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Cadmium oxide nanoplatelets: synthesis, characterization and their electrochemical sensing property of catechol

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Abstract Cadmium oxide (CdO) nanoplatelets were synthesized by thermal decomposition of cadmium malonate. The synthesized CdO nanoplatelets were characterized by X-ray diffraction (XRD); from the XRD analysis, it is clear that the phase structure of CdO nanoplatelets was found to be face-centered cubic with the average crystalline size of 40-50 nm. FT-IR analysis shows the presence of surface carboxyl and hydroxyl groups on to the CdO nanoplatelets. From DRS-UV-Vis analysis, both the direct and indirect band gaps of the CdO nanoplatelets were found to be 2.0 and 1.67 eV, respectively. From the FE-SEM analysis, the morphology of the synthesized CdO was found to be nanoplatelets, which were randomly agglomerated. Further, HR-TEM was used to confirm the formation of nanoplatelets. The electrochemical sensing property of CdO nanoplatelets was carried out by cyclic voltammetry (CV) by coating CdO nanoplatelets on Glassy carbon electrode (GCE) and using it as working electrode for sensing of catechol. The enhanced electrochemical behaviour is mainly attributed to the nanometer dimensions and surface hydroxyl groups on the CdO nanoplatelets. Chronoamperometry (CA) was used to determine the sensitivity and repeatability of the modified electrode. The

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modified electrode shows linear range of catechol concentration between 7.5×10^{-6} and 1.5×10^{-4} M with sensitivity of 9.8 nA μ M⁻¹.

Keywords CdO nanoplatelets · Electrochemical sensing · Catechol · Chronoamperometry

Introduction

Nanostructured metal oxides such as Fe₂O₃, TiO₂, V₂O₅, CuO and ZnO have received considerable attention over the past decades, due to their unique electronic, optical, thermal properties and their promising applications in fabricating nanoscale devices [1-5]. In meticulous, the nanostructured metal oxides are of great interest in the fields of drug delivery, photocatalyst, electrocatalyst and solid oxide fuel cells [6-8]. Among the various nanostructured metal oxides, CdO is an important n-type semiconductor metal oxide, which belongs to the II-VI group with large band gap, low electrical resistivity and high transmission in the visible region. Because of these properties, it has been widely investigated in various fields such as photovoltaic cells, transparent electrodes, etc. [9, 10]. Several synthetic routes such as hydrothermal method, template assisted method, solvothermal methods, chemical co-precipitation method, vapor phase transport, thermal evaporation, microwave method and sonochemical method were adopted to prepare CdO nanostructures. Depending on the synthetic procedures, the morphology of the CdO varies such as nanowires, nanotubes, nanofibers, nanorods, nanoclusters, nanocubes, nanobelts and nanoparticles [11-15]. The physical and chemical properties of CdO depend on the size, shape and stoichiometry that further lies on the synthetic procedures [16]. Nanostructured CdO has been employed in processes such as energy storage system, electrochromic thin films [17], magnetoresistive devices [18], heterogeneous catalysis and gas sensors [19]. Furthermore, CdO and other cadmium-based oxides were demonstrated to have excellent electrocatalytic activity toward various compounds, ozone and oxygen evolution [20]. Nanostructured CdO-modified electrodes have been used to detect diverse organic molecules such as glucose, dopamine, cysteine, propylamine, hydroquinone and methanol [21-25] as model compounds. Large amounts of phenolic compounds were released in the environment by various industries, such as coal mining, oil refinery, paint, polymer and pharmaceutical preparation. These compounds are harmful to human beings. Hence, it becomes more important to monitor the levels of the phenolic compounds in the environment. Though, chemically modified electrodes and enzyme-modified electrodes were reported to analyse the levels of catechol [26, 27], the enzyme modification process was tedious and the modified electrodes were unstable under room temperature conditions due to the poor stability of the immobilized enzymes.

In this work, we report the synthesis of CdO nanoparticles using cadmium malonate as single precursor via facile thermal decomposition route. The synthesized CdO nanoparticles were used to modify the glassy carbon electrode and employed for the electrochemical sensing towards catechol.

Experimental

Materials

Cadmium acetate, malonic acid, sodium hydrogen phosphate and sodium dihydrogen phosphate were purchased from Qualigens (Mumbai, India) and were used without further purification. Catechol was purchased from Sigma (USA) and was used as received. Doubly distilled water was used as the solvent.

Characterization

FT-IR spectrum of CdO was recorded on Schimadzu FT-IR 8300 series instrument using potassium bromide pellets. The DRS-UV–Visible spectrum of the sample was recorded on UV-1601OC, Shimadzu instrument. Powder X-ray diffraction (XRD) analysis was carried out using Brucker D8 ADVANCE with monochromatic CuK α_1 radiation ($\lambda = 1.5406$ Å). The morphology of the sample was analysed by FE-SEM using a HITACHI SU6600 field emission-scanning electron microscopy and HR-TEM using a FEI TECNAI G² model T-30 at accelerating voltage of 250 kV. Cyclic voltammetry was performed using CHI 600A instrument with bare and modified GCE as working electrode, platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammetric measurements were carried out using 0.1 M phosphate buffer solution (PBS) as the background electrolyte.

Synthesis of cadmium malonate

Cadmium malonate $[CdC_3H_2O_4\cdot 2H_2O]$ was prepared by stirring cadmium acetate and malonic acid in 1:1 ratio in 50 mL of distilled water at 60 °C for 2 h. Cadmium malonate was obtained by evaporating the above solution in water bath at 80 °C for 3 h.

Synthesis of CdO nanoplatelets

Cadmium malonate was heated in muffle furnace at 550 °C for 6 h; the temperature of the muffle furnace was raised at the rate of 5 °C min⁻¹. After that, the temperature of the muffle furnace was reduced to room temperature and the obtained CdO nanoplatelets were used for characterization.

Results and discussions

X-ray diffraction studies

XRD pattern of CdO was shown in Fig. 1. The diffraction peaks of CdO reveal that it has a face-centered cubic structure, which exactly matches with JCPDS No. 75–0592 along with space group of Fm3m (225) and no impurity phases such as CdO₂ and Cd(OH)₂ were observed. The observed diffraction peaks at $2\theta = 33.020^\circ$, 38.34° , 55.32° , 65.95° and 69.30° are associated with [111], [200], [220], [311] and [222] plane, respectively, with the *d*-spacing values of 0.46, 0.40, 0.27, 0.23 and 0.22 nm, respectively. The sharp diffraction peaks clearly indicate the high crystalline nature of the prepared CdO. Using Scherrer equation, the average crystallite size was calculated and found to be 40–50 nm.

FT-IR spectroscopy

FT-IR spectrum of CdO is shown in Fig. 2. The spectrum exhibits a broad band near $3,400 \text{ cm}^{-1}$ due to the OH-stretching vibrations of free and hydrogen-bonded hydroxyl groups. The peak at $1,380 \text{ cm}^{-1}$ corresponds to the C=O/C–O vibrations. The other bands at 852 and 723 cm⁻¹ may be related to the water molecules combined with the hydroxide [28]. A peak at 520 cm⁻¹ corresponds to the formation of Cd–O [29].

Thermogravimetric analysis

The thermal decomposition of cadmium malonate was investigated by thermogravimetric analysis (TGA) under



Fig. 1 X-ray diffraction pattern of CdO nanoplatelets



Fig. 2 FT-IR spectrum of CdO nanoplatelets

nitrogen atmosphere. Figure 3 shows a small weight loss at about 150 °C, which might be due to the hydrated water molecules. The compound undergoes decomposition above 310 °C, with a weight loss of approximately 67.0 %. From the first weight loss, it is evident that the decomposed product contains surface hydroxyl groups. These surface hydroxyl groups were lost on further heating in the temperature range of 600-700 °C. The remaining mass was found to be 33.0 %.

DRS-UV-Visible spectroscopy

The diffused reflectance spectrum was carried out for CdO in room temperature. The variation of optical absorbance with wavelength (λ) of CdO is shown in Fig. S1. The nature and value of the optical band gap can be determined by the fundamental absorption, which is due to the electron excitation from the valance band to conduction band. The



Fig. 3 TGA curve of cadmium malonate

relation between the absorption coefficient (A) and the incident photon energy (hv) can be given as

$$(\alpha hv)^{1/n} = A \big(hv - E_{\rm g} \big)$$

where α is a constant and E_g is the band gap of the material and exponent n depends on the type of transition. For direct allowed transition, n = 1/2; indirect allowed transition, n = 2; and for direct forbidden, n = 3/2. To determine the possible transitions, $(\alpha h v)^{1/n}$ versus hv were plotted, and corresponding band gap were obtained from extrapolating the straight portion of the graph on hv axis. The direct band gap calculated from $(\alpha hv)^2$ versus hv plot is found to be 2.00 eV and the indirect band gap is 1.67 eV calculated from $(\alpha hv)^{\frac{1}{2}}$ versus hv plot as shown in Figs. S2 and S3, respectively. However, the obtained band gap of the CdO nanoplatelets is smaller than the reported value [30]. This difference in band gap of CdO originates from non-stoichiometric composition and strongly influenced by the synthetic procedures [31]. In fact, the presence of cadmium interstitials, i.e., Cd²⁺ ions, or oxygen vacancies gives rise to defect states and there may be some finite transition probabilities from these states, which leads to the indirect transitions in CdO.

FE-SEM analysis

Figure 4a and b shows the FE-SEM image of the synthesized CdO; it can be seen that diameter of CdO nanoparticles annealed at 550 °C is in the range of 90-220 nm. Since the decomposition temperature is around 550 °C, the size of the CdO nanoparticles increases due to the phenomenon called high degree of supersaturation of the decomposed products of cadmium malonate complex. This high degree of supersaturation accelerates the crystal growth formation reaction within a short time. At this stage, the controlling step of the reaction takes place by the transformation from grain growth to crystal nucleus formation. The rate of particle aggregation is a predominant factor, which controls both the morphology and structure of the CdO nanoparticles [32]. At the temperature of 550 °C, the crystal nucleus continue to grow and nucleus aggregation would be predominant which was caused by the rapid formation of crystal nucleus due to high temperature which results in aggregation among the crystal nucleus [33, 34].

HR-TEM analysis

The formation of CdO nanoplatelets were confirmed by HR-TEM analysis (Fig. 4c). The size of the nanoplatelets was found to be ~ 200 nm, which is consistent with the FE-SEM analysis. The edges of the nanoplatelets were thin and irregular in nature.

Electrochemical sensing property

Figure 5 shows the cyclic voltammograms (CV) of bare and CdO/GCE in the absence of 0.1 mM catechol in 0.1 M PBS. It can be seen that no oxidation-reduction peak was observed at the CdO/GCE in 0.1 M PBS in the potential range of -0.4 to +1.0 V. Curve b of Fig. 5 clearly indicates that the CdO/GCE is not electroactive in the selected potential range which pointed out that the CdO/GCE can be utilized for the sensing of catechol. Though the CdO/GCE is not active in the selected potential range, it shows higher current response when compared with that of bare GCE (Fig. 6). In Fig. 6, the CdO/GCE (curve b) shows shift in potential with enhanced peak current in presence of 0.1 mM catechol than the bare GCE (Fig. 6a) indicates the electrocatalytic ability of the modified electrode. This electrocatalytic effect was attributed to the larger available surface area of the modifying layer due to the nanometer size of the sample [1], as evident by the FE-SEM analysis. Further, the surface -OH group of CdO shown in FT-IR forms the hydrogen bonding with the hydroxyl group of catechol. This hydrogen bonding effectively contributes to the weakening of hydroxyl bond to facilitate the electron transfer through the hydroxyl group of catechol O-H-O to surface hydroxyl group of CdO. The mechanism of elctrooxidation of catechol at CdO/GCE is shown in Scheme 1. Figure 7 shows the effect of scan rate on the electrochemical response of 0.1 mM catechol at the CdO/ GCE. As can be seen in Fig. 7, the oxidation peak current shifted positively and the reduction peak current moved negatively, and the value of ΔE was less than 300 mV. Figure 7 shows that both the oxidation and reduction peak currents were almost linearly proportional to the square root of scan rate in the range of $10-100 \text{ mV s}^{-1}$. It



Fig. 4 a, b FE-SEM images of CdO nanoplatelets with a magnification of 500 nm. c HR-TEM images of CdO nanoplatelets

suggests that the CdO layer has good electrochemical activity and fast electron transfer at pH 7.4. It is reported that the redox process of catechol proceeds through



Fig. 5 Cyclic voltammograms of (**a**) bare GCE and (**b**) CdO/GCE in absence of 0.1 mM catechol in 0.1 M PBS



Fig. 6 Cyclic voltammograms of a bare GCE and b CdO/GCE in presence of 0.1 mM catechol in 0.1 M PBS



Scheme 1 Mechanism of electrooxidation of catechol at CdO/GCE

 $2e^-$, $2H^+$ process [35]. In order to calculate, the number of electrons involved in the overall reaction can be obtained by the following equation,



Fig. 7 Cyclic voltammograms at CdO/GCE for 0.1 mM catechol at different scan rates: (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80,(i) 90 and (j) 100 mV s⁻¹



Fig. 8 Typical amperometric i-t responses of CdO/GCE for the detection of catechol at an applied potential of 0.4 V versus SCE in pH 7.4 PBS under stirring condition. *Inset figure* shows the plot of current response versus concentration of catechol

$$I_{Pa} = nFQv/4RT$$

$$n = I_{Pa}4RT/FQv$$
(2)

where *n* is the number of electrons involved in the reaction, I_{Pa} is the anodic peak current, *R* is the gas constant, *T* is the temperature (*K*), *F* is the Faraday constant, *Q* is the charge and *v* corresponds to the scan rate. The total number of electrons involved in the redox process of catechol is 1.73 (~2). To determine the sensitivity and repeatability, response of CdO/GCE chronoamperometric measurements was carried out in 0.1 M PBS at stirring condition and the optimum electrode potential was selected as +0.4 V versus SCE. Figure 8 displays the chronoamperometric current–time response of the CdO/GCE upon the addition of

0.2 mL of 0.1 mM catechol. A successive addition of catechol to continuously stirred 0.1 M PBS produces a significant increase in the current. The almost equal current steps for each addition of catechol illustrate that the CdO/ GCE is stable and has an efficient electrocatalytic activity towards the catechol. The prompt response was attributed to the heterogeneous electron transfer of CdO/GCE. The calibration graph for the determination of catechol by the CdO/GCE is shown as the inset in Fig. 8. The linear range was almost found between 7.5×10^{-6} and 1.5×10^{-4} M with a correlation coefficient of 0.9952 corresponding with a sensitivity of 9.8 nA μ M⁻¹, shows that the CdO/GCE is highly sensitive towards catechol. The results clearly indicate that the electrocatalytic reaction takes place between the CdO/GCE and catechol, which is due to the electron transfer between catechol and the modified electrode; as a result, the electrochemical oxidation of catechol becomes easier. In addition, it is clear that CdO/GCE can be effectively used for the electrochemical sensing of catechol.

Conclusion

CdO nanoplatelets were synthesized by simple thermal decomposition of cadmium malonate at 550 °C. The XRD, FT-IR and DRS-UV–Vis analyses were used to study the synthesized sample spectrally and FE-SEM analysis was used to study the morphology of the sample. CdO nanoplatelets were successfully fabricated onto the GCE for sensing of catechol. From the electrochemical measurements, it is clearly understood that the CdO nanoplatelet-modified electrode shows a wide linear range of concentration for catechol sensing.

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