



## Electrocatalytic oxidation of ascorbic acid on a lithium-doped tantalum oxide film coated electrode



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### ABSTRACT

In this work, lithium-doped tantalum oxide (lithium-Ta<sub>2</sub>O<sub>5</sub>) particles were synthesized using a low-temperature hydrothermal method. X-ray photoelectron spectroscopy (XPS) indicated that the state of lithium on the Ta<sub>2</sub>O<sub>5</sub> surface is the Li<sup>+</sup> form. The crystal phase of the samples was analyzed using X-ray diffraction (XRD). The analysis revealed that the lithium-Ta<sub>2</sub>O<sub>5</sub> particles are well crystallized into an orthorhombic phase. Calculation from density functional theory (DFT) indicated that the band gap of Ta<sub>2</sub>O<sub>5</sub> narrows when it is doped with lithium, resulting in improved conductivity and electrocatalytic activity over Ta<sub>2</sub>O<sub>5</sub>. The electrocatalytic activity of a lithium-Ta<sub>2</sub>O<sub>5</sub> film coated electrode was investigated in a 0.1 mol dm<sup>-3</sup> KCl solution containing ascorbic acid (AA) using cyclic voltammetry (CV). The lithium-Ta<sub>2</sub>O<sub>5</sub> film coated electrode has excellent electrocatalytic activity toward the oxidation of AA with much reduced overpotential. The anodic peak potential of AA shifted from 0.72 V (versus Ag|AgCl) on a bare glassy carbon electrode (GCE) to 0.42 V on the lithium-Ta<sub>2</sub>O<sub>5</sub> film coated electrode.

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### 1. Introduction

Metal-oxide electrodes have received extensive attentions in the field of electrocatalysis due to their special properties [1–6]. Most metal oxides are semiconducting, and display electrocatalytic activity. However, the concentration of free electrons in metal-oxide semiconductors is low, approximately 10<sup>21</sup> m<sup>-3</sup> [1]. Research has shown that doping can improve the conductivity of metal-oxide semiconductors [7–11]. Furthermore, doping may change the band gap from the introduction of new doping energy levels in metal oxides and improve their electrocatalytic activity [1,12,13]. For example, studies by Senevirathne et al. showed that Nb-doped TiO<sub>2</sub>/carbon composite supports had electrocatalytic activity for oxygen reduction reaction in proton exchange membrane fuel cells [14]. Feng et al. studied Ti-doped PbO<sub>2</sub> (SnO<sub>2</sub>) electrodes, which had good electrocatalytic activity for phenol degradation [15]. Also, cerium-doped tantalum oxide electrodes exhibited excellent electrocatalytic activity for methylene blue reduction [13].

Tantalum oxide is a stable oxide in most acidic and alkaline solutions, and its film is semiconducting [16–18]. Moreover, Ta<sub>2</sub>O<sub>5</sub> has excellent chemical and thermal stabilities, which makes it promising for use as electrodes [19–22]. For example, Ishihara et al. found Ta<sub>2</sub>O<sub>5</sub>-based C and N compounds and found that they

exhibit electrocatalytic activity for oxygen reduction reaction in polymer electrolyte fuel cells [23]. Tungsten oxide doped Ta<sub>2</sub>O<sub>5</sub> exhibited good catalytic performance for oxygen reduction reaction [24]. Previously reports showed that cerium-, and europium-doped Ta<sub>2</sub>O<sub>5</sub> film coated electrodes exhibited excellent electrochemical reversibility and electrocatalytic activity [13,25]. Thus, doping could change the electrochemical properties of Ta<sub>2</sub>O<sub>5</sub>, and eventually new electrode materials are promising to be constituted for electrocatalytic applications.

Ascorbic acid, commonly known as vitamin C, is a vital component in the diet of both the human and animal kingdoms [26–31]. AA takes part in several biological reactions and mammalian functions [32]. AA can be synthesized with plants and many mammals, but not with man. Clinical studies have shown that the lack of AA could result in diseases. AA is also used as an antioxidant and has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [33]. Therefore, the concentration of AA in foods, drinks and pharmaceuticals can be an index of quality [34]. Recently, many analytic techniques have been used in monitoring the concentration of AA, such as enzymes, spectrophotometry, fluorometry, liquid chromatography and chemiluminescence [35–40]. However, these analytic methods require complicated pretreatment techniques and expensive instruments [41]. Electrochemical methods have been proved to be effective and inexpensive ways for identifying the presence of AA [34]. However, the oxidation of AA is difficult using direct oxidation on conventional electrodes because of its high overpotential (the

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additional potential needs to drive a reaction at a certain rate), low selectivity, poor sensitivity and poor reproducibility [32,42–45]. Thus, it is important to develop new electrode materials with excellent electrocatalytic activity toward the oxidation of AA.

In this paper, we report the application of a lithium-doped Ta<sub>2</sub>O<sub>5</sub> film coated electrode for the electrocatalytic oxidation of AA. Moreover, the electronic structure of lithium-Ta<sub>2</sub>O<sub>5</sub> was calculated using density functional theory. To the best of our knowledge, the electronic structure of lithium-doped Ta<sub>2</sub>O<sub>5</sub> has not previously been calculated.

## 2. Experimental

### 2.1. Chemical reagents and synthesis of lithium-Ta<sub>2</sub>O<sub>5</sub> particles

Poly-vinylidene-fluoride (PVDF, 99.2%) and 1-methyl-2-pyrrolidinone (NMP, 99.0%) were obtained from Sigma–Aldrich. Tantalum oxide (99.9%) was sourced from Shanghai Maikun chemical reagents Co. Lithium nitrate hexahydrate (99.9%) was received from Tianjin chemical reagents corporation, China.

The synthetic method of lithium-Ta<sub>2</sub>O<sub>5</sub> particles was similar to a previously reported procedure [13]. 0.4418 g Ta<sub>2</sub>O<sub>5</sub> powder was triturated and put into a 30-mL Teflon vessel, then 20 mL of 0.1 mol dm<sup>-3</sup> LiNO<sub>3</sub> solution was added. The other processes were same as those described previously [13,25]. The resulting lithium-Ta<sub>2</sub>O<sub>5</sub> particles were further characterized with scanning electron microscope (SEM), XPS, XRD and CV.

### 2.2. Electrochemistry and other measurements

The fabrication of the lithium-Ta<sub>2</sub>O<sub>5</sub> film and pure Ta<sub>2</sub>O<sub>5</sub> film coated electrodes were similar to the described previously [25]. 0.90 g lithium-Ta<sub>2</sub>O<sub>5</sub> (pure Ta<sub>2</sub>O<sub>5</sub>) particles and 0.04 g PVDF were added into 2 mL NMP to form a uniform suspension at magnetic stirring for 60 min. The suspension was spread on the GCE, then dried for 60 min at 60 °C. Finally, an oxide film coated GCE was obtained. The amount of lithium-Ta<sub>2</sub>O<sub>5</sub> particles onto GCE surfaces was 5.0 mg cm<sup>-2</sup>. The lithium-Ta<sub>2</sub>O<sub>5</sub>, pure Ta<sub>2</sub>O<sub>5</sub> film coated electrodes and bare GCE served as the working electrodes. An Ag|AgCl electrode (with saturation KCl solution) and a platinum coil were used as the reference and counter electrode, respectively. The CV measurements were carried out with a three-electrode system with using CHI750D electrochemical workstation (CH Instruments, Shanghai, China).

The components of samples were analyzed using X-ray photoelectron spectroscopy on an ESCA-LAB MKII apparatus. The doping amount of lithium in Ta<sub>2</sub>O<sub>5</sub> was measured with inductively coupled plasma (VISTA-MPX CCD Simultaneous ICP-OES, Varian, American). The electronic conductivity of lithium-doped Ta<sub>2</sub>O<sub>5</sub> was measured with a LCR digital bridge (ZL5, Shanghai, China). The phase structure was identified by X-ray diffraction (Empyrean, Netherlands) with Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation at a scan rate of  $0.022 \theta \text{ s}^{-1}$ . The accelerating voltage and applied current were 40 kV and 40 mA, respectively. The reference of Ni was added. The morphology of samples was investigated with scanning electron microscopy (S4800, Hitachi, Japan).

## 3. Results and discussion

### 3.1. XPS of lithium-Ta<sub>2</sub>O<sub>5</sub> particles

In order to confirm the lithium doping, we used XPS to study the lithium-Ta<sub>2</sub>O<sub>5</sub>. As shown in Fig. 1a, Li 1s peak appears in the XPS spectrum indicating that lithium is doped to the Ta<sub>2</sub>O<sub>5</sub>. The standard binding energy of the C 1s is 284.62 eV, while the binding

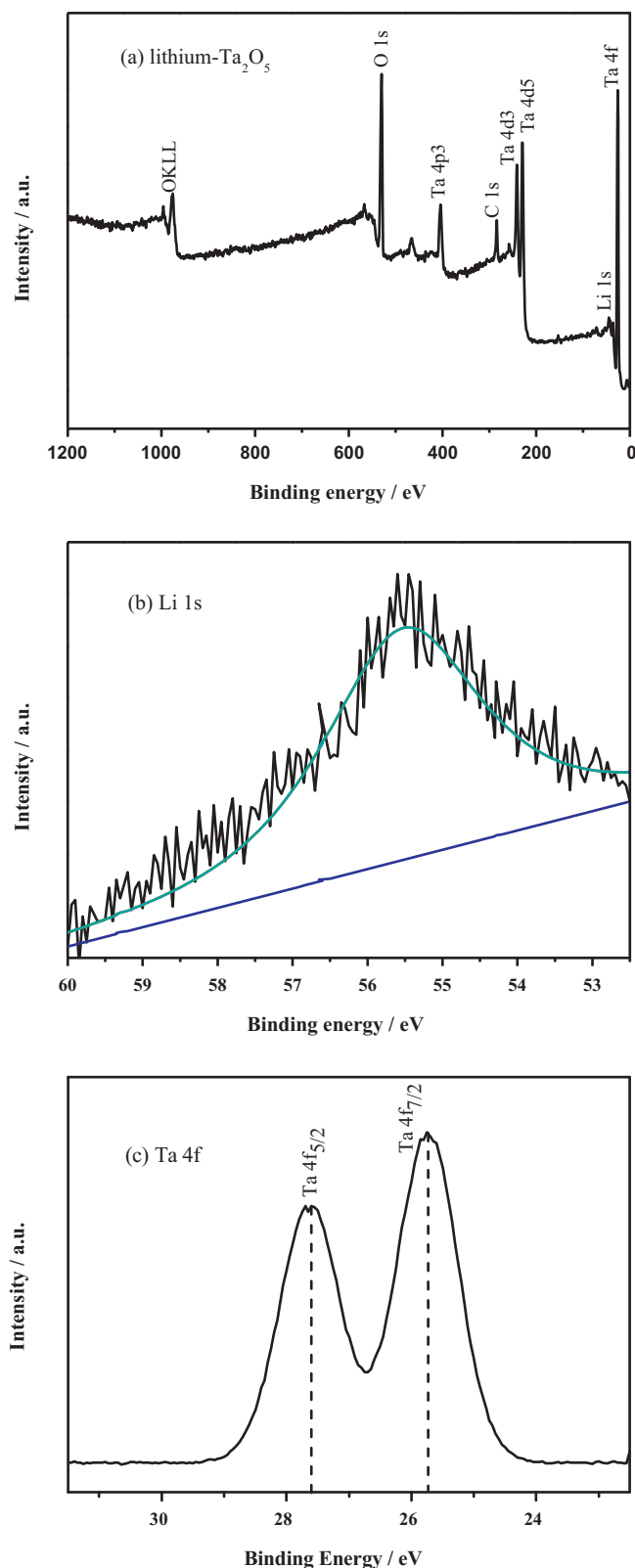


Fig. 1. (a) XPS survey spectrum of lithium-Ta<sub>2</sub>O<sub>5</sub> particles, with background-subtracted spectrums of (b) Li 1s and (c) Ta 4f.

energy level of the C1s obtained herein is 284.65 eV. The XPS spectrum of Li 1s was also measured under the same conditions, as shown in Fig. 1b. The binding energy of the Li 1s is 55.45 eV. This indicated that lithium exists in the form of Li<sup>+</sup> on the surface of the lithium-Ta<sub>2</sub>O<sub>5</sub> [46–48]. Moreover, the doping amount of lithium

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