



Pristine carbon nanotubes as non-metal electrocatalysts for oxygen evolution reaction of water splitting



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ABSTRACT

Oxygen evolution reaction (OER) is one of the most important reactions in electrochemical energy storage and conversion systems. Thus, the development of efficient electrocatalysts with high activity and durability is of great technological and scientific significance. We demonstrate here for the first time that pristine carbon nanotubes (CNTs) composed of between 2 and 7 concentric tubes and an outer diameter of 2–5 nm have an outstanding activity for the OER in alkaline solution as compared with single-walled and multi-walled CNTs (SWNTs & MWNTs). For example, current density measured at 1.8 V (vs RHE) for the OER on triple-walled CNTs is 56 mA cm^{-2} , ~ 10 times higher than 5.9 mA cm^{-2} measured on SWNTs and 35 times higher than 1.6 mA cm^{-2} measured on MWNTs. The activity of such CNTs is significantly higher than that of conventional 20% Ru/C and 50% Pt/C electrocatalysts at high polarization potentials. Such CNTs also show an excellent stability toward OER. One hypothesis is that for the OER on CNTs with specific number of walls, efficient electron transfer occurs on the inner tubes of the CNTs most likely through electron tunneling between outer wall and inner tubes, significantly promoting the charge transfer reaction of OER at the surface of outer wall of the CNTs. For SWNTs, such separation of functionality for OER is not possible, while effective electron tunneling between outer wall and inner tubes of the CNTs diminishes as the number of walls increases due to the reduced dc bias (i.e., the driving force) across the walls or layers of MWNTs. This hypothesis is strongly supported by the observed distinctive volcano-type dependence of the electrocatalytic activity and turnover frequencies (TOF) of CNTs as a function of number of walls.

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1. Introduction

Hydrogen production from water splitting driven by renewable energy, such as hydro, solar or wind power is a most environmental friendly pathway to meet the constantly growing demand for renewable energy storage and conversion technologies. For example, the most mature solar-driven water splitting technology is the combination of commercial photovoltaic (PV) modules with water electrolyzers [1]. However, the practical application of water electrolysis or water splitting is greatly constrained by the high overpotentials (η) required and the slow rate of the oxygen evolution reaction (OER) because the release of O_2 involves the

formation of an oxygen–oxygen bond with an overall four-electron process [2]. Hence, developing efficient catalysts with high activity and durability for OER is of great technological and scientific significance in the application of renewable energy storage and conversion technologies.

There are substantial progresses on developing electrocatalysts for water splitting through decades of sustained efforts. This includes noble metals and metal oxides-based OER catalysts, such as Pt [3,4], Pd [5], Au [5], Ir [4], Ru [4], RuO_2 [6], IrO_2 [7] and their combination [8], but their wide spread application is limited due to their high cost and scarce resources. Water splitting under alkaline conditions allows the use of non-noble metals and inexpensive various oxide catalysts. Transition metal oxides, such as MnO_2 [9,10], Co_2O_3 [11,12], NiCoO_3 [13], Ni–Fe oxide [14] and $\text{Fe}_x\text{Co}_y\text{Ni}_z\text{O}_x$ [15] have shown relatively good activity that are comparable to RuO_2 and IrO_2 in alkaline solutions. However, the low conductivity of these oxides is problematic in practical applications.

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Carbon nanotubes (CNTs) are seamless cylinders composed of one or more curved layers of graphene with either open or closed ends. These materials have been extensively studied as catalyst supports due to their unique properties, such as large specific surface area, excellent mechanical and electrical properties [12,16–19]. Co_2O_3 particles supported on oxidized multi-walled carbon nanotubes (MWNTs) yielded a current density of 10 mA cm^{-2} at an overpotential (η) of 0.39 V in 0.1 M KOH solution [20], significantly better than Co_2O_3 nanocrystals. Ultrathin nickel–iron layered double hydroxide nanoplates supported on oxidized MWNTs achieved a current density of 10 A g^{-1} at $\eta = 0.228 \text{ V}$ in 1 M KOH with catalysts loading of 0.25 mg cm^{-2} [18]. Li et al. [21] developed a mononuclear ruthenium complex supported on MWNTs, which show high electrocatalytic activity and low η for water oxidation reaction. Modifying CNTs by nitrogen doping can also substantially enhance the electrocatalytic activity for the O_2 reduction reaction and OER in alkaline solutions [22,23]. However, it is generally believed that pristine CNTs without nitrogen doping or supported metal or metal oxide nanoparticles would have little electrocatalytic activity for the water oxidation reactions.

Here we demonstrate, for the first time, that the as-received pristine CNTs with a diameter of 2–5 nm and composed mainly of 2–7 concentric tubes have extremely high electrochemical activities for the OER in alkaline solutions, as compared with SWNTs and MWNTs. The results indicate that CNTs with such specific characteristics are efficient OER catalysts for water splitting in alkaline solutions.

2. Experimental

2.1. Materials

CNTs with different number of walls and diameters were obtained from commercial sources including Nanostructured & Amorphous Materials, Inc., USA, Beijing Dk Nano Technology Co., LTD, China and Shenzhen Nano, China. In order to reduce the possible effect of the metal catalysts, such as cobalt and nickel, in the CNTs samples on the OER, the as-received CNTs samples were purified as follow: 50 mg CNTs were dispersed in 50 mL HCl (30 wt%) solution before ultrasonicated for 1 h, then the dispersion was separated and the sludge was dispersed in a fresh 50 mL HCl (30 wt%) solution, followed by stirring overnight. The CNTs solids were collected and transfer into a Teflon digestion tank and 10 mL HCl solution was added and digested at 120°C overnight. After the digestion, the CNTs were washed by fresh HCl, and then by HNO_3 for 3 times before rinsed thoroughly by DI water. The purified CNTs were dried and collected. Activated carbon (Sigma–Aldrich), graphite (Sigma–Aldrich), 50% Pt/C (Alfa Aesar), Ru/C (20 wt% Ru on Vulcan carbon black, Premetek Co.), KOH (Sigma–Aldrich), Nafion solution (5% in isopropanol and water, Sigma–Aldrich) were received and used without further treatment.

2.2. Characterization

The BET surface area of CNTs, activated carbon and graphite were characterized using a Gemini 2360 surface area analyzer. The Raman spectra were recorded in air at room temperature using a Perkin-Elmer GX FT-IR/Raman spectrometer with a back-scattered configuration and equipped with a Nd:YAG laser at 1064 nm as its light source for Raman. CNTs were characterized using a transmission electron microscope (TEM JEOL3000) operating at 200 kV. The average outer diameter (OD) and number of walls of CNTs were estimated by measuring 100 randomly chosen CNTs in the TEM images.

Thermogravimetric (TG, Q5000) analyses were performed under air upon equilibration at 100°C for 15 min, followed by a ramp of $10^\circ\text{C min}^{-1}$ up to 800°C to estimate the content of the impurities in the CNTs samples. The elements of the impurities or trace metals were analyzed using Inductively Coupled Plasma (ICP-OES, IRIS Intrepid II XSP, USA). The solutions for ICP analysis were prepared as follow: as-received CNTs and the purified CNTs were digested using microwave dissolver (SINEO, HDS-8G) with acid mixture containing 10 mL HNO_3 (65%), 1 mL HClO_4 and 2 mL HF (the procedure was set as: 150°C , 5 min; 180°C , 5 min; 200°C , 10 min; and 230°C , 20 min).

The electrochemical measurements were conducted in a three-electrode cell with a Luggin capillary, using a Gamery Reference 3000 Potentiostat. The tip of the Luggin capillary was placed 3 mm beneath the working electrode. The working electrode is prepared as follows. Generally, 1 mg of electrocatalyst was ultrasonically mixed in 2 mL Nafion solution to form a homogeneous ink, followed by pipetting 5 μL of the catalyst ink onto the surface of a glassy carbon electrode (GCE). The diameter of GCE was 5 mm. The iR drop between the working electrode and the tip of the Luggin capillary was estimated by measuring the impedance value at the frequency of 30 kHz. A Pt mesh and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Potentials in the present study were given versus RHE reference electrode ($E_{\text{RHE}} = E_{\text{vs SCE}} + E_{\text{SCE}} + 0.059 \times \text{pH}$, where $E_{\text{SCE}} = 0.247 \text{ V}$ vs RHE at 20°C).

The linear scan voltammetry was conducted at a sweep rate of 1 mV s^{-1} in the potential range between 0 and 1 V (vs SCE). Tafel plots were recorded at a scan rate of 1 mV s^{-1} . Before the potential scan, the electrode was initially conditioned at a potential of 0.65 V (vs SCE) for 5 min and Tafel plots were iR corrected. Impedance curves were recorded under open circuit and different dc bias with frequency range from 0.1 Hz to 100 kHz and the signal amplitude of 10 mV using a Gamery Reference 3000 Potentiostat. Electrode polarization resistance, R_p , was measured by the differences between the high and low frequency intercepts. Without specification, the catalyst loading was 0.025 mg cm^{-2} and the measurements were conducted at GCE with rotating speed of 2000 rpm. The reason for the use of low CNTs loading for the activity study is to avoid the mass transportation effect on the activity of CNTs. As shown in Fig. S1 (Supporting information), the activity of CNTs for OER increases linearly with the CNTs loading in the catalyst loading range of the present study. The chronopotentiometry were conducted at different current densities with catalysts loading of 0.1 mg cm^{-2} . For the purpose of comparison, commercial 20% Ru/C and 50% Pt/C electrocatalysts were also investigated for OER under identical conditions. The reproducibility of the electrochemical activity of the CNTs for the OER in alkaline solutions was confirmed by repeating the experiments for at least 3–5 times.

3. Results and discussion

3.1. Characterization of CNTs

Fig. 1 is the TEM micrographs of CNTs samples used in the present study. According to the TEM images, no metal nanoparticles were observed, indicating the good purity of the CNTs samples. The outer diameter, OD and number of walls were taken as the average of the measurement from the TEM images (Figs. S2 and S3, Supporting information). Based on the size distribution, the CNTs were categorized as belonging to one of several different groups labeled as CNTs- n , where $n = 1-7$. CNTs-1 mainly consists of single-walled CNTs (SWNTs, 79%), some double-walled CNTs (DWNTs, 16%), and generally occurs as bundles with an average OD of $1.97 \pm 0.40 \text{ nm}$ (Fig. 1A). CNTs-2 are mainly DWNTs (65%) with OD = $3.3 \pm 0.89 \text{ nm}$

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