



Metal oxides/CNT nano-composite catalysts for oxygen reduction/oxygen evolution in alkaline media



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ABSTRACT

A series of highly active state-of-the-art catalysts have been synthesized by depositing high loadings of transition metal oxides (MnO₂, Co₃O₄, NiO, CuO and Fe_xO_y) onto nitrogen-doped carbon nanotubes (CNTs) for bi-functional catalysis in alkaline media. The metal oxides have been dispersed onto functionalized CNTs by an improved impregnation method. This novel, synthetic approach allows for both the preparation of functionalized nitrogen-doped CNTs as well as the even dispersion of metal oxides onto the walls of the CNTs. The catalysts have been characterized by Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), transition electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) methods. Catalytic activity has been measured using a Rotating Disc Electrode (RDE) experiment. The resulting catalysts are stable in alkaline media under experimental conditions and have high bi-functional electrocatalytic activity—both for the oxygen reduction reactions (ORR) and oxygen evolution reactions (OER). From this series of catalysts, the most active catalyst for ORR is the 50 wt% MnO₂/CNT catalyst with a half-wave potential of 0.84 V at the current density of -2.1 mA cm^{-2} and an onset at 0.98 V versus RHE. The most active for OER is the 50 wt% NiO/CNT catalyst with an onset potential at 1.45 V versus RHE.

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1. Introduction

The majority of our world's vehicles are dependent on petroleum-derived fuels. The craving for these fuels has led to political unrest, wars, poverty and mass pollution. Furthermore, the conversion efficiency of chemical potential energy into kinetic energy from these fuels is quite low for an internal combustion engine. Fuel cell technology has been extensively researched to address these issues. Fundamentally, these fuel cells are driven by electrochemical kinetics and intrinsic kinetics at the catalyst layer. Recently, interest to catalysts that can reduce oxygen during the cathodic cycles and evolve oxygen during anodic cycles (bi-functional catalysts) has significantly grown from manufacturers of metal-air batteries, electrolyzers and fuel cells. Presently, the most conventional cathodic and anodic catalysts are made from Pt-group metals (PGM). It has also been discovered that by placing these on commercial carbon supports that have high surface area, it enhances their activity [1]. The main drawback and need for more catalyst research is the incredibly high cost and low

abundance of Pt-group elements. In recognition of the unfavorable factors that PGM-based materials possess, composite nanomaterials incorporating transition metal nanoparticles on multiwalled carbon nanotubes (MWCNTs) is described in this manuscript that rival the electrochemical activities of published PGM results.

We show through our analysis that this family of catalysts is stable in alkaline media, have large surface area, is easy to synthesize, can be produced at lower cost from abundant transition metals and still have high bi-functional electrocatalytic activity. Reported here is a method of functionalized CNT preparation based on the sacrificial support method (SSM) developed at UNM [2–14], synthesis, characterization, and electrocatalytic activity of 50 wt% MO_x/CNT hybrid catalysts in ORR and OER. The method of CNT synthesis allows for controllable production and high deposition of metal oxides. It has been reported that the preparation of composite materials based on transition metal oxides and carbon supports can be synthesized by a variety of methods; however, such high transition metal oxide loadings have not been reported in literature with bi-functional capabilities. Electrocatalysts have been synthesized by coating commercial CNTs with small loadings of transition metal oxides [15–17] and a bi-functional catalyst has been made by separately synthesizing MnO₂ nanotube structures and CNTs, followed by physically mixing the two together to create a heterogeneous

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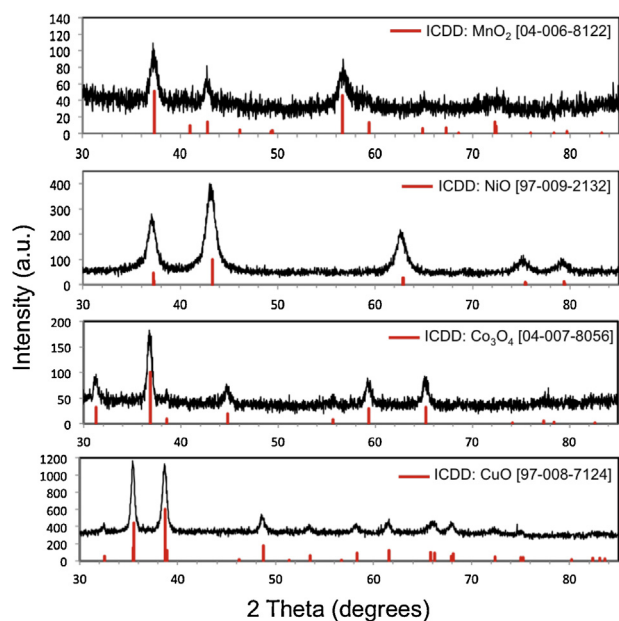


Fig. 1. XRD data for (a) 50 wt% MnO₂/CNT, (b) 50 wt% NiO/CNT, (c) 50 wt% Co₃O₄/CNT and (d) 50 wt% CuO/CNT.

mixture of compounds [18], rather than a singular nanocomposite structural network as described in the present work. The Shao-Horn group has reported state-of-the-art perovskite catalysts based on La, Cu, Mn, Co and Ni mixed oxides supported on Vulcan carbon with $E_{1/2} = 0.64\text{--}0.71\text{ V}$ [19]. The 50 wt% MnO₂/CNT catalyst presented in this research has a half-wave potential $\sim 100\text{ mV}$ better than these results. The electrochemical activity is a result of the novel synthetic approach to yield specialized bi-functional nanocomposite materials, which reiterates the understanding that the method of preparing oxides and their composites affects their morphology and electrocatalytic activities.

2. Materials and methods

2.1. Catalyst synthesis

The CNTs were synthesized by a conversion of C₂H₄ on Fe nanoparticles using the sacrificial support method. Fe(NO₃)₃ was mixed with a colloidal suspension of a silica sacrificial support (Cab-O-Sil® EH-5, 380 m² g⁻¹), dried and ball milled for 4 h at 450 RPM (Across International PQ-N04 Planetary Ball Mill) and placed in a furnace. The powder sample was exposed to a heat treatment at 500 °C in a H₂ atmosphere for 30 min, 760 °C in a C₂H₄ atmosphere for 60 min and 900 °C under an NH₃ atmosphere for 60 min. The results from the XPS analysis confirms the presence of nitrogen defects on the surface of the nanotubes from the introduction of ammonia, which in turn, acts as anchors for the oxides. All gases used were ultra high-grade purity. The material was removed from the furnace, leached with HF and washed to reach a neutral pH. Concentrated nitric acid is introduced, resulting in CNTs with no amorphous carbon. An impregnation method was then utilized in which liquid transition metal nitrates (99.98%, Sigma-Aldrich) were deposited on the CNT powder to yield 50 wt% metal oxides, referred to as MO_x, deposited on the CNTs. The resulting material was dried overnight in the presence of oxygen at 85 °C leaving a metal salt catalyst. After drying, the MO_x/CNTs (M: Fe, Mn, Ni, Co, Cu) were calcined at 350 °C for 120 min. This synthesis method was chosen to keep the metal oxide agglomerations as small as possible to allow for maximum active sites per catalyst mass.

2.2. Catalyst characterization

The catalysts were characterized by Brunauer–Emmet–Teller (BET) measurements, SEM (Hitachi S-5200), TEM (JEOL 2010 EX HREM), XRD (Scintag Pad V, Cu anode) and XPS (XPS spectra were acquired on a Kratos Axis DLD Ultra X-ray photoelectron spectrometer using an Al K α source monochromatic operating at 150 W with no charge compensation) methods. Catalytic activity for ORR and OER were measured in 1.0 M KOH, prepared from deionized water and KOH pellets (99.99%, Sigma-Aldrich) using the RDE method. The

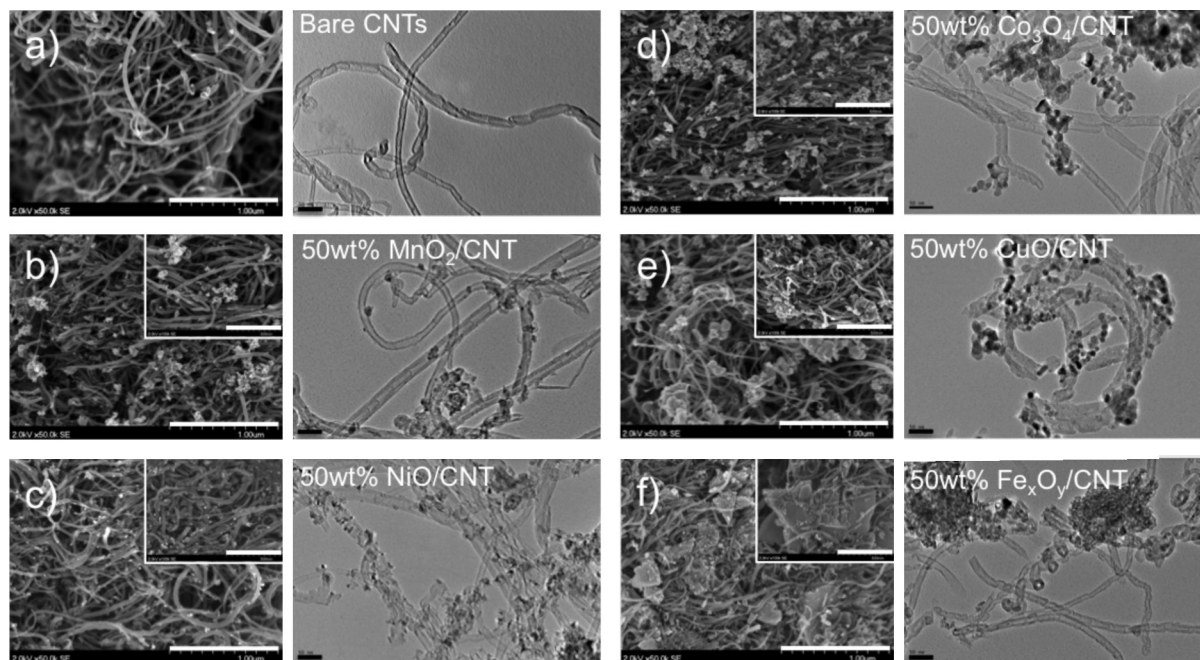


Fig. 2. SEM (left) and TEM (right) images of: (a) bare CNTs, (b) 50 wt% MnO₂/CNT, (c) 50 wt% NiO/CNT, (d) 50 wt% Co₃O₄/CNT, (e) 50 wt% CuO/CNT and (f) 50 wt% Fe_xO_y/CNT. SEM: scale bar is 1.00 μm and insets have a scale bar of 500 nm. TEM: scale bar is 50 nm.

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