. In order to determine the phase behaviour of four component system on a pseudo-ternary phase, the relative concentration of the two constituents must be fixed throughout the investigations. Here the weight ratio of surfactant to co-surfactant was fixed. The microemulsion system was chosen because of enough stable space, high reaction efficiency and yield. In order to dissolve the water as much as possible, five different ratios of surfactant to co-surfactant were chosen as shown in Table 1. Table 1 shows that the ratio of 2:3 is the appropriate.

The procedure was, titrating a series of SDS/n-butyl alcohol/cyclohexane mixtures with water. The formation of clear, homogenous and transparent solution, after the mixture was stirred vigorously, was considered as microemulsion region. If the mixture became turbid, it was considered as the occurrence of phase separation and ME represents the microemulsion region. In this region the system formed clear and homogenous microemulsion. The typical microemulsion system employed in the study has a composition of 50% cyclohexane, 20% SDS and 30% n-butyl alcohol.

The oil phase, the surfactant and the co-surfactant were mixed with weight ratio 5:2:3 by magnetically stirring until it became transparent (ME). Three microemulsions were prepared as follows: ME 100 g, 20 g of 0.1 mol/L NiCl2 aqueous solution was added (ME1). ME 100 g, 20 g of 0.1 mol/L ZnCl2 aqueous solution was added (ME2). ME 200 g, 40 g of 0.2 mol/l of NH4H2O aqueous solution was added (ME3). All the three experimental processes were under magnetic stirring, ME1 was added dropwise to the ME2 under stirring for another 30 min at room temperature. Then ME2 was added dropwise to the mixture of ME1 and ME3 under stirring for 30 min at room temperature. Thus the obtained precipitate was repeatedly washed using ethanol and followed by centrifuging for 15 min at 2000 rpm. The precursor powders were dried in an oven for 24 hrs at 80°C until a constant weight of the particles is achieved. The NiO/ZnO hybrid nanoparticles were obtained after calcination at 500°C for 3 hours.

2.4. Preparation of bare carbon paste electrode and modified carbon paste electrode

The bare carbon paste electrode (bare CPE) was prepared by hand mixing of 80% graphite powder with 20% silicon oil in an agate mortar for about 30 min to produce a homogenous carbon paste. The paste was packed into the homemade cavity and smoothed on a weighing paper. The modified carbon paste electrode (MCPE) was prepared by adding 20 mg NiO/ZnO hybrid nanoparticles to above mentioned graphite powder and silicon oil mixture.

3. Results and Discussion

3.1. Characterization

The XRD pattern of the synthesized nanoparticles is shown in Figure 1. The position and intensity of the characteristic peaks of the sample are well consistent with that of the standard JCPDS Card No. 780429 and No. 891397. The sharp diffraction peak in the XRD pattern indicates the crystalline nature. No other metal oxide impurity peaks present in NiO/ZnO pattern were observed, indicating the high purity of the products and by using Debye Scherrer’s formula, the crystalline sizes of NiO/ZnO hybrid nanoparticles were calculated. The obtained average particle size is 28 nm.

<table>
<thead>
<tr>
<th>SDS:Hexanol (w)</th>
<th>Cyclohexane (g)</th>
<th>Water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>5</td>
<td>0.3</td>
</tr>
<tr>
<td>2:3</td>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>1:1</td>
<td>5</td>
<td>0.2</td>
</tr>
<tr>
<td>3:2</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>4:1</td>
<td>5</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Figure 1. XRD patterns for NiO/ZnO hybrid nanoparticles sample.

Figure 2. IR Spectra of NiO/ZnO hybrid nanoparticles sample.

The IR transmittance spectrum for the NiO/ZnO hybrid nanoparticles synthesized by using SDS is displayed in Figure 2. The peaks at around 2931, 2854 and 1117 cm⁻¹ are due to C-H stretching and bending. These band vibrations provide evidence for the incorporation of SDS into the NiO/ZnO hybrid. The broad peaks at approximately 3438 and 1624 cm⁻¹ were proposed to be due to H-OH stretching and broad intense peak observed at around 420 cm⁻¹ and small peak at around 601 cm⁻¹ are attributed to the framework vibration of metal oxide nanoparticles [38, 39].

The SEM observations reveal that flake shaped structures were grown and each flake is ~ 40 - 50 nm thick, 500 nm long structure and some irregular shaped particles show less than ~40 nm size as shown in Figure 3. The EDS indicates that the atomic ratio of Zn and Ni of about 1:2 exists in the sample as shown in Figure 4.

3.2. The response of DA and UA at the bare CPE and MCPE

The electrochemical responses of 1×10⁻⁵ M DA in 0.2 M phosphate buffer solution of pH 7.4 at the bare CPE and the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE) with scan rate 0.1 V/s is shown in Figure 5a. At the (bare CPE), the anodic peak potential (Epa) was 0.157 V and the cathodic peak potential (Epc) was 0.096 V and ∆Ep was 0.061V. However a well-defined redox wave of DA was observed and the peak currents significantly increased at the MCPE with the anodic peak potential shifting negatively to 0.146 V and the corresponding cathodic peak potential is 0.097 V and ∆Ep is 0.049 V indicating the modified electrode shows fast electron transfer process.

Figure 5b shows the electrochemical responses of 1×10⁻⁶ M UA in 0.2 M phosphate buffer solution of pH 7.4 at the bare CPE and the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles with scan rate 0.1 V/s. At the bare CPE, the anodic peak potential (Epa) was 0.335 V and the MCPE with anodic peak potential (Epa) was 0.304 V. Compared with bare CPE, the enhancement in the peak currents with reduction of oxidation peak potential showed catalytic effects of the NiO/ZnO hybrid nanoparticles.

3.3. The effect of scan rate

The effect of scan rate for 1×10⁻⁵ M DA and 1×10⁻⁶ M UA in 0.2 M phosphate buffer solution of pH 7.4 was studied by CV at the MCPE. It showed an increase in the peak current as shown in Figure 6a and 6b for scan rate from 0.100 to 0.600 Vs⁻¹. The graph obtained exhibited good linearity between the square root of the scan rate (v²) versus peak current for MCPE with correlation coefficients (r²=0.999) as shown in Figure 7a and 7b for DA and UA which indicates the MCPE electron transfer reaction was diffusion-controlled process. The surface area available for the electron transfer to species in solution can be estimated by the Randles–Sevcik equation (1) for reversible electrode process and equation (2) for irreversible electrode process assuming charge transfer coefficient for irreversible electrode process is 0.5 (αt=0.5) [32-34]. This equation relates the peak current for an electron transfer-controlled process with the square root of the scan rate as follows:
Figure 4. EDS of NiO/ZnO hybrid nanoparticles sample.

Figure 5. Cyclic voltammograms of 1×10⁻⁵ M DA (a) and 1×10⁻⁴ M UA (b) at solid line for modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles (MCPE) and at dashed line for bare CPE.

Figure 6. Cyclic voltammograms of 1×10⁻⁵ M DA (a) and 1×10⁻⁴ M UA (b) for the prepared with NiO/ZnO hybrid nanoparticles MCPE with different scan rates (0.1, 0.150, 0.200, 0.250, 0.300, 0.350, 0.400, 0.450, 0.500, 0.550 and 0.600 V/s) in pH 7.4 PBS.

\[ i_p = (2.69 \times 10^3) n^{1/2} A^{1/2} D^{1/2} C_0^{1/2} v^{3/2} \]  
\[ i_p = (2.99 \times 10^3) n (\text{on})^{1/2} A D_0^{1/2} v^{1/2} C_0^{1/2} \]

where \( i_p \) is the peak current, \( A \) is the electroactive area (cm²), \( C \) is the concentration of the electroactive species (mole cm⁻³), \( n \) is the number of exchanged electrons, \( D \) is the diffusion coefficient (cm² s⁻¹) and \( v \) is the scan rate (V s⁻¹). The values of the diffusion coefficients were obtained from the slopes of \( i_p \) vs \( v^{1/2} \) and by using equation (1), the surface area of electrode for the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles was calculated.

and the surface area of MCPE at 0.1 V s⁻¹ was found to be 0.0673 cm² for DA and 0.136 cm² for UA. Compared with bare CPE, the MCPE exhibits enhanced surface area of electrode. Hence the probable mechanism may be NiO/ZnO hybrid nanoparticles combine with the hydrogen bond of the hydroxyl group of DA, which activates hydroxyl group, weakens the bond energy of O–H and improves the electron transfer rate. At the same time, high surface area of the NiO/ZnO hybrid nanoparticles improved the electrode contact area of DA and UA.
The effect of concentration of DA and UA used for the analysis of DA. DA concentration was varied prepared with NiO/ZnO hybrid nanoparticles. By increasing 0.129 (iM to 0.0429 M the graph of Ipa vs concentration of |iM to 600 |iM and UA from the concentration of DA from 1 |iM to 600 |iM and UA concentration was varied from 1 |iM to 600 |iM which is better than reported value [45] and 1.18 µA/µM.cm² for UA which is better than reported value [46].

kinetic limitations decrease its sensitivity (slope of calibration of plot) and due to this, it shows different linear ranges in calibration plot. The obtained linear ranges equations for DA and UA concentration are shown in Table 2. The detection limit for DA and UA in the lower concentration linear range was found to be 0.062 µM for DA which is less than that reported in literature [37-40] and 0.97 µM for UA which is less than that reported in the literature [41-44] for MCPE and was calculated according to the recent reports [37]. The sensitivity is found to be 59.26 µA/µM.cm² for DA which is better than reported value [46].

3.5. Detection of DA, UA and AA mixture
A0 and UA are present along with DA in mammalian brain and the concentration of these was much higher than that of DA. Hence the NiO/ZnO hybrid nanoparticles MCPE is applied for electrochemical analysis of DA (1x10⁻⁷ M) in the presence of AA (0.5x10⁻⁴ M) and AA (1x10⁻⁴ M) in 0.2M phosphate buffer solution at pH 7.4. The obtained results show that voltammetric peak separation between DA and AA is 0.2V and AA oxidation peak is merged with DA oxidation peak as shown in Figure 10a and 11a. Therefore based on the reported literature [14], the SDS/polyglycine/NiO/ZnO hybrid nanoparticle MCPE was prepared and applied for electrochemical analysis of DA (1x10⁻⁷ M) in the presence of UA (0.5x10⁻⁴ M) and AA (1x10⁻⁴ M) in 0.2M phosphate buffer solution at pH 7.4. The obtained results exhibit enhanced peak currents response, separation and selectivity for analysis of DA, UA and AA. The oxidation peak potentials of DA, AA and UA were at 0.236, 0.019 and 0.348 V, respectively. The peak-to-peak separation of DA-AA is 0.217 V and that of DA-UA is 0.112 V. These results were sufficient to identify DA in the presence of AA and UA at SDS/polyglycine/NiO/ZnO hybrid nanoparticle MCPE as shown in Figure10b and 11b.

3.6. Real sample analysis
Abnormal concentrations of DA and UA in body fluids influence the function of central nervous system. Hence the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticle was applied to the determination of DA.
Table 2. Calibration curve parameters for the determination of DA and UA.

<table>
<thead>
<tr>
<th></th>
<th>Linear range</th>
<th>Concentration ranges</th>
<th>Regression equations (Ip vs C)</th>
<th>r</th>
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<tbody>
<tr>
<td></td>
<td>First</td>
<td>1 μM to 6 μM</td>
<td>( I_p (\mu A) = 3.011 \times 10^6 + 1.778 \times 10^3 C (\mu M/L) )</td>
<td>0.990</td>
</tr>
<tr>
<td>Dopamine</td>
<td>Second</td>
<td>6 μM to 100 μM</td>
<td>( I_p (\mu A) = 1.3033 \times 10^5 + 0.1442 C (\mu M/L) )</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>Third</td>
<td>100 μM to 600 μM</td>
<td>( I_p (\mu A) = 2.738 \times 10^5 + 0.02368 C (\mu M/L) )</td>
<td>0.990</td>
</tr>
<tr>
<td>Uric Acid</td>
<td>First</td>
<td>12.9 μM to 0.629 mM</td>
<td>( I_p (\mu A) = 4.0075 \times 10^6 + 0.03549 C (\mu M/L) )</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>Second</td>
<td>0.629 mM to 6.29 mM</td>
<td>( I_p (\mu A) = 3.172 \times 10^5 + 0.000898 C (\mu M/L) )</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>Third</td>
<td>6.29 mM to 0.0429 M</td>
<td>( I_p (\mu A) = 4.672 \times 10^4 + 0.00004423 C (\mu M/L) )</td>
<td>0.990</td>
</tr>
</tbody>
</table>

Figure 10. (a) Cyclic voltammogram for simultaneous determination of \( 1 \times 10^{-7} \) M DA, \( 1 \times 10^{-4} \) M AA and \( 0.5 \times 10^{-4} \) M UA at NiO/ZnO hybrid nanoparticles MCPE (dashed line) and (b) at SDS/polyglycine/ NiO/ZnO hybrid nanoparticle MCPE (solid line) with the scan rate of 0.1 Vs\(^{-1}\).

Figure 11. Differential voltammograms for simultaneous determination of \( 1 \times 10^{-7} \) M DA, \( 1 \times 10^{-4} \) M AA and \( 0.5 \times 10^{-4} \) M UA at (a) NiO/ZnO hybrid nanoparticles MCPE and (b) at SDS/polyglycine/ NiO/ZnO hybrid nanoparticle MCPE at 0.1 Vs\(^{-1}\).

and UA content in healthy human blood serum samples applying the differential pulse voltammetric procedure. Using the proposed method, the uric acid and dopamine concentration were analyzed in healthy human blood serum and the results obtained are listed in Table 3. Procedure for real sample analysis: 1 ml of healthy human blood serum sample without any pretreatment was diluted to 100 ml with buffer and diluted solutions were pipetted into each of series of 10 ml volumetric flasks and to this, different known standard concentrations of DA and UA solutions were added and diluted to the mark with pH 7.4 phosphate buffer. The results are shown in Table 3 and the recovery and relative standard deviation (RSD) were acceptable, showing that the proposed methods could be efficiently used for the determination of DA and UA in real blood serum sample with

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recovery in the range ~97.00 to 99% for both DA and UA analysis.

4. Conclusions

The NiO/ZnO hybrid nanoparticles were synthesized using simple microemulsion method and electrochemical parameters were studied. The modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles exhibits stable electrocatalytic activity, sensitivity, surface area of electrode, lower detection limit and higher linear range in 0.2 M phosphate buffer solution at pH 7.4 compared with bare CPE. The proposed method can be applied to the detection of DA and UA in blood serum samples. Therefore, the present method can be extended to many metal oxides, ferrites for DA and UA in human blood serum sample.

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Determination of Dopamine in Presence of Uric Acid at Poly (Eriochrome Black T) Film Modified Graphite Pencil Electrode

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Abstract

A simple commercial graphite pencil electrode was used to investigate the electrochemical oxidation of dopamine. The electropolymerised film of eriochrome black T was prepared on the surface of graphite pencil electrode by using cyclic voltammetry technique. The prepared electrode exhibits an excellent electrocatalytic activity towards the determination of dopamine. The effects of concentration, pH and scan rate were investigated. Simultaneous detection of dopamine and uric acid was investigated by using both cyclic voltammetric and differential pulse voltammetry technique. The modified electrode was also used for the detection of dopamine in injection.

Keywords: Poly (Eriochrome Black T), Graphite Pencil Electrode, Dopamine, Uric Acid, Cyclic Voltammetry, Differential Pulse Voltammetry

1. Introduction

Dopamine is an important neurotransmitter in the amygdala, a phylogenetically older structure in the brain, which is thought to play a critical role in limbic, cognitive and neuroendocrine functions [1,2]. Serious diseases such as Schizophrenia and Parkinsonism may result by loss of DA-containing neurons [3-8]. Patient with this disease shows a low level of DA. Therefore, determination of DA concentration has become important. Many methods were introduced to determine DA, such as spectroscopy, chromatography and electrochemistry [9-13]. Because of its electrochemical activity, DA can also be determined with electrochemical method [7,14]. Uric acid (UA) is the primary end product of purine metabolism in the human body [15]. In a healthy human being, the typical concentration of UA in urine is around 2 mM and in the blood is in between 120 µM to 450 µM ranges [16,17]. Extreme abnormalities of UA levels are symptomatic of several diseases, such as, cardiovascular disease [18], hyperuricemia, uric acid stones [19], gout and Lesch-Nyhan syndrome [20]. Thus accurate determination of UA concentration is of great importance. Recently, electrochemical sensors have attracted much attention due to their advantages of simplicity, cheapness, fast analysis along with high sensitivity and selectivity [21]. The oxidation potential of DA and UA are very close such that, the bare electrode often suffers from fouling effects. The chemically modified electrodes have the ability to detect both DA and UA selectively [22,23].

The electopolymer film coated electrodes are playing an important role in sensor field. Ongera et al. studied the simultaneous determination of dopamine in presence of ascorbic acid at electropolymer modified carbon paste electrode [3,4,21]. Gabriela Broncova et al. used poly (neutral red) modified electrode for determination of citrate in soft drinks [24]. M. Pandurangachar et al. prepared poly (patton’s and reeder’s) film coated carbon paste electrode for simultaneous detection of citrate in soft drinks [24]. M. Pandurangachar et al. prepared poly (patton’s and reeder’s) film coated carbon paste electrode for simultaneous detection of dopamine [7]. Sarah M. Kirwan studied the electrochemical properties of AA and H2O2 at Poly (o-phenylenediamine) film modified Platinum-iridium electrodes alloy wires [25].

In the present work, poly (EBT) film coated graphite pencil electrode is used for the selective detection of DA in the presence of UA. The electrochemical study of EBT was done by our research group [26]. Many electrochemical experiments have been done by electropolymerizing the EBT indicator and discussing their voltm-
Simultaneous Detection of Dopamine and Uric Acid at Poly (Fast Sulfone Black F) Film Coated Graphite Pencil Electrode


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Abstract- The poly (fast sulfone black f) film was synthesized on the surface of graphite pencil electrode by cyclic voltammetric method. The synthesized polymer film coated electrode exhibit excellent electrocatalytic activity towards the detection of dopamine at 7.0 pH. The scan rate effect was found to be diffusion controlled electrode process. The concentration effect of dopamine was linear with current. The redox peak potentials of dopamine were depend on pH. This polymer film coated electrode was very good at simultaneous study of dopamine in presence of high concentrated uric acid. The separated peak potential of DA-UA was 150 mV by cyclic voltammetric technique.

Key words- Poly (Fast Sulfone Black F), Graphite Pencil Electrode, Dopamine, Uric acid, Cyclic Voltammetry, Simultaneous

1. INTRODUCTION

Dopamine is an important neurotransmitter in the amygdala, a phylogenetically older structure of the brain, which is thought to play a critical role in limbic, cognitive and neuroendocrine functions [1,2]. Serious diseases such as Schizophrenia and Parkinsonism may result by loss of DA-containing neurons [3-8]. Patient with this disease shows a low
Poly(amaranth) film based sensor for resolution of dopamine in the presence of uric acid: A voltammetric study

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Abstract

The electropolymerized film of amaranth was prepared on the surface of graphite pencil electrode (GPE) using cyclic voltammetric technique. This poly(amaranth) film coated electrode exhibited an excellent electrocatalytic activity towards the detection of dopamine (DA) in the presence of uric acid (UA) in 0.2 mol/L phosphate buffer solution at pH 7.0. The effect of interference study was carried out using differential pulse voltammetric technique. The poly(amaranth) modified GPE was applied for the detection of DA in dopamine injection with satisfactory results.

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Keywords: Poly(amaranth); Graphite pencil electrode; Dopamine; Uric acid; Sensor

The graphite pencil electrode (GPE) has been successfully acting as a biosensor in modern electroanalytical field. Due to its high electrochemical reactivity, good mechanical rigidity, low cost, low technology, and ease of modification, renewal and low background current [1], the GPE has good application in analysis of neurotransmitter and detection of traces of metal ions. In recent years polymer modified electrodes have received great attention due to their good stability, reproducibility, more active sites, homogeneity in electrochemical deposition and strong adherence to the electrode surface. Hence they have been used as sensors for the determination of dopamine (DA) [2,3]. DA is one of the naturally occurring catecholamines in the mammalian central nervous system, which plays a key role in neurotransmission. Changes in the concentration of DA may lead to serious diseases such as Schizophrenia and Parkinson’s [2]. There have been some reports for the determination of DA and UA by electrochemical methods [4–6]. In the present work, the poly(amaranth) modified GPE was fabricated for the electrochemical determination of dopamine in the presence of uric acid (UA).

The pencil-lead rods (HB 0.5 mm in diameter and 6 cm length) were purchased from local bookstore. Amaranth, DA and UA were purchased from Himedia chemicals. All other chemicals were of analytical grade. Phosphate buffer solution (PBS 0.2 mol/L) was used as a supporting electrolyte throughout the experiment. Freshly prepared solutions
Electrochemical Investigations of Potassium Ferricyanide and Dopamine by 1-butyl-4-methylpyridinium tetrafluoro borate Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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A carbon paste electrode (CPE) modified by 1- butyl 4- methylpyridinium tetrafluoro borate (BMPTB) was used for the detection of K$_3$Fe(CN)$_6$ and dopamine. Cyclic voltammetric technique demonstrated highly improved response of K$_3$Fe(CN)$_6$ and dopamine at BMPTB /CPE compared to bare CPE with different shape of cyclic voltammorams. The effect of BMPTB concentration on the electrode quality also reveals that BMPTB formed on a CPE surface with a high density of negative charged end directed outside the electrode. The detection limit for modified electrode for K$_3$Fe(CN)$_6$ is 1x10$^{-4}$ M and dopamine 1 x10$^{-3}$ M.

Keywords: Carbon paste electrode, 1- butyl 4- methylpyridinium tetrafluoro borate ionic liquid, Dopamine, Cyclic voltammetry.

1. INTRODUCTION

Potassium ferricyanide is used as an oxidizing agent to remove silver from negatives and positives, a process called dot etching. In color photograph, potassium ferricyanide is used to reduce the size of color dots without reducing their number, as a kind of manual color correction. Potassium ferricyanide is the chemical compound with the formula K$_3$Fe(CN)$_6$. This bright red salt consists of the coordination compound [Fe(CN)$_6$]. It is soluble in water and its solution show some green yellow fluorescence. Potassium ferricyanide is often used in physiological experiments as a means of
Clay modified carbon paste electrode for the voltammetric detection of dopamine in presence of ascorbic acid

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ABSTRACT

α-Cobalt (II) hydroxide (α-Co-SO4) was synthesized. Characterized by powder X-ray diffraction, FT-IR spectroscopy, as well as elemental analysis indicates the formation of α-cobalt (II) hydroxide. The synthesized α-Co (II) hydroxide was used to fabricate modified carbon paste electrode for the determination of dopamine. The α-Co-SO4/SDS/CPE was characterized by electrochemical methods and modified electrode was used to determine dopamine (DA) and ascorbic acid (AA) simultaneously. The detection limit and quantification limits for DA were found to be 2.5 × 10⁻⁷ mol/L and 5.3 × 10⁻⁷ mol/L respectively.

1. Introduction

Among all the chemical sensors reported in the literature, electrochemical sensors are the most attractive because of their remarkable sensitivity, experimental simplicity and low cost [1]. In the recent years, a new approach to electrocatalysis emerged using molecular materials attached to electrode surfaces, since the kinetics of an electrochemical reaction and sometimes even the electrode reaction product may depend on the composition of the electrode. Research arose focusing on the preparation and the characterization of electrodes modified with inorganic structured materials such as zeolites and clays. The key features of inorganic materials are their shape and size selectivity in chemical reactions. Zeolites have well-defined pores and channels, clays exhibit layer like structures, in both cases a three dimensional architecture is built on the electrode surface allowing study of molecular recognition effects in the design of electro catalysts for specific substrates and of analytical devices [2,3]. The electrochemical biosensors have been increasingly developed for continuous monitoring in environmental and health care applications. Numerous immobilization methods have been developed for electrochemical biosensor applications such as covalent linkages, cross-linking methodologies, bioaffinity attachment, self-assembled multilayer’s, mixing in carbon composites and entrapment within polymeric and inorganic matrices. Among these methods, entrapment within hydrophilic gels such as sol gel and clays appears to be efficient and popular methods [4-6].

α-Hydroxides of nickel and cobalt have a structure similar to LDHs [7]. The hydroxides of nickel and cobalt crystallize in different polymorphic modifications, mainly the β- and the α-form. The β-form is of the formula M (OH)₂ and it is an ordered stacking of neutral layers of the composition [M (OH)₂] with an interlayer spacing of 4.6 Å. The α-form is a hydroxyl deficient compound and consists of a stacking of positively charged layers of composition [M (OH)₂]n⁻, (H₂O)ₙ⁺ which intercalate anion such as NO₃, Cl, OAc, SO₄ etc. along with water molecules in the interlayer region to restore charge neutrality. Consequently, the α-hydroxides have a higher interlayer spacing, which varies with the size of the interlayer anion (7.5-8 Å) as compared to the brucite-like β-hydroxides [8]. The α-hydroxide of nickel, though unstable in an alkaline electrolyte, is theoretically expected to exhibit superior electrochemical properties compared to the β-form [9].

Surfactant is a linear molecule with a hydrophilic head and a hydrophobic end. Due to its unique molecular structure, surfactant was extensively used in the fields of electrochemistry and electroanalytical chemistry for various purposes [10]. Two of their properties are useful in electro-chemistry: adsorption at interfaces and aggregation into supramolecular structures [11]. Hu’s group [12-16] has introduced surfactants to electroanalytical chemistry to improve the detection limits of some biomolecules. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactants. They proposed a synergistic adsorption mechanism to interpret these enhancement effects of
This is to certify that Dr./Ms./Mr. SATHISH REDDY, K. Kuvempu University, Shimoga has presented a paper/participated in the NCNM 2010, National conference on Nanostructured Materials and Nanocomposites, organized by the department of Chemistry, NSS College, Ottapalam, Kerala, India, sponsored by University Grants Commission, held at NSS College, Ottapalam.

Smt. V.K Syamala
Head of the Department and Convener
NCNM 2010

Dr. G. Jogadees Chandran
Principal and Chairman
NCNM 2010
International Conference on Current Trends in Chemistry and Biochemistry

ICCTCB -2009
(In Celebration of the Completion of 100 Glorious Years of Teaching and Research at the Department of Chemistry, Central College Campus, Bangalore University, Bangalore, India)

Certificate of Participation

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Sathia Reddy

Of ........................................ University

I presented a poster

Participated in the International Conference on Chemistry and Biochemistry at Central College Campus, Bangalore University, Bangalore, during December 18-19, 2009.

Convenor

Organising Secretaries
State Level Conference on
NANOTECHNOLOGY

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Department of Chemistry and Staff
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Sirigere - 577 541 Chitradurga Dist
And
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Mr. godtigh.reddy. Research Scholar

Kuvempu University presented paper

and has participated in the U.G.C. sponsored
State Level One Day Conference on
NANOTECHNOLOGY
held in Sirigere, Chitradurga Dist on 14th August 2009
as Deligate/Resource Person of the Session

Prof: B.M. Murugeswarappa
Convener

Dr. N. Lokesha Odeyar
Principal, Grade-I

Prof: B.S. Sherigara
Vice-Chancellor
This is to certify that Prof./Dr./Ms./Mrs./Mr. SATHISH REDDY

RESEARCH SCHOLAR, DEPT OF INDUSTRIAL CHEMISTRY, KUVEMPU UNIVERSITY,

SHANKARA GHATTA - 574 451, INDIA

has presented a paper (invited)/poster/participated/chaired a session at the International Conference on Nanomaterials: Synthesis, Characterization and Applications held at Kottayam, Kerala, India from 27th to 29th April 2010.

Convener
Prof. (Dr.) Sabu Thomas

Organized By:
Centre for Nanoscience & Nanotechnology
Mahatma Gandhi University
Priyadharshini Hills P.O., Kottayam, Kerala, India 686 560
Certificate

This is to certify that Prof. / Dr. / Mr. / Mis. / ... SATHISH PEDDY ...

has attended the Two days National Symposium on
FRONTIER AREAS IN CHEMICAL SCIENCE AND NANOTECHNOLOGY
held at the Department of Industrial Chemistry,
Kuvempu University, Shankargatta - 577 451 Shimoga Dist., During May 1 & 2, 2010.

Presented Paper [✓]  [ ] Registered Delegate

Convenor

Vice-Chancellor
CERTIFICATE

This Certificate is awarded to **MR. SATHISH REDDY**

KUVEMPU UNIVERSITY, SHIMOGA


President

Secretary
GOVERNMENT OF GOA

GOVERNMENT COLLEGE OF ARTS, SCIENCE & COMMERCE
SANQUELIM - GOA
CERTIFICATE

This is to certify that Prof./Dr./Mr./Ms. SATHISH REDDY of KUVEMPURI UNIVERSITY, SHINOGA has participated as an Invited-Speaker / Chairman / Poster presenter / attended / Volunteer / member of Organising Committee in Organising / delegate, at the two day National "SYMPOSIUM CUM WORKSHOP ON CARBON MATERIALS" organized by the Department of Chemistry, Government College of Arts, Science and Commerce, Sanqueelim - Goa, on 20th and 21st January, 2012.

Dr. Purnakala V. Samant
Convenor, Symposium cum Workshop

Ms. Lucy James
Principal
UGC AND DST SPONSORED NATIONAL CONFERENCE
ON
CHEMISTRY: CHALLENGES AND OPPORTUNITIES
NCCCO - 2012
In commemoration of the Silver Jubilee of the Post Graduate Centre

CERTIFICATE

We are happy to place on record the participation of
Dr/ Mr/Ms. Sathish Reddy of Kuvempu University, Karnataka
in the National conference NCCCO- 2012 held at
St Joseph’s College (Autonomous), Bangalore from
16-18 February 2012.
He/She also presented a paper under the category of
Oral/Poster presentation.

Organising Secretary
Prof. Anantha P Rao
Organising Secretary

Head of the Department
Head of the Department of Chemistry

Principal
ST. JOSEPH’S COLLEGE
This is to certify that Mr./Mrs. SATHISH REDDY, Kuvempu University,
Shanmugapura, Shimoga has participated in the UGC sponsored one day State-level seminar on "ANALYTICAL TECHNIQUES IN THE PRESENT SCENARIO" held at Sahyadri Science College (Autonomous), Shimoga on 27th March 2010.

Dr. H. Sayyadappa
Convener

Prof. B.R. Siddaramappa
Principal

Prof. Y.S. Agassimundin
Chief Guest
Certificate of Participation

National Seminar on Crystal Growth - XIV

Kuvempu University, Vellore - 632 014, Tamil Nadu, India.

This is to certify that Dr./Ms. Sathaish Reddy participated in the seminar held on 10-12, March 2010 at VIT University, Vellore - 632 014, Tamil Nadu, India.

Jointly organized by
School of Advanced Sciences, VIT University
Indian Association for Crystal Growth

Dr. K. Sathiyarayanan
Chairperson

Dr. V. Rama Ramaiah
President, IACG

Dr. S. Kalainathan
Convener
This is to certify that Mr. Mt. J. Mathew, Sathish Reddy, Research Scholar, as attended the Two day seminar on "UNDERSTANDING OUR UNIVERSE" held during 7th to 8th December 2009 at Kuvempu University, Jnana Sahyadri, Shankaraghatta 577 451, Karnataka.

Dr. H. S. Jayanna
Convener

Prof. B. S. Shenigara
Vice-Chancellor
Certificate Of Participation

This is to certify that

BHUMIKA REDDY

of  

attended
2nd National Conference on
Emerging Trends in Engineering and Technology - 2008

held at CIT Campus - Gubbi, Tumkur,
during 24-25 April, 2008

and presented / participated / chaired a
technical session


Prof. Shantala Suresh
Vice-Principal, CIT, Gubbi.

Dr. C.R. Pradeep
Principal, CIT, Gubbi.
UGC Sponsored National Conference on

NANO CHEMISTRY – A Science of Diminished Dimensions

( NCASDD - 2009 )

11th March, 2009

Certificate

We have a great pleasure to put it on record that

Dr. / Mr. / Ms. / Mrs. / .......... SATHISH REDDY.

has participated and presented a paper in one day

National Conference held at Sahyadri Science College,

Shimoga – 577 203, Karnataka, India,

Organized by Department of Chemistry, on 11th March, 2009.

Dr. Basavaraj Padmashali
Convener, NCASDD – 2009

Prof. B.R. Siddaramappa
Principal

Prof. B.S. Sherigara
Vice-Chancellor
KUVEMPU UNIVERSITY

DEPARTMENT OF POST GRADUATE STUDIES IN PHYSICS
JNANASAHYADRI, SHANKARAGHATTA- 577 451.

CERTIFICATE

This is to certify that Mr. / Ms. / Dr. [Name]

Dept. of T.C., K.V., Shankaraghatta has attended the one day seminar "on Recent Development in Nano Science & Technology" on 29th March, 2008 held at Department of Physics, Kuvempu University, Shankaraghatta.

Date: 29th March 2008

No

[Signature]
B.S. Shergara
Vice-Chancellor
Kuvempu University

[Signature]
Convenor

[Signature]
Dr. H.S. Jayamra
Kuvempu University

School of Chemical Sciences
Department of Chemistry, Jnana Sahyadri, Shankaraghappa - 577 451.

National Seminar on

Nanotechnology - Past, Present & Future

Certificate

This is to certify that Prof. / Dr. / Mr./ Mrs. Sathish Reddy has participated in the National Seminar on "Nanotechnology - Past, Present & Future" held at the Department of Chemistry, Kuvempu University, Shankaraghatta on 04-04-2008.

Prof. J. Keshavayya

Dr. Y. Arthoba Naik.

Convenors
KUVEMPU UNIVERSITY

Dept. of Nanoscience & Technology / Dept. of Industrial Chemistry
Kuvempu University, Jnana Sahyadri, Shankaraghatta 577 451 Shivamogga-Dist., Karnataka, India

NATIONAL WORKSHOP ON "USAGE OF INSTRUMENTS FOR NANOTECHNOLOGY APPLICATIONS"

In association with
SINSIL INTERNATIONAL, Bangalore

CERTIFICATE OF PARTICIPATION

This is to certify that Prof/ Dr/ Mr/Ms. SATHISH REDDY, Research Scholar has participated in the National Workshop on Usage of Instruments for Nanotechnology Applications organized by Dept. of Nanoscience & Technology/ Dept. of Industrial Chemistry, Kuvempu University, Shankaraghatta 577 451 on 25th April 2011.

Dr. J. Manjanna
Organizing Secretary
Dept. of Nano sci. & Tech.

Prof. H.S. Bhojya Naik
Chairman
Dept. of Ind. Chemistry

Mr. Y.R. Roopsingh
General Manager
Sinsil International
KUVEMPUN UNIVERSITY
Department of PG Studies and Research in Biochemistry
Jnana Sahyadri, SHANKARAGHATTA - 577451, Shivamogga District,

Two Days National Seminar

on

"R A C B B - 2009"

Certificate

This is to certify that Prof./Dr./Sri./Smt.

SATHISH REDDY, Research Scholar

Dept. of Industrial Chemistry, Kuvempu University

attended the Two Days National Seminar

on

"Recent Advances and Challenges in Biochemistry and Biotechnology - 2009"

organised by Department of P.G. Studies and Research in Biochemistry, Jnanasahyadri, Kuvempu University,
Shankaraghatta on 1st and 2nd April, 2009.

Dr. A.N. Rajeshwara
Convener

Dr. S.E. Neelagund
Organising Secretary

Prof. B. S. Sherigara
Vice-Chancellor
"THROUGH THE INSTRUMENTS"
UGC sponsored workshop on applications of analytical tools

In association with
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This is to certify that Prof./Dr./Mr./Ms. SATHISH REDDY, Kuvempu University, Shimoga, has participated in the UGC sponsored workshop "Through the Instruments - Applications of Analytical Tools" organized by the Department of Chemistry, Sahyadri Science College (Autonomous), Shivamogga on 23rd March 2011.

Dr. K. R. Venugopala Reddy
Convener

Dr. Basavaraj Padmashali
Convener

Prof. B. R. Siddaramappa
Principal

Prof. A. Varadarajulu
Emeritus Professor
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