



K_{0.4}TaO_{2.4}F_{0.6} Nanocubes as Highly Efficient Noble Metal-Free Electrocatalysts for Hydrogen Evolution Reaction in Acidic Media

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ABSTRACT

A novel and simple synthesis methodology based on ion adsorption process is reported for K_{0.4}TaO_{2.4}F_{0.6} nanocubes supported on carbon (K_{0.4}TaO_{2.4}F_{0.6} NCs/C), and used as electrocatalyst for hydrogen evolution reaction (HER) in the acidic media. The K_{0.4}TaO_{2.4}F_{0.6} NCs/C exhibits outstanding catalytic activities and stabilities for HER. The X-ray absorption fine structure (XAFS) analysis indicates stronger binding energy and electron transfer from metal element to fluorine, which leads to higher HER performance, proved by the density functional theory (DFT) calculations.

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1. Introduction

Hydrogen is an ideal clean fuel based on its high energy storage density and environmental friendly reaction product. [1–6] It is a great scientific and technological challenge to find an efficient, clean and low-cost method for the hydrogen production [7,8] Electrochemical hydrogen evolution reaction (HER) is one of the most economical and efficient ways to produce H₂ [9]. Actually, appropriate electrocatalysts for HER is the key issue in the field of hydrogen production. Noble metal based electrocatalysts (especially platinum, Pt) exhibit best HER performances due to their low overpotential (almost zero) and fast kinetics. However, the scarcity and high price of Pt limit its large-scale application. [10] Thus, high active noble metal-free electrocatalysts with lower prices for HER are requested. [11] In the past decade, various novel and promising noble metal free electrocatalysts have been developed and reported, like metal (alloys), [12,13] metal carbides, [14,15] metal sulfides, [16,17] metallic phosphides [18,19] and doped graphene and carbon nanotubes, [20–23] etc.

Fluorine (F) is the most electronegative element with smallest van der Waals radius. The effect of F for electrochemical process

was proved. [24–26] K_{0.4}TaO_{2.4}F_{0.6} is one of M_xMeO_{2+x}F_{1-x} type compounds and has the same structure (M = K, Na and Ag, etc; Me = Ta and Nb). [27] However, there was opinion doubting the real existence of K_{0.4}TaO_{2.4}F_{0.6} even in 2011. [28] For probing the possible bonding between Ta and other elements, the X-ray absorption fine structure (XAFS) analysis was performed. The K_{0.4}TaO_{2.4}F_{0.6} nanocubes supported on carbon (K_{0.4}TaO_{2.4}F_{0.6} NCs/C) was synthesized and served as electrocatalysts for HER in acidic media. Catalytic activities of various electrocatalysts were investigated by density functional theory (DFT). K_{0.4}TaO_{2.4}F_{0.6} shows the lowest Gibbs free energy for H* adsorption ($|\Delta G_{H^*}|$) in various tantalum oxides, which mainly result from the superior capacity of hydrogen adsorption on fluorine. [29] In addition, stability was observed.

2. Experimental

2.1. Materials synthesis

2.1.1. Synthesis of K_{0.4}TaO_{2.4}F_{0.6} NCs/C and ^gC materials

The K_{0.4}TaO_{2.4}F_{0.6} NCs/C was synthesized by using 10 g D301 anion exchange resin (AR, > 99%, Shanghai Hualing Co. Ltd., China) adsorbed with 0.75 mM potassium heptafluorotantalate (K₂TaF₇, Aladdin Chemistry Co. Ltd., China) in 500 mL boiling water for 5 h. Then, the resulting resin complex and the resin without adsorbed were sintered at 900 °C in N₂ flow for 2 h. Finally, resulting

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productions were grounded and treated in 1 mol L⁻¹ HCl solution and washed by deionized water and dried.

2.1.2. Synthesis of KTaO_3

K_2TaF_7 (0.75 mM) was sintered at 900 °C for 2 h in the air. The resulting product was grounded and washed by deionized water and dried.

2.2. Characterizations

The X-ray diffraction (XRD) analysis was performed on a D/Max-III (Rigaku Co., Japan) using Cu K α radiation, and operating at 40 kV and 30 mA. The 2θ angular regions between 10° and 90° were explored at a scan rate of 8° min⁻¹. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a XPS apparatus (ESCALAB 250, Thermo-VG Scientific Ltd.). Structural and morphological characterizations were carried out on a transmission electron microscopy (TEM, FEI Tecnai G2 F30) operating at 300 kV. The thermal gravimetric (TG) measurement was performed on Thermogravimetry and Fourier transforms infrared spectrometry (NETZSCH-Feinmahltechnik GmbH, Selb). The X-ray absorption measurements were investigated at the Ta L₃-edge of the samples were recorded at room temperature in the transmission mode with silicon drift fluorescence detector at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF) operated with a Si (111) double crystal monochromator. The synchrotron was detected at 3.5 GeV between 150–210 mA. The photon energy was calibrated with the first inflection point of Ta L₃-edge in Ta metal foil and data acquired were processed and analyzed by Athena and Artemis software. [30,31]

2.3. Electrochemical measurements:

A three-electrode cell was used on a Bio-Logic VMP3 potentiostat for electrochemical measurements with a glassy carbon electrode ($\varphi = 5$ mm) as the working electrode, a graphite rod as the counter electrode and a reversible hydrogen electrode (RHE) electrode as the reference electrode. $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ NCs/C, commercial Ta_2O_5 (CAS: 1314-61-0), KTaO_3 and C catalysts (10.0 mg) were dispersed in 1.5 mL ethanol and 0.5 mL Nafion (0.5 wt%, DuPont, USA) solution, respectively. The resulting mixture was then ultrasonicated for 45 min until obtain a well dispersed ink. Electrocatalysts ink was transferred to the surface of the work electrode. Then, to obtain an electrocatalysts thin film on electrode, the work electrode was dried under infrared lamp. The electrochemical tests were performed in 1 M HClO_4 solution at 25 °C.

2.4. Computational methods:

We performed all theoretical calculation with Vienna Ab-initio Simulation Package (VASP). [32–34] Relaxed slab models were shown in Fig. 9b. The Monkhorst-Pack sampling scheme was used

to sample the k -points of Ta_2O_5 , $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ and KTaO_3 with $6 \times 6 \times 1$, $4 \times 4 \times 1$ and $6 \times 6 \times 1$, respectively. In this study, (001) facets of $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$, Ta_2O_5 and KTaO_3 were selected for calculations. The (001) facet was selected based on the result of TEM images (Fig. 3b). It means that the selection of (001) facet as adsorption facet for H is in agreement with experimental situation. Free energies of the intermediates were obtained by $\Delta G_{\text{H}^*} = \Delta E_{\text{H}^*} + \Delta \text{ZPE} - T\Delta S$, where ΔE_{H^*} , ΔZPE and ΔS are the binding energy, zero point energy change and entropy change of adsorption H, respectively. ΔZPE and ΔS were obtained from the method reported by Nørskov et al. by using normal-mode analysis with DFT calculation. The vibrational entropy for H adsorbed on all slabs are less than 1 meV, so $\Delta S = S_{\text{H}^*} - 1/2 S_{\text{H}_2} \approx -1/2 S_{\text{H}_2}$. For H_2 at 300 K and 1 atm, $T S_{\text{H}_2} = 0.41$ eV, then we get $T\Delta S \approx 0.20$ eV. The values of ZPE for H adsorbed on surface of three slabs are displayed in Table S1. For ZPE of H_2 we used the value of 0.27 eV is from Nørskov. [35]

3. Result and discussion

3.1. Synthesis mechanism

The synthesis route of $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ NCs/C is shown in Fig. 1, based on a novel ion adsorbed methodology (Fig. S1). The process involves ion adsorption and heat treatment steps. In the ion adsorption step, K_2TaF_7 was subsequently incorporated on the resin via ion adsorption process served as the precursor of K, Ta and F (Fig. 1a). In the heat treatment step, the as-exchanged resin was typically heated at 900 °C for 2 h under pure N_2 (Fig. 1b). At this step, carbonization of the resin complex was occurred with the formation of $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ NCs simultaneously. During the heat-treatment, $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ phase starts to form at temperatures over 700 °C, decomposes and transforms to TaC phase at 1000 °C (Fig. S2). The Raman shift suggests that the carbon support in $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ NCs/C shows high degree of graphitization (Fig. S3).

3.2. XRD, EDS and TG analysis

The crystalline structure of the $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ NCs/C was examined by X-ray diffraction (XRD) pattern (Fig. 2a). As shown in the result, the XRD pattern of the $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ (PDF #28-0805) indicates the formation of $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ at 900 °C under N_2 atmosphere. Strong and sharp diffraction peaks indicated that obtained products were well crystallized, which were perfectly indexed as the Tetragonal phase of $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ with unit cell parameters of $a = b = 12.5$ Å, $c = 3.94$ Å and $\alpha = \beta = \gamma = 90^\circ$ and a space group of P4/mbm. $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ is a very complex compound and nano-materials are easily oxidized in air based on their high surface energy. Some impurity peaks in the XRD pattern of $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ NCs/C were proved to be derived from tantalum oxides (e.g. peaks at $\sim 20^\circ$ was caused by Ta_2O_5 (008) facet; Ta_4O (011) and TaO_2 (111) peaks appeared at $\sim 40^\circ$). Impurities of

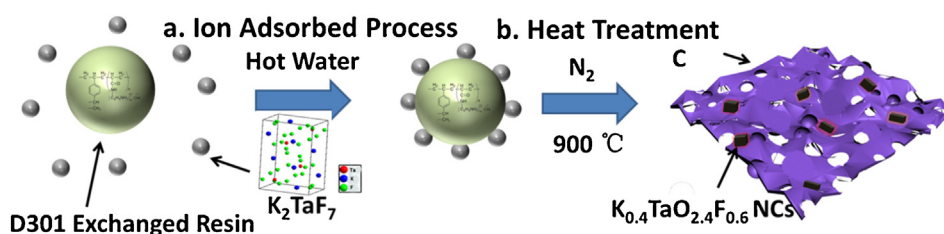


Fig. 1. The synthesis process of $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ NCs/C electrocatalyst. (a) ion adsorption of D301 resin with K_2TaF_7 in boiling water, (b) heat-treatment under N_2 atmosphere, carbonization of resin and formation of $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ phase at 900 °C in N_2 simultaneously, forming $\text{K}_{0.4}\text{TaO}_{2.4}\text{F}_{0.6}$ NCs/C.

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