

# Template-Free Hydrothermal Synthesis of Nanorod (RuTi)O<sub>2</sub> Composite Cathode for Hydrogen Evolution in Alkali Solution

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**Abstract.** A novel nanorod (RuTi)O<sub>2</sub> composite cathode has been prepared via a facile and controllable approach. X-ray diffraction (XRD), scanning electron microscopy (SEM), and linear scanning voltammetry (LSV) were used to scrutinize the electrodes and the electrochemical performance. The results reveal that the designed nanorod (RuTi)O<sub>2</sub> composite cathode displays high electrocatalytic performance for the hydrogen evolution evolution (HER) in alkali solution with a low onset overpotential. For driving a cathodic current density of 100 mA cm<sup>-2</sup>, it only needs overpotential of 220 mV. Such excellent performance of the NR-(RuTi)O<sub>2</sub>/Ti could be ascribed to the unique surface structure with more active sites to be utilized during the HER.

## 1 Introduction

Hydrogen energy is a clean, renewable, environmentally friendly resource and considered as one of the most promising candidates for replacing fossil fuels in the future [1, 2]. Several techniques such as water electrolysis, natural gas reforming, coal gasification, etc. have been widely used for producing hydrogen. Among these techniques, the electrocatalytic production of hydrogen by water electrolysis or chlor-alkali electrolysis as an easy, clean, mature, large-scale industrial technique has received extensive attentions, however, the key problems of this technique mainly related to high energy consumption and relatively low production rates, limit its commercial applications [3].

To reduce the energy consumption and improve the efficiency of hydrogen production, many research efforts have been devoted to decrease the over-potential of the electrode for hydrogen evolution reaction (HER) by the modification of material properties [4], the development of new electrode materials [5, 6], the formation of composite electrode materials [7, 8], and the fabrication of the electrode materials with nanoarchitectures [9, 10]. As the hydrogen evolution reaction (HER) can occur only at confined spatial sites called the reactive two-phase zone (solid/liquid interface), nanoscale control in morphology and dispersion is considered greatly promising in optimizing the properties of the catalysts [11]. Hydrothermal synthesis is yet a simple and effective method to design nanoscale controllable catalysts. The variation of hydrothermal conditions such as temperature, pH, concentration and molar ratio of reactants imparts tunable morphologies and nano/micro-structures [12, 13]. A mesocrystalline rutile TiO<sub>2</sub> nanorod arrays on the Ti substrate was synthesized via the hydrothermal treatment in aqueous HCl solutions containing tetrabutyl titanate, which shows an excellent quasi-omnidirectional antireflection performance [14]. By changing the concentration of NaOH in aqueous, Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> nanoplates and nanowires fabricated under hydrothermal conditions showed high photocatalytic activity for the degradation of wastewater [15]. Kuang et al [16] reported a special porous SrTiO<sub>3</sub> 3D architecture fabricated through a facile

hydrothermal reaction, which showed enhanced photocatalytic activity in hydrogen evolution from water splitting.

Thus, the hydrothermal synthesis is considered as a promising path to fabricate a unique Ru-modified composite catalyst toward electrocatalytic hydrogen evolution. Herein, we try to utilize this strategy to design a nano-architected (RuTi)O<sub>2</sub> composite cathode, which is grown in situ onto the surface of the Ti substrate under certain hydrothermal conditions. The surface morphology of (RuTi)O<sub>2</sub>/Ti catalyst is controlled by controlling the hydrothermal conditions. This novel catalyst is therefore expected to exhibit high electrocatalytic performance for the HER.

## 2 Experimental sections

In a typical synthesis, a Ti substrate (50.0 mm×10.0 mm×0.25 mm) was cleaned initially by sonication in acetone, distilled water, and then etched in 18 wt % HCl at 358 K for 15 min to remove the oxide layer on the surface. The Ti substrates were placed within a Teflon-lined stainless-steel autoclave, followed by adding 10 mL solution of RuCl<sub>3</sub> and hydrochloric acid with 5 mol L<sup>-1</sup> NaCl solution. The autoclave was sealed and heated at 453 K for 20 h. After the hydrothermal reaction was over, the samples were completely washed with distilled water and dried in an oven. Finally, the samples were annealed at 773 K for 1 h under ambient air. As a reference, the traditional (RuTi)O<sub>2</sub>/Ti was prepared via the thermal decomposition of a mixture of RuCl<sub>3</sub> and tetrabutyl titanate dissolved in iso-propanol at 3:7 molar ratios. The Ti substrate was brushed with the precursors, followed by drying at 373 K for 10 min to allow the solvent to vaporize, and then annealed at 773 K for 1 h under ambient air.

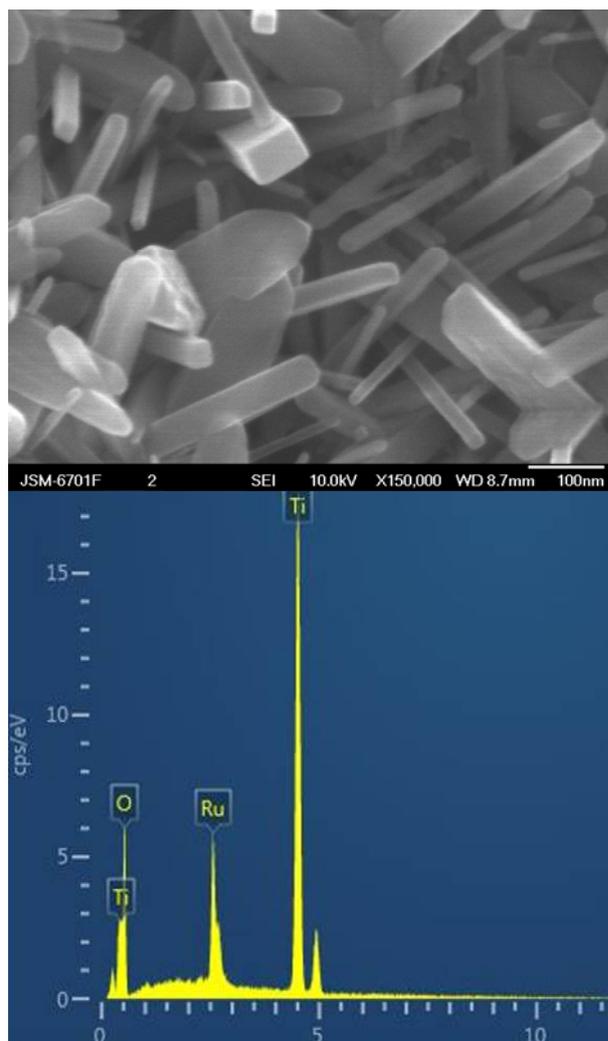
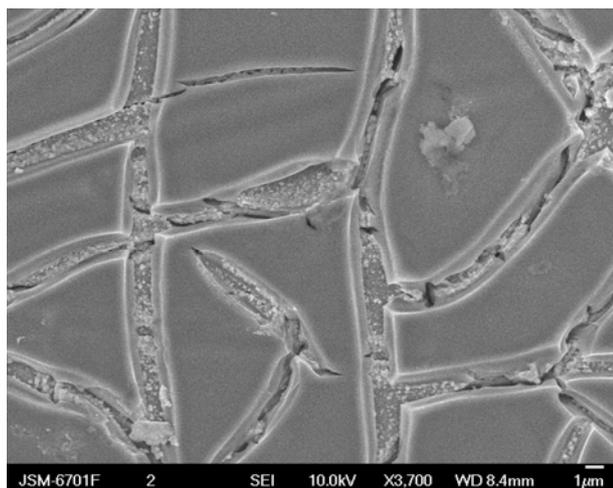
The surface morphology and the microstructure of the samples were analyzed by scanning electron microscopy (SEM, JSM-7800, Japan) and X-ray diffraction (XRD-6000, Shimadzu), respectively. Electrochemical measurements were conducted in a three-electrode cell system. The electrode area of the working electrode is 1 cm<sup>2</sup>. A Pt foil in parallel orientation to the working

electrode was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials mentioned in this work were converted to the values with reference to a reversible hydrogen electrode (RHE). The catalytic performances of prepared catalysts toward HER were systematically investigated in 6 mol L<sup>-1</sup> NaOH electrolyte. All data are presented without IR compensation.

### 3 Results and discussion

#### 3.1 Surface morphology

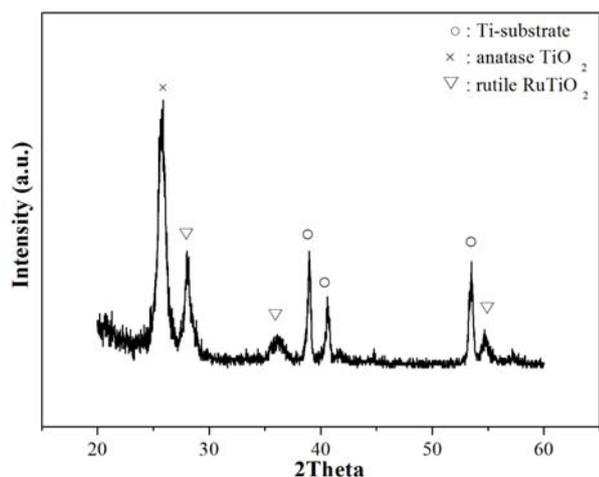
SEM analysis is performed to investigate the microstructure of prepared (RuTi)O<sub>2</sub> composite cathode. For (RuTi)O<sub>2</sub> composite cathode prepared by the traditional thermal decomposition method, it can be seen that from Figure 1, the surface of coating is typical mud-crack island-gap microstructure (denoted as MC-(RuTi)O<sub>2</sub>/Ti). In contrast, the hydrothermal synthesized (RuTi)O<sub>2</sub> composite cathode displays completely different surface morphology. As illustrated, the surface of Ti substrate are uniformly covered with nanorod (RuTi)O<sub>2</sub> (denoted as NR-(RuTi)O<sub>2</sub>/Ti), which almost grow individually and vertically to the substrate without obvious agglomeration. The diameter of (RuTi)O<sub>2</sub> nanorods is about 50-100 nm. The corresponding EDX image of (RuTi)O<sub>2</sub> nanorods clearly verifies the presence of elemental Ru, Ti and O in the whole nanorods. This suggests that solvothermal crystallization in the presence of chloric ions plays a critical role in the formation of nanorod for the binary (RuTi)O<sub>2</sub> catalysts. Such nano-architected (RuTi)O<sub>2</sub> with high aspect ratio will be beneficial for maximizing the number of exposed active sites, allowing the easy diffusion of the electrolyte during the HER.



**Figure 1.** SEM images of (a) MC-(RuTi)O<sub>2</sub>/Ti and (b) NR-(RuTi)O<sub>2</sub>/Ti and (c) the corresponding EDX analysis.

#### 3.2 XRD analysis

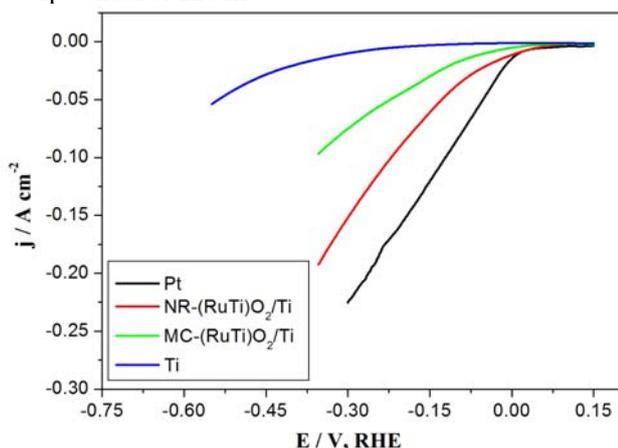
The crystal structures of the NR-(RuTi)O<sub>2</sub>/Ti composite cathode were analyzed by XRD. No peaks for pure rutile RuO<sub>2</sub> (PDF card No. 040-1290) and pure rutile TiO<sub>2</sub> (PDF card No. 021-1276) are observed in Figure 2, except for the diffraction peaks of anatase TiO<sub>2</sub> at 25.58° (PDF card No. 021-1272). This suggests that these dioxides are mainly present in the solid solution because they possess the same valence and similar ionic radius, which means they satisfy the Hume-Rothery conditions for the formation of a substitution solid solution [17, 18]. It is therefore rational that the X-ray diffractograms of the mixed oxides show slight shift in the peak positions.



**Figure 2.** XRD pattern of NR-(RuTi)O<sub>2</sub>/Ti.

### 3.3 Electrocatalytic performance for HER

The electrocatalytic activity of HER at the NR-(RuTi)O<sub>2</sub>/Ti composite cathode is evaluated by means of linear scan voltammograms (LSV) measurements in 6 mol L<sup>-1</sup> NaOH solution. For comparison, the Ti substrate, MC-(RuTi)O<sub>2</sub>/Ti, and Pt catalysts are also investigated under the same conditions. As expected in Figure 3, the Pt catalyst exhibits the best HER activity with negligible overpotential, whereas the Ti substrate exhibits relatively poor HER activity. In sharp contrast, the NR-(RuTi)O<sub>2</sub>/Ti composite cathode is highly active toward the HER, which is considerably better than that of the MC-(RuTi)O<sub>2</sub>/Ti. For driving a cathodic current density of 100 mA cm<sup>-2</sup>, the NR-(RuTi)O<sub>2</sub>/Ti only needs an overpotential of 220 mV.



**Figure 3.** LSV of the Ti substrate, Pt, MC-(RuTi)O<sub>2</sub>/Ti, NR-(RuTi)O<sub>2</sub>/Ti catalysts in a 6 mol L<sup>-1</sup> NaOH electrolyte at a sweep rate of 5 mV s<sup>-1</sup>.

To further study HER behavior on the interface of composite cathode and electrolyte, the kinetic parameters (Tafel slope *b* and exchange current density *i*<sub>0</sub>) calculated from the linear scan curve at the lower overpotential region are summarized in Table 1. Generally, the lower Tafel slope indicates a favoring hydrogen generation [19]. It can be seen that, the Tafel slopes of the NR-(RuTi)O<sub>2</sub>/Ti is 54.8 mV dec<sup>-1</sup>, which is obviously lower

than that of the MC-(RuTi)O<sub>2</sub>/Ti and Ti substrate. In addition, the exchange current density, *i*<sub>0</sub>, a critical kinetic parameter in the dynamic electrochemistry, is derived directly from the intercept by the extrapolation of Tafel slope to equilibrium potential. The calculated *i*<sub>0</sub> of the NR-(RuTi)O<sub>2</sub>/Ti is 0.36 mA cm<sup>-2</sup>, which is 3 times that of the MC-(RuTi)O<sub>2</sub>/Ti. Because the exchange current density usually depends on the surface roughness, the relative surface area of NR-(RuTi)O<sub>2</sub>/Ti, MC-(RuTi)O<sub>2</sub>/Ti, Ti substrate and Pt catalysts was indirectly measured by determining the capacitance of the double layer at the solid/liquid interface [20]. The integrated charge over the double layer range is proportional to the active surface area. From the results shown in Table 1, the effective surface area of the NR-(RuTi)O<sub>2</sub>/Ti is larger than that of the MC-(RuTi)O<sub>2</sub>/Ti and Ti substrate. This demonstrates that 1D (RuTi)O<sub>2</sub> nanorod grown on the Ti substrate are more effective in enlarging the catalytically active surface area due to the high aspect ratio and rich surface area. Thus, better exposure and enhanced utilization of the active sites on 1D (RuTi)O<sub>2</sub> nanorod greatly contribute to its high HER activity.

**Table 1** Kinetic parameters for HER in 6 mol L<sup>-1</sup> NaOH

Catalysts	Tafel slope (mV dec <sup>-1</sup> )	<i>i</i> <sub>0</sub> (mA cm <sup>-2</sup> )	Relative surface area
Ti substrate	147	0.009	6.8
Pt	42.4	0.58	127
MC-(RuTi)O <sub>2</sub> /Ti	72.3	0.12	261
NR-(RuTi)O <sub>2</sub> /Ti	54.8	0.36	354

## 4 Conclusion

In summary, the nanorod (RuTi)O<sub>2</sub> composite cathode have been successfully grown in situ onto the surface of Ti substrate by hydrothermal process. The unique characteristics of the composite cathode incorporate the merits of high intrinsic activity from RuO<sub>2</sub> and the exposure of more active sites provided by 1D nanorod with high surface area. It exhibited excellent catalytic performance for HER with low onset overpotential and high exchange current density, making it a promising approach to design the desirable electrode materials for electrolytic applications.

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