

*Full Paper*

## **Electrocatalytic Oxidation of Ascorbic Acid on Copper Iodide Modified Sol-Gel Derived Carbon Ceramic Electrode**

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**Abstract-** In this research, we reported a novel modified carbon ceramic electrode using CuI as modifier was fabricated by sol-gel technique. The electrocatalytic activity of the copper iodide modified sol-gel derived carbon ceramic (CIM-SGD-CC) electrode was examined for the oxidation of ascorbic acid (AA). Results showed that the CIM-SGD-CC electrode has high catalytic ability for electrooxidation of ascorbic acid. The response current exhibited good linear relationship for the concentration of ascorbic acid in the range from  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  mol L<sup>-1</sup>, with the correlation coefficient of 0.9902 and the detection limit of 1.66 μmol L<sup>-1</sup>. The kinetic parameter such as the electron transfer coefficient ( $\alpha$ ) and exchange current density ( $j_0$ ) for the modified electrode were calculated. The advantages of the modified CCE are its good stability and reproducibility of surface renewal by simple polishing, excellent catalytic activity and simplicity of preparation.

**Keywords-** Ascorbic Acid, Electrocatalytic oxidation, Copper iodide, Sol-gel, Carbon ceramic electrode

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## 1. INTRODUCTION

The concept of modified electrodes is one of the exciting developments in the field of electroanalytical chemistry [1]. Modification of electrodes surface with redox active materials reduce overpotential and minimize surface fouling and oxide formation compared to unmodified electrodes [2]. The modified electrode films cannot be renewed after contamination in short periods of time. Hence, it is necessary that the sensor preparation method be modified. Since the work of Lev's group on carbon ceramic electrodes (CCEs) [3], much effort has been made to fabricate chemically modified CCEs and to use them as sensors for voltammetric studies of different analytes. Carbon ceramic electrodes (CCEs) have received particular attention [4,5], since the combination of the flexibility of the sol-gel process (which enables control of the porosity and surface area of the oxide) with the conducting properties of the carbon materials gives CCEs advantages over other types of carbon-based electrodes. It is possible to obtain a renewable electrode surface, similar to that of carbon paste electrodes (CPEs) [6], that is more robust and possesses high chemical, thermal, and mechanical stability. The CCEs prepared by sol-gel techniques are interesting materials in the fields of chemical sensors and biosensors owing to their renewability, polishibility, chemical stability, physical rigidity, porosity, and permeability in electroanalysis [7-9].

Vitamin C or ascorbic acid (AA), a water-soluble vitamin, is widely present in many biological systems and in multivitamin preparations. AA is commonly used to supplement inadequate dietary intake and as an antioxidant [10]. Its deficiency leads to the development of a well-known syndrome called scurvy. It is administered in the treatment of many disorders, including Alzheimer's disease, atherosclerosis, cancer, and infertility as well as some clinical manifestations of HIV infections [11]. Many studies have been pursued to establish rapid and sensitive methods for the reliable determination of AA due to the biological and technological importance of AA. Up to date, various analytical techniques, including spectrophotometric, solid-phase iodine method and liquid chromatography have been developed to study the AA content in food, drugs and plants [12-15]. Compared to other choices, electrochemical analysis has attracted considerable attention for its simplicity and high sensitivity. However, it is difficult to determine AA electrochemically by direct oxidation on a conventional electrode because the direct redox reactions of AA at the bare electrodes are totally irreversible and require a high overpotential [16]. Moreover the direct redox reactions of AA at the bare electrodes often suffer from a pronounced fouling effect, which results in rather poor reproducibility [17-21].

The present work reports the preparation of copper iodide modified sol-gel derived carbon ceramic electrode and investigate the electrocatalytic properties of the modified electrode toward the oxidation of ascorbic acid. The results show that the modified electrode can be used as an amperometric sensor for the determination of ascorbic acid.

## 2. EXPERIMENTAL

### 2.1. Reagents and instrumentation

Methyltrimethoxysilane (MTMOS), ascorbic acid, and other chemicals were purchased from Merck or Fluka and used without any further purification. All solutions were prepared with doubly distilled water. Electrochemical measurements were carried out in a conventional three-electrode cell powered by an electrochemical system comprising an AUTOLAB system with PGSTAT12 boards (ECO Chemie, Utrecht, and The Netherlands). The system was run on a PC using GPES 4.9 software. CIM-SGD-CC electrode as working electrode (prepared as follows) was employed for the electrochemical studies. A platinum wire was employed as counter electrode and an Ag/AgCl electrode served as the reference electrode. All experiments were performed at room temperature of  $25\pm 2^\circ\text{C}$ .

### 2.2. Preparation of CIM-SGD-CC electrode

The fabrication of CIM-SGD-CC electrode is described as follows: 0.3 mL of MTMOS, 0.45 mL of methanol, and 10  $\mu\text{L}$  of hydrochloric acid (11 M) were mixed and stirred for 3 min until a homogeneous gel solution appeared, then 0.3 g of carbon powder and CuI powder at a sufficient ratio were added and the resultant mixture shaken for an additional 1 min. The hydrochloric acid acts as catalyst for the hydrolysis of the MTMOS. Then the mixture was added into Teflon tubes (with 2 mm inner diameter and 5 cm length, and the length of composite material in the tube was about 0.5 cm) and dried for at least 24 h at room temperature. Then the electrode was polished with polishing paper and rinsed with distilled water. The same procedure was used for preparation of bare carbon ceramic electrode without copper iodide. The electric contact was made with a copper wire through the back of the electrode.

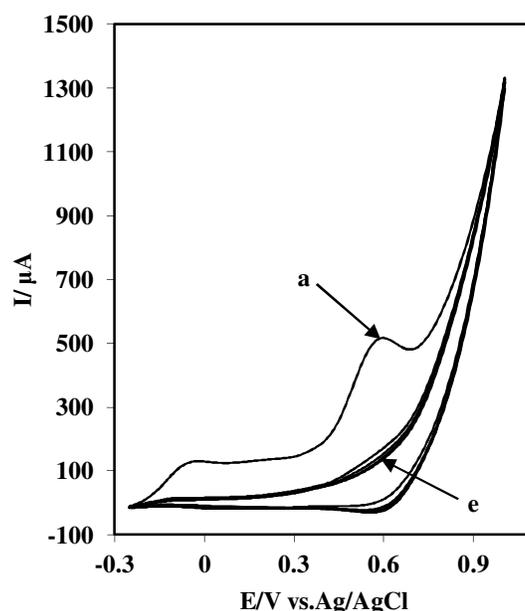
## 3. RESULTS AND DISCUSSION

Electrochemical properties of the prepared CIM-SGD-CC electrode were investigated. In this study, for the activation of the electrode surface, the electrode was placed in 0.1 mol  $\text{L}^{-1}$  NaOH solution in the potential range of  $-250$  to  $1000$  mV (*vs.* Ag/AgCl) at a scan rate of 50  $\text{mVs}^{-1}$  (Fig. 1). There are prominent peaks at approximately  $-68$  and  $570$  mV during the first cycle but in the second and next cycles, featureless voltammograms were recorded. This indicates that an irreversible electrochemical transformation of the CuI has been achieved during the cyclic voltammetry. Surface elemental analysis of this modified electrode was studied by energy dispersive X-ray (EDX) technique. Fig. 2 illustrates the elemental composition of the electrode surface respectively. Also, EDX analysis of CCE revealed one silica peak at 1.7 keV that it severe overlaps with the gold peak. This peak can be attributed to sol-gel precursor used for electrode preparation. It seems that a film of oxy copper iodide

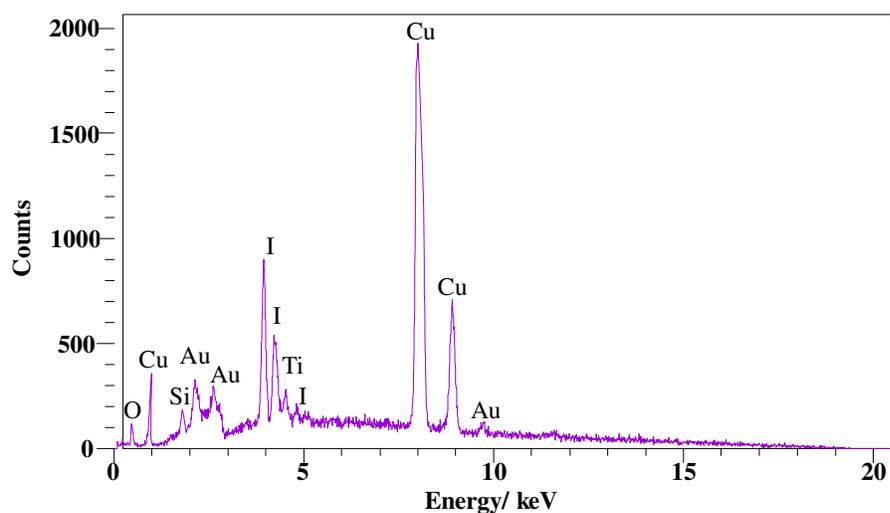
is formed at the surface of electrode during the cyclic voltammetry step, according to the reaction 1 [22]:



One of the objectives of the present study was to fabricate a modified electrode capable of the electrocatalytic oxidation of ascorbic acid. In order to test the electrocatalytic activity of the CIM-SGD-CC electrode, the cyclic voltammograms were obtained in the presence and absence of AA at bare (Fig. 3a, 3b) and CIM-SGD-CC (Fig. 3c, 3d) electrodes. At the bare electrode, no anodic current due to the oxidation of AA is observed but for CIM-SGD-CC electrode a large anodic peak is observed. It was found that in comparison to unmodified carbon ceramic electrode, electrochemical behavior of AA was greatly improved at CIM-SGD-CC electrode, indicating that the anodic oxidation of AA could be catalyzed at CIM-SGD-CC electrode. This proves that the copper iodide bears the main role in electro-catalytic oxidation of AA. We previously proved that the presence of halides causes an increase activity in the electrocatalytic behavior of copper. The increased activity probably related to a more favorable adsorption of reactant or of intermediates leading to a higher surface concentration of electroactive molecules ready for being oxidized or it is due to the partial delocalization of the electronic density of reactant into the solid with possible consequent bond pre-dissociations which facilitates the oxidation or both [23].

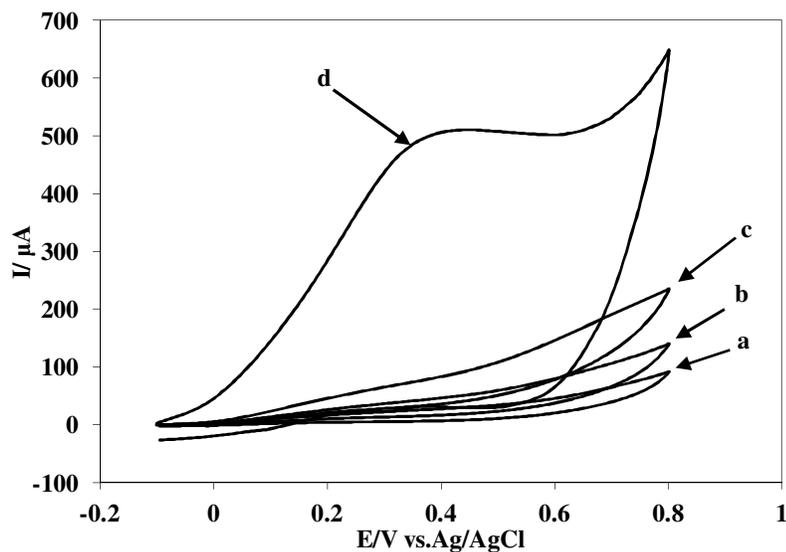


**Fig. 1.** Repetitive cyclic voltammograms of CIM-SGD-CC electrode in  $0.1 \text{ mol L}^{-1} \text{ NaOH}$  in the potential range of  $-250\text{--}1000 \text{ mV}$ . Potential sweep rate is  $50 \text{ mV s}^{-1}$ . (a) first cycle; (e) end cycle



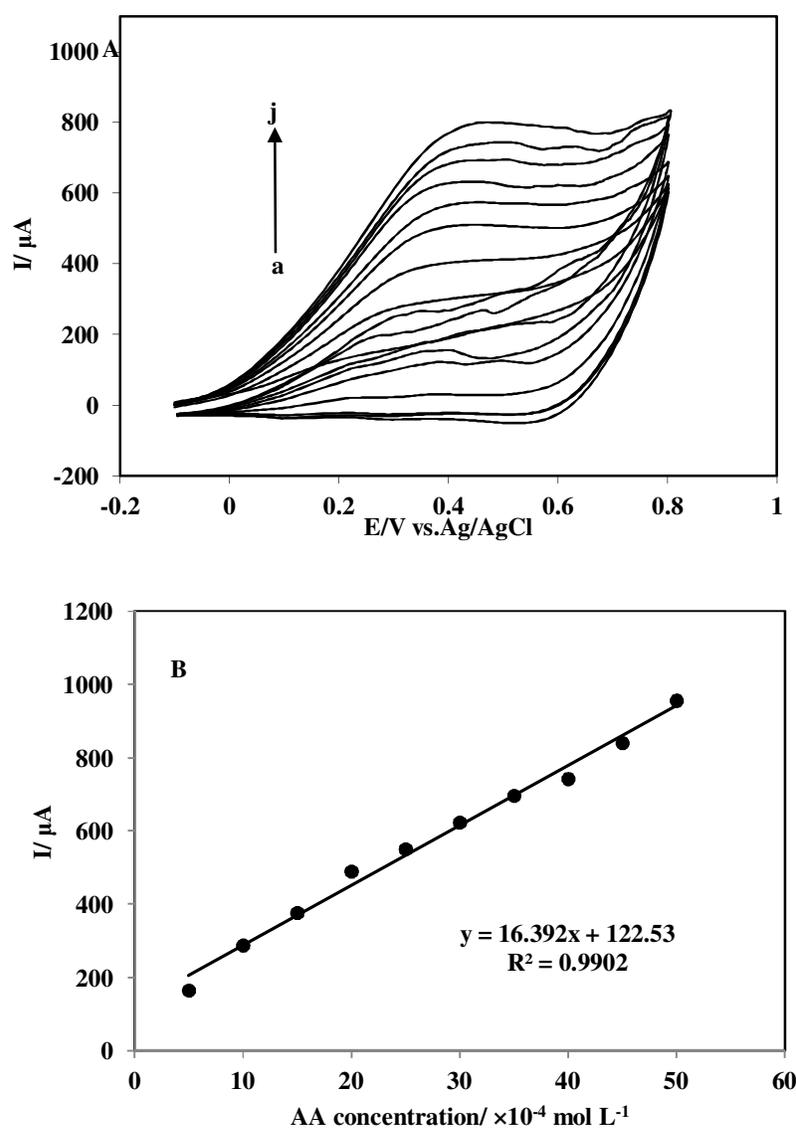
**Fig. 2.** Energy disperses X-ray (EDX) on the surface of CIM-SGD-CC electrode

The cyclic voltammograms of CIM-SGD-CC electrode were recorded in different concentrations of NaOH solution containing  $25 \times 10^{-4} \text{ mol L}^{-1}$  AA (not shown). It is shown that, the high catalytic peak current is achieved above a NaOH concentration of  $0.1 \text{ mol L}^{-1}$ . Thus,  $0.1 \text{ mol L}^{-1}$  NaOH was chosen as an optimum supporting electrolyte.

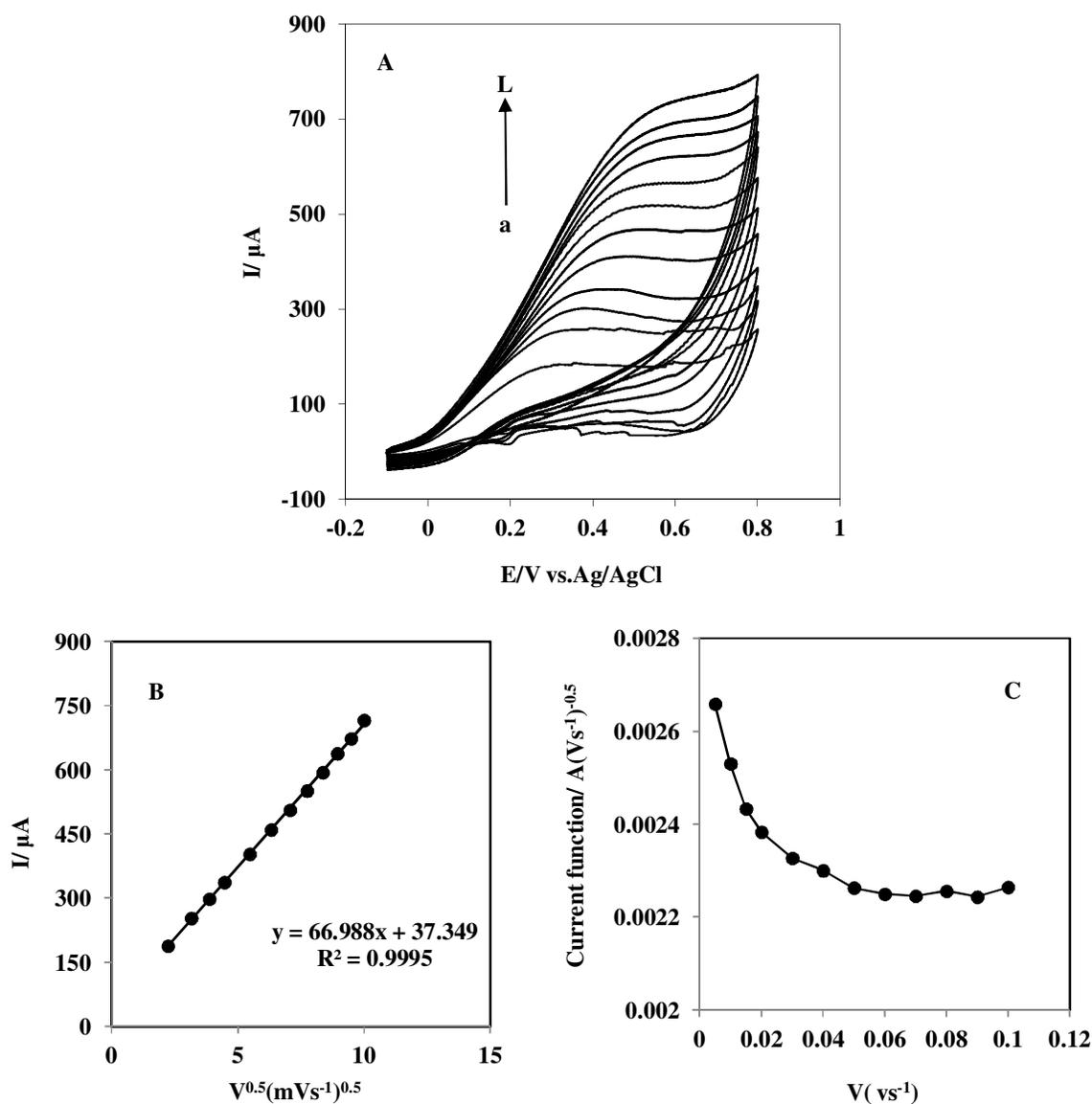


**Fig. 3.** Cyclic voltammograms of bare CCE (a, b) and CIM-SGD-CC electrode (c, d) in  $0.1 \text{ mol L}^{-1}$  NaOH solution in the absence (a, c) and presence of  $25 \times 10^{-4} \text{ mol L}^{-1}$  ascorbic acid (b, d). Conditions: potential range  $-100$  to  $800 \text{ mV}$  scan rate of  $50 \text{ mV s}^{-1}$

With the increase of AA concentration, the anodic peak current gradually increased (Fig. 4). The characteristic shape of cyclic voltammogram in this potential region indicates that the signal is due to the oxidation of AA. The catalytic peak current is proportional to the concentration of AA in the range of  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  mol L<sup>-1</sup>. The linear regression equation is  $I (\mu\text{A}) = 16.392 C_{\text{AA}} (\mu\text{mol L}^{-1}) + 122.53$  ( $R^2 = 0.9902$ ).



**Fig. 4.** (A) Cyclic voltammograms of a CIM-SGD-CC electrode in the presence of various ascorbic acid concentrations: (a)–(j): 5, 10, 15, 20, 25, 30, 35, 40, 45, and  $50 \times 10^{-4}$  mol L<sup>-1</sup>, respectively, at a scan rate of  $50 \text{ mV s}^{-1}$ ,  $0.1 \text{ mol L}^{-1}$  NaOH solution. (B) Variation of anodic peak current vs. ascorbic acid concentration



**Fig. 5.** (A) Cyclic voltammograms of CIM-SGD-CC electrode in  $0.1 \text{ mol L}^{-1}$  NaOH containing  $25 \times 10^{-4} \text{ mol L}^{-1}$  of ascorbic acid at various potential scan rates (from inner to outer)  $5\text{-}100 \text{ mVs}^{-1}$ . (B) Variation of the catalytic current with the square root of sweep rate. (C) Current function vs.  $v$  for  $0.1 \text{ mol L}^{-1}$  NaOH solution in the presence of  $25 \times 10^{-4} \text{ mol L}^{-1}$  ascorbic acid

In order to provide more evidence, the effect of the scan rate on the performance of CIM-SGD-CC electrode was also studied. The peak currents could lead to the information on electron transfer kinetics. Fig. 5A shows the CVs of the electrode prepared in optimum condition at various scan rates when immersed in a solution containing  $25 \times 10^{-4} \text{ mol L}^{-1}$

ascorbic acid and 0.1 mol L<sup>-1</sup> NaOH. It can be noted from Fig. 5A that the anodic currents increase and the peak potential shifts toward positive direction with increasing the scan rate, suggesting a kinetic limitation in the reaction between the redox sites of the modifier and the ascorbic acid. When peak current values were plotted against  $v^{1/2}$  (Fig. 5B), the following linear relationship was obtained (Eq. (1)), suggesting that the process is controlled by diffusion of analyte as expected for a catalytic system.

$$I_p = 37.342 + 66.988 v^{1/2} \text{ (mV}^{1/2} \text{ s}^{-1/2}\text{)} \quad (1)$$

Moreover, a plot of the scan rate normalized current ( $I/v^{1/2}$ ) versus the scan rate exhibits the typical shape of an electrochemical (EC') catalytic process (Fig. 5C).

To obtain some information on the rate-determining step, a Tafel plot (not shown) was drawn using the data from the rising part of the current–voltage curves recorded at low scan rate for AA concentration of  $25 \times 10^{-4}$  mol L<sup>-1</sup>. The Tafel slope for the linear parts of the plot recorded at scan rate of  $5 \text{ mVs}^{-1}$  was estimated as being equal to  $0.155 \text{ V decade}^{-1}$ , indicating that one-electron process involved in the rate-limiting step, assuming a transfer coefficient ( $\alpha$ ) of approximately 0.38. The exchange current density ( $j_0$ ) evaluated from Tafel plots is  $0.61 \times 10^{-7} \text{ Acm}^{-2}$ .

The Tafel slope was also obtained from the linear relationship observed for  $E_p$  versus  $\log v$  (not shown) by using Eq. (2) [24]:

$$E_p = \frac{b}{2} \log v + \text{constant} \quad (2)$$

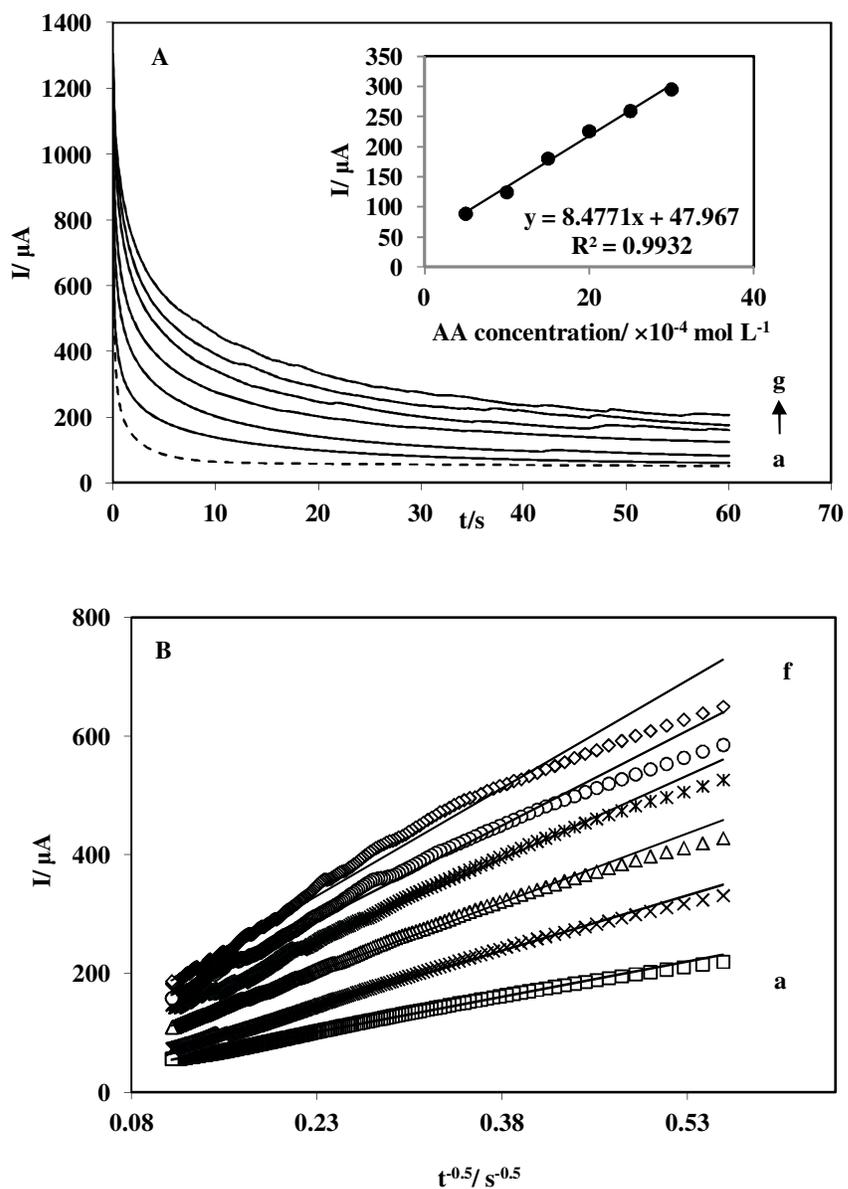
On the basis of Eq. (2) the slope of  $E_p$  versus  $\log v$  plot is  $b/2$ , where  $b$  indicates the Tafel slope. The slope of  $E_p$  versus  $\log v$  plot is  $\partial E_p / \partial \log v$  which was found to be 83.462, so  $b = 166.924$ , which is in good agreement with the corresponding value evaluated from polarization measurements. This slope indicates that a one electron transfer process is the rate limiting step assuming a transfer coefficient of  $\alpha = 0.35$ .

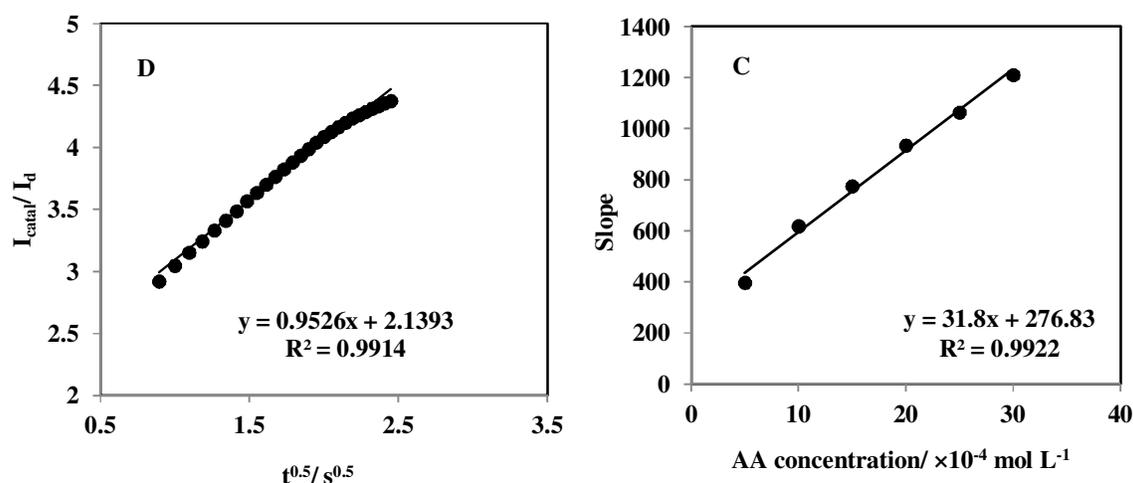
In order to evaluate the reaction kinetics, the oxidation of AA on CIM-SGD-CC electrode was investigated by chronoamperometry. Chronoamperometry, as well as cyclic voltammetry has been employed for the investigation of the processes occurring via an  $E_r C_i$  mechanism [25]. Double steps chronoamperograms were recorded by setting the working electrode potentials to desired values and were used to measure the catalytic rate constant on the modified surface. Fig. 6A shows a series of well-defined chronoamperograms for the CIM-SGD-CC electrode in the absence and presence of different concentrations of ascorbic acid at an applied potential of 0.4 V versus Ag/AgCl. The plot of net current with respect to the mines square roots of time presents a linear dependency (Fig. 6B). This indicates that the transient current must be controlled by a diffusion process. The transient current is due to catalytic oxidation of AA, which increases as the AA concentration is raised. No significant

cathodic current was observed when the electrolysis potential was stepped to 0.00 mV (vs. Ag/AgCl), indicating the irreversible nature of the oxidation of AA. By using the slopes of these lines; we can obtain the diffusion coefficients of the significant according to the Cottrell equation [26]:

$$I = nFAD^{1/2}C^*(\pi t)^{-1/2} \tag{3}$$

Where D is the diffusion coefficient, and C\* is the bulk concentration. The slopes of the resulting straight lines were then plotted versus the concentration of AA (Fig. 6C), from which we calculated a diffusion coefficient of  $5.40 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for AA.





**Fig. 6.** (A) Chronoamperograms of CIM-SGD-CC electrode in  $0.1 \text{ mol L}^{-1}$  NaOH containing different concentrations of ascorbic acid:  $0.0, 5, 10, 15, 20, 25$  and  $30 \times 10^{-4} \text{ mol L}^{-1}$ , from (a) to (g), respectively. Potential steps were  $0.4$  and  $0.0 \text{ V}$ , respectively. Insets: Variation of chronoamperometric currents at  $t=10 \text{ s}$  vs. concentration of AA. (B) Plot of  $i$  vs.  $t^{-1/2}$  obtained from chronoamperometric measurements CIM-SGD-CC electrode in  $0.1 \text{ mol L}^{-1}$  NaOH containing different concentrations of AA:  $5, 10, 15, 20, 25$  and  $30 \times 10^{-4} \text{ mol L}^{-1}$ , from (b) to (g), respectively. (C) The relationship between the slope of the linear segments and the AA concentration. (D) Dependency of  $I_{catal}/I_d$  on  $t^{1/2}$  derived from CAs of (a) and (d) in panel (A)

The rate constants of the reactions of AA and the ensuing intermediates with the redox sites of the CIM-SGD-CC electrode can be derived from the chronoamperograms according to Eq. (4) [24]:

$$\frac{I_{catal}}{I_d} = \lambda^{1/2} \left[ \pi^{1/2} \operatorname{erf}(\lambda^{1/2}) + \frac{\exp(-\lambda)}{\lambda^{1/2}} \right] \quad (4)$$

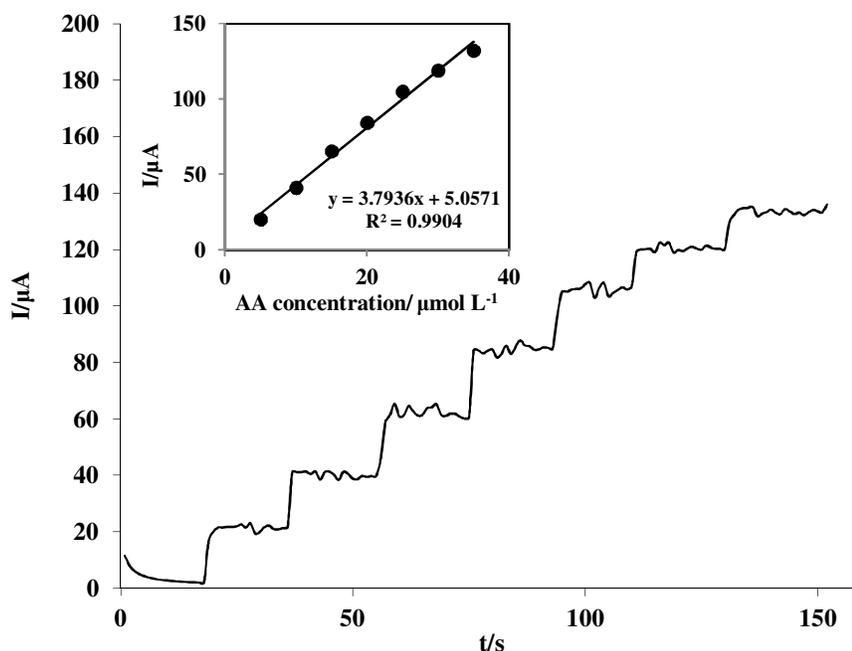
where  $I_{catal}$  is the catalytic current in the presence of AA,  $I_d$  the limiting current in the absence of AA and  $\lambda = kCt$  ( $k$ ,  $C$  and  $t$  are the catalytic rate constant, bulk concentration of AA and the elapsed time, respectively) is the argument of the error function. For  $\lambda > 1.5$ ,  $\operatorname{erf}(\lambda^{1/2})$  almost equals unity and Eq. (5) reduces to [27]:

$$\frac{I_{catal}}{I_d} = \lambda^{1/2} \pi^{1/2} (kCt)^{1/2} \quad (5)$$

From the slope of the  $I_{catal}/I_d$  vs.  $t^{1/2}$  plot (Fig. 6D), the value of  $k$  for  $15 \times 10^{-4} \text{ mol L}^{-1}$  AA was calculated to be  $1.927 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

Analytical characteristics of CIM-SGD-CC electrode for the amperometric determination of AA were estimated. Fig. 7 shows the current-time responses of the modified electrode to

AA which was successively added to the electrochemical cell containing  $0.1 \text{ mol L}^{-1}$  NaOH under hydrodynamic conditions, while the electrode potential was kept at 0.39. As shown in the figure a well-defined response was observed during the stepwise increasing of AA concentration in the range  $5\text{--}35 \text{ }\mu\text{mol L}^{-1}$ . The linear regression equation of calibration curve is expressed as  $I (\mu\text{A})=3.7936C_{\text{AA}} \mu\text{mol L}^{-1}+5.0571$  with a correlation coefficient of 0.9904 ( $n=7$ ). The sensitivity and limit of detection (LOD) were found to be  $3.79 \text{ }\mu\text{A}/\mu\text{mol L}^{-1}$  and  $1.66 \text{ }\mu\text{mol L}^{-1}$ , respectively.



**Fig. 7.** The current–time profiles recorded at the CIM-SGD-CC electrode during the successive addition of ascorbic acid. Inset: Typical calibration graph derived from the current time profile

By repetitive CV of the CIM-SGD-CC electrode for approximately 20 times in NaOH solution at a scan rate of  $50 \text{ mV s}^{-1}$ , the peak current value decreases less than 7%, indicating good stability.

The modified electrode retained its initiate activity for more than 50 days when kept in air at ambient conditions. A decrease of 9% was observed in the current response of the electrode at the end of 50th day. In addition, repetitive recording of cyclic voltamograms in AA solution tested the reproducibility of the electrocatalytic effect of the modified CCE. It was found that the relative standard deviation (R.S.D.) of the peak currents of  $25 \times 10^{-4} \text{ mol L}^{-1}$  AA for six replicate determinations was 3.1%. Table 1 compared the proposed electrode for AA determination with electrodes reported in literatures. As show, the proposed electrode comparable with other electrodes such as multiwalled carbon nanotube-modified carbon–

ceramic electrode. Despite this, the advantages of the CIM-SGD-CC electrode are its good stability and reproducibility of surface renewal by simple polishing, excellent catalytic activity and simplicity of preparation.

**Table 1.** Analytical parameters of several modified electrodes for AA determination. LOD: limit of detection; LDR: linear dynamic range; CPE: carbon paste electrode; SWV: square wave voltammetry, CCE: carbon ceramic electrode, DPV: Differential pulse voltammogram

Electrode	Method	LOD ( $\mu\text{M}$ )	LDR ( $\mu\text{M}$ )	References
Modified GCE	Amperometry	2.52	5 – 81.7	[27]
Modified CCE	Amperometry	8.6	16–5000	[28]
Modified CCE	SWV	5	10–200	[29]
Modified SWCNT/CCE	DPV	3	5 – 700	[30]
Modified GCE	DPV	8.2	20 – 140	[31]
Modified CCE	Amperometry	1.66	5 – 35	This work

#### 4. CONCLUSIONS

Copper iodide modified sol-gel derived carbon ceramic (CIM-SGD-CC) electrode was prepared and characterized by EDX and cyclic voltammetry techniques. The modified electrode exhibits excellent and persistent electrocatalytic behavior toward ascorbic acid oxidation compared with the bare CCE. The proposed sensor possesses high sensitivity and stability, good reproducibility and fast response. These advantages make it promising for providing a simple method for practical applications.

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