



# Promoting effect of nitrogen doping on carbon nanotube-supported RuO<sub>2</sub> applied in the electrocatalytic oxygen evolution reaction

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## ABSTRACT

RuO<sub>2</sub> nanoparticles supported on multi-walled carbon nanotubes (CNTs) functionalized with oxygen (OCNTs) and nitrogen (NCNTs) were employed for the oxygen evolution reaction (OER) in 0.1 M KOH. The catalysts were synthesized by metal-organic chemical vapor deposition using ruthenium carbonyl (Ru<sub>3</sub>(CO)<sub>12</sub>) as Ru precursor. The obtained RuO<sub>2</sub>/OCNT and RuO<sub>2</sub>/NCNT composites were characterized using TEM, H<sub>2</sub>-TPR, XRD and XPS in order to probe structure–activity correlations, particularly, the effect of the different surface functional groups on the electrochemical OER performance. The electrocatalytic activity and stability of the catalysts with mean RuO<sub>2</sub> particle sizes of 13–14 nm were evaluated by linear sweep voltammetry, cyclic voltammetry, and chronopotentiometry, showing that the generation of nitrogen-containing functional groups on CNTs was beneficial for both OER activity and stability. In the presence of RuO<sub>2</sub>, carbon corrosion was found to be significantly less severe.

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## 1. Introduction

Hydrogen production by water electrolysis using renewable electricity has been proposed as an eco-friendly route for energy storage [1]. However, the sluggish kinetics of the oxygen evolution reaction (OER), which is the anode reaction in water electrolysis, remains a major challenge for the development of electrolyzers [2]. Ti-supported RuO<sub>2</sub>, IrO<sub>2</sub>, or their mixtures are used as dimensionally stable anodes in current industrial processes [3]. Non-precious metal oxides, such as MnO<sub>x</sub>, Co<sub>3</sub>O<sub>4</sub>, as well as Mn- and Co-based mixed oxides have been shown to be promising alternatives to noble metal catalysts [4–9]. However, the poor electrical conductivity of these oxides hinders their large scale applications in water electrolysis.

Despite of its high cost, RuO<sub>2</sub> remains one of the most promising electrocatalysts for the OER due to its low overpotential and high activity [10–12]. Considering large scale industrial applications, it is necessary to use a conductive support to minimize the

amount of RuO<sub>2</sub> and lower the electrode cost while simultaneously maintaining the high activity of RuO<sub>2</sub>. Multi-walled carbon nanotubes (CNTs) have shown great potential as support materials in heterogeneous catalysis and electrocatalysis due to their high electrical conductivity and chemical stability under corrosive conditions [13,14]. Nitrogen doping can significantly modify the electronic and chemical properties of CNTs [15]. RuO<sub>2</sub> exhibits a very low overpotential during the OER thus avoiding severe carbon oxidation at high potentials [16], which is of great importance for practical applications especially in polymer electrolyte membrane cells and metal-air batteries.

In this work, two types of CNTs including oxygen- and nitrogen-functionalized CNTs were used as support for the deposition of RuO<sub>2</sub> nanoparticles by metal-organic chemical vapor deposition (MOCVD). The obtained composites were used as electrocatalysts for the OER under alkaline conditions. The electrocatalytic activity was evaluated by linear sweep voltammetry while the stability was monitored by chronopotentiometry as well as cyclic voltammetry. The results revealed that RuO<sub>2</sub> nanoparticles supported on NCNTs (RuO<sub>2</sub>/NCNTs) are superior both in terms of activity and stability to those supported on OCNT (RuO<sub>2</sub>/OCNTs) for the OER, which clearly suggests that nitrogen doping promotes the performance of RuO<sub>2</sub>.

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## 2. Experimental

### 2.1. Synthesis of catalyst

CNTs (Baytubes® C 150 P) with mean outer diameter of 15 nm and mean inner diameter of 4 nm were provided by Bayer Material Science (Leverkusen, Germany). The as-received CNTs were purified by washing in 1.5 M HNO<sub>3</sub> under stirring at room temperature for 72 h in order to remove the residual growth catalysts used in their synthesis. The purified CNTs were partially oxidized by HNO<sub>3</sub> vapor at 200 °C for 72 h to obtain oxygen-functionalized CNTs (OCNTs) [17]. The obtained OCNTs were further treated at 400 °C for 6 h in 10 vol% NH<sub>3</sub> in He with a total flow of 50 sccm to obtain nitrogen-functionalized CNTs (NCNTs) [18]. The OCNTs and NCNTs were used as substrates for the deposition of RuO<sub>2</sub> nanoparticles.

CNT-supported RuO<sub>2</sub> nanoparticles were synthesized via a MOCVD procedure using ruthenium carbonyl (Ru<sub>3</sub>(CO)<sub>12</sub>) as the Ru precursor [19]. Briefly, about 500 mg of CNTs (i.e. OCNTs or NCNTs) and a certain amount of Ru<sub>3</sub>(CO)<sub>12</sub> were mixed and ground for 30 min at room temperature to achieve homogeneous mixing. The theoretical loading of Ru was 10.0 wt% in all the cases. The mixture was loaded into a horizontal quartz tube reactor, which was heated following a multiple-step program: room temperature to 40 °C at 2 °C/min, hold for 60 min; 40–60 °C at 0.2 °C/min, hold for 60 min; 60–120 °C at 1 °C/min, hold for 60 min; 120–300 °C at 2.8 °C/min, hold for 120 min; cooling down to room temperature [19]. Synthetic air at atmospheric pressure was used as the reaction gas at a flow rate of 10 sccm during the whole temperature program. The obtained samples are denoted as RuO<sub>2</sub>/OCNTs and RuO<sub>2</sub>/NCNTs, respectively.

### 2.2. Characterization

XRD was performed using a PANalytical theta–theta powder diffractometer with a Cu K<sub>α</sub> source. Scans were run from 10° to 80° with a step size of 0.013°. The obtained XRD patterns were analyzed by PANalytical X'Pert HighScore Plus v3.0 software. For elemental analysis, the samples were dissolved in a H<sub>2</sub>SO<sub>4</sub>/HCl solution. The Ru content was measured by inductively coupled plasma–optical emission spectroscopy (ICP-OES, PU701 UNICAM). N<sub>2</sub> physisorption measurements were conducted at –196 °C using an Autosorb-1 MP Quantachrome system. Prior to the measurements, all samples were degassed at 200 °C for 2 h. The surface areas were calculated from the linear part of the BET plots. The structure of the as-prepared samples was examined using transmission electron microscopy (TEM) with a Tecnai microscope. The diameter distribution was obtained by counting 200–230 particles in several TEM images.

Temperature-programmed reduction (TPR) experiments were performed in a flow setup using 4.63 vol% H<sub>2</sub> in Ar at a flow rate of 84.1 sccm. The H<sub>2</sub> concentration in the exhaust gas was monitored by a thermal conductivity detector (Hydros 100, Fisher-Rosemount). The reactor loaded with about 40 mg of the sample was heated from room temperature to 200 °C with a heating rate of 2 °C/min and held for 30 min before cooling down.

X-ray photoelectron spectroscopy (XPS) measurements were performed in a UHV set up equipped with a monochromated Al K<sub>α</sub> X-ray source (1486.6 eV, 14.5 kV, 30.5 mA) as incident radiation and a GammaData-Scientia SES 2002 hemispherical analyzer. The base pressure in the measurement chamber was 5 × 10<sup>–10</sup> mbar. A pass energy of 200 eV and a slit width of 0.2 mm were chosen resulting in an energy resolution better than 0.6 eV. Charging effects were compensated using a flood gun, and binding energies were calibrated using the main C 1s peak at 284.5 eV as internal standard. A Gaussian–Lorentzian mixed function with a ratio of 70:30 and a Shirley background were applied in spectra deconvolution.

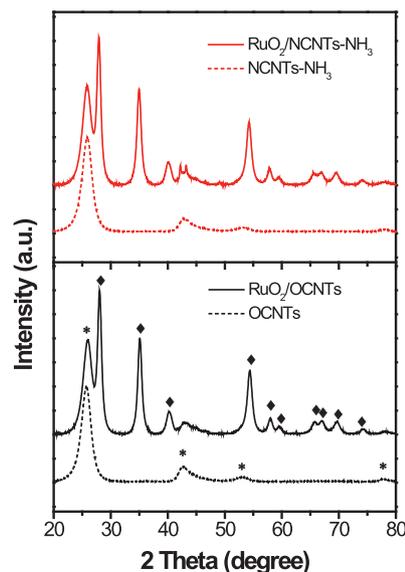
**Table 1.** Elemental analysis and BET surface area (*A*<sub>BET</sub>) of CNT substrates and RuO<sub>2</sub>/CNT composites.

Materials	Elemental analysis (wt%)					<i>A</i> <sub>BET</sub> (N <sub>2</sub> ) <sup>c</sup> (m <sup>2</sup> /g)
	Ru <sup>a</sup>	Co <sup>a</sup>	Mn <sup>a</sup>	N <sup>b</sup>	O <sup>b</sup>	
OCNTs	–	0.13	0.04	0.31	4.26	290
NCNTs	–	0.14	0.05	0.97	2.02	309
RuO <sub>2</sub> /OCNTs	9.80	–	–	–	–	227
RuO <sub>2</sub> /NCNTs	10.10	–	–	–	–	259

<sup>a</sup> The Ru, Co and Mn contents were determined by ICP-OES.

<sup>b</sup> The N and O contents were determined by a Vario EL analyzer.

<sup>c</sup> *A*<sub>BET</sub> was obtained from N<sub>2</sub> physisorption.



**Fig. 1.** XRD patterns of OCNTs, RuO<sub>2</sub>/OCNTs, NCNTs, and RuO<sub>2</sub>/NCNTs.

### 2.3. Electrochemical tests

Electrocatalytic tests were performed in a conventional three-electrode cell controlled by an Autolab potentiostat/galvanostat (PGSTAT12, Eco Chemie) in combination with a Metrohm RDE-2 rotator and its control unit. A home-made Ag/AgCl, 3 M KCl electrode (+ 0.210 V versus NHE) and a platinum wire served as the reference electrode (RE) and counter electrode (CE), respectively. Polished glassy carbon (GC) disc electrodes (diameter: 3.8 mm) embedded in a Teflon cylinder were employed as working electrodes (WE). The catalyst suspension was prepared by ultrasonically dispersing the catalyst (5.0 mg) in a mixture of water (490 mL), ethanol (490 mL) and Nafion® (5 %, 20 mL). Subsequently, the resulting catalyst suspension was dropped onto the polished GC electrode to obtain a catalyst loading of 210 μg/cm<sup>2</sup>. The electrode was dried in air at room temperature before measurement. Prior to the measurements, the electrolyte KOH (0.1 M) was purged with pure O<sub>2</sub> for 20 min to reach O<sub>2</sub> saturation. All the modified electrodes were pre-conditioned by cyclically sweeping in the potential range 1.0–1.5 V versus reversible hydrogen electrode (RHE) at a scan rate of 100 mV/s until reproducible cyclic voltammograms (CV) were obtained.

Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV/s and a rotation speed of 1600 rpm. Tafel plots were obtained from LSV recorded at a scan rate of 1 mV/s and a rotation speed of 1600 rpm. All the potentials were corrected for IR drop and are reported versus the RHE. Unless explicitly stated, all the current densities reported in this work were calculated using the geometric area of the electrode.

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