

Reaction Kinetics Study of All cis-Polyaniline Nanotube Film Modified Electrode for Fast Ascorbic Acid Detecting

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A reaction kinetics study was performed for all cis-polyaniline nanotube (ACPN) film modified electrode for fast ascorbic acid detecting. An ACPN film modified electrode exhibited excellent electrocatalytic activity, a low detection limit and a high sensitivity to ascorbic acid (AA). It is found that AA can be electro-catalytically oxidized on an ACPN film even at a concentration less than 1 mM. A mechanism of AA electrooxidation on the ACPN film modified electrode was proposed. Furthermore, the detection sensitivity was regulated by tuning the film thickness, and the optimized fabrication conditions for the ACPN film modified electrode was obtained. Based on the reaction kinetics study, the catalytic rate constant for the best electrode was found to be $6.3 \times 10^6 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. It is expected that such a sensor based on the ACPN film can be widely applied for AA detection.

Introduction

Ascorbic acid (vitamin C, AA) from fruits and vegetables is an important antioxidant agent used in food, pharmaceutical, cosmetic, and health care fields (Rath and Pauling, 1990, 1991). The determination of AA concentration in blood or food has become essential. To date, various AA analytical methods such as enzymatic methods (Marchesini *et al.*, 1974), HPLC analysis with fluorimetric (Kirk and Sawyer, 1991) and UV-vis detection (Wagner *et al.*, 1979; Finley and Duang, 1981) have been developed and applied. However, these methods are always time-consuming and lack reproducibility, sensitivity and selectivity. Compared to these traditional techniques, electrochemical methods are considered to be simpler, more convenient and more reliable for tracing target chemicals detecting, and to date, various active mediators modified electrodes have also been developed for the detection of AA (Mazloum-Ardakani *et al.*, 2009; Motahary *et al.*, 2010; Satheesh Babu *et al.*, 2012; do Carmo *et al.*, 2012; Dalmasso *et al.*, 2012).

Conducting polymers possess many interesting features and can be applied in numerous electroanalytical sensors. Electrodes modified with polyaniline (PANI) based conducting polymers have been developed for detecting AA (Kalakodimi and Nookala, 2002; Jurevičiūtė *et al.*, 2005; Kit-Anan *et al.*, 2012; Lucero *et al.*, 2012; Rivero *et al.*, 2012;

Wang *et al.*, 2012a; Anu Prathap and Srivastava, 2013). These previous studies indicate that two issues are of critical importance for the efficient electrocatalytic oxidation of AA on the PANI modified electrodes: one relates to the chemical redox interaction between AA and PANI film; the other relates to the charge propagation within the PANI film. Thus, to improve electrocatalytic efficiency during the detecting, a PANI layer with higher electric conductivity, better water wettability, higher apparent diffusion coefficient and super-stability is desired.

There are four main types of isomers, i.e., positional, cis/trans, and rotational isomers, which can affect the electrochemical properties of PANI. In our previous study (Wang *et al.*, 2013), an electrode modified with all cis-PANI nanotube (ACPN) film was prepared using a facile unipolar pulse electro-polymerization method (UPEP) for supercapacitors and AA sensors. However, the fabrication conditions for the ACPN film modified electrode were not optimized and the electro-oxidation of AA on the electrode was also unclear. In this study, the fabrication method for an ACPN film modified electrode for AA detection was optimized and the reaction kinetics of AA with an ACPN film were investigated. Furthermore, the catalytic mechanism on the electro-oxidation of AA was also analyzed and discussed.

1. Experimental

The method to prepare an ACPN film modified electrode was described in our previous study (Wang *et al.*, 2013). All electrochemical experiments for characterization of the obtained electrode for AA detection were conducted with a

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VMP3 electrochemical workstation (Princeton Ltd.) using a conventional three-electrode system. Before the measurement, the prepared electrode was immersed in 0.5 M H_2SO_4 with applied potentials from -0.2 to 0.55 V at 0.1 V \cdot s $^{-1}$ for 150 cycles, followed by rinsing with deionized water, and finally drying in a vacuum oven. The performance test for the electro-oxidation of AA was then carried out using cyclic voltammetry between -0.2 and 0.7 V with a scan rate of 5 mV \cdot s $^{-1}$. Amperometric responses of the electrode to various concentrations of AA by successive injection of AA into a three-electrode electrochemical cell (40 mL) containing electrolytes with stirring were measured. Before the successive addition of AA, the electrode was first polarized at the operating potential until the background current became stable. Each experiment was repeated at least three times, and the results were found to be reproducible. The average data were used for the analysis.

2. Results and Discussion

2.1 Electrocatalytic oxidation of ascorbic acid

Schematic representations for the fabrication of the ACPN film modified electrode by the UPEP method (outside the solid panel) as well as electrocatalytic oxidation mechanism for AA on the ACPN film (inside the solid panel) are illustrated in **Figure 1**. The formation mechanism of the ACPN film on electrode was analyzed and discussed in our previous study (Wang *et al.*, 2013). Here, the electrocatalytic oxidation mechanism for AA on the ACPN film is proposed. The oxidation of AA to dehydro-AA should involve two electrons transferred, in which the electrooxidation of AA occurs through the mediated electron transfer on the ACPN film. The oxidized form of all cis-PANI (PANI_{ox}) is beneficial to oxidize AA with the change from PANI_{ox} to the reduced form (PANI_{red}) simultaneously (inside the solid panel).

To understand the promoting effect of the ACPN on the electrocatalytic oxidation of AA, the oxidation degree of ACPN as a function of the electrochemical potential (black line) and the electrocatalytic oxidation current at different potentials (blue line) for a 1 mM AA solution were obtained as indicated in **Figure 2**. Herein, the data of oxidation degree was obtained by analyzing the same N1s curve of X-ray photoelectron spectroscopy (XPS) of the PANI at different applied electrochemical potentials (Snauwaert *et al.*, 1990). Since nitrogen atoms in intercalary PANI chains are present in two forms, imine ($=\text{N}-$) and benzenoid amine ($-\text{NH}-$), the N 1s spectra are reasonably deconvoluted into two Gaussian peaks at 399.8 and >400.0 eV, respectively. Thus, it can be calculated using Eq. (1).

$$\text{oxidation degree} = \frac{\text{imine amount}}{\text{total amount of polyaniline}} \times 100\% \quad (1)$$

In the low potential region from -0.2 to $+0.1$ V, the oxidation degree is near zero, corresponding to the region

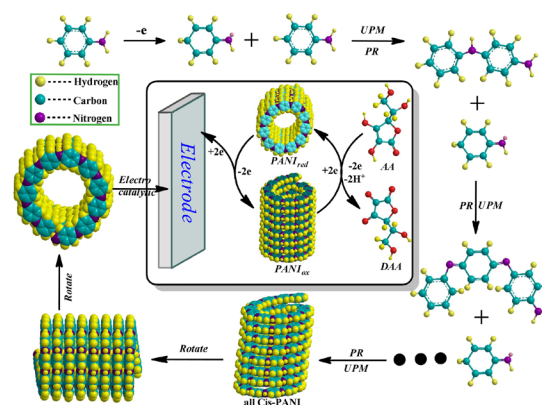


Fig. 1 Schematic illustration of the polymerization process and the rotating shows of the PANI (outside the solid panel) and electrocatalytic oxidation mechanism in the ascorbic acid sensor (inside the solid panel); UPEP: Unipolar pulse electro-polymerization method; PR: Polymerization Reaction

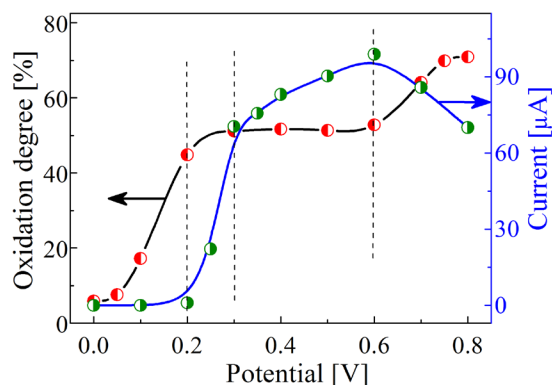


Fig. 2 Oxidation degree as a function of the electrochemical potential (black line) and electro-catalytic oxidation current at the different potential (blue line) with 1 mM of ascorbic acid

where PANI is in the leucoemeraldine form. Then, the oxidation degree increased sharply and approached 44% at 0.2 V and remained at the value of near 50% up to 0.6 V, where PANI is changed to the emeraldine state (Huang *et al.*, 1986). Interestingly, AA cannot be oxidized on ACPN film at potentials less than 0.2 V, but the oxidation current increases close to 73% of the maximal current rapidly at 0.3 V, and remains at the sluggish augment to the maximal current until the potential is increased up to 0.6 V. That is why AA can be electrocatalytically oxidized by the emeraldine due to the highest imine ($=\text{N}=$) concentration corresponding to the electrocatalytic oxidation of ACPN. As we know, the insertion of anions in the emeraldine state starts at 0.2 V, which serves to charge the electrical double layer of the film and to neutralize any net charge on the polymer chains which might arise from the protonation of the PANI film in its oxidized form, was observed by using an electrochemical quartz crystal microbalance (EQCM) (Orata and Buttry, 1987). With the increase in the potential from 0.3 to 0.6 V, the oxidation degree remains unchanged because the oxidized amount of the PANI film is almost equal to the protonation of the PANI film. However, the oxidation

current remained at the sluggish increases to the maximal current with the increase of the overpotential. When the potential increases from 0.6 to 0.8 V, the imine concentration begins to decrease because the imine is excessively protonated to neutralize any net charge on the polymer chains, resulting in the electro-catalytically oxidized current decreasing. Thus, the imine concentration reaches the maximum at the potential region from 0.25 to 0.3 V. In our previous study (Wang *et al.*, 2013), it was found that the peak potential for electro-catalytic oxidation of AA at the low concentration (less than 1 mM) is at about 0.28 V.

2.2 Optimization of PANI modified electrodes

To optimize the ACPN film modified electrodes, the factors influencing the film thickness and active molar ratio in the UPEP of it were investigated in detail. In general, the structure and amount of ACPN film deposited on the electrode can be regulated by tuning the polymerization potential, the pulse cycle and/or polymerization time (Liu *et al.*, 2009; Wang *et al.*, 2012b). Especially, the potential and time play main roles in the thickness of the polymer film. In the present study, to decide the active molar ratio in the obtained film, the following equation is applied.

$$Y_a = \frac{m_a}{m_t} \quad (2)$$

Here, Y_a stands for the active molar ratio in the film, m_a for active moiety matter quantity in the film and m_t for the total molar quantity of the PANI. m_a can be obtained by estimating the surface coverage of the electrode because the electrochemical redox response of the PANI between the leucoemeraldine and the emeraldine states is a surface-confined process like a diffusionless process. As such, the peak current at various scan rates can be calculated by the following equation (Sharp *et al.*, 1979).

$$I_p = \frac{n^2 F^2 A \nu G_0}{4RT} \quad (3)$$

Here, G_0 , ν , A and I_p represent the surface coverage concentration, the scan rate, the electrode area, and the peak current, respectively. m_t of the PANI deposited on the electrode can be calculated according to the Faraday's law as shown in Eq. (4) assuming that the current efficiency is 100%.

$$Q = \frac{m_t}{M} zF \quad (4)$$

Here, Q is the charge loading; m_t the mass of the deposited PANI; M the molar mass of aniline monomer; F the Faraday constant; and z the exchanged number of electron (Tu *et al.*, 2011). **Figure 3** shows the sensitivity (black line) and the active molar ratio (blue line) of the PANI at the different polymerization potentials from 0.85 to 1.05 V (vs. SCE) with the polymerization time of 30 s. It is found that the sensitivity of the AA detection strongly depends on the UPEP potential. One can see that the sensitivity increases with the increase in polymerization potential from 0.85 to 0.95 V, corresponding to the enhancements of the active molar ratio

and the film thickness in the ACPN film modified electrode.

However, when the polymerization potential is higher than 0.95 V, the sensitivity and the active molar ratio gradually decrease with the increase in the thickness. It indicates that the obstacle of electron-transfer increases and the formation of a non-conductive layer arises from the PANI polymerization with the increasing of the thickness (Zare and Golabi, 1999; Liu *et al.*, 2011). Here, the electron transfer rate should be decreased and penetration of the counterion (SO_4^{2-}), which is required in transition between leucoemeraldine and emeraldine for preserving charge neutrality, becomes more and more difficult as the distance between the PANI outer layer and the electrode surface increases. On the other hand, a more non-conductive layer should be generated with the increase in the thickness. Thus, the electrode modified by ACPN film with the polymerization potential of 0.95 V exhibits the highest sensitivity to AA. Furthermore, it should be noted that a film with a higher thickness could result in larger noise, slower response and lower detection limit of a sensor (Luo *et al.*, 2005).

The effect of the polymerization time on the sensitivity (black line) and active molar ratio (blue line) is shown in **Figure 4**. One can see that the optimum polymeriza-

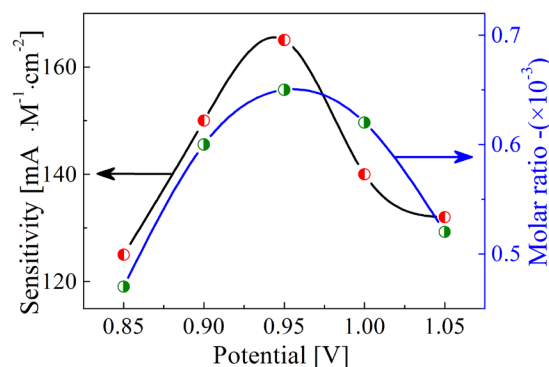


Fig. 3 Dependences of sensitivity (black line) and active molar ratio (blue line) of active moiety matter quantity and gross molar quantity of the PANI on the different polymerization potentials from 0.85 V to 1.05 V (vs. SCE) with the polymerization time of 30 s

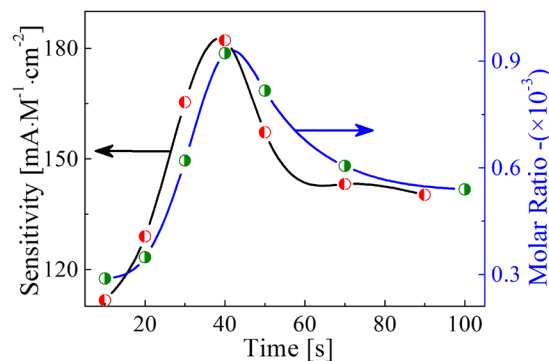


Fig. 4 Dependences of sensitivity (black line) and active molar ratio (blue line) of active moiety matter quantity and gross molar quantity of the ACPN on the different polymerization time at polymerization potential of 0.95 V (vs. SCE)

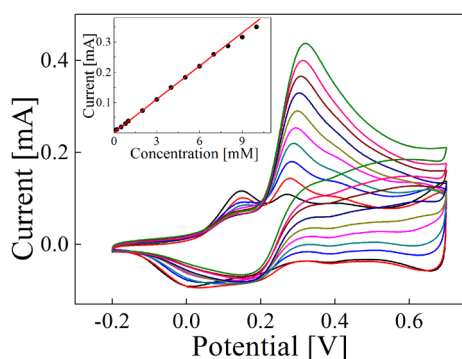


Fig. 5 Cyclic voltammograms of the ACPN film modified electrode when successive addition of ascorbic acid to the solution of 0.1 M H_2SO_4 at a sweep rate of $5 \text{ mV} \cdot \text{s}^{-1}$; inset: the calibration curve of peak current to concentration of ascorbic acid

tion time is around 40 s. Based on the above results, in the construction of the ACPN film modified electrode for AA detection, the deposition time of 35–45 s at 0.95 V should be selected to achieve the highest activity.

2.3 CV responses to ascorbic acid

Figure 5 displays the cyclic voltammograms of the ACPN film modified electrode by increasing AA concentration during the test, in which the inset shows the plot of catalytic peak current versus the concentration of AA. One can see that the anodic peak current is increased linearly with the concentration of AA in the range of 1×10^{-6} – 1×10^{-2} M and the detection limit is as low as 6.58×10^{-7} M on a signal-to-noise ratio of 3 with a correlation coefficient of 0.9988. When the AA concentration exceeds 1×10^{-2} M, the response of the modified electrode decreases from the expected value and deviates from the linearity; which may be mainly attributed to the saturation of active sites on the ACPN film modified electrode surface. Furthermore, a very high sensitivity of $182 \text{ mA} \cdot \text{M}^{-1} \cdot \text{cm}^{-2}$ is demonstrated for the ACPN film modified electrode, which is much higher than those reported $166.5 \text{ mA} \cdot \text{M}^{-1} \cdot \text{cm}^{-2}$ (Wen *et al.*, 2010) in the literature. As indicated in our previous study (Wang *et al.*, 2013), such ultrahigh electrocatalytic activity, wide linear range and high sensitivity should be attributed to the molecular conformation of the helical tubular microstructure and the intrinsic properties of ACPN such as low charge transfer resistance, good water wettability, high apparent diffusion coefficient and excellent biocompatibility.

2.4 Chronoamperometric responses to ascorbic acid

Figure 6 shows the current–time curves in the detection of a blank sample (a) and 1–6 mM AA (b–g) at 0.5 V in the 0.1 M H_2SO_4 solution and the dependence of I_{cat}/I_L on $t^{1/2}$ derived from the data of chronoamperograms of (a) and (b) (inset). Here, the chronoamperometry is used for the calculation of the diffusion coefficient of AA in the solution. For an electroactive material with diffusion coefficient D , the current corresponding to the electrochemical reaction can

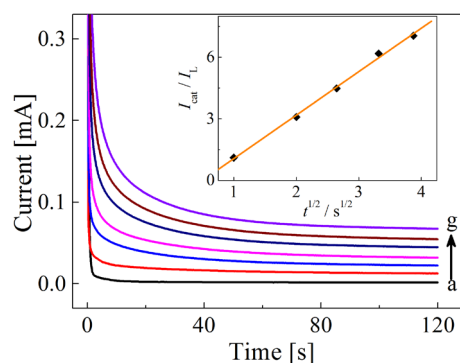


Fig. 6 (A) Chronoamperograms when the ACPN film modified electrode in the absence (a) and presence of 1 (b), 2 (c), 3 (d), 4 (e), 5 (f), 6 (g) mM ascorbic acid in 0.1 M H_2SO_4 solution at 0.5 V (vs. SCE); inset: dependence of I_{cat}/I_L on $t^{1/2}$ derived from the data of chronoamperograms of (a) and (b); I_{cat} is the current of the ACPN modified electrode in the presence of AA, I_L is the limiting current in the absence of AA

be described by Cottrell's law (Bard and Faulkner, 2001).

$$i = nFAD^{1/2}C_0\pi^{-1/2}t^{-1/2} \quad (5)$$

Here, D and C_0 are the diffusion coefficient [$\text{cm}^2 \cdot \text{s}^{-1}$] and bulk concentration [$\text{mol} \cdot \text{cm}^{-3}$] of AA, respectively. One can see that the plot of I versus $t^{1/2}$ at various AA concentrations is linear. From the slope of I versus $t^{1/2}$ plot, the value of the diffusion coefficient (D) can be calculated. In this study, the average value of D is calculated to be $1.1 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, which is higher than those reported in the literature [4.5 – $6.9 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$] for the PANI-based electrodes (Zhang and Dong, 2004; Zhang and Lian, 2007).

The chronoamperometry can also be used for the evaluation of the catalytic rate constant (k) for the chemical reaction between AA and the redox sites of surface confined ACPN using the following equation (Galus, 1976).

$$I_{\text{cat}}/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kC_0t)^{1/2} \quad (6)$$

Here, k , C_0 , and t are the catalytic rate constant [$\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$], catalyst concentration (M) and time elapsed (s), respectively. γ is the argument of the error function, which is almost equal to 1. Based on the slope of the I_{cat}/I_L versus $t^{1/2}$ plot, k is obtained for given AA concentrations (inset). The value of k is calculated to be $6.3 \times 10^6 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, which is about 10 times higher than those reported PANI-based composite modified electrodes used for the electrocatalytic oxidation of AA (5.6 – $8.3 \times 10^5 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) (Zhang and Dong, 2004; Zhang and Lian, 2007). In a future work, the actual measurements of concentrations of ascorbic acid in a simulated or a real solution to test its reliability, robustness and lifespan as a working sensor will be performed. Furthermore, to gain more insight into this electrode on the transfer of electrons and ions, some in-situ quantitative characterization methods will be developed.

Conclusions

In this study, the reaction kinetics of an ACPN film modified electrode with excellent electrocatalytic activity for fast ascorbic acid detecting are investigated in details. The following results are obtained: (1) AA is found to be electro-oxidized on the electrode even at the concentration of AA less than 1 mM; (2) the electrooxidation of AA occurs through the mediated electron transfer on the ACPN film and the oxidized form of all cis-PANI (PANI_{ox}) is beneficial to oxidize AA; (3) the detection sensitivity can be regulated by tuning the film thickness, and the deposition time of 35–45 s at 0.95 V should be the optimum condition to achieve the highest activity; (4) the catalytic rate constant for the best electrode is $6.3 \times 10^6 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ based on the kinetic study. It indicates that the prepared sensor could be an alternative for application in AA detection.

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