

Highly Sensitive and Indirect Electrochemical Sensing of Ascorbic Acid Based on the Catalytic Oxidation of Glucose on the Ni Nanoparticles-ionic Liquid Composite

Jie Yang¹, Weijuan Li², Tao Yang², Shifeng Hou^{3,*}

¹Bio-nanotechnology & Medical Engineering Institute, Jining Medical College, Jining, 272067, P. R. China

²College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P. R.China

³Chemistry and Biochemistry Department, Montclair State University, New Jersey, 07043, US

*E-mail: yangjiequst@126.com

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In this system, a Ni nanoparticle-ionic liquid platform (Ni_{NP}-IL) was developed for synergistical and indirect determination of ascorbic acid (AA) via electrocatalytic recycle between Ni and glucose. The Ni_{NP}-IL film was characterized by scanning electron microscope and cyclic voltammetry. The activation of Ni_{NP}-IL/CPE in alkaline media, forming a Ni(OH)₂/NiO(OH)-IL film, was found to induce the adsorption of AA at the electrode surface. Based on the electrocatalytic oxidation of glucose at the activated Ni_{NP}-IL/CPE in 0.08 mol/L NaOH solution, a novel detection strategy was constructed for indirect determination of AA. Under optimal conditions, AA was amperometrically determined by using the as-prepared Ni_{NP}-IL/CPE with a detection limit of 4.5×10^{-8} mol/L (S/N = 3). Possible interferences from the coexisting ions were also investigated. The results indicated that the designed biosensor could be used for the detection of AA in the presence of dopamine, borate, nitrate, chloride, acetate and carbonate ions.

Keywords: Ni nanoparticles, ionic liquid, glucose, ascorbic acid, indirectly determination.

1. INTRODUCTION

Ascorbic acid (AA, vitamin C) is a potent reducing and antioxidant agent for biological systems. Due to the importance of AA, the determination of AA has a great significance. A large number of analytical methods have been applied to detect AA. In recent years, the electrochemical approach has aroused growing interest with its great potentials because of high sensitivity, low cost,

rapid response[1-3]. However, most investigations were focused on the direct electrocatalytic oxidation of AA. Therefore, how to decrease the oxidation potential and achieve the low detective sensitive becomes the goal of scientific research worldwide.

As environmentally friendly media, ionic liquids (ILs) have recently appeared as clean alternatives to volatile organic solvents for a wide variety of non-aqueous reactions. They are very useful in organic synthesis, separation field and electroanalysis due to the high chemical and thermal stability, negligible vapor pressure, high conductivity and wide electrochemical window[4,5]. In electroanalysis field, they are generally used as electrolyte and electrode material[6-9]. Electrochemical sensors using ILs for analytical purposes have been reported in a number of studies for detection of different compounds, such as uric acid, phenols, dopamine, hydrogen peroxide and glucose[10-17].

At the same time, the electrochemical sensors made of nanomaterials have been introduced due to their special physical and chemical properties, such as increasing the surface area, mass transport and catalysis[18]. Ni nanoparticles, Au nanoparticles and Pt nanoparticles have been widely used in biosensors[19-22].

In this study, a Ni nanoparticles-ionic liquid modified carbon paste electrode ($\text{Ni}_{\text{NP}}\text{-IL/CPE}$) was fabricated. In detail, the $\text{Ni}_{\text{NP}}\text{-IL}$ suspension was dropped on CPE to obtain the $\text{Ni}_{\text{NP}}\text{-IL/CPE}$. Then the $\text{Ni}_{\text{NP}}\text{-IL/CPE}$ was activated in NaOH solution. The modified electrodes were characterised using scanning electron microscope (SEM) and cyclic voltammetry (CV). The composite electrode showed good electrochemical oxidation to glucose. Based on the electrochemical response of glucose on the $\text{Ni}_{\text{NP}}\text{-IL/CPE}$, a new method for detection of AA was further established. The $\text{Ni}_{\text{NP}}\text{-IL/CPE}$ showed the advantages of easy preparation, rapid response, low cost, and low detection limit.

2. EXPERIMENTAL

A CHI 832 electrochemical analyzer (Shanghai CH Instrument Company, China), which was in connection with a carbon paste electrode (CPE) or modified CPE working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE), was used for electrochemical measurements. Scanning electron microscopy (SEM) was carried out using a JSM-5900 machine (JEOL, Tokyo, Japan).

Ionic liquids (IL, 1-butyl-3-methylimidazoliumhexafluorophosphate) were purchased from Shanghai Cheng Jie Chemical Co., Ltd. Ni_{NP} were provided by College of Materials, Qingdao University of Science and Technology. Dopamine (DA), glucose and ascorbic acid (AA) were purchased from Sigma. All the reagents were of analytical grade.

The different ratios of $\text{Ni}_{\text{NP}}\text{-IL}$ hybrids were prepared by dispersing different amounts of Ni_{NP} in a given IL under ultrasonic agitation for 1 h. 10 μL of above $\text{Ni}_{\text{NP}}\text{-IL}$ hybrids were spread uniformly onto the fresh surface of the CPE and air-dried naturally to obtain the $\text{Ni}_{\text{NP}}\text{-IL/CPE}$. For comparison, $\text{Ni}_{\text{NP}}\text{/CPE}$ and IL/CPE were prepared by the same method with the single component existing. Before electrochemical determination, the $\text{Ni}_{\text{NP}}\text{-IL/CPE}$ and the $\text{Ni}_{\text{NP}}\text{/CPE}$ were activated in 0.08 mol/L NaOH solution with CV under the potential range of 0.00 V to 0.80 V for 50 cycles.

CV was performed with CHI 832 electrochemical analyzer in a quiescent solution at a scan rate of 100 mV/s. The supporting electrolyte solution of CV was 0.08 mol/L NaOH.

The current-time curves were recorded in a stirred cell with successive addition of ascorbic acid standard solution and other anions solution to the cell at an operating potential of 0.65 V.

3. RESULTS AND DISCUSSION

3.1 Morphology Characterization of Ni_{NP} and Ni_{NP} -IL hybrids

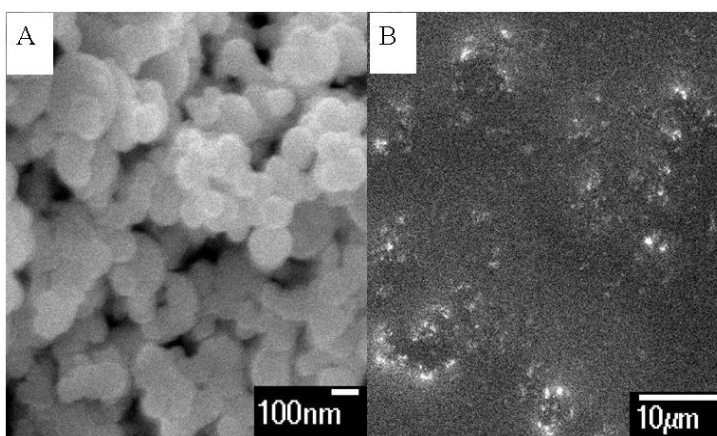


Figure 1. SEM images of (A) the synthesized Ni_{NP} and (B) the Ni_{NP} -IL composite.

The typically morphology of the synthesized Ni_{NP} was shown in Figure 1A. It can be seen that the products consist of homogeneous and intact nickel nanoparticles. The Ni_{NP} -IL composite can form a uniform film on the surface of CPE, which was displayed in Figure 1B. The result indicated that Ni_{NP} were uniformly dispersed in IL, which could greatly promote the electrocatalytic ability for the oxidation of glucose and AA.

3.2 Cyclic voltammograms of Ni_{NP} -IL/CPE in different solutions

Cyclic voltammograms of Ni_{NP} -IL/CPE in different solutions were recorded and shown in Figure 2. In NaOH solution, there is a pair of redox peaks which are originated from redox nickel nanoparticles during activation (Figure 2a)[23]. After the AA was added, the oxidation potential moved to the positive direction with a basically unchanged peak current (Figure 2b). The peak potential and currents did not change significantly when the AA was added continuedly. With the presence of glucose, the anodic peak current increased sharply and the oxidation potential moved to the positive direction(Figure 2c), which indicated Ni_{NP} -IL/CPE can electrocatalyze the oxidation of glucose and was consistent with the literature reported[24]. It can be seen that in the NaOH solution containing glucose and AA the redox peak current increased ulteriorly, especially the anodic peak current enhanced dramatically (Figure 2d). The current signal of glucose was on increase with the

continuous addition of AA. This result showed that AA can be detected by the Ni_{NP}-IL/CPE based on the electrocatalytic oxidation of glucose.

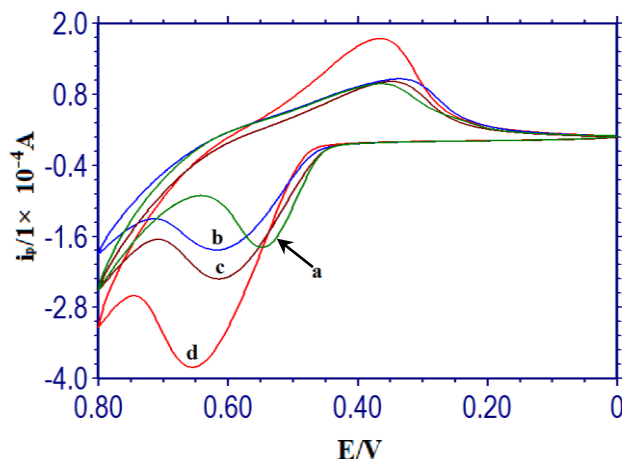


Figure 2. Cyclic voltammograms of Ni_{NP}-IL/CPE: (a) in NaOH solution, (b) in NaOH and AA solution, (c) in NaOH and glucose solution, (d) in NaOH, glucose and AA solution.

3.3 Optimization of experimental conditions

Electrochemical and electrocatalytic properties of modified electrodes could be influenced by many factors. Therefore, the optimized experimental for fabricating the modified electrodes, including the activation solution (NaOH) concentration, activation time in CV and the ratio of Ni_{NP} and IL were investigated.

3.3.1 Influence of concentration of NaOH

Cyclic voltammograms of Ni_{NP}-IL/CPE in different concentration NaOH solution were shown in Figure SI-1 given in *Supplementary Information*. Accompanying with the increase of the concentration of NaOH solution, the oxidation peak potentials negatively shift and the oxidation peak currents increased gradually, the maximum value of oxidation peak currents was observed in 0.08 mol/L NaOH solution. With further increase of the concentration of NaOH, the peak current tended to decrease. Therefore the 0.08 mol/L NaOH solution was selected for modified electrodes activation.

3.3.2 Effect of activation time

The activation time of the modified electrodes was selected from 20 cycles to 70 cycles. At the beginning, there was no redox peak, With the increase of activation time redox peaks appeared. The oxidation peak appeared at 0.548 V and the reduction peak appeared at 0.349 V. With the increase of activation time redox peaks potential kept stable, the peak current increased gradually and the

maximum value was obtained at the 50th cycle. It leveled off afterward. Therefore, a run of 50 cycles was chosen to activation modified electrodes.

3.3.3 Optimization of Ni_{NP} ratio

The different ratios of Ni_{NP} to IL in ethanol were used to make modified electrodes. The mass ratios of Ni_{NP} to IL were 1:15, 1:20 and 1:25 respectively. For all these electrodes, CVs were carried out in the NaOH solution containing glucose and AA, The correspondence of the mass ratio of Ni_{NP} to IL ($M_{Ni_{NP}}:M_{IL}$) on the CV absolute value of oxidative peak current (i_{pa}) of glucose and AA was shown in Fig. SI-2 in *Supplementary Information* section. Results showed that i_{pa} reached a maximum value at $M_{Ni_{NP}}:M_{IL}$ of 1:20. So the $M_{Ni_{NP}}:M_{IL}$ of 1:20 was beneficial to the electrochemical detection of glucose and AA. The reason might be ascribed as two aspects: when the amount IL was much less enough, the Ni_{NP} might agglomerate easily and can not be easily activated. Hence only a small amount of Ni_{NP} present catalytic effect, which the rate of electron transfer could not be enhanced due to the poor quantity of IL. When the amount of IL was in excess, it might form a thick film on the surface of Ni_{NP} -IL/CPE and led to less electrocatalytic activity of the Ni_{NP} -IL/CPE, the catalytic effect was not ideal. Therefore, Ni_{NP} and IL mass ratio of 1:20 was selected for the electrode modification.

3.4 Electrochemical characteristics of the modified electrodes

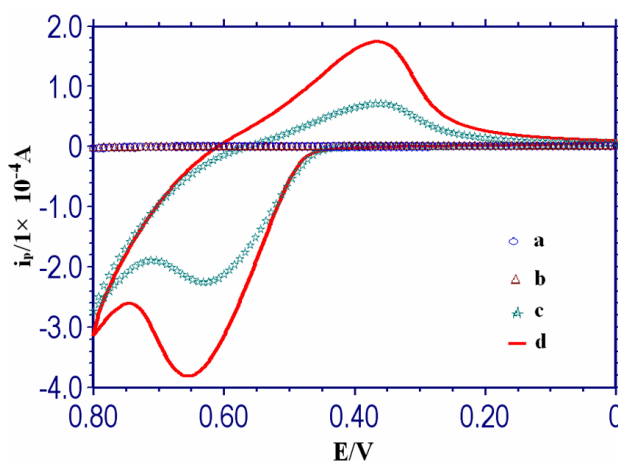


Figure. 3 Cyclic voltammograms of bare CPE (a), IL/CPE (b), Ni_{NP} /CPE (c) and Ni_{NP} -IL/CPE (d) in NaOH 0.08 mol/L solution.

Figure 3 shows cyclic voltammograms of coexisting system of glucose and AA in NaOH solution at the different electrodes. From curve a (bare CPE) and curve b (IL/CPE), no obvious electrochemical signals of the glucose and AA were observed, which indicated that bare CPE and IL/CPE had no catalytic activity to the oxidation of glucose and AA. However, a pair of redox peaks appeared on the Ni_{NP} /CPE (Figure 3c), which was ascribed to the electrochemical oxidation glucose and AA at the Ni_{NP} /CPE. Further, while on the Ni_{NP} -IL/CPE (Figure 3d), the redox peaks current

increased observably. It can be seen that the oxidation peak currents had a great increase of the oxidation peak, which was attributed to the presence of ionic liquid as the electron-transfer promoter and excellent linker. This result indicates that the incorporation of Ni_{NP} with IL can result in a synergy of electrocatalytic oxidation towards AA.

3.5 Effect of scan rate

Figure SI-3A in Supplementary Information shows the cyclic voltammograms of the Ni_{NP}-IL/CPE measured with different scan rates from 10 mV/s to 150 mV/s in the potential range of 0 V to 0.8 V in 0.08 mol/L NaOH solution containing glucose and AA. As is obvious, the peak potential for the catalytic oxidation of glucose and AA shifts to increasingly positive potentials with increasing scan rate. This result suggests a kinetic limitation in the reaction between redox sites of the Ni_{NP}-IL/CPE and glucose, AA[26]. The redox peak currents of glucose and AA increased with increasing scan rate, a linear relationship of oxidation peak current with the square root of the scan rate in the range from 10 to 150 mV/s was established, which was expressed as $I_{pa} (10^{-4}A) = 0.2358 v^{1/2} - 0.6767$ ($r = 0.9969$) (Supplementary Information, Figure A3-B). The results indicated the electrode process was controlled by diffusion.

3.6 Interferences

Interference experiments were done by comparing the responses between before and after addition of some possible interferents into the 0.08 mol/L NaOH solution containing 1×10^{-5} mol/L AA. We study the influence of dopamine by CV. Under the optimal conditions, no interference was encountered for additions of 1×10^{-4} mol/L dopamine into the assay solution. The amperometric method was performed to examine the interference effect of borate (BO_3^{3-}), nitrate (NO_3^-), chloride (Cl^-), acetate (CH_3COO^-) and carbonate (CO_3^{2-}) ions. The results showed that the aforementioned species did not have current response (Appendices, Figure A4). In conclusion, the tested interferents could not cause interference to the determination of AA and the Ni_{NP}-IL/CPE was of good anti-jamming performance.

3.7 Chronoamperometric measurements

From figure 2 and figure 3, it can be seen that 0.65V is the optimum potential to keep the Ni_{NP}-IL/CPE with high electro-catalytic activity in the oxidation state. So the amperometric determination of AA was conducted at Ni_{NP}-IL/CPE with the working potential fixed at 0.65 V. With the successive addition of AA, the current-time curve was recorded and shown in Figure 4A. The i_p value was linear with the concentration of AA (Figure 4B). In the concentration range of 1.25×10^{-7} mol/L \sim 2.38×10^{-6} mol/L, the linear regression equation was $i_p (10^{-5}A) = 0.0533C (\times 10^{-7}) - 2.9067$ and the regression coefficient (γ) was 0.9983. The detection limit was estimated to be 4.5×10^{-8} mol/L (S/N = 3). The stability of the modified electrode was investigated. When the modified electrode was stored at 4 and

measured intermittently, no apparent change was found over 15 days. The voltammetry response declined to 86% after 20 days.

Recently many electrochemical sensors were reported to detect AA. Eser Ergün et al prepared a novel polymer film of poly(glyoxal-bis(2-hydroxyanil)) P(GBHA) by electropolymerization of glyoxal-bis(2-hydroxyanil) (GBHA) on a glassy carbon electrode[26]. This electrode was utilized for detection of the AA and the linear response range was 1.0-2000 $\mu\text{mol/L}$ with the detection limit of 0.26 $\mu\text{mol/L}$. Shaopeng Qi and coworkers constructed a electrochemical sensor based on pristine graphene (PG) to detect AA[27]. The PG based sensor exhibited excellent performance for detection of AA and the linear response range was 9.0-2314 $\mu\text{mol/L}$ with the detection limit of 6.45 $\mu\text{mol/L}$. In Xie's paper, one-step facile ultrasonic method was developed to fabricate graphene/ SnO_2 nanocomposite in acidic solution. CV and DPV were used to detect AA with the detection limite 100 μM [28]. Compared with more other reported methods listed in Table SI-1[29-36], our proposed method is better than the former literatures.

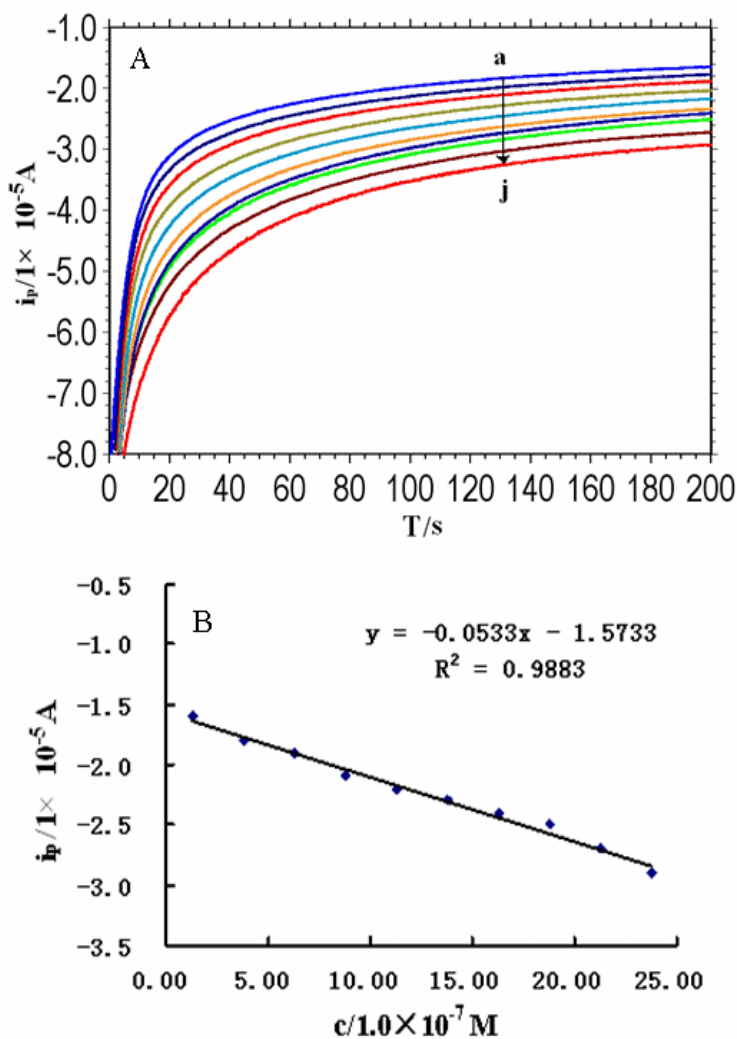


Figure 4. **A** Amperometric $i-t$ curves for AA oxidation at $\text{Ni}_{\text{NP}}\text{-IL/CPE}$. The concentrations of AA from a to j: 1.25, 3.75, 6.25, 8.75, 11.25, 13.75, 16.25, 18.75, 21.25, 23.75 $\times 10^{-7}$ mol/L. The potential was fixed at 0.65V. **B** The i_p value vs the concentration of AA.

4. CONCLUSIONS

This research illustrated a simple method to fabricate the Ni_{NP}-IL/CPE and the utilization of the Ni_{NP}-IL/CPE for the determination of AA. The modified electrodes were characterised using SEM and CV. The Ni_{NP} in alkaline media to form a Ni(OH)₂/NiO(OH) film was used to electrocatalyze glucose oxidation in 0.08 mol/L NaOH. It was found that electrochemical response of glucose at the Ni_{NP}-IL/CPE gradually developed with adding different concentration of AA. Under the selected conditions, the Ni_{NP}-IL/CPE exhibited a fast response and good selectivity in determination of AA. AA was amperometrically determined by using the Ni_{NP}-IL/CPE in the concentration range of 1.25×10^{-7} mol/L \sim 2.38×10^{-6} mol/L with a detection limit of 4.5×10^{-8} mol/L (S/N = 3).

SUPPLEMENTARY DATA:

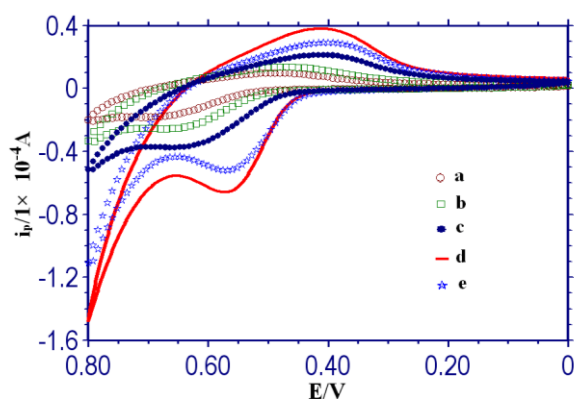


Figure A1. Cyclic voltammograms of Ni_{NP}-IL/CPE in different concentration of NaOH solution: (a) 0.01 mol/L, (b) 0.02 mol/L, (c) 0.05 mol/L, (d) 0.08 mol/L, (e) 0.10 mol/L.

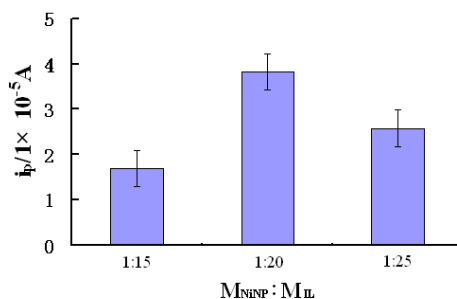


Figure A2. Effect of the ratio of $M_{NiNP}:M_{IL}$ in composite on CV absolute value of oxidative peak current difference (i_{pa}) of glucose and AA.

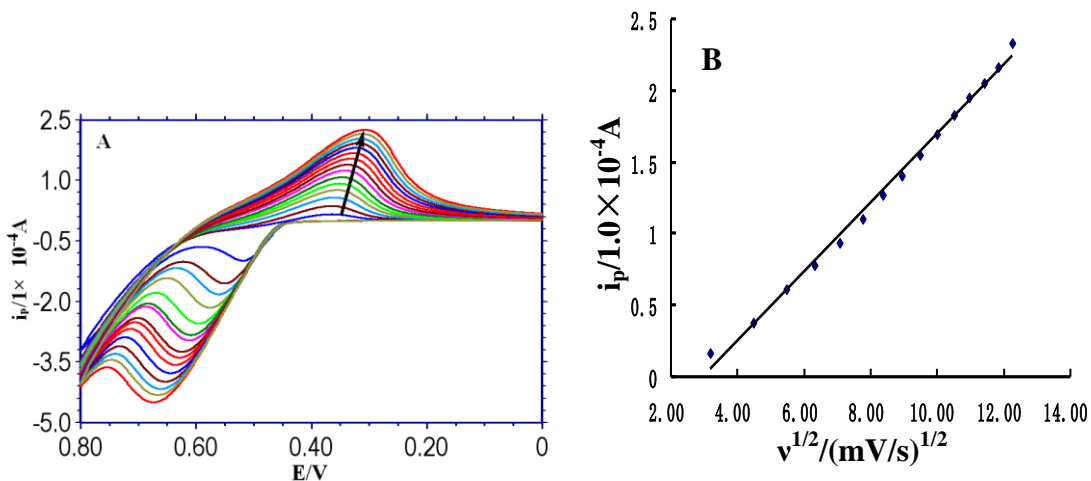


Figure A3. (A) Cyclic voltammograms of Ni_{NP}-IL/CPE with different scan rates (from inner to outer 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150 mV/s) in NaOH 0.08 mol/L solution containing glucose and AA. (B) Relationship between the oxidation current and the square root of the scan rate ($v^{1/2}$).

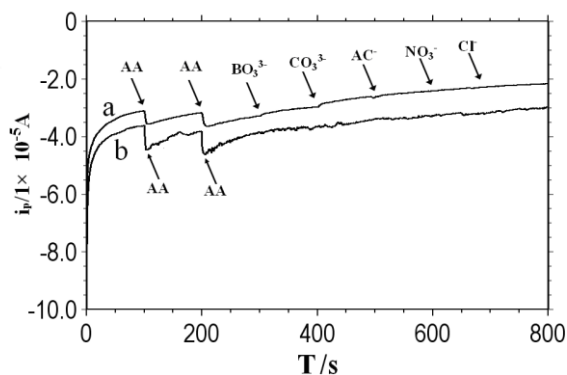


Figure A4. Amperometric $i-t$ curves at Ni_{NP}-IL/CPE in 0.08 mol/L NaOH solution containing glucose at 0.65 V inter AA and other interferences (a), and without other interferences (b) as indicated.

Table A1. Comparison of the analytical data's obtained by some modified electrodes proposed for the determination of ascorbic acid

Reference	Electrode material	Modifier	Linear range(μM)	Detection limit(μM)	R^2
29	GC electrode	graphene oxide	100-1000	-	0.996
30	GC electrode	polymerized direct blue 71	1-2000	1	0.996
31	GC electrode	polycalconcarboxylic acid	1-500	0.5	
32	pyrolytic graphite electrode	mesopore-rich active carbon	0.5-2000	0.3	0.998
33	GC electrode	polyaniline-copper nanoparticles	5-3500	2	0.9995

34	GC electrode	Pd nanowire	25-900	200	0.9998
35	CP electrode	ionic liquid mixed-valent	50-7400	20	-
36	GC electrode	nickelhexacyanoferrate /phosphomolybdate	0-600	-	-
This work	CP electrode	ionic liquid-Ni nanoparticles	0.125-2.38	0.045	0.9983

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