



# Platinum supported on multifunctional titanium cobalt oxide nanosheets assembles for efficient oxygen reduction reaction

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## ABSTRACT

To move towards the successful commercialization of fuel cells, emphasizing solely on the catalytic activity is not sufficient, and requirements on performance stability are also urgently to be solved. In this work, we describe a facile and robust strategy to the development of a novel Pt based catalyst with binary titanium cobalt oxide as the support. The binary titanium cobalt oxide nanotubes are characterized with hierarchical tubular porous and hollow structures that constructed by ultrathin interconnected nanosheets assembles (labeled as  $Ti_{0.8}Co_{0.2}O_2$  NTAs). The resultant catalyst (Pt/ $Ti_{0.8}Co_{0.2}O_2$  NTAs) exhibited much higher mass activity for oxygen reduction reaction (ORR) compared with the commercial Pt/C catalyst, and it also possesses excellent structure stability. The experimental data demonstrates that the novel support plays a significant role in the enhanced ORR activity, which not only acts as a robust and desirable support to afford a high dispersion for Pt nanoparticles, but also as a co-catalyst to boost the activity of the resultant catalyst via the modulation of the electronic structures of the supported Pt atoms. This work opens a new path for maximizing the ORR activity and durability by introducing porous binary titanium based oxides as the Pt support, which combines the merits of high stability, co-catalysis and doping effects.

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## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are promising candidates for supplying an efficient, clean and sustainable energy to advanced portable electronic devices, electrical vehicles and power sources [1,2]. Effective and robust catalyst is the key components of PEMFCs technology and largely dominates its ultimate lifetime and activity [3–5]. To date, the most effective electrocatalysts for both the cathodic oxygen reduction reaction (ORR) and anodic oxidation reaction are still the Pt-based nanomaterials [6–11]. However, their universal and practical applications are

heavily hampered by the high cost, poor ORR kinetics, decay of electrochemical surface area and catalytic performance for prolonged operation times. Additionally, intensive investigations have demonstrated the severe corrosion of carbon support in the acidic and oxidant conditions, especially occurs in the transient conditions such as start-up/shutdown or local fuel starvation events at the anode, will expedite the dissolution, migration and detachment of Pt atoms, resulting in a serious durability problem [12–19]. Consequently, exploring alternatives to carbon supports and enhancing the durability of Pt based catalysts is one of the most important issues in this field.

Recently, many efforts has been afforded on the development of robust non-carbon support materials, such as titanium oxides ( $TiO_2$ ) [14,20,21], tin-doped indium oxide (ITO) [22], transition metal nitrides and carbides [23–27]. Due to the corrosion resistance and strong metal-support interaction (SMSI), Pt based catalysts anchored on these novel supports exhibit much better durability and simultaneously higher ORR activity than that of

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carbon supported Pt catalyst. TiO<sub>2</sub> is probably an ideal alternative to carbon support because it's chemically inert and structurally stable in acidic and oxidative conditions, and possesses excellent electrochemical corrosion resistant properties over a wide range of operating potential [14,21,28,29]. It is also worth noting previous studies that oxygen containing species (mainly OH) groups can be adsorbed on the surface of Ti atoms (Ti–OH), consequently the OH coverage on supported Pt atoms can be lowered due to the lateral repulsion between adjacent OH groups adsorbed on the Pt atoms and Ti atoms, freeing more Pt active sites for O<sub>2</sub> adsorption, thus the ORR activity can be further enhanced [30]. Unfortunately, the intrinsic ultra-low electrical conductivity derived from the semiconductor nature of raw TiO<sub>2</sub> dramatically deteriorates the whole performance of the catalyst, precluding its applications in the field of electrochemistry [20,21].

One promising way to overcome the drawback and achieve a high conductivity is to decorate TiO<sub>2</sub> nanostructures via doping. Ru, Mo, W and F doped TiO<sub>2</sub> supported Pt catalysts demonstrate much high conductivity compared with the bare TiO<sub>2</sub> support, meanwhile exhibit better durability than that of the commercial Pt/C catalyst [14,21,31–33]. Furthermore, the electronic structure of Pt nanoparticles (NPs) anchored on the doped TiO<sub>2</sub> support can be also modified by the dopants, thus enhanced activity may be obtained. A key merit of the doped TiO<sub>2</sub> supported Pt catalysts is that the hybrid materials exhibit excellent stability due to not only the corrosion resistance of TiO<sub>2</sub> itself, but also the SMSI between the TiO<sub>2</sub> support and the Pt NPs. However, a dilemma is that the discontinuity caused by the poor particle–particle contacts, abundant grain boundaries and defects among the TiO<sub>2</sub> NPs could lower the efficiency of electron transport and weaken the catalytic performance of the hybrid material. In addition, despite various efforts in anchoring Pt NPs on various TiO<sub>2</sub> based supports, to the best of our knowledge, the synthesis of one dimensional (1D) doped TiO<sub>2</sub> composite used as support for Pt catalyst, especially porous nano-sheets assemblies, has not been reported until now.

Inspired by the above considerations, we postulate that an integration of SMSI, doping effect, and 1D porous TiO<sub>2</sub> nanostructure that seems naturally to be beneficial for the creation of durable Pt-based catalysts with high activity. Herein, we developed a facile and scalable one-step solvothermal method to synthesize 1D hollow and porous TiO<sub>2</sub> and cobalt (Co) doped TiO<sub>2</sub> tubular architectures (labeled as TiO<sub>2</sub> and Ti<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> NTAs, respectively) assembled by randomly oriented ultrathin TiO<sub>2</sub> nanosheets. The resulting Pt decorated 3D-like architectures can not only provide accessible and large pores/channels for fast mass transfer of reactants to the active sites, but also the synergistic effects derived from the doping effect and high conductivity to maintain the high ORR activity of the overall catalysts. Consequently, the Pt/Ti<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> NTAs exhibit excellent electrocatalytic ORR activity and stability compared with the state-of-the-art Pt/C catalyst.

## 2. Experimental procedures

### 2.1. Preparation of TiO<sub>2</sub> and Ti<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> NTAs

All chemicals were purchased commercially (Aladdin, China) and used as received without further purification. First, TiO<sub>2</sub> NTAs were synthesized by a facile solvothermal approach followed by an annealing process. 0.5 g titanyl sulfate (TiOSO<sub>4</sub>) was added to a mixed solution composed of glycerol (10 mL), benzyl alcohol (18 mL), and ethyl ether (10 mL), and then the mixture was sonicated for 30 min to get a milky white homogeneous solution. Finally, the solution was transferred into an autoclave and kept at 150 °C for 12 h, before it was cooled to room temperature. The resulting massive products were collected by filtration and washed

three times with absolute ethanol, and were put into a vacuum drying oven at 70 °C overnight. And then, roughly 0.5 g of titanium oxide precursor was placed in a quartz boat, and the precursors was annealed at 450 °C for 2 h exposed to air with a progressive heating rate in a programme controlled heating tubular furnace (room temperature to 390 °C, 3 °C min<sup>-1</sup>; 390–450 °C, 1 °C min<sup>-1</sup>). The synthesis conditions for Ti<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> (x = 0.05, 0.1, 0.15, 0.2 and 0.25) NTAs were the same to that of TiO<sub>2</sub> NTAs except the addition of cobalt chloride (CoCl<sub>2</sub>) and the atomic ratio of Ti/Co was kept at (1-x):x. Take Ti<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> NTAs as an example, the atomic ratio of Ti/Co was kept at 4:1.

### 2.2. Synthesis of home-made Pt/C, TiO<sub>2</sub> and Ti<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> NTAs supported Pt catalysts

The deposition of Pt on the TiO<sub>2</sub> and Ti<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> NTAs was achieved by the method of ethylene glycol (EG) reduction. The total Pt loading was controlled at 20 wt%. In detail, 40 mg of TiO<sub>2</sub> or Ti<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> NTAs, 120 mg of sodium citrate and 1.34 mL of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O/EG solution (20 mg/mL) were mixed with 30 mL of EG in a 100 mL flask, followed by ultrasonic for 60 min, and then tuning the pH to ca. 12 using 1 M NaOH/EG solution. The resulting homogeneous mixture was then heated from room temperature to 130 °C in 30 min and maintained at 130 °C for 8 h in an oil bath, followed by centrifugation, washing thoroughly with de-ionized water and vacuum drying at 80 °C. The synthesis processes of the home-made Pt/C (labeled as HM Pt/C) were similar with Pt/TiO<sub>2</sub> NTAs except the Vulcan XC-72 carbon was used as the support.

### 2.3. Characterization of the catalysts

XRD was conducted on a Rigaku-Ultima III X-ray diffractometer with Cu K $\alpha$ 1 radiation ( $\lambda = 1.5405 \text{ \AA}$ ) at 30 kV and 20 mA, and the selected  $2\theta$  range was from 20° to 86°, with a scanning increments of 0.02°. Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were conducted with a field-emission scanning electron microscope (FESEM, Hitachi S-4800). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were obtained with a JEOL 2100 microscope. All the X-ray photoelectron spectroscopy (XPS) spectra of the materials were collected by XPS employing a monochromated Al-K $\alpha$  X-ray source ( $h\nu = 1486.6 \text{ eV}$ , Thermo Scientific, ESCALAB 250 XI). The precise Pt loadings of all the catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Leeman PROFILE SPEC) measurements. Specific surface areas and pore distribution of the samples were measured by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption (TristarII 3020). The conductivity of the compressed powders under a pressure of 130 MPa was calculated by a standard four-point probe measurement (KeithLink Technology, Taiwan).

### 2.4. Electrochemical measurements

All the electrochemical experiments were conducted on an electrochemical work station (Ivium, Netherlands) at room temperature (25±1 °C), using a three-electrode electrochemical cell. The working electrode is a glassy carbon electrode (GCE, 5 mm inner diameter, 0.196 cm<sup>2</sup>), a leak-free 3 M NaCl saturated Ag/AgCl electrode was used as the reference electrode and a Pt wire was used as the counter electrode, respectively. All potentials in this work are quoted with respect to a reversible hydrogen electrode (RHE). The catalysts (5 mg) were dispersed in a mixture solvent containing ethanol and Nafion (0.25 wt%) to form a homogeneous catalyst ink by sonicating for 30 min, and 5  $\mu$ L of catalyst ink was

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