



# Facial synthesis of porous hematite supported Pt catalyst and its photo enhanced electrocatalytic ethanol oxidation performance



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## ABSTRACT

The porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> supported Pt catalyst is synthesized by a facial thermal treatment assisted precipitation method. The particle size of Pt is less than 3 nm. The pore diameters of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles are concentrated to 2.46 nm in a mesoporous scale. Its electrochemical performance is tested. The ethanol oxidation current of the Pt/Fe<sub>2</sub>O<sub>3</sub> catalyst obviously improves under illumination, compared with that in the dark, during the optical switching operation. Moreover, with the addition of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the ethanol oxidation current of Pt/C grows about 51% under illumination and 32% in the dark; the onset potential shifts negatively for about 20 mV. This work demonstrates an optical strategy which can be a potential alternative to accelerate electrode reactions towards ethanol oxidation reaction.

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## 1. Introduction

Fuel cells have attracted much attention in the search for alternative energy resources and are recognized as promising power sources for portable electronic devices and electric vehicles [1,2]. Among them, the alkaline alcohol fuel cells (AAFCs) have been extensively investigated because of their superiorities compared to the direct alcohol fuel cells (DAFCs) in terms of faster kinetics of electrode reactions, wider selections towards electrode materials, high energy density and ease of transportation and storage [3–9]. In decades, various kinds of electrocatalysts have been developed to enhance the ethanol oxidation performance, among which, metal oxides promoted precious metal catalysts have been demonstrated to be quite active during the alkaline alcohol catalytic processes [10–13]. They can not only reduce costs but also preserve the integrity of catalysts and protect the Pt surface from poisoning by the intermediates or by-products during the reaction [11]. While, besides developing highly active catalysts, considerable efforts should be focused on the reaction condition to accelerate electrode reactions. The photoelectrocatalytic strategy using photocatalytic materials, such as TiO<sub>2</sub> and WO<sub>3</sub>, has recently

been used to enhance the methanol oxidation process [14]. But the increasing current of the catalyst is at the expense of the positive shift of its onset potential, which is unfavourable in the application.

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has been widely researched in water oxidation catalysis [15–18], sensors [19], lithium-ion batteries [20–23], ultrahigh density data storage media and magnetic devices [24], the tunable selection device element in nonvolatile memory circuits [25] and field-emission applications [26].  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has also been considered to be a potential candidate for a photoelectrochemical system because of its good stability, small band gap (approximately 2.2 eV) and low cost.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> supported Pt catalysts have already been reported as good electrocatalysts towards alcohol oxidation [27]. Porous structures can promote the catalytic processes because pores can facilitate mass transfer and their high surface area allows a high concentration of active sites per mass of catalysts [15,28,29]. There is few articles about porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles less than 50 nm. Recently, it is reported that porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (about 40 nm) has a high performance as supercapacitors [30]. But it was synthesized by a hydrothermal method combined with a slow annealing route, which is complex and time consuming.

In this paper, we synthesized porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by a novel thermal treatment assisted precipitation method with FeCl<sub>3</sub>·H<sub>2</sub>O and NH<sub>4</sub>HCO<sub>3</sub> as main reactants. This facial method can ensure a large scale preparation. The electrochemical results demonstrate

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that, under illumination, the porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> supported Pt catalyst (Pt/Fe<sub>2</sub>O<sub>3</sub>) shows an enhanced electrocatalytic performance towards the ethanol oxidation.

## 2. Experimental

### 2.1. Material Preparation.

All chemicals were purchased from Guangzhou Dongzheng Chemical & Glass Instrument Co. Ltd as analytical grade and used as received without further purification.

### 2.2. Synthesis of porous $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

The porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was prepared by a facial precipitation method. FeCl<sub>3</sub>·H<sub>2</sub>O (10 mmol) and NH<sub>4</sub>HCO<sub>3</sub> (100 mmol) were separately dissolved in distilled water (700 mL). Ethanol (70 mL) and the above NH<sub>4</sub>HCO<sub>3</sub> solution were then added into the FeCl<sub>3</sub>·H<sub>2</sub>O solution in sequence. The mixture was then kept under stirring for 1 h at room temperature and centrifuged. The as-obtained precursor was washed with water and ethanol for several times and dried at 80 °C. We got the porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> after thermal decomposition of the precursor at 400 °C for 5 h in air.

### 2.3. Synthesis of Pt/Fe<sub>2</sub>O<sub>3</sub>

The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder was agitated in an ethanol solution that contained 16.6 wt% of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (the mass ratio of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Pt was 4:1). After evaporation of ethanol, the mixture was calcined at 400 °C for 5 h in air to decompose the Pt precursor. The heating rate was 5 °C/min. The as-prepared powders were then agitated in an ethanol solution again and kept at 50 °C under a flowing CO gas for 2 h. We finally got the Pt/Fe<sub>2</sub>O<sub>3</sub> hybrids after centrifuging, cleaning and drying. The benchmark Pt/C catalyst (46.7%, TKK, Japan) was used without further treatment.

### 2.4. Material characterization

The crystalline structure of the sample was studied by X-ray diffraction (XRD) on a D/Max-III (Rigaku Co., Japan) using Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm) and operating at 40 kV and 30 mA. The energy dispersive X-ray spectrometer (EDX, JEM-2010HR) was employed for approximate elemental analyses. The transmission electronic microscopy (TEM) investigations were carried out on a JEOL JEM-2010 at 200 kV. The N<sub>2</sub> adsorption experiments using an

ASAP 2020 Surface Area Analyzer (Micromeritics Co., USA) were conducted to investigate the porosity of the samples. All the samples were out gassed at 200 °C in a nitrogen flow for 4 h prior to the measurement. Nitrogen adsorption data were recorded at the liquid nitrogen temperature (77 K). The Pt content in the catalysts was examined by Inductively Coupled Plasma-atomic Emission Spectrometry (ICP-AES, TJA Company in America).

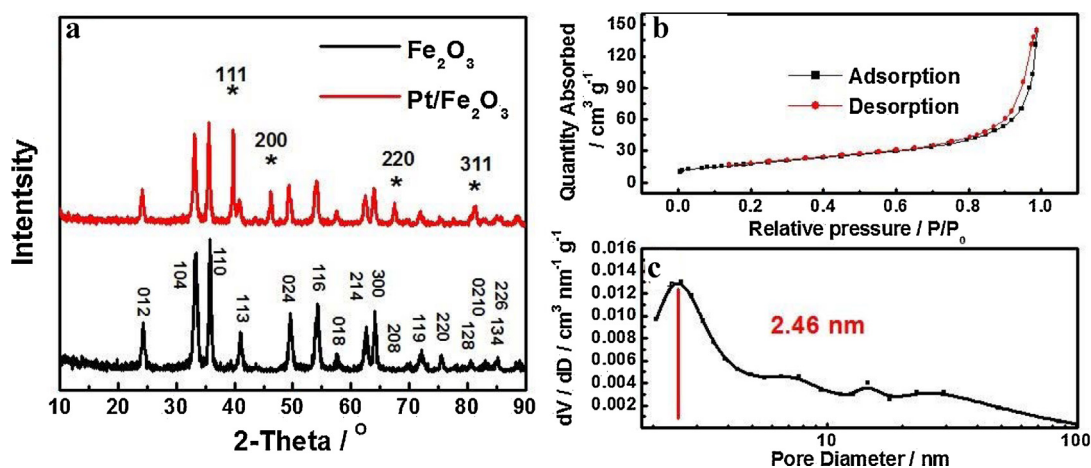
### 2.5. Electrochemical measurements

The optical system is conducted on a LSP-X150 Power Supply for Arc Lamp, Zolix Instrument. A 100-W xenon lamp is the light source and the power density of the reaction point is 40 mW cm<sup>-2</sup>. The electrochemical characterizations were conducted on a bipotentiostat (AUT 85443, Autolab, Metrohm) in the thermostat-controlled standard three-electrode cell at 25 °C with a reversible hydrogen electrode (RHE) as the reference electrode and a platinum foil as the counter electrode. The working electrode was a sample-coated glassy carbon (GC) electrode. Its geometric area is 0.1963 cm<sup>2</sup>. For all of the catalysts in this article, Pt loadings were 0.30 mg cm<sup>-2</sup>. To overcome limitation of electronic conductivity, the prepared catalyst was mixed with carbon powders (Cabot Vulcan XC-72) at a 1:1 mass ratio. The mixture was ultrasonically dispersed in 2 mL Nafion<sup>®</sup> solution (0.05 wt %, DuPont, USA) for at least 30 min to form a homogeneous ink. The electrocatalyst ink was then quantitatively transferred onto the surface of the working electrode using a micropipette, and dried under an infrared lamp to obtain the electrocatalyst film. The electrochemical measurements were taken at 25 °C if the temperatures were not mentioned.

## 3. Results and discussion

The X-ray diffraction (XRD) patterns of the porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder and Pt/Fe<sub>2</sub>O<sub>3</sub> hybrid are shown in Fig 1a. The characteristic peaks (111), (200), (220) and (311) assigned to Pt (PDF # 65–2868) are detected in addition to the intensive signals of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (PDF # 33–0664), confirming the formation of hybrid phase. The crystal lattice orientations that each peak corresponds are marked.

We investigated the pore-size characterization of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by measuring the nitrogen adsorption/desorption isotherms. The nitrogen adsorption/desorption curve (Fig. 1b) exhibits combined characteristics of type II and type IV isotherms. The Brunauer–Emmett–Teller (BET) specific surface area was 88.35 m<sup>2</sup> g<sup>-1</sup> with a total pore volume of 0.23 cm<sup>3</sup> g<sup>-1</sup>. Among them, the mesopore



**Fig.1.** (a) XRD patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Pt/Fe<sub>2</sub>O<sub>3</sub>. The peaks marked by "\*" represent Pt. (b) nitrogen adsorption/desorption isotherms cumulative pore volume and (c) DFT pore size distribution curve of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

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