

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 400⁰C 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-

14]. 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 (99.955%), 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 CH_3COONa and CH_3COOH solution. 1×10^{-5} M stock solution

of DA was prepared by dissolving in 0.1M perchloric acid solution. 1×10^{-4} M 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 80⁰C in hot air oven about 1hour. Then dried precipitate was transferred to silica crucible and ignited at 400⁰C 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 Bruker D/MAX 2500 X-ray diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), 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] $D = K\lambda/(\beta \cos \theta)$ where K is constant(0.9), λ is the wavelength($\lambda = 1.5418 \text{ \AA}$) ($\text{Cu K}\alpha$), β is the full width at the half-maximum of the line and θ 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)

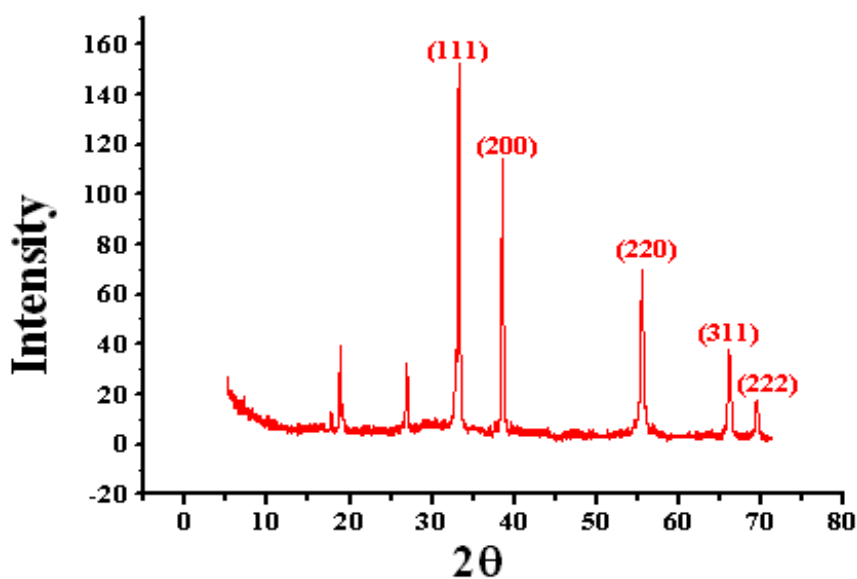


Figure 1. XRD pattern for CdO nanoparticles

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].

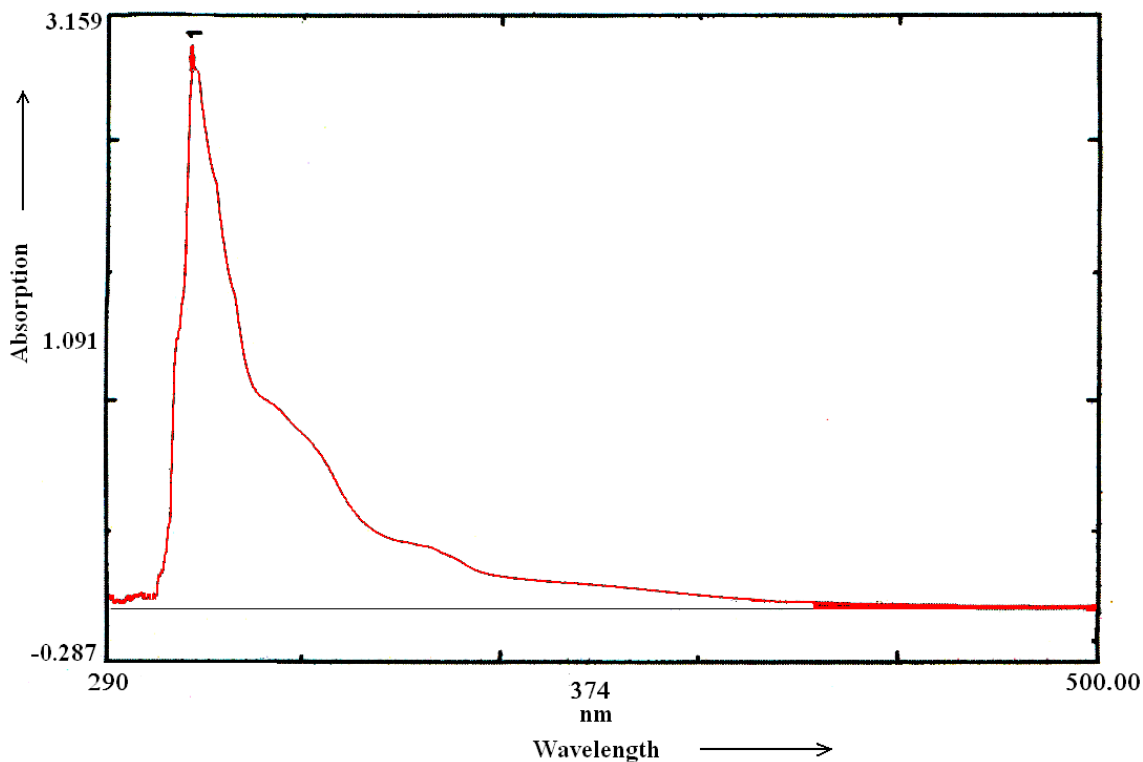


Figure 2. UV-Absorption spectra for CdO nanoparticles

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 $1 \times 10^{-5} \text{ M}$ DA at bare and CdO nanoparticles modified CPE at scan rate 100 mV/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 249 mV and reduction peak potential at 177 mV . The separation in peak potential (ΔE_p) is 72 mV 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 248 mV and reduction peak potential at 172 mV respectively, with the peak potential separation (ΔE_p) 76 mV . 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.

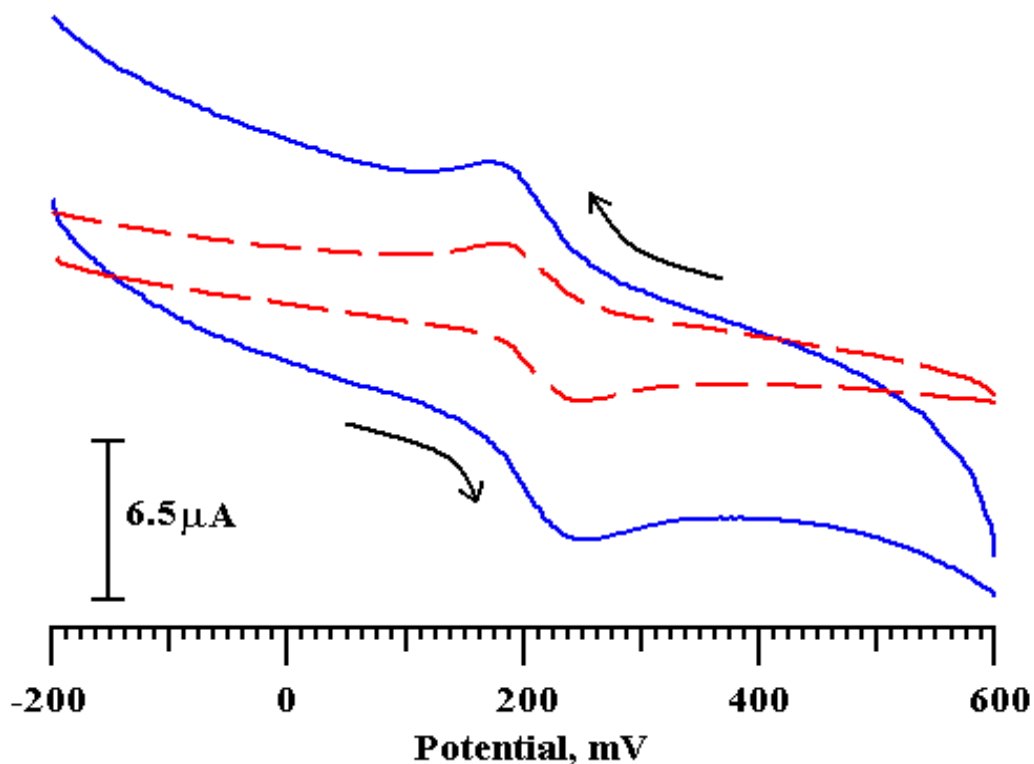


Figure 3. Cyclic voltammogram of $1 \times 10^{-5} \text{M}$ DA at CdO nanoparticles modified CPE (solid line) and at bare CPE (dashed line).

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

Fig. 4 shows the CVs of $1 \times 10^{-4} \text{M}$ 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 300mVs^{-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.

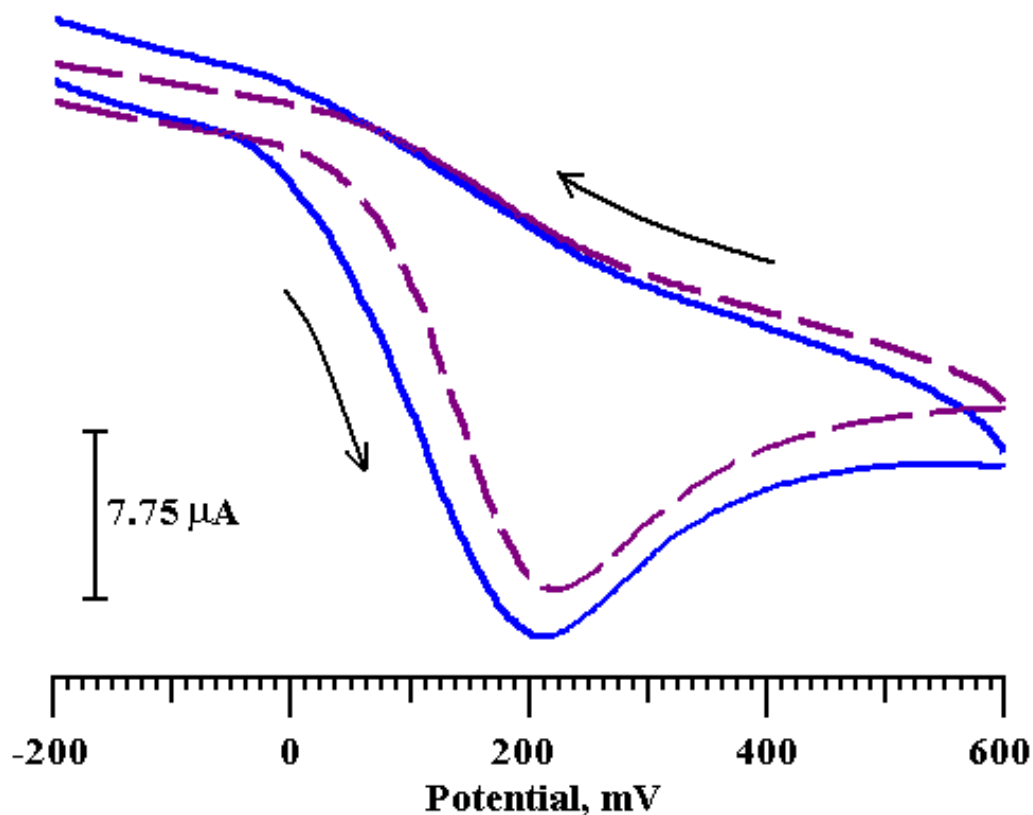


Figure 4. Cyclic voltammogram of 1×10^{-4} M AA at CdO nanoparticles modified CPE (solid line) and at bare CPE (dashed line).

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

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