Bimetallic CoPt nanoparticles-modified Pt disk electrode for the amperometric sensing of ascorbic acid

MERZAK DOULACHE^{a,b,*}, MOHAMED TRARI^b and BOUBAKEUR SAIDAT^a

^aLaboratory of Physical Chemistry of Materials (LPCM), Faculty of Sciences, (UATL), BP 37G, 03000 Laghouat, Algeria

^bLaboratory of Storage and Valorization of Renewable Energies (LSVRE), Faculty of Chemistry, (USTHB), BP 32, El Alia, 16111 Algiers, Algeria
E-mail: doulache@yahoo.fr

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Abstract. Cobalt-Platinum bimetal nanoparticles (CoPtNPs) were electrodeposited on bare Pt electrode. A highly sensitive amperometric sensor-based on CoPtNPs/Pt modified electrode was constructed to determine ascorbic acid (AA). The Co-Pt nanoparticles were characterized by scanning electron microscopy (SEM) and cyclic voltammetry (CV). Due to the synergistic effects of Co-Pt nanoparticles, the electrocatalytic activity of modified electrode showed a significant enhancement toward the oxidation of AA compared to Co/Pt and bare Pt electrodes in alkaline medium. The electrocatalytic activity of CoPtNPs/Pt was studied as a function of Co:Pt molar ratio in the deposition bath. The analytical performance of the proposed sensor has been investigated by chronoamperometry method under the optimized conditions. This sensor showed a linear response to AA concentration range from 10 μM to 0.5 mM with a detection limit of 0.37 μM ($S/N = 3$), a high sensitivity of 103 $\mu\text{A mM}^{-1}$, and a fast response time. In addition, the reproducibility, selectivity and applicability of this sensor were assessed with satisfactory results.

Keywords. Co-Pt bimetallic nanoparticles; modified electrode; electrocatalysis; ascorbic acid; electrochemical sensor.

1. Introduction

Ascorbic acid (AA), known as Vitamin C, is one of the important vitamins found in fruits and vegetables, which help to maintain normal physiological functions. AA, widely known as antioxidant, also plays a crucial role in the metabolism of cholesterol. The important role of AA has been revealed through recent researches in various fields such as toxicology, genetics, oncology, nutritional science, and even material science as a mild reducing agent.¹ The toxicity of reactive oxygen species² and synthetic pyrethroid pesticide³ can be protected by AA reducing toxic substances. Hence, the development of a simple and reliable method for the determination of AA with a high sensitivity and a good selectivity is of great importance. Among the reported methods, the electrochemical method is considered to be a crucial topic of interest due to its simplicity and rapidity without the sample preparation procedures.⁴⁻¹³

However, the direct oxidation of AA at bare electrodes is irreversible and the subsequent hydrolysis product, 2,3-diketogluconic acid¹⁴ is readily adsorbed onto the electrodes surface. Moreover, some of biological molecules, like the dopamine and uric acid are oxidized at almost the same potential at conventional electrodes and results in an overlap of voltammetric response. Therefore, using bimetallic nanoparticles modified electrodes has been described as promising route for the electrochemical AA sensor fabrication.¹⁵⁻¹⁹ It has been reported that bimetallic nanoparticles such as PdNi, AuPt, AuAg, AgPt and PtNi, exhibit better electrochemical properties than their single-metal component.¹⁹⁻²³ Specifically, bimetallic CoPt NPs are believed to offer unprecedented benefits in catalysis by tuning the catalysts durability.²⁴

In order to get a better electrochemical sensor with high sensitivity, selectivity and stability, we have investigated the electrocatalytic activity of CoPt-based bimetallic nanomaterials. This kind of electrodes can interact synergistically to form redox mediators with improved activity attributed to a larger surface area,

*For correspondence

excellent catalytic activity, enhanced conductivity and good stability.^{25,26}

Aiming to achieve a high catalytic effect with increased stability and lower cost, we dispersed CoPt nanoparticles on bare Pt disk electrode to produce CoPt/Pt nanomaterial. In this, contribution, the electrochemical activity of the CoPt/Pt modified Pt electrode for AA oxidation was studied and compared with Co/Pt and bare Pt electrodes. The results indicate enhanced electrocatalytic activity of CoPtNPs/Pt and a higher sensitivity, compared to Co/Pt modified electrode²⁷ and bare Pt electrode toward the AA oxidation. This study demonstrated that CoPt/Pt nanomaterial is a promising catalyst for amperometric sensing of ascorbic acid.

2. Experimental

2.1 Reagents and apparatus

Chloroplatinic acid hexahydrate H_2PtCl_6 (99%, Merck, Germany) and CoSO_4 (>99%, Merck, Germany) were used in the preparation of modified electrode. Ascorbic acid (99.5%), H_3BO_3 (99.5%) and NaOH (99%) were analytical grade products from Fluka. Deionized water was used in the preparation of solutions.

The electrochemical experiments were realized with a PGZ402 potentiostat/galvanostat (Radiometer analytical). A platinum foil and saturated calomel electrode (SCE) were used as a counter and reference electrode, respectively, in a standard three-electrode cell; the working electrode was Pt disk electrode ($\varnothing=2$ mm). For steady-state amperometric experiments, the working potential was fixed at 0.2 V and the solution was stirred gently with a magnetic stirrer. Every test was repeated three times in order to confirm the reproducibility of our results. The surface morphology of CoPtNPs/Pt electrode was analyzed with a JOEL JSM 6360-LV microscope.

2.2 Preparation of CoPtNPs/Pt

Before each experiment, the working electrode was hand-polished in aqueous suspensions of successively finer grades of alumina (5 to 0.3 μm), until a mirror-finishing surface was obtained. Then, it was ultrasonically cleaned for 5 min in the mixture HNO_3 /absolute ethanol (1/1), thoroughly rinsed with water and dried at room temperature. CoPt NPs were first deposited electrochemically on the bare Pt electrode surface by cathodic reduction of a mixed solution containing CoSO_4 , H_2PtCl_6 and H_3BO_3 (0.05 M) during 120 s at a potential of -1.2 V. Various molar ratios of cobalt and platinum were employed. The total concentrations CoSO_4 and H_2PtCl_6 were 0.03 M with Co:Pt molar ratios of 2:1, 3:1, 4:1 and 5:1. After rinsing with distilled water, the modified electrode was immersed in an alkaline solution (NaOH 0.1 M) and scanned repetitively for 20 cycles in the potential range (-0.6 to 0.6

V) at a rate of 50 mV s^{-1} until a stable cyclic voltammogram (CV) was reached.

2.3 Preparation of real samples

Pharmaceutical tablets of Vitamin C (UPSA® 500 mg, Saidal Company, Algiers) were tested for the ascorbic acid. The tablets were dissolved in NaOH solution (0.1 M) and diluted to prepare solutions of 50, 100 and 250 μM . The validity of CoPtNPs/Pt modified electrode for the AA determination was assessed by direct determination using a previously calibrated graph. All solutions were prepared using ultra-high-quality water (Millipore).

3. Results and Discussion

3.1 Electrochemical deposition of bimetallic cobalt–platinum

The electrochemical behavior of Co^{2+} , Pt^{4+} and Co-Pt binary electrolyte was studied by cyclic voltammetry method in 0.05 M H_3BO_3 (pH 5.25). The CV in an electrolyte containing Co^{2+} ions (Figure 1a) shows a huge rise in cathodic current at -1.1 V (peak I_c) which corresponds to the reduction of Co^{2+} and its corresponding oxidation peak (I_a) appears at 0.27 V during the anodic sweep. At a potential higher than -1.35 V, hydrogen evolution takes place with increased current.

CV obtained in Pt^{4+} electrolyte (Figure 1b) shows two overlapping reduction waves at 0.18 V (I_c) and -0.09 V (II_c) correspond to the reduction of PtCl_6^{2-} to PtCl_4^{2-} and PtCl_4^{2-} to Pt respectively, which can be expressed as:^{28,29}

In the cathodic region, the CV curves showed the adsorption/desorption peaks of atomic hydrogen (III_c and IV_c), characteristic of the bulk Pt electrode around -0.29 to -0.69 V, suggesting an electrodeposition of Pt particles on the electrode.

CV in Co-Pt binary electrolyte shows three reduction peaks assigned to the reduction of cobalt (I_c) and Pt^{4+} ions (II_c , III_c) by comparison with the peaks obtained for individual metal ion electrolytes (Figure 1c). The Co^{2+} reduction potential is slightly shifted toward positive potentials, which could be attributed to the alloy formation. The peaks obtained during the anodic scan can be attributed to the oxidation of cobalt (I_a) and for Co-Pt alloy (II_a). It is obvious from the above discussion that to achieve a codeposition of cobalt and platinum on bare Pt electrode, a minimal potential of -1 V is required.

Figure 1. CVs recorded on bare Pt electrode at a scan rate of 50 mV s^{-1} in an electrolyte of $0.05 \text{ M H}_3\text{BO}_3$ containing (a) 0.02 M CoSO_4 , (b) $0.01 \text{ M H}_2\text{PtCl}_6$ and (c) $0.02 \text{ M CoSO}_4 + 0.01 \text{ M H}_2\text{PtCl}_6$ at a pH 5.25.

Hence, for all deposition studies, a potential of -1.2 V is used.

After electrodeposition, the CoPt bimetallic film was conditioned in 0.10 M NaOH solution by potential cycling between -0.6 and 0.6 V with 20 cycles (50 mV s^{-1}). These parameters were obtained experimentally as optimum values for development of similar quantities of Co redox mediators, and the maximum activation of the electrode surface for the electrocatalytic oxidation of AA.

3.2 Scanning electron microscopy characterization (SEM)

The SEM analysis is performed in order to define the morphological properties of the Co-Pt deposit (4:1 molar ratio). In this respect, we have compared the SEM micrograph of CoPt with Co particles deposited individually under similar electrochemical pulsed conditions.

Figure 2b shows SEM micrograph of Co-Pt on Pt disk electrodes. The particles of Co and Pt covering the whole electrode surface with irregular sizes lying between 50 and 100 nm . The individual Co deposit on the Pt

surface (Figure 2a) shows that the Co particles are formed of nearly spherical structures dispersed uniformly with well-defined geometric shapes. The mean grains size of single Co particles lies between 300 and 800 nm . So, the difference between the CoPt systems and single deposits of Co indicates that the morphological properties of the binary deposit are mutually and markedly influenced by the existence of individual metals. The CoPt deposit appears formed of resolved and well-dispersed single particles with a higher surface roughness. The surface distribution of CoPt NPs deposit affects the real surface area, thus generating the increased active surface of the exposed particles and in this way, more active sites are available in comparison with individual Co deposit. This may make the roughened CoPtNPs/Pt electrode an efficient material for the electron transfer with a greater catalytic activity for the AA electrooxidation.

3.3 Characterization of CoPt NPs/Pt electrode

The 20th cyclic voltammograms (CVs) of Co/Pt and CoPtNPs/Pt electrodes (with different Co:Pt molar

Figure 2. The SEM image of (a) Co/Pt surface electrode and (b) CoPtNPs/Pt (the Co:Pt molar ratio is 4:1) surface electrode.

Figure 3. CVs of Co/Pt electrode and CoPtNPs/Pt electrodes (with different Co:Pt molar ratios 2:1, 3:1, 4:1 and 5:1) in 0.1 M NaOH at a scan rate of 50 mV s^{-1} . Inset shows the zoom view of the peak currents.

ratios) in 0.1 M NaOH solution are illustrated in Figure 3. The electrochemical behavior of CoPtNPs/Pt electrodes looks like that of Co/Pt where the anodic-cathodic peaks provide evidence of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ (peak I_a) and $\text{Co}^{\text{IV}}/\text{Co}^{\text{III}}$ (peak II_a) redox transition assigned to different cobalt oxide species on the electrode surface.²⁶ The peaks I_c and II_c are cathodic peaks of the reduction of cobalt oxide/hydroxide formed during the anodic cycles that subsequently lead to the production of Co(II) species according to following sequences:

Some authors mentioned that an ill-defined anodic peak appeared at a lower potential (peak III_a), assigned to the adsorption of oxygen-containing species, H_2O , OH^- during consecutive cycles in alkaline solution.^{30,31} Notably, in this work, a drastic increase of the response current is observed with raising the Co:Pt molar ratio. The highest signal current is observed for Co:Pt ratio of 4:1 above which a regression is noticed. On the contrary, the redox peaks of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ and $\text{Co}^{\text{IV}}/\text{Co}^{\text{III}}$ are more ill-defined and the peak currents on Co/Pt are smaller than those on CoPtNPs/Pt. The higher peak current on CoPt (molar ratio of 4:1) electrode is due to an increased roughness of the electro-catalytic film, which leads to a larger exposed surface area in the electrochemical experiments, suggesting better electro-catalytic behavior. It is also seen that CoPt NPs deposited at Co:Pt molar ratio of 4:1 exhibits a much higher adsorption peak (III_a), indicating the former have a larger specific active surface area.

The effect of the scan rate (ν) on the electrochemical behavior of Co/Pt and CoPtNPs/Pt (at various Co:Pt molar ratios) in alkaline solution (NaOH 0.1 M) is reported in Figure 4a. The peak currents are proportional to the scan rate (ν) in the region ($10\text{--}100 \text{ mV s}^{-1}$), pointing to the electrochemical activity of the surface redox couple. The surface coverage (Γ) of Co(III) species on CoPtNPs/Pt is evaluated using the Laviron's equation.³²

$$I_p = n^2 F^2 A \Gamma \nu (4RT)^{-1} \quad (5)$$

where A is the electrode surface area, F the Faraday constant, n the number of exchanged electrons, T the absolute temperature and R the universal gas constant. Figure 4b shows that the surface coverage Γ of Co(III)

Figure 4. (a) Plots of anodic peak currents vs. the scan rate of CoPtNPs/Pt with different Co:Pt molar ratios. (b) Effects of the Co:Pt molar ratio on surface coverage.

species increases with the Co:Pt ratio. In contrast to the result of Figure 2, it can be concluded that the electroactive Co(III) deposited on the electrodes increase with increasing the Co:Pt ratio, leading to higher electrocatalytic activity. The lower Γ value of the Co/Pt electrode is related to its low electrodeposited yield and different morphology i.e., smaller specific surface area; the highest Γ value is found in CoPtNPs/Pt with Co:Pt molar ratio of 4:1 and this optimal is selected for further experiments. The decrease in the surface coverage to 5:1 ratio of Co:Pt could be attributed to the enhanced smoothness of the surface morphology of CoPtNPs/Pt electrode.

3.4 Electrocatalytic oxidation of AA on CoPtNPs/Pt

The electrocatalytic performance of CoPtNPs/Pt (4:1 molar ratio) for the AA oxidation is examined by cyclic voltammetry. Figure 5 shows the voltammograms at bare Pt, Co/Pt and CoPtNPs/Pt in the absence (curve a, c and e) and in the presence (curve b, d and f) of AA (5 mM). In the absence of AA, there is no electrochemical response at bare Pt disk electrode (curve a). By contrast, in AA solution a broad, weak and irreversible oxidation peak of AA appears at 0.24 V (curve b), suggesting a sluggish electrochemical system. On the contrary, on Co/Pt (curve c), two pairs of peaks corresponding to the reversible Co^{III}/Co^{II} and Co^{VI}/Co^{III} redox reaction are observed in blank solution. After addition of AA (curve d), two anodic peaks at -0.08 (peak I_a) and 0.24 V (peak II_a) assigned to the oxidation of AA are observed; the heights of these peaks increase linearly with raising the AA concentration. The anodic peak current related to the oxidation of Co(II) increases in the presence of AA while the corresponding cathodic

Figure 5. CVs of bare Pt (a and b), Co/Pt (c and d) and CoPt NPs/Pt (e and f) in 0.1M NaOH in the absence (a, c, e) and presence (b, d, f) of AA (5 mM). Scan rate: $50 mVs^{-1}$.

currents decrease compared to that in the absence of AA, which is a typical catalytic reaction. In this mechanism, Co(II) is oxidized to Co(III), and then Co(III) oxidizes ascorbic acid followed by the regeneration Co(II). According to the bi-logarithm dependence of peak currents on the scan rate (data not shown), the electrochemical process occurring at the potential of peak I_a is complicated by adsorption ($\Delta \log I_p / \Delta \log v = 0.75$), whereas the electrochemical process at the potential of peak II_a is complicated by the chemical reaction ($\Delta \log I_p / \Delta \log v = 0.35$).³³

Therefore, the AA oxidation on Co/Pt electrode in alkaline medium occurs through redox mediation by electrogenerated Co(III) in two ways:²⁷ the first one involving strong product adsorption in the region -200 to 100 mV (peak I_a), and the other involving soluble forms of both the reactant and product in the region 100 to 350 mV (peak II_a).

The replacement of Co/Pt by CoPtNPs/Pt changes neither the shape of the voltammogram of AA oxidation (curve *f*) nor the peak potentials. Two peaks ($E_p = -0.01$ and 0.24 V) correspond to the electrocatalytic oxidation of AA; they are higher than the peaks obtained on the Co/Pt electrode. These enhanced properties are evidently attributed to the high roughness and consequently large active surface area of CoPtNPs/Pt electrode, which produces higher diffusion of AA molecules toward CoPtNPs/Pt and in this way to a better electrocatalytic activity. Comparatively, CoPtNPs/Pt is more appropriate for the detection of AA.

Ascorbic acid has two acid protons (H_2A); its oxidation undergoes two successive one electron oxidation steps accompanied by rapid dehydration, which makes the oxidation process irreversible.^{34,35}

This mechanism involves a pre-deprotonation process giving ascorbate (AH^-) followed by $1e^-/1H^+$ oxidation of the ascorbate to form the radical anion (A^-), which is further oxidized to dehydroascorbic acid (DHA). The DHA species is rapidly hydrated to form the final product of hydrated bicyclic species (P) as demonstrated by Rueda *et al.*³⁵ and Ruiz *et al.*³⁶

On the basis of the reported results, the following mechanism can be proposed for the mediated oxidation of AA on the modified surface, which is outlined in Figure 6; the redox transition of cobalt species is

In addition, AA is oxidized on the modified surface *via* the following reaction:

Figure 6. Mechanism for the mediated oxidation of ascorbic acid on the modified surface.

Where, the intermediate is further oxidized to DHA, through the final electron transfer process:

In consequence, AA is oxidized on CoPt/Pt through an irreversible oxidation process, and no obvious reduction peak of AA can be seen in the negative scans of cyclic voltammograms.

The electrocatalytic activity of CoPtNPs film on different substrates, namely, platinum, gold and glassy carbon for AA oxidation was investigated in alkaline medium (data not shown). The results showed that the electrocatalytic activity of CoPtNPs film on different substrates follows the order: CoPtNPs/Pt > CoPtNPs/Au > CoPtNPs/GC. Thus, the enhanced electrocatalytic activity of the CoPtNPs/Pt electrode is due to the good surface electric conductivity of Pt substrate relative to the surface of Au and GC electrodes.

3.5 Chronoamperometric studies

The potential step chronoamperometry, as well as other electrochemical methods, were also employed for investigating electrochemical processes at chemically modified electrodes. The Chronoamperograms were recorded by setting the working electrode potentials to the desired values and measuring the transient current on the CoPtNPs/Pt surface. Figure 7 shows the chronoamperograms for CoPtNPs/Pt in the absence (curve *a*) and presence (curves *c–f*) of AA in the concentration range (0.1–0.5 mM). The applied potential step was 200 mV; plotting the net current *vs.* the inverse square roots of

Figure 7. Chronoamperograms of CoPtNPs/Pt in the absence (curve *a*) and presence (curves *c–f*) of AA in the concentration range (0.1–0.5 mM). Inset (a): the plot of I_{cat} *vs.* $t^{-1/2}$; Inset (b): the plot of I_{cat}/I_L *vs.* $t^{1/2}$.

Figure 8. (a) Amperometric responses at bare Pt electrode (curve *a*), Co/Pt (curve *b*) and CoPt NPs/Pt (curve *c*) by successive additions of AA (10 μM) in NaOH (0.1 M) solution. (b) The calibration graph of AA on CoPtNPs/Pt plotted at the working potential 0.20 V.

time shows a linear dependence (Figure 7, inset a). Therefore, a diffusion-controlled process predominates for the AA electrooxidation. The mean the diffusion coefficient (D) of AA can be easily deduced from the slope by using the Cottrell equation:³²

$$I = nFAD^{1/2}C_0(\pi t)^{-1/2} \quad (13)$$

where I is the transient current, C_0 the bulk concentration and t the elapsed time. The mean diffusion coefficient D for AA is found to be $5.37 \pm 0.05 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The chronoamperometry can also be employed to evaluate the catalytic rate constant (k) according to the following relation:³⁷

$$I_{\text{cat}}/I_L = \gamma^{1/2}[\pi^{1/2}\text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \quad (14)$$

where I_{cat} and I_L are the currents in the presence and absence of AA, respectively, $\gamma = kC_0t$ is the argument of the error function and t is the elapsed time. For $\gamma > 1.5$, $\text{erf}(\gamma^{1/2})$ is almost equal to unity, and Eq. (14) becomes:

$$I_{\text{cat}}/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kC_0t)^{1/2} \quad (15)$$

From the slopes of the I_{cat}/I_L vs. $t^{1/2}$ plot (Figure 7, inset b), the mean catalytic rate constant for the electrooxidation reaction is found to be $11.85 \pm 0.12 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, two-fold higher than that calculated on Co/Pt electrode ($6.27 \pm 0.26 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$).²⁷

3.6 Amperometric detection of AA on CoPtNPs/Pt

The amperometry under stirred conditions has a much higher current sensitivity than cyclic voltammetry and is used to estimate the lower limit of detection. Figure 8a exhibits a typical steady-state catalytic

current time response of the CoPtNPs/Pt electrode with successive injections of AA, with an increment of 10 μM at a fixed potential of 200 mV in alkaline solution. During the successive addition of AA, a well-defined response is observed, by comparison to both electrodes Co/Pt and bare Pt electrodes, proving stable and efficient catalytic ability of the electrocatalyst CoPt NPs immobilized onto the Pt electrode surface. This result demonstrated that the CoPtNPs/Pt exhibits a better electrocatalytic activity attributed to its synergistic action since it has a high surface area and an excellent conductivity to promote the electron transfer between AA analyte and bulk-electrode surface.³⁸

The calibration plot for CoPtNPs/Pt electrode is given in Figure 8b. The response current for AA is linear on the concentrations range (10–500 μM) with a correlation coefficient (R^2) of 0.998. The limit of detection (LOD), defined as the signal-to-noise ratio (3:1), is equal to 0.37 μM . From these results, one can conclude that the oxidation of AA on the CoPtNPs/Pt electrode can be employed for the determination of AA with good sensitivity over a large concentrations range. Compared with AA sensors given in the literature (Table 1), CoPtNPs/Pt is more sensitive with a larger linearity. Furthermore, the modified electrode is facile to fabricate, relatively inexpensive and mediator-free.

3.7 Reproducibility, repeatability and stability of CoPt NPs/Pt

The reproducibility and repeatability of CoPtNPs/Pt were determined. In a series of five different CoPtNPs/Pt electrodes elaborated by the same electrochemical technique, a relative standard deviation of 3.2% was found to

Table 1. Comparison of the proposed modified electrode with other electrodes for the determination of Ascorbic acid.

Electrode	Sensitivity ($\mu\text{A mM}^{-1}$)	Linear range (μM)	LOD (μM)	Ref.
GCE/MWCNT	62.5	5–120	3.5	4
NiCoO ₂ /C	39	10–2630	0.5	5
[Ni(phen) ₂] ²⁺ /MWCNTs/GCE	–	10–630	4	6
MWCNT/PNB/GCE	60.84	10–140	2.4	7
Chitosan/CPB/GCE	70.34	4–1000	0.8	8
CuNPs/c-MWCNT/PANI/Au	37.5	5–600	1	9
PoDPoAP	30.62	0.1–10,000	36.4	10
Au/HDT/OT	3.86	300–1400	90	11
AgNPs/rGO/GCE	43.12	10–800	9.6	12
Nafion/MWNT/GCE	8.69	80–6000	40	13
CoPd/C	83.71	0.1–3420	0.1	15
hAu-Ru/GC	426	< 5–2000	2.2	16
CS/Au-AgNTs/GCE	–	5–2000	2	17
PdNi/C modified GCE	54	10–1800	0.5	18
Co/Pt	74.3	10–480	2.5	25
CoPtNPs/Pt	103	10–500	0.37	This work

MWCNT/GCE multiwalled carbon nanotubes/glassy carbon electrode, MWCNT/PNB multiwalled carbon nanotubes/poly(Nile blue A), Chitosan/CPB chitosan incorporating cetylpyridine bromide, PoDPoAP poly(*o*-phenylenediamine-co-*o*-aminophenol), Au/HDT/OT gold/hexanedithiol/1-octanethiol, AgNPs/rGO silver nanoparticle/reduced graphene oxide, hAu-Ru hollow gold/ruthenium, [Ni(phen)₂]²⁺ nickel(II)-bis(1,10-phenanthroline) complex, CS/Au-AgNTs chitosan/gold-silver nanotubes.

Table 2. Determination of ascorbic acid in the vitamin C tablets using the amperometry method.

Sample	Nominal amount (μM)	Found ^a (μM)	RSD% (n=5)	Recovery (%)
1	50	49.5	0.90	99
2	100	102	0.99	102
3	250	253	2.00	101

^aRegression equation of linear calibration plot: $I(\mu\text{A}) = 2.833 + 0.103 C(\mu\text{M})$ with a correlation coefficient of 0.998.

be 50 μM AA, showing the reliability of the method. The repeatability was determined by recording five successive amperometric tests for AA concentration of 50 μM with the same CoPtNPs/Pt electrode; RSD value of 1.8% was obtained.

The stability of CoPtNPs/Pt was studied through the response to 50 μM . When not in use, the electrode was kept in NaOH solution (0.1 M) at ambient temperature. The data indicate that the current response of the electrode remains almost unchanged after three weeks, suggesting that the CoPtNPs/Pt electrode possesses good long-term stability.

3.8 Real samples analysis

To check the applicability and feasibility of the proposed electrochemical sensor, the CoPt NPs/Pt was applied to the AA determination in real pharmaceutical samples with the amperometric method and five

replications were performed (Table 2). Good recovery rates for 50, 100 and 250 μM of ascorbic acid were obtained; proving that the proposed method meets the requirement of analysis and is practical for the determination of ascorbic acid in commercial tablets.

3.9 Interference study

The interference of species such as dopamine (DA), uric acid (UA), acetaminophene (AP) and glucose (GL) in the determination of AA was also studied by amperometry. Interfering species were injected with AA in NaOH solution under stirring and their response is reported in Figure 9. AA is found to respond in the same way independently of the presence or absence of interferences, thus illustrating that the quantitative determination of AA was in no way affected by interfering species. Further, the response current obtained for these

Figure 9. Amperometric responses of CoPtNPs/Pt to AA (10 μ M) and with the addition of UA (10 μ M), DA (10 μ M), AP (10 μ M) and GL (10 μ M) in 0.1 M NaOH.

interfering species was less than 5% of that observed for AA.

4. Conclusions

In this work, bimetallic CoPt nanoparticles were formed on bare Pt electrode by potentiostatic deposition and successfully tested for the electro-oxidation of ascorbic acid in alkaline medium. Comparatively, CoPtNPs/Pt showed a higher catalytic activity and a better stability toward the electrochemical oxidation of ascorbic acid. The electrocatalytic activity of CoPtNPs/Pt has been improved by adjusting the Co:Pt molar ratio in the deposition bath solution. Higher charge-transfer kinetic and better catalytic rate constant were obtained on CoPtNPs/Pt. The final surface concentration of the Co hydroxide species was influenced by the co-existence of platinum. High disorder of the Co hydroxide layer structure was formed on bimetallic CoPtNPs, compared to that on Co/Pt. More specifically, the electrodes CoPtNPs/Pt (molar ratio of 4:1) exhibited the best analytical performance, with a fast response, a linear dependence under optimized conditions over a wide AA concentration (10–500 μ M) with a low detection limit of 0.37 μ M. Besides, the sensitivity, the repeatability and selectivity of the proposed sensor were satisfying. The results suggest that our proposed CoPtNPs/Pt sensor can be a potential candidate for routine AA analysis.

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