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CeO$_2$-MWCNT nanocomposite based electrochemical sensor for acetaldehyde

RayammarakkarM.Shereema[a,b], SindhuR.Nambiar[a], S. Sharath Shankar [a]*andTalasila P. Rao [a,b] *

[a]*Chemical Sciences & Technology Division (CSTD),*

CSIR-National Institute for Interdisciplinary Science & Technology (CSIR-NIIST),

*Trivandrum 695019, INDIA.*e-mail: tprasadarao@rediffmail.com*

[b]*Academy of Scientific and Innovative Research (AcSIR), New Delhi 110001, India.*

Abstract

The present study endeavours to build a new, highly sensitive and selective electrochemical sensor with CeO$_2$-MWCNT nanocomposite film, which enhances the sensing platform to detect acetaldehyde. The chemically synthesised CeO$_2$ nanoparticles were subjected to adsorb on MWCNT. Thus prepared nanocomposite was characterized by XRD, SEM and Impedance spectroscopy. Drop to drop method was employed in the preparation of CeO$_2$-MWCNT modified glassy carbon electrode which could sense nanomolar levels of acetaldehyde by cyclic voltammetry. Under optimal conditions, the developed sensor detected acetaldehyde in the concentration range of 10^{-8} to 10^{-5} M with a detection limit of 7.4×10^{-9} M accompanied with a good precision of 1.6 % at 10^{-6} M of acetaldehyde. Moreover, it exhibited reasonably good selectivity towards acetaldehyde in conjunction with different co-existing organic species and was successfully applied to synthetic fruit juice samples.

Key words: Multiwalled carbon nanotubes-CeO$_2$ nanocomposite film, Acetaldehyde, Synthetic fruit juices.

1 INTRODUCTION

The incomplete combustion of petroleum fuels and biomass produces aldehydes which are ubiquitous air pollutants[1]. Inhalation of acetaldehyde may result in bronchitis, dottiness, protein denaturation and sometimes even death [2-4]. Acetaldehyde is found in many food items including, ripe fruits, beverages, vegetables, cheese and other dairy products. Ripened fruit contains about 80% of acetaldehyde than unripe ones. In beverages, it is formed due to the enzymatic oxidation of alcohol. Therefore, the main pathways by which acetaldehyde enter our body includes air, water, alcohol drinking and tobacco smoke. The increased concentration of acetaldehyde in our body favours its reaction with DNA due to its strong electrophilic property which could induce mutagenesis and carcinogenesis [5-6]. Being toxic at low concentration and carcinogenic when exposed for prolonged time, aldehyde detection is significantly important for monitoring environmental and domestic pollution [7-9], as well as food sophistication or contamination from packaging. Hence, the development of sensitive, rapid, simple, and low-cost devices for acetaldehyde detection is urgent and important.

There are limited reports available on acetaldehyde detection. Abbas et al. employed neutral red- sulfite-acetaldehyde system to detect traces of acetaldehyde by developing a kinetic method [10]. Yashuhara and shibamoto detected it using gas chromatography with a nitrogen-phosphorus detector [11]. A gas chromatographic method using electron capture detector was adopted for the determination of the same by Mori et al. [12]. High performance liquid chromatography has been used for the same purpose [13-16]. Determination of aliphatic aldehydes in aqueous solution by the inhibition of luminol chemiluminescence induced by hydrogen peroxide in the presence of potassium hexacyanoferrate has been reported [17]. Since all these methods converted acetaldehyde to some other form to detect it, they are considered to be

indirect methods. However, there were studies reported to have detected acetaldehyde as it is by amperomety-based sensor [18].

Cerium oxides mark their distinctive application as excellent catalysts. Over the years, cerium oxide and cerium oxide-based materials have been investigated as structural and electronic promoters of heterogeneous catalytic reactions. One of the most familiar applications in this field is the utilization of CeO_2 as the key component in three-way catalysts for the treatment of exhaust gas from automobiles [19]. Among different lanthanide oxides, ceric oxides are widely used due to their excellent catalytic properties [20-22]. CeO_2 and its nanocomposite films like CeO_2-$BaTiO_3$, cerium oxide (NanoCeO$_2$)–chitosan were also explored for applications in electronic devices [23] and biosensors [24, 25]. Composite materials based on CNTs and metal oxide nanomaterials integrate their unique characters and functions and may also exhibit some new properties caused by the cooperative effects between the two kinds of materials [26-30]. Therefore, these composite materials have shown very attractive potential applications in many fields.

In this article we describe a direct method for the determination of acetaldehyde with CeO_2-MWCNT/GCE by cyclic voltammetry. We mainly concentrated on CeO_2-MWCNT nanocomposite based on the report that, CeO_2 converts acetaldehyde into acetic acid by donating its labile oxygen atom present in their crystal lattices due to its fluorite structure. Here, Ce^{4+} is reduces itself into Ce^{3+} by oxidizing molecules on its surface [31].

2 Experimental

2.1 Chemicals and reagents

Acetaldehyde, multi walled carbon nanotube and cerium oxide was purchased from Aldrich, Milwauke, WI, USA. Deionised double distilled water was used in the preparation of working solutions. All other chemicals were of analytical reagent grade (E Merck, Mumbai, India) and were used as received, without any further purification. Potassium nitrate solution of

pH 6 was used as the supporting electrolyte in all the electrochemical experiments. Stock solution of 0.1 M acetaldehyde was freshly prepared for each series of experiments.

2.2 Instrumentation

Electrochemical measurements were done using a three-electrode cell, with a glassy carbon electrode (3 mm in diameter) as working electrode, Pt wire as auxiliary electrode and Ag/AgCl electrode as reference electrode using a VSP-potentiostat/galvanostat (Biologic Science Instruments). The Oakton pH 700 meter, Germany, was used to measure pH. The size and morphology were examined with the aid of a scanning electron microscope (SEM), JEOL, Model JSM 5600 LV, Tokyo, Japan. UV- Visible spectra were recorded with a computer controlled double beam UV-Vis spectrophotometer UV-2401PC (Shimadzu, Kyoto, Japan), X-ray diffraction (XRD) pattern of the samples were recorded on a Philips X'pert diffractometer (XRD, X'Pert Pro MPD) with CuKα radiation (1.5406A).

2.3 Preparation of CeO$_2$-MWCNT nanocomposite and fabrication of CeO$_2$-MWCNT/GC electrode

CeO$_2$ nanoparticles were synthesized by chemical method reported in the literature [32]. An appropriate amount of MWCNT (0.25 %) was added to the synthesized CeO$_2$ and sonicated for 30 minutes to form a homogeneous solution. The Van der Waals force of attraction between CeO$_2$ and MWCNT made CeO$_2$ to easily attach to the walls of MWCNT. This benefit was used for the fabrication of CeO$_2$-MWCNT/GC modified electrode. The GC electrode was polished with alumina slurry followed by sonication. On to this fine surface of GC, 5 μL of the above suspension was added by drop to drop and air dried to obtain the CeO$_2$-MWCNT/GC modified electrode. Thus developed modified electrode was used to detect acetaldehyde in 0.1M KNO$_3$ of pH 6.

2.4 Electrochemical measurements

A freshly prepared solution of acetaldehyde (1μM) was added to an electrochemical cell containing 10 ml of 0.1M KNO_3 as supporting electrolyte (pH 6). Cyclic voltammetric curves were plotted by scanning the potential from -0.4 to 1.2 V at a scan rate of 50 mV s^{-1}. The acetaldehyde quantification was achieved by measuring the oxidation peak current at 0.78V.

3 Results and Discussions

3.1 Characterization studies

The prepared CeO_2-MWCNT nanocomposite was characterized by the following methods.

3.1.1 Spectral and morphological characterization

Fig.1 showed the XRD pattern of CeO_2 and CeO_2-MWCNT nanocomposite in the range of 10-70^0.The four angles at 28.5^0, 33.1^0,47.5^0 and 56.3^0 correspond to (111), (200), (220) and (311) planes of the face centered cubic phase of CeO_2 (JCPDS 78–0694). After incorporating MWCNT two additional peaks were observed at 26.2^0 and 42.1^0 corresponding to the plane (002) and (101) which is the clear evidence of adsorption of CeO_2 on MWCNT. From Scherrer formula,

$$D = K\lambda/\beta \cos\theta$$

Where D is the crystallite size, K is the Sherrer constant (0.89), λ is the wave length of Cu Kα radiation (0.15406 nm), β is FWHM (full width of peak intensity at half maximum) in

radians, θ is the peak (1 1 1) position in degrees, particle size of CeO_2 was calculated and was

found to be 15-25 nm.

Fig.2 (a), (b), and (c) showed the scanning electron micrographs of CeO_2, MWCNT and

CeO_2-MWCNT nanocomposites. It was observed that CeO_2 possessed the spherical shape with

size 10-30 nm (a) and MWCNT the tubular form (b). The spherically shaped CeO_2 sticked on

the surface of MWCNT and it is the concrete indication of the CeO_2-MWCNT nanocomposite.

3.1.2 UV-Visible absorption spectrum

Fig. 3 showed the UV-Visible absorption spectrum of CeO_2 and CeO_2-MWCNT

nanocomposite. A well-defined sharp and strong absorbance peak at 300 nm was observed which

is due to the Ce^{4+}, indicating a narrow and uniform particle size distribution obtained via this

route. There was no change in CeO_2 absorbance after the addition of MWCNT, which suggests

that MWCNT has no influence on the size and structure of the CeO_2 nanoparticles. Hence, the

role of MWCNT was to provide a better surface for the oxidation of acetaldehyde, thereby

increasing the current, which was confirmed from electrochemical characterization studies.

3.2 Electrochemical characterization

3.2.1 Electrochemical Impedance Spectroscopy

EIS is a commonly used characterization technique for studying the impedance changes of

the electrode surface during modification process. In Nyquist plot, the semi-circular or real

portion is related to electron transfer resistance R_{ct} and linear or imaginary part is related to

controlled diffusion process. Electron transfer Resistance is dependent on the diameter of the

semi-circular portion. Large semicircle with high R_{ct} means (contributes) the system has higher

resistance to the flow of electrons. Fig.4 shows EIS of bare GCE (a), CeO_2/GCE (b) and CeO_2-

MWCNT/GCE (c) in $Fe(CN)_6^{3-/4-}$ system. Inset is the equivalent circuit used to analyse the impedance behavior. The small semicircular portion of GCE implies it has low resistance towards the electron transfer process. After modifying with CeO_2, the diameter of semicircle was increased with R_{ct} value 489Ω, indicating the CeO_2 nanoparticles hindered the electron transfer of the electrochemical probe of $Fe(CN)_6^{3/4-}$ and this hindrance was decreased (R_{ct} =401 Ω) after incorporating MWCNT with CeO_2 nanoparticles. These results showed the efficiency of CeO_2-MWCNT/GCE.

3.2.2 Cyclic Voltammetric analysis

In comparison to the bare GC and CeO_2/GC electrodes, the CeO_2-MWCNT/GC electrode provided more electroactive surface for the oxidation of acetaldehyde. This was confirmed through the cyclic voltammteric experiments of different electrodes in 1mM $K_3[Fe(CN)_6]$ solution. Fig.5 represented the cyclic voltammograms of bare GC (curve a), CeO_2/GC (curve b) and CeO_2-MWCNT/GC (curve c) electrode in 1 mM $K_3[Fe(CN)_6]$ with 0.1 M KCl as the supporting electrolyte. At bare GC, ferricyanide showed anodic peak at 170 mV with peak current 11 μA and cathodic peak at 98 mV with 13 μA. ΔE_p for bare GC was found to be 72 mV, which was an indication of quasi reversible nature of bare GC. In CeO_2/GCE, the anodic peak potential shifted to more positive side i.e., 196 mV and cathodic peak current potential shifted to more negative side i.e., 93 mV with ΔE_p 103 mV. Sensitivity of $K_3[Fe(CN)_6]$ increased remarkably, which could be explained by the change of particle size and increase in electroactive surface area at CeO_2/GCE, but at the same time process still remained quasi reversible. After adding MWCNT to CeO_2/GCE, a rapid and a sharp increase of the both anodic (28 μA) and cathodic current (29 μA) was observed with shift in both anodic (202 mV) and cathodic peak (123 mV) potentials. ΔE_p at CeO_2-MWCNT/GCE was 60 mV, which implied the

electrochemical process had changed to reversible indicating the good performance of the modified electrode. Therefore, the electrocatalytic effect is higher in CeO_2-MWCNT/GC electrode as compared to CeO_2/GC and bare GC electrodes.

Fig.6 showed the cyclic voltammograms of acetaldehyde in a potential range of -0.4 to 1.2 V at a scan rate of 50 mV/s in 0.1M KNO_3 solution at bare GC (curve a), MWCNT/GC (curve b) CeO_2/GC (curve c) and CeO_2-MWCNT/GC (curve d) electrodes. There were no peaks observed at bare GC, MWCNT/GC electrodes. One broad anodic peak at 0.88 V due to the oxidation of Ce was generated at the CeO_2/GC electrode, which further sharpened and shifted to 0.8 V with an increase in current at the CeO_2-MWCNT/GCE. The broadened reduction peak appeared at 300 mV on CeO_2/GC was shifted to 400 mV on CeO_2-MWCNT/GCE representing the quasi reversible nature of both CeO_2/GCE and CeO2-MWCNT/GCE.

### 3.3 Voltammetric analysis of acetaldehyde at CeO_2-MWCNT/GCE

Fig.7 (a) showed the cyclic voltammetric curves of acetaldehyde with different concentrations in 0.1 M KNO_3 buffer of pH 6.0. For each addition of acetaldehyde there was a decrease in peak current. When the acetaldehyde concentration increased, more CeO_2 would be used for the conversion of acetaldehyde to acetic acid, this could be the reason for decline in the peak current. The plot of peak current vs. [acetaldehyde] (Fig.7(b(i))) gives dual linearity, one at lower concentration range from 0.01 to 0.5 μM and other in higher concentration range from 0.5 to 10 μM. Which means the fabricated electrode could be applied for a wide range of concentrations. For the calculation of limit of detection, a plot of peak current vs. log [acetaldehyde] was drawn. Again, a good linear graph with a wider range of concentrations, 10^{-8} to 10^{-5}M was obtained (Fig.7(b(ii)). The limit of detection was calculated as 7.4×10^{-9}M based on 3 times the standard deviation of the blank value. The relative standard deviation was found to be

1.6% for 10 replicate determinations of 10^{-6} M of acetaldehyde, which revealed the extremely high precision of designed acetaldehyde sensor. Moreover, the developed CeO_2-MWCNT/GCE was able to produce same current for a period of one week; this showed the stability of the electrode.

3.4 Mechanism

Possible mechanism for this electrode process could be explained as follows, Ce^{4+} is reduced itself into Ce^{3+} by oxidizing the molecules on its surface. The energy between 4f and 5d is almost same so we can easily switch off Ce^{4+}/Ce^{3+} inter conversion by applying low potential energy. In fluorite structure of CeO_2, the oxygen atom can easily move around the crystal allowing the cerium to reduce or oxidize the molecule on its surface. Hence the CeO_2 can easily convert acetaldehyde into acetic acid by donating its labile oxygen atoms to the acetaldehyde. Scheme 1 gave the schematic representation of this mechanism.

$$Ce\ (IV) + CH_3CHO \longrightarrow Ce\ (III) + CH_3COOH$$
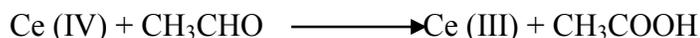
3.5 Effect of scan rate

The effect of scan rate on the electrocatalytic behavior of the modified electrode towards the oxidation of acetaldehyde was studied by cyclic voltammetry. Fig.S1 (a) & Fig.S2(a) show the cyclic voltammograms of oxidation of acetaldehyde at various scan rates (20 to 90 mVs^{-1}) at the CeO_2-MWCNT/GC modified electrode and CeO_2/GC electrode respectively. It could be perceived from the above CV's that with an increase in scan rate, the peak potential for the electro-oxidation of acetaldehyde shifts to more positive potentials, suggesting a kinetic limitation in the reaction between the redox sites of modified electrode and acetaldehyde. In addition, catalytic current increases with increasing scan rate, because in short scale experiments there is no enough time for catalytic reaction to take place completely.

In order to obtain information about the rate determining step, the Tafel slope was drawn

using the following equation, for a diffusion controlled process,

$$E_p = (b/2) \log \nu + \text{constant}$$

Based on the above equation, from the Tafel plot (Fig. S1 (b)) the slope of E_p vs. $\log \nu$ is

b/2 where b indicates the Tafel slope. The slope of E_p vs. $\log \nu$ for CeO_2-MWCNT/GC electrode

was found to be 0.0809. This slope indicates an electron transfer co-efficient of $\alpha = 0.73$ for a

one electron transfer process, which is the rate determining step. Similarly for CeO_2/GC

modified electrode, α value was 0.59 (Fig. S2 (b)).On the basis of the slopes of the linear

dependence of the anodic peak currents on the square root of the potential sweep rates (Fig. S1

(c), fig.S2(c)), by Randle-Sevcik equation

$$I_p = (2.99 \times 10^5) \, \alpha^{0.5} n^{1.5} ACD^{0.5} \nu^{0.5}$$

where I_p is the peak current, A is the electrode surface area, D is the diffusion co-efficient and C

is the bulk concentration, the diffusion coefficient of acetaldehyde was calculated to be $5.46 \times 10^{-3} \, cm^2/s$ and $1.55 \times 10^{-2} \, cm^2/s$ for CeO_2/GC and CeO_2-MWCNT/GC modified electrode

respectively.

The reaction (adsorption controlled or diffusion controlled) that controlled

acetaldehyde oxidation on CeO_2/GC and CeO_2-MWCNT/GC was studied from the plots of I_p Vs

ϑ (Fig.S1 and S2 (d)) and I_p Vs $\vartheta^{0.5}$. In case of CeO_2/GC electrode, I_p Vs ϑ is more linear than Ip

Vs $\vartheta^{0.5}$ indicating adsorption controlled processes. But in CeO_2-MWCNT/GC the greater

linearity of the Ip vs. $\nu^{0.5}$ plot indicates the mass transfer being predominately diffusion

controlled.

3.6 Optimization studies for the determination of acetaldehyde at the CeO$_2$-MWCNT/GC modified electrode

In order to attain maximum sensitivity, the effect of concentration of CeO$_2$ and weight percentage of MWCNT was studied by varying the volume of CeO$_2$ and the weight percentage of MWCNT in the nanocomposite. While keeping the weight percentage of MWCNT constant, volume of CeO$_2$ suspension was varied from 250-1000 μl. As it can be seen from, fig.S3, 500 μL gave maximum current, further increment in concentration of CeO$_2$ from 500 μL the peak current decreased and the anodic peak became broad just like the peak obtained in CeO$_2$ alone, still it senses acetaldehyde from 10^{-8} M. By maintaining the concentration of CeO$_2$ at 500 μL we varied the weight percentage of MWCNT from 0.15 to 0.90 %   and observed a maximum sensitivity at 0.25 %, fig.S4. Further increase in weight percentage of MWCNT, decreased the sensitivity with increase in current, this could be due to the fact that the MWCNT provided its surface area for the adsorbtion of CeO$_2$ and also considerably contributed to the electron transfer process. Hence 500 μL of CeO$_2$ with 0.25% MWCNT was considered to be optimum conditions for further analysis.

Likewise, the effect of drop to drop volume of the nanocomposite on the GC was optimized and 5 μL exhibited better sensitivity. While increasing the drop to drop volume above 5μL the sensitivity shrunk, this could be attributed to the increasing film thickness and the possibility of peeling off from the electrode surface (Fig.S5).

3.7 Effect of electrolyte and pH

The different parameters which may possibly affect the electrochemical determination of acetaldehyde were also studied. Effect of different supporting medium including, sodium chloride, potassium chloride, sodium acetate, potassium nitrate, ammonium acetate and sodium

di-hydrogen phosphate electrolyte towards the electrochemical determination of acetaldehyde on the surface of CeO_2-MWCNT/GC electrode was analysed. Among which potassium nitrate gave better response for acetaldehyde sensing and was used as the supporting electrolyte for further analysis.

The effect of the pH of the supporting electrolyte on the electrochemical behaviour of the sensor was investigated over the range of 4.0–9.0. The response current and sensitivity of the sensor increased with increasing pH values from 4.0 to 6.0 and then decreased with further increase in pH (Fig. S6). This could be due to the fact that CeO_2 would act as a strong oxidising agent when they are in the acidic medium.

3.8 Comparison with reported acetaldehyde sensors

Table 1 depicts the comparative studies of the current method with the reported acetaldehyde sensing methods. In comparison with hitherto reported methods, the current method had wider calibration range and lower detection value. The only sensor which comes closest to the developed sensor is Au-nafion sensor with limit of detection 23nM but it offers only a small calibration range 0.025- 0.5 μM.

3.9 Selectivity studies and analysis of synthetic mixtures of fruit juice

Since acetaldehyde is present in most of the fruits, the selectivity of the CeO_2-MWCNT/GC modified electrode for acetaldehyde sensing was investigated under optimised conditions by testing the response to several compounds that are usually present in fruit juice. Among the different interferents, ethanol interferes even in equal amount but glucose, fructose, and glycerol do not interfere up to 100 folds. Cations like K^+ and Na^+ are not interfering in the acetaldehyde oxidation.

Fig.8 showed the peak current of 10^{-6} M of acetaldehyde and other interferents, which indicated that the developed electrode showed good selectivity towards acetaldehyde from the

potential interfering species and could be applied to determine its concentration in the fruit juice samples. Therefore, the developed modified electrode was applied for the determination of acetaldehyde in synthetic mixture of fruit juice using the standard addition method and the recoveries of acetaldehyde are presented in Table 2.

4 Conclusions

A voltammetric sensor based on CeO_2-MWCNT nanocomposite was designed for acetaldehyde sensing. MWCNT can improve the stability of the modified electrode, reduce the agglomeration level of CeO_2 nanoparticles, and increase the electron transfer rate. The catalytic oxidation of acetaldehyde was found to be highly sensitive at the nano-CeO_2-MWCNT/GC because of the synergistic effect of nano-CeO_2 and MWCNT. A lower detection limit of 7.4×10^{-9} mol/L, wide linear range from 10^{-8} to 10^{-5} mol/L, excellent selectivity, good stability and repeatability gives it the potential application in acetaldehyde sensing. Also interference study showed reasonably good selectivity and hence the developed modified electrode is suitable for measurement of acetaldehyde in fruit juice samples.

Acknowledgements

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TABLES

Table 1. Comparison with reported acetaldehyde sensing methods

Method	Modification	Linear calibration Range	Detection limit(nM)	Reference
HPLC-electrochemistry	GC	68 to 6800μM	86	[33]
Amperometry	Au-nafion	0.025 to 0.50μM	23	[18]
Amperometry	AIDH, NADH oxidase and NADs in a polyvinyl alcohol bearing styryl pyridiruum groups (PVA-SbQ) matrix/Pt disk	0.5 to **330** μM	-	[34]
Amperometry	PNR/sol–gel-AldDH-NADHOx electrodes	10 to 60μM	2600	[35]
Cyclic Voltammetry	Copper chloride modified copper electrode	2 to 50mM	-	[36]
Amperometry	Aldehyde dehydrogenase and diaphorase on platinum electrode	1 to 500μM	-	[37]
Cyclic Voltammetry	CeO_2-MWCNT/GC	0.01 to 10μM	7.4	Present work

Table 2: Analysis of synthetic fruit juice sample

Components (g/100ml)	CH₃CHO spiked (M)	CH₃CHO found (M)	Recovery (%)
Glucose: 1 Fructose: 1	10^{-8}	9.88×10^{-9}	98.8
Ethanol : 0.01 Glycerol: 0.01 Potassium: 0.02	10^{-7}	1.01×10^{-7}	101.0

Figure captions.

Fig.1   XRD pattern of CeO_2 and CeO_2-MWCNT nanocomposite

Fig.2 **(a)** SEM image of CeO_2 **(b)** MWCNT **(c)** CeO_2-MWCNT

Fig.3   UV-Visible absorption spectra of suspension of CeO_2 and CeO_2-MWCNT

Fig.4   Nyquist diagram of electrochemical impedance spectra of bare GC, CeO_2/GC and CeO_2-MWCNTs/GC electrodes in 0.1 M KNO_3 solution containing 5.0 mM $Fe(CN)_6^{3-/4-}$ (1:1). The inset is equivalent circuit of CeO_2-MWCNT/GC electrochemical impedance measurement system

Fig.5   Cyclic voltammograms of bare GC, CeO_2/GC and CeO_2-MWCNT/GC electrodes in 1 mM $K_3Fe(CN)_6$ and 0.1 M KCl as supporting electrolyte at a scan rate of 50 mVs^{-1}

Fig.6   Cyclic voltammograms of acetaldehyde (10^{-6}M) at bare GC, CeO_2/GC and CeO_2-MWCNT/GC modified electrodes in 0.1M KNO_3 as supporting electrolyte at a scan rate of 50 mVs^{-1}

Fig.7 **(a)** Cyclic voltammograms at the CeO_2-MWCNT/GC nanocomposite electrode in the presence of different concentrations of acetaldehyde **(b)** calibration curve in the range of 10^{-8} to 10^{-5} M of acetaldehyde (i) Ip vs. [acetaldehyde] (ii) Ip vs. log [acetaldehyde] plots

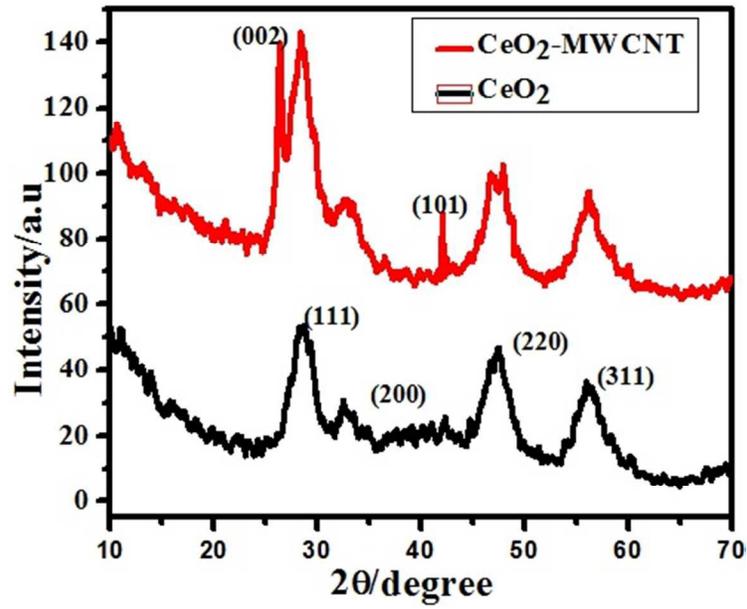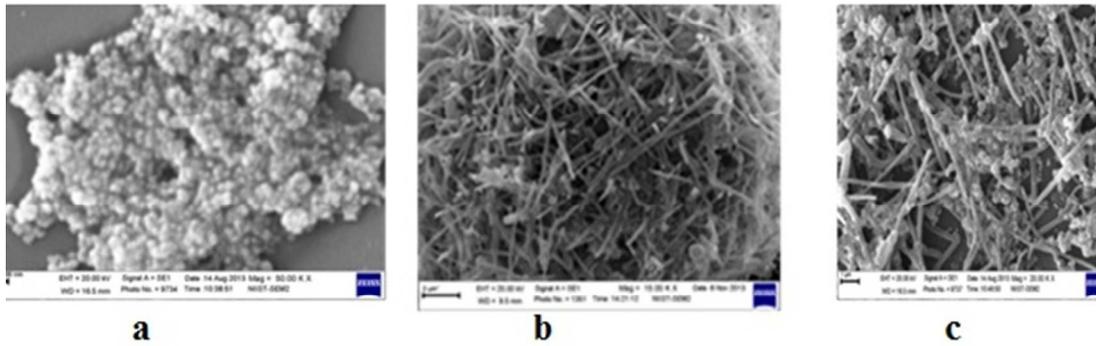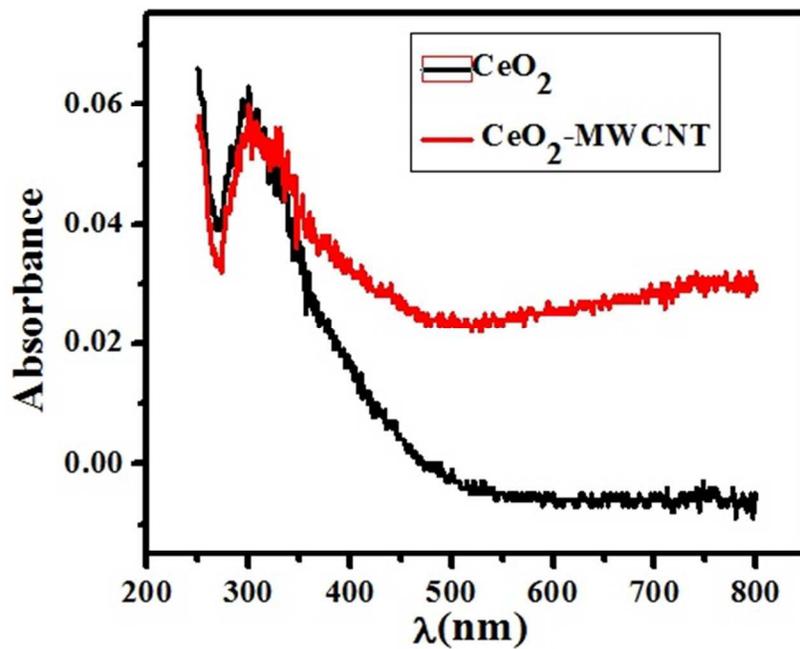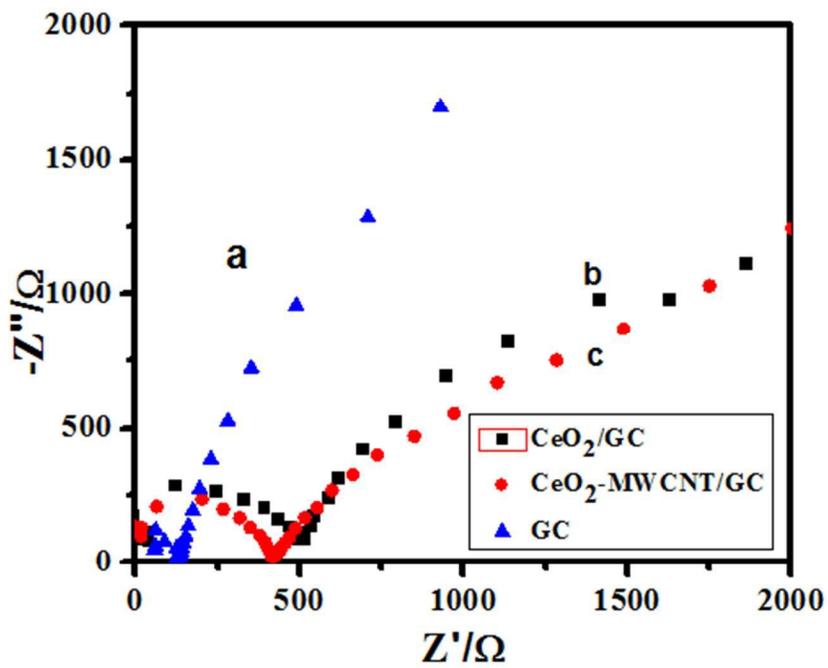**Fig. 8** Selectivity studies of acetaldehyde and other organics

Fig. 1

a   b   c

Fig. 2

Fig. 3

Fig. 4
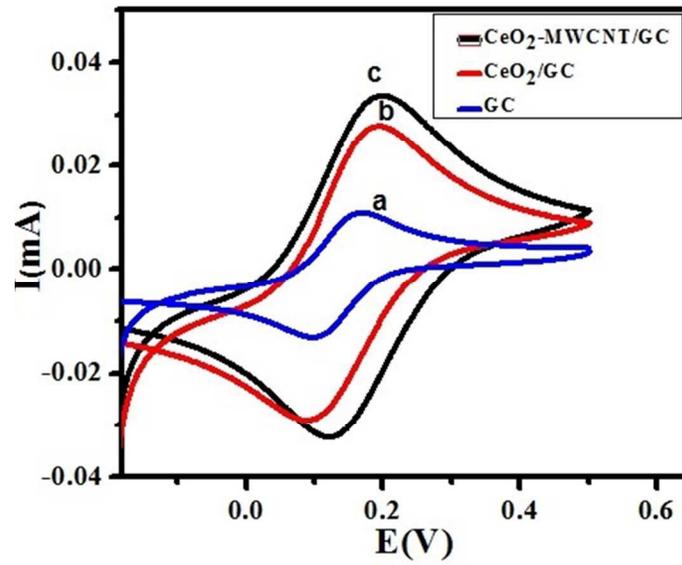
Fig. 5
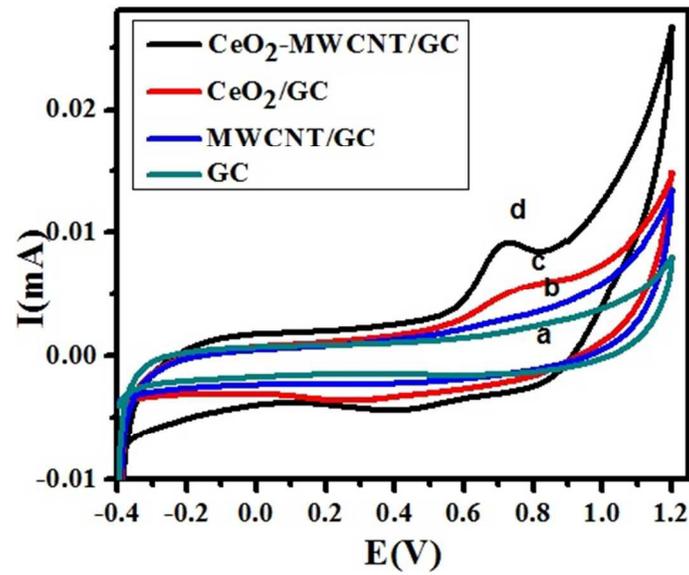
Fig. 6
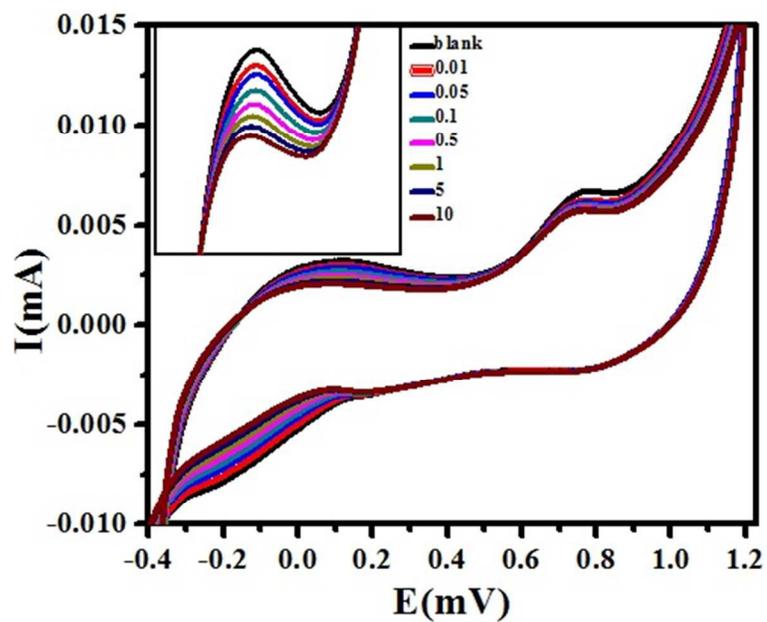
Fig. 7a

Fig. 7b

Fig. 8

Scheme 1