Electrocatalytic Activity of Europium Doped Tantalum Oxide for Ascorbic Acid Oxidation in Aqueous

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Europium doped tantalum oxide (europium-Ta₂O₅) particles were synthesized using a low temperature hydrothermal method. The crystal phase of the samples was analyzed using X-ray diffraction (XRD). The XRD result revealed that the europium-Ta₂O₅ particles had a good crystalline structure and belonged to the orthorhombic phase. The electrocatalytic activity of an europium-Ta₂O₅ film electrode was investigated by cyclic voltammetry (CV) in 0.1 mol dm⁻³ KCl solution containing ascorbic acid (AA). The CV results indicated that the europium-Ta₂O₅ film electrode had excellent catalytic activity toward AA oxidation with obvious reduction of the overpotential. The anodic peak potential (E_{pa}) of AA shifted from 0.72 V on a bare glass carbon electrode (GCE) to 0.38 V on the europium-Ta₂O₅ film electrode. Moreover, europium doping could improve the stability and electrocatalytic activity of Ta₂O₅.

Keywords: Tantalum Oxide; Dope; Electrocatalysis; Cyclic Voltammetry

1. INTRODUCTION

Ascorbic acid is a vital component in the diet of both the human and animal kingdoms [1-6]. AA takes part in several biological reactions and mammalian function [7]. Clinical studies have shown that the lack of AA could result in disease, such as scorbutus. Ascorbic acid has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [8]. Therefore, the concentration of AA in foods, drinks and pharmaceuticals can be an index of quality [9]. At present, electrochemical methods have been proved to be effective and inexpensive ways for AA determination [9]. However, the oxidation of ascorbic acid is difficult using direct oxidation on conventional electrodes because of its high overpotential, low selectivity, poor sensitivity and poor reproducibility [7, 9-13]. The development of the modified electrodes is attracting increasing attention because of their electrocatalytic activity [14-18]. For example, gold nanoparticles, Pt nanoparticles and carbon

nanotube- modified electrodes have been used in the determination of AA [19-21]. The conducting polymer (polyaniline, PANI) has been used in modified electrodes, but PANI electrodes will lose their redox activity and conductivity above pH 4.0 [22]. However, these chemically modified electrodes exhibit some limits in their applications. Therefore, it is necessary to develop new electrode materials with excellent electrocatalytic activity toward the oxidation of AA.

Tantalum oxide films demonstrate conductivity, and it is a stable oxide in usual acidic and alkaline solution. So, it has potential application as an electrode [23, 24]. For example, Ishihara and coworkers studied Ta_2O_5 -based C and N compounds and found that they exhibit electrocatalytic activity for oxygen reduction reactions in polymer electrolyte fuel cells [25]. Tungsten oxide doped Ta_2O_5 exhibited the catalytic performance for the oxygen reduction reaction in proton exchange membrane fuel cells [26]. The previously documented report found that lanthanum-, cerium-doped Ta_2O_5 film electrodes exhibited excellent electrochemical reversibility [24, 27]. Thus, the rare earth metals-doped Ta_2O_5 might constitute new electrode materials in the electrochemical applications field. In this study, therefore, we studied a rare earth metal (europium) doped Ta_2O_5 film electrode material to improve the electrocatalytic activity of Ta_2O_5 for AA oxidation.

2. EXPERIMENTAL PART

2.1 Chemical reagents

Tantalum oxide (99.9%) was sourced from Shanghai Maikun Chemical reagents Co. Polyvinylidene-fluoride (PVDF, 99.2%) and 1-methyl-2-pyrrolidinone (NMP, 99.0%) were obtained from Sigma-Aldrich.

2.2 Synthesis of europium-Ta₂O₅ particles

The synthetic method of europium-Ta₂O₅ particles was similar to a previously reported procedure [27]. 0.4418 g Ta₂O₅ powder was triturated and put into a 30-mL Teflon vessel, then 20 mL of 0.1 mol dm⁻³ Eu(NO₃)₃ solution was added. The mixture was stirred to form a uniform suspension and was kept at 200 °C for 12 h. Then it was cooled to room temperature and was filtered under vacuum to obtain the precipitate. The precipitate was rinsed several times by distilled water and ethanol, respectively, then the precipitation was dried at 60 °C for 2 h. Finally, europium-Ta₂O₅ particles were obtained after calcining 400 °C for 4 h. The resulting particles were further characterized with X-ray photoelectron spectroscopy (XPS), X-ray diffraction and cyclic voltammetry.

2.3 Electrochemistry and other measurements

The europium- Ta_2O_5 film electrode was prepared by the following method. 0.90 g europium- Ta_2O_5 and 0.04 g PVDF were added into 2 mL NMP to form a uniform suspension at magnetic stirring for 30 min. The suspension was spread on the GCE, then dried for 60 min at 60 °C. Finally, an oxide

film coated GCE was prepared. The europium- Ta_2O_5 film electrode and standard GCE served as the working electrodes. A platinum coil and an Ag|AgCl electrode (with saturation KCl solution) were used as the counter and reference electrode, respectively. CV measurements were carried out with a three-electrode system by using CHI750D Electrochemical Workstation (CH Instruments, Shanghai Chenhua Instrument Corporation, China).

The phase structure was identified by X-ray diffraction (D8-ADVANCE, Bruker, Germany) with Cu K α (λ = 1.5406 Å) radiation at a scan rate of 0.02 2θ s⁻¹. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. The added Ni was used as the reference material. The components of samples were analyzed using X-ray photoelectron spectroscopy on an ESCA-LAB MKII apparatus.

3. RESULTS AND DISCUSSION

3.1 XRD of europium-Ta₂O₅ particles

The XRD patterns of undoped Ta_2O_5 (a) and europium- Ta_2O_5 (b) particles obtained are shown in Fig. 1.



Figure 1. XRD patterns of (a) undoped and (b) europium-doped Ta₂O₅ particles.

As can be seen, all the sharp diffraction peaks can be indexed in the unit cell of tantalum oxide (JCPDS 01-089-2843). The results gave the following information: (1) Europium-Ta₂O₅ obtained had good crystallinity. (2) Ta₂O₅ and europium-Ta₂O₅ belonged to the orthorhombic crystalline phase. (3) Europium-doped Ta₂O₅ did not change the crystal structure of Ta₂O₅.

3.2 XPS of europium-Ta₂O₅ particles



Figure 2. XPS survey spectrums of (a) undoped and (b) europium-doped Ta₂O₅ particles.



Figure 3. XPS spectrum background-subtracted of Ta 4f.

In order to confirm the europium doping, we studied XPS for the undoped and europium-doped Ta_2O_5 , and the results are shown in Fig. 2. It can be seen that Eu 3d peaks appeared in the region of the XPS spectrum in graph (b). It indicated that europium was doped to Ta_2O_5 . The binding energy level of C1s obtained is 284.75 eV, here. Fig. 3 shows The XPS spectrum for Ta 4f. From this Figure, we could know the binding energy levels of Ta $4f_{5/2}$ and $4f_{7/2}$ was 27.3 and 25.4 eV, which shifted to the

higher values of elemental Ta (24.0 ($4f_{5/2}$) and 22.0 ($4f_{7/2}$) eV) [28]. This indicated that the site Ta exists in a cationic state rather than the elemental state Ta₂O₅ [29].

3.3 Electrocatalytic activity of the europium-Ta₂O₅ film electrode



Figure 4. Cyclic voltammograms of (a) 0 and (b) 1 mmol dm⁻³ AA in 0.1 mol dm⁻³ KCl solution on the europium-doped Ta_2O_5 film electrode. The potential scan rate was 50 mV s⁻¹.

Fig. 4 shows typical cyclic voltammograms of 1 mmol dm⁻³ AA in a 0.1 mol dm⁻³ KCl solution saturated with N₂ atmosphere on the europium-Ta₂O₅ film electrode at the potential scan rate of 50 mV s⁻¹. Curve (a) shows the blank experiment which was carried out in 0.1 mol dm⁻³ KCl solution without AA. No peak was observed. There was an anodic wave at 0.38 V in curve (b), and it was ascribed to the oxidation of AA [30-32]. However, the E_{pa} of AA oxidation was 0.72 V on the bare GCE [30]. Thus, there was a negative-shift of 0.34 V of the E_{pa} of AA toward the europium-Ta₂O₅ film electrode. The result indicated that the europium-Ta₂O₅ film electrode had excellent electrocatalytic activity toward AA oxidation. As can be seen, the overpotential shifted negatively which implied that the europium-Ta₂O₅ improved the reversibility of the electron transfer processes of AA. The electrochemical reaction of AA oxidation is the following [33].



The anodic peak of AA is wide, and it implies that the electrochemical reaction of AA is an irreversible process. For the irreversible process, E_p and the logarithm of the potential scan rate (log*v*) obey the following equation [13, 34]:

$$E_{n} = K + (2.303RT/2\alpha n_{\alpha}F)\log v$$

Where K is a constant, α is the transfer coefficient, and n_{α} is the electron number transferred in the electrochemical process.



Figure 5. (A) Cyclic voltammograms of 1 mmol dm⁻³ AA in 0.1 mol dm⁻³ KCl solution on the europium-doped Ta_2O_5 film electrode at different potential scan rates. (B) Variation peak potential with the logarithm of potential scan rates.

Fig. 5A shows CVs of 1 mmol dm⁻³ AA in 0.1 mol dm⁻³ KCl solution on the europium-Ta₂O₅ film electrode at different potential scan rates. The potential scan rates were 30, 50, 80, 100, 120 and 140 mV s⁻¹, respectively. The anodic peak potential shifted to more positive values with increasing potential scan rates, which indicated that a kinetics limitation exists in the reaction between the redox

sites of europium-Ta₂O₅ film and AA [7]. Fig. 5B shows that variation of E_p with logv, and the slope was 0.0514. The Tafel slope was 0.1028. The value of $2.303RT/\alpha n_{\alpha}F$ was equivalent to the Tafel slope. Consequently, we obtained the value of the transfer coefficient as 0.29. The range of α was between 0.25 and 0.75 on most electrodes [35]. The value of α was in accordance with the range of the transfer coefficient.

3.4 Electrochemical properties of AA on the europium- Ta_2O_5 film electrode

In order to investigate the electrochemical properties of AA on the europium- Ta_2O_5 film electrode, we plotted the proportion between the anodic peak currents and the square-root of the potential scan rate, as shown in Fig. 6.



Figure 6. Dependence of the anodic peak current on the square root of potential scan rate in $0.1 \text{ mol } \text{dm}^{-3} \text{ KCl}$ solution containing 1 mmol $\text{dm}^{-3} \text{ AA}$ on the europium-doped Ta₂O₅ film electrode.

In this figure, we could state that the anodic peak currents were linear with the square-root of the potential scan rate. Further investigation was carried out using cyclic voltammetrys in 0.1 mol dm⁻³ KCl solution containing different concentration of AA on the europium- Ta_2O_5 film electrode. The potential scan rate was 50 mV s⁻¹. The concentration of AA was 0.1, 0.5, 1.0, 3.0 and 5.0 mmol dm⁻³, respectively. The proportion between the anodic peak currents and the concentration of AA is shown in Fig. 7. From this figure, we can state that it is also linear. These linear relationships indicated that the anodic peak currents of AA were controlled by the diffusion process on the europium- Ta_2O_5 film electrode was carried out in 0.1 mol dm⁻³ KCl solution containing 1 mmol dm⁻³ AA. The E_{pa} of AA oxidation was around located at 0.54 V on the undoped Ta_2O_5 film electrode. This result implied that europium doping could improve the electrocatalytic activity of the Ta_2O_5 film electrode.



Figure 7. Variation anodic peak currents with the concentration of AA on the europium-doped Ta_2O_5 film electrode. The potential scan rate was 50 mV s⁻¹.

3.5 Electrochemical stability of the europium-Ta₂O₅ film electrode

The conductivity and stability of the europium-Ta₂O₅ film electrode were investigated with the following experiments. The cyclic voltammogram of 5 mmol dm⁻³ K₃Fe(CN)₆ in 0.1 mol dm⁻³ KCl solution were performed on the undoped Ta₂O₅ and europium-Ta₂O₅ film electrodes, respectively. The peak potential separation (ΔE_p) was about 100 mV on the europium-Ta₂O₅ film electrode, which was less than the ΔE_p of 144 mV at the undoped Ta₂O₅ film electrode [24, 36]. The high peak currents and low overpotential indicated that europium-Ta₂O₅ film electrode had stable electrochemical activity. Therefore, europium-Ta₂O₅ is an excellent electrode material for the oxidation of AA.

4. CONCLUSIONS

The europium- Ta_2O_5 particles with orthorhombic crystalline phase were synthesized successfully by using the low temperature hydrothermal method. The europium- Ta_2O_5 film electrode had excellent electrocatalytic activity toward the oxidation of AA. Europium doping improved the conductivity, stability and electrocatalytic activity of the Ta_2O_5 film electrode. The electrochemical process of AA was diffusion-controlled on the europium- Ta_2O_5 film electrode. Europium- Ta_2O_5 might be a kind of potential electrocatalytic material in AA determination processes.

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