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## Development of Highly Active Bifunctional Electrocatalyst Using $\text{Co}_3\text{O}_4$ on Carbon Nanotubes for Oxygen Reduction and Oxygen Evolution

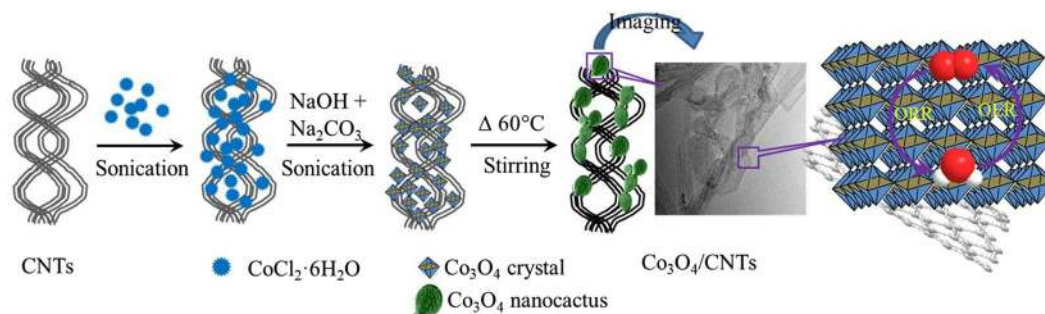
Mohammad Shamsuddin Ahmed, Byungchul Choi & Young-Bae Kim

Replacement of precious platinum catalyst with efficient and cheap bifunctional alternatives would be significantly beneficial for electrocatalytic oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) and the application of these catalysts in fuel cells is highly crucial. Despite numerous studies on electrocatalysts, the development of bifunctional electrocatalysts with comparatively better activity and low cost remains a big challenge. In this paper, we report a nanomaterial consisting of nanocactus-shaped  $\text{Co}_3\text{O}_4$  grown on carbon nanotubes ( $\text{Co}_3\text{O}_4/\text{CNTs}$ ) and employed as a bifunctional electrocatalyst for the simultaneous catalysis on ORR, and OER. The  $\text{Co}_3\text{O}_4/\text{CNTs}$  exhibit superior catalytic activity toward ORR and OER with the smallest potential difference (0.72V) between the  $E_{j_{10}}$  (1.55V) for OER and  $E_{1/2}$  (0.83V) for ORR. Thus,  $\text{Co}_3\text{O}_4/\text{CNTs}$  are promising high-performance and cost-effective bifunctional catalysts for ORR and OER because of their overall superior catalytic activity and stability compared with 20 wt% Pt/C and  $\text{RuO}_2$ , respectively. The superior catalytic activity arises from the unique nanocactus-like structure of  $\text{Co}_3\text{O}_4$  and the synergetic effects of  $\text{Co}_3\text{O}_4$  and CNTs.

Fabrication of hybrid nanomaterials that preserves improved properties other than the original properties of their base materials is an important issue in nanoscience and technology. Among the different allotropes of carbon nanomaterials, carbon nanotubes (CNTs) are one of the most promising nanomaterials for catalysis and sensing<sup>1–4</sup>. The catalytic sites in renewable and green energy systems need to be supported on conducting materials. These sites can be made of metallic nanostructures (such as nanoparticles and nanoflowers) or organometallic complexes. CNTs are potential ideal support material for electrocatalysts because of its electrical conductivity, high surface area, and relatively enhanced durability<sup>5</sup>. Noncovalent chemical approach to ensure a close incorporation between the CNTs and the metallic sites is promising because of its simple fabrication method and better preservation of the electronic properties of the CNTs without damaging the  $\pi$ -configuration.

Persistent environmental impact and increasing demands of traditional energy resources, such as, oil, gas, and coal have stimulated extensive efforts worldwide to develop renewable and green energy technologies, such as fuel cells (FCs) and water splitting systems<sup>1,6–12</sup>. Among many electrochemical reactions in FCs, the oxygen reduction reaction (ORR) is considered as the heart of FCs because it is the only reaction in cathode. By contrast, electrocatalytic oxygen evolution reaction (OER) through water splitting has been recognized as one of the most promising ways to generate oxygen<sup>4</sup>. Precious metals such as platinum (Pt) and/or its alloy materials have been most frequently used active electrocatalyst for both reactions<sup>13–16</sup>. However, Pt-based materials are susceptible to the poor durability and crossover effect in FCs<sup>17,18</sup>. Moreover, the high cost and bottleneck reserve in nature of Pt have also prohibited the full commercialization of FCs<sup>19,20</sup>. Meanwhile, transition metals and their alloys<sup>21–24</sup> have been demonstrated as promising catalysts for ORR and/or OER. So far, the catalytic activities of many nonprecious metal electrocatalysts remain too low compared with those of noble metal catalysts. Moreover, the catalytic activity of the former electrocatalysts is largely hindered by their inherent corrosion and oxidation susceptibility.

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**Figure 1.** The schematic diagram of  $\text{Co}_3\text{O}_4/\text{CNTs}$  preparation and its catalytic activity.

A number of cobalt oxides with uniform porous structure and large surface area have been employed as non-precious catalysts to the electrochemical energy conversion reactions<sup>25–29</sup>. These catalysts have currently attracted much interest in the field of electrocatalysis because of their chemical and physical properties<sup>29</sup>. In particular,  $\text{Co}_3\text{O}_4$  with spinel crystal structure is beneficial for the electron transport between  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions. Thus,  $\text{Co}_3\text{O}_4$  has been widely considered as an efficient electrocatalyst for ORR and OER<sup>30–33</sup>. However,  $\text{Co}_3\text{O}_4$  itself shows lower electrocatalytic activity because of its low electrical conductivity and dissolution, short active site density and agglomeration nature during electrocatalytic processes<sup>30</sup>. Nevertheless, further studies have exhibited that the synergy between carbon nanomaterials (i.e. graphene and CNTs) and  $\text{Co}_3\text{O}_4$  can give a huge promotion of the electrocatalytic activity<sup>26,28,34–37</sup>. Many researches have investigated on  $\text{Co}_3\text{O}_4$ -based hybrid catalysts and obtained uniformly dispersed  $\text{Co}_3\text{O}_4$  nanostructures (i.e. nanoparticles, core-shell, and hollow sphere) to improve electrocatalyst activity<sup>30,38–41</sup>. The results show that the size and shape of the nanocatalysts are deeply related to their electrocatalytic performances, and using these hybrid catalysts is considered one of the best strategies for improving catalytic activity and stability<sup>42</sup>.

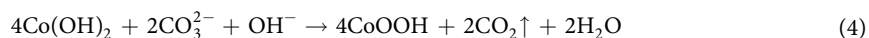
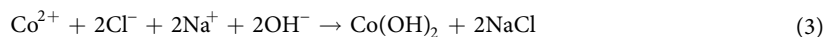
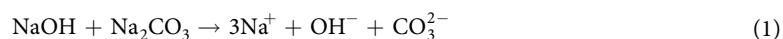
Multifunctional (i.e. bifunctional or trifunctional)<sup>28,41,43</sup> catalyst systems have been reported. However, a bifunctional catalyst system with enhanced activity for ORR and OER is difficult to develop because of the pH-dependent activity and stability<sup>43</sup>. OER electrocatalysts exhibit poor performance in alkaline electrolyte than acid electrolyte<sup>44</sup>. So far, doped-free and noncovalent CNTs with  $\text{Co}_3\text{O}_4$ -hybrid bifunctional catalyst for ORR, and OER has not been reported to date, although the N-doped graphene or CNTs with  $\text{Co}_3\text{O}_4$ -hybrid catalysts are rarely discussed<sup>28,30</sup>. Therefore, new strategies to develop a simply prepared, highly efficient, and cost-effective  $\text{Co}_3\text{O}_4$ - and CNT-based hybrid bifunctional electrocatalysts for ORR and OER is desirable for the large-scale production of clean energy. In this study, we have developed a simple strategy to synthesize  $\text{Co}_3\text{O}_4$  nanocactus grown on CNTs ( $\text{Co}_3\text{O}_4/\text{CNTs}$ ; in Fig. 1). For the first time, the  $\text{Co}_3\text{O}_4/\text{CNTs}$  were successfully employed as bifunctional  $\text{Co}_3\text{O}_4$ -based electrocatalyst for ORR and OER. The porous  $\text{Co}_3\text{O}_4/\text{CNTs}$  exhibited superior electrocatalytic activity and stability than the benchmarks Pt/C or  $\text{RuO}_2$  for ORR and OER, respectively, because of their high density of active sites and excellent charge transport capability.

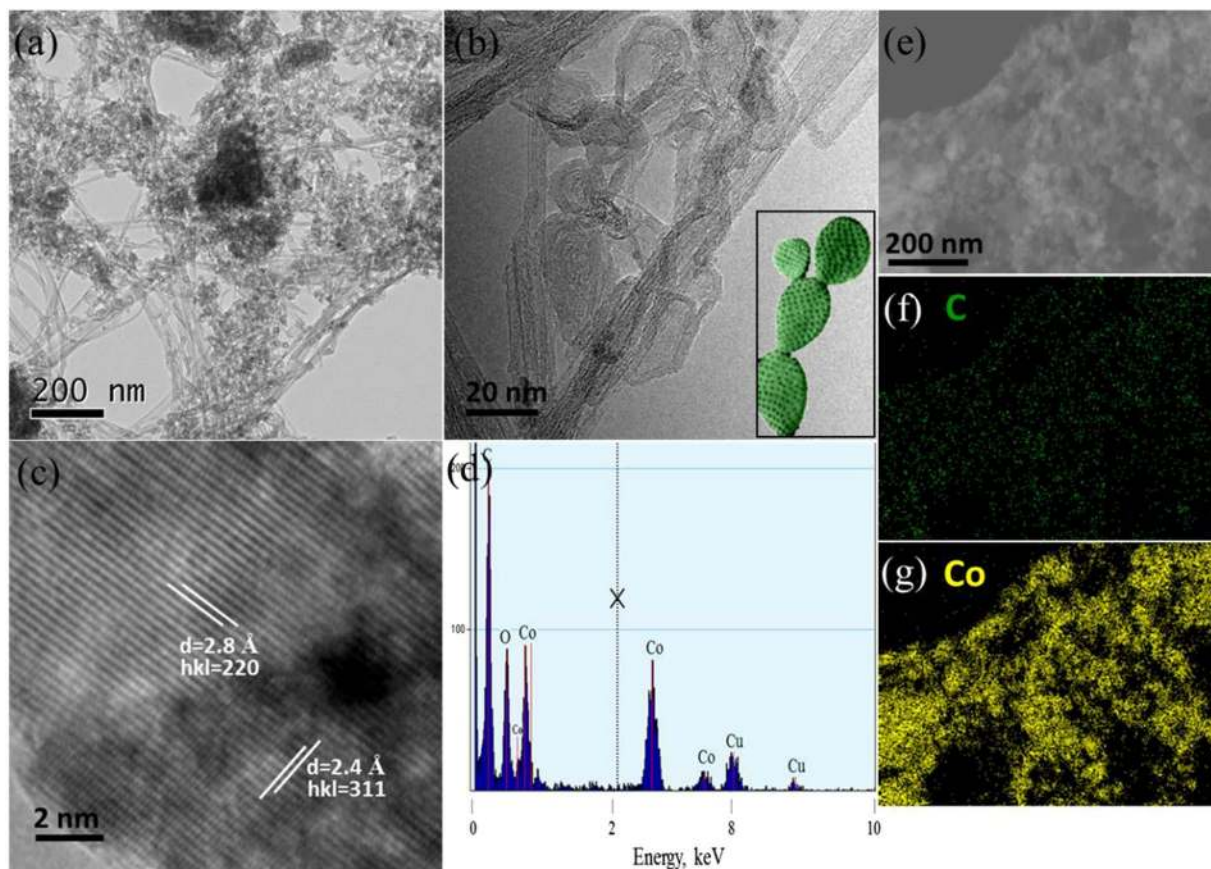
## Experimental Section

The  $\text{Co}_3\text{O}_4/\text{CNTs}$  were synthesized by a simple chemical method. In a typical preparation,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (62 mg) was mixed with 30 mL of water. Then, 30 mg of multiwalled CNTs, which were treated with acid for 30 min<sup>45</sup>, were mixed with 30 mL of water. The solution was added into the  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  solution and vigorously stirred for 1 h. The pH was controlled by slowly adding a solution of  $0.21 \text{ mol L}^{-1}$  NaOH and  $0.066 \text{ mol L}^{-1}$   $\text{Na}_2\text{CO}_3$  under vigorous stirring until pH 10 was reached at room temperature (RT). The prepared suspension was kept at  $60^\circ\text{C}$  for next 24 h under gentle stirring. Finally, the  $\text{Co}_3\text{O}_4/\text{CNTs}$  were filtered and washed with water for and dried at  $60^\circ\text{C}$ . The bare CNTs were prepared using the same protocol but without addition of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  solution. Also, the  $\text{Co}_3\text{O}_4/\text{CNTs}$  in various pH values (i.e. pH 7, 12, 14) were prepared by controlled addition of aforementioned alkaline solution. The electrochemical and instrumental characterizations were described in the supporting information.

## Results and Discussions

Figure 1 shows that the  $\text{Co}_3\text{O}_4$  precursor and clean CNTs were mixed with a simple cooperative assembly of prepared alkaline solution in water at RT. The solution was then kept at  $60^\circ\text{C}$  under gentle stirring for next 24 h to form  $\text{Co}_3\text{O}_4$  nanocactus onto CNTs. The growth of  $\text{Co}_3\text{O}_4$  nanocactus probably goes through a modified mechanism as below<sup>46</sup>–





**Figure 2.** TEM (a and b), HRTEM (c) images, EDX spectrum (d), bright-field TEM image (e) and C (f), Co (g) elemental mapping of  $\text{Co}_3\text{O}_4/\text{CNTs}$ , insets: a photograph of a microdasys cactus, enlarged HRTEM images.

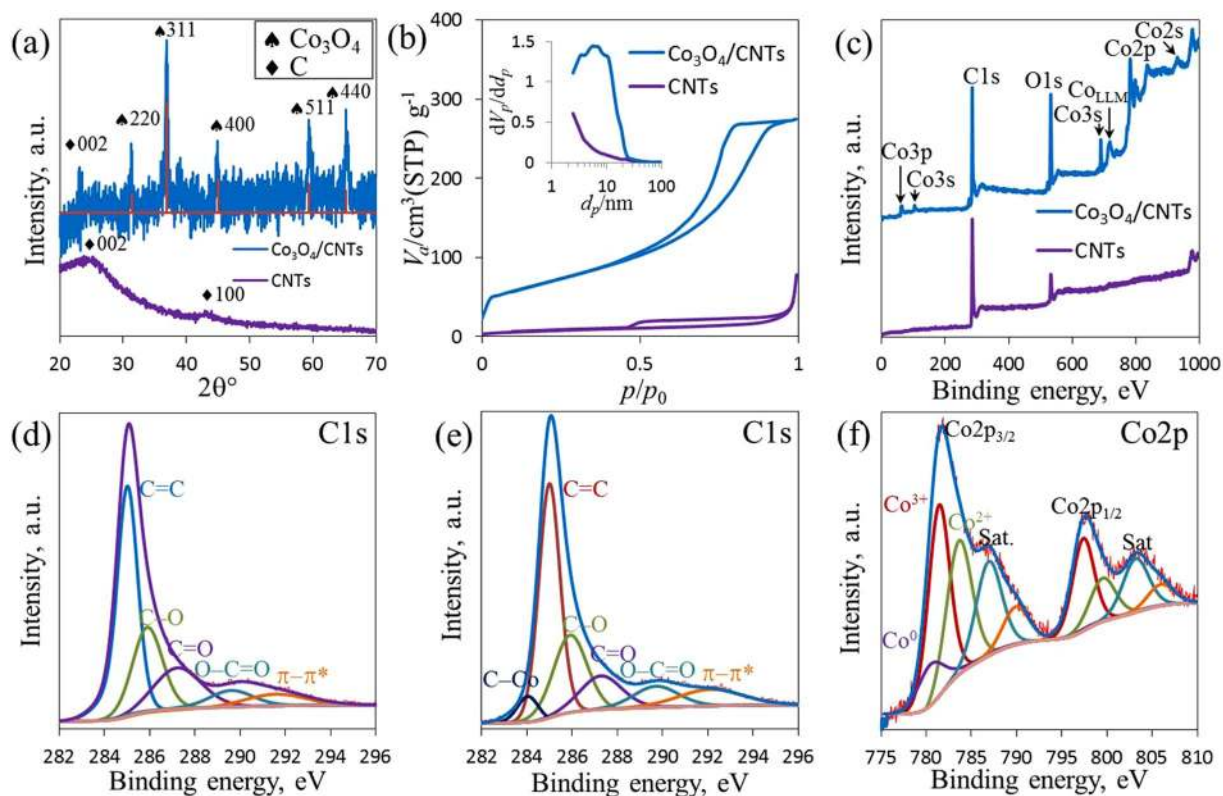


However, the as prepared  $\text{Co}_3\text{O}_4/\text{CNTs}$  were found with a highly crystalline form. The growth of  $\text{Co}_3\text{O}_4$  nanocactus grown on CNTs (Figure S1) was confirmed by transmission electron microscopy (TEM) analysis in Fig. 2. TEM revealed that the numerous nano-sized  $\text{Co}_3\text{O}_4$  cactus were grown onto CNTs (Fig. 2a) and the average size of a single unit of nanocactus was  $\sim 25$  nm in length with  $\sim 5$  nm thick sidewall (Fig. 2b). High resolution TEM (HRTEM) showed the crystalline spinel structure of the  $\text{Co}_3\text{O}_4$  nanocactus (Fig. 2c) and the lattice spacing of 2.4 Å and 2.8 Å can be assigned to the (311) and (220) planes of typical  $\text{Co}_3\text{O}_4$ <sup>47</sup>. The bulk elemental component of  $\text{Co}_3\text{O}_4/\text{CNTs}$  was investigated by energy dispersive X-ray spectroscopy (EDX) in Fig. 2d. The C peak at 0.2 keV was accompanied by an O peak in the EDX spectra. Three Co peaks at  $\sim 0.77$ , 6.9 and 7.63 keV corresponding to  $\text{CoL}_{\alpha 1}$ ,  $\text{CoL}_{\beta 1}$  and  $\text{CoL}_{\gamma 1}$ , respectively, were also obtained in the EDX spectra. The as-prepared  $\text{Co}_3\text{O}_4/\text{CNTs}$  consisted of 6.93 wt% Co, 81.93 wt% C, and 11.14 wt% O. Also, Fig. 2 shows bright-field TEM image (e) and C (f), Co (g) elemental mapping of  $\text{Co}_3\text{O}_4/\text{CNTs}$  sample which confirming once again the presence of C and Co elements.

The TEM results are consistent with the X-ray diffraction (XRD) data. XRD was performed to investigate the phase structure of  $\text{Co}_3\text{O}_4/\text{CNTs}$ . In Fig. 3a, several peaks of the pristine  $\text{Co}_3\text{O}_4$  were consistent with the standard  $\text{Co}_3\text{O}_4$  (ICDD: 98-008-8940, red line). Except for the broad peak (002) at  $\sim 25^\circ$ , which may be ascribed to disordered stacked graphitic structure of CNTs, the major diffraction peaks of  $\text{Co}_3\text{O}_4/\text{CNTs}$  were in good agreement with those of  $\text{Co}_3\text{O}_4$ <sup>48–50</sup>. The type IV  $\text{N}_2$  adsorption/desorption isotherm curve with a distinct hysteresis loop in the relative pressure range of 0.45–0.99 confirmed the presence of mesopores in  $\text{Co}_3\text{O}_4/\text{CNTs}$  and bare CNTs samples (Fig. 3b). The Brunauer–Emmett–Teller specific surface area (SSA) for  $\text{Co}_3\text{O}_4/\text{CNTs}$  was measured to be  $373 \text{ m}^2 \text{ g}^{-1}$ , which was approximately 3-magnitudes higher than the corresponding typical values for  $\text{Co}_3\text{O}_4$ -decorated carbon nanomaterials (i.e.,  $\text{Co}_3\text{O}_4/\text{N-rGO}$ ,  $103.9 \text{ m}^2 \text{ g}^{-1}$ ;  $\text{Co}@\text{Co}_3\text{O}_4/\text{NC-1}$ ,  $111 \text{ m}^2 \text{ g}^{-1}$ ;  $\text{Co}_3\text{O}_4/\text{CNW-A}$ ,  $166 \text{ m}^2 \text{ g}^{-1}$ )<sup>28,30,32</sup>. On the contrary, the SSA for bare CNTs was  $133.2 \text{ m}^2 \text{ g}^{-1}$ . Barrett–Joyner–Halenda pore size distribution curves confirm the presence of the main mesopores with various sizes between 3 nm and 25 nm (average pore diameter, 6.9 nm) and a pore volume of  $1.32 \text{ cm}^3 \text{ g}^{-1}$ . The average pore diameter and pore volume were much higher than those of bare CNTs (Fig. 3b inset). Therefore, a large SSA, high pore volume, and wide pore size distribution are the clear indication of facile electrocatalysis on  $\text{Co}_3\text{O}_4/\text{CNTs}$  sample.

X-ray photoelectron spectroscopy (XPS) was performed to elucidate the chemical changes and confirmed the cobalt state during  $\text{Co}_3\text{O}_4$  growth on CNTs. The peaks obtained in the XPS spectra at 284.2, 531.0 and 780.7 eV (Fig. 3c) could be ascribed to C1s, O1s and Co2p, respectively, due to the existence of carbon, oxygen and cobalt

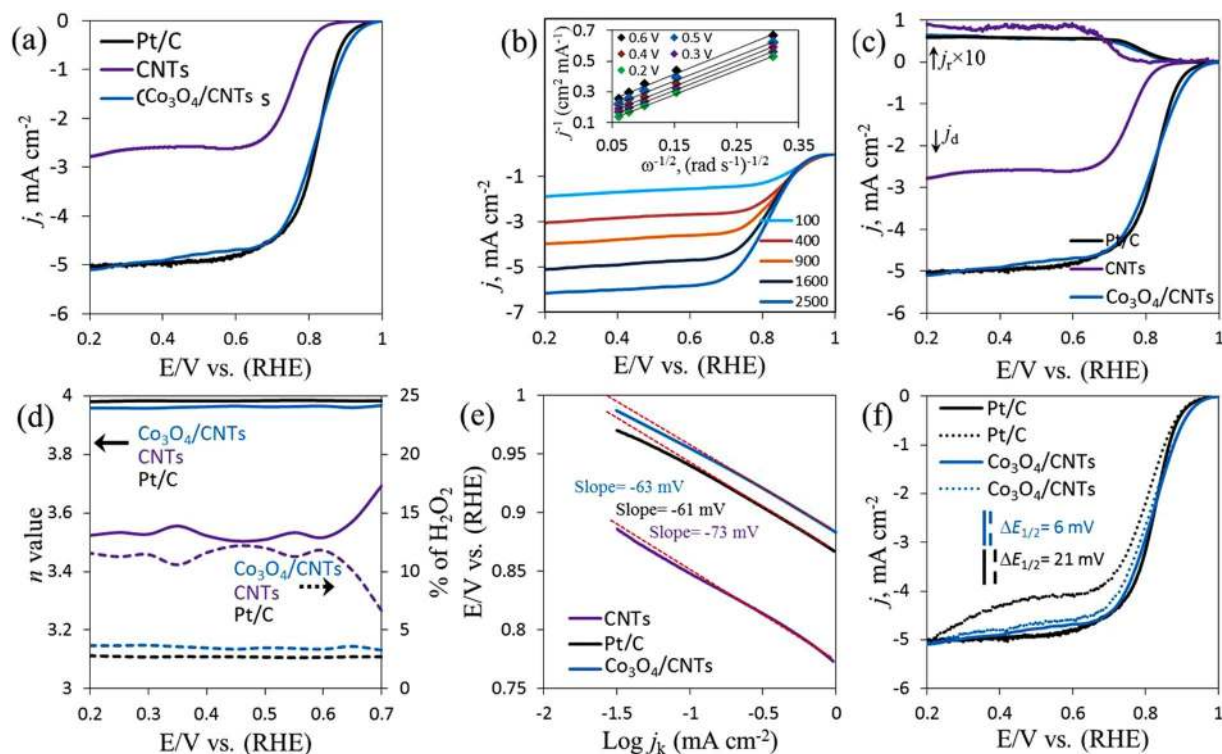




**Figure 3.** The XRD spectra (a), the nitrogen adsorption–desorption isotherms (b), XPS spectra (c), core level of C1s (d and e), and Co2p XPS spectrum (f) of CNTs and Co<sub>3</sub>O<sub>4</sub>/CNTs; inset: the corresponding pore-size distribution (b).

in Co<sub>3</sub>O<sub>4</sub>/CNTs. Significant difference was observed in the presence of Co<sub>3</sub>O<sub>4</sub> in Co<sub>3</sub>O<sub>4</sub>/CNTs compared with bare CNTs. The high-resolution C1s XPS spectra of bare CNTs (Fig. 3d) and Co<sub>3</sub>O<sub>4</sub>/CNTs (Fig. 3e) represent the defective sp<sup>3</sup>-carbon and basal-plane sp<sup>2</sup>-carbon of CNTs<sup>51</sup>. Both figures showed four absorbance peaks for oxygenated sp<sup>3</sup>-carbon at 285.8, 287.3, and 289.7 eV, which were attributed to C–O, C=O, and O–C=O, respectively, including distinct oxygen-free sp<sup>2</sup>-carbon (C=C) at 285.0 eV<sup>52</sup>. Moreover, a tiny shakeup peak was obtained at 292.2 eV for π–π\*, signifying higher degree of graphitization<sup>53,54</sup>. The tiny peak at low binding energy of 284.1 eV could probably be attributed to the C–Co bond in Co<sub>3</sub>O<sub>4</sub>/CNTs<sup>55</sup>. The overall elemental composition of Co<sub>3</sub>O<sub>4</sub>/CNTs is listed in Table S1. Furthermore, XPS confirmed the oxidized state of the Co-species with the detection of binding energies of 781.7 eV and 797.6 eV which were attributed to Co2p<sub>3/2</sub> and Co2p<sub>1/2</sub> peaks, respectively (Fig. 3f)<sup>56,57</sup>. However, the Co<sup>0</sup>, Co<sup>3+</sup> and Co<sup>2+</sup> species were detected at 781.4, 781.6, and 783.8 eV in Co2p<sub>3/2</sub> with corresponding satellite peak (786.7 eV) due to the presence of Co<sub>3</sub>O<sub>4</sub> in the Co<sub>3</sub>O<sub>4</sub>/CNTs sample. At Co2p<sub>1/2</sub>, the Co<sup>3+</sup> and Co<sup>2+</sup> species also appeared at 797.45 eV and 799.6 eV with its shakeup satellite at 803.3 eV. Moreover, the numerical analysis of XPS data was also recorded, and Co was detected as 6.94 wt% with a good ratio of Co<sup>3+</sup>/Co<sup>2+</sup> (1.1) at pH 10 which was the lowest value among all pHs (Figure S2 and Table S2).

**Electrochemical ORR on Co<sub>3</sub>O<sub>4</sub>/CNTs.** The linear sweep voltammogram (LSV) curves on rotating disk electrode (RDE) exhibited ORR for Co<sub>3</sub>O<sub>4</sub>/CNTs, bare CNTs (catalyst mass loading, 153 μg cm<sup>-2</sup>) and 20 wt% Pt/C electrodes in O<sub>2</sub>-saturated 0.1 M KOH solution at a scan rate of 5 mV s<sup>-1</sup> and at 1600 rpm (Fig. 4a) and signify the electrocatalytic ORR performance on all electrodes. The superior electrocatalytic ORR was observed on Co<sub>3</sub>O<sub>4</sub>/CNTs in terms of the improved onset potential ( $E_{\text{onset}}$ ) of 0.93 V and a half-wave potential ( $E_{1/2}$ ) of 0.83 V than the CNTs ( $E_{\text{onset}}$ , 0.83 V and  $E_{1/2}$ , 0.76 V (Figure S3)). These values were also superior to those of commercially available Pt/C ( $E_{\text{onset}}$  of 0.91 V and  $E_{1/2}$  of 0.83 V) and several other reported Co<sub>3</sub>O<sub>4</sub>-based catalysts for ORR<sup>26,58</sup>. Moreover, the current density ( $j$ , normalized by electrode area, 0.196 cm<sup>2</sup>) at the Co<sub>3</sub>O<sub>4</sub>/CNTs electrode was higher than that of the CNTs modified electrode and closer to that of Pt/C. Thus, the Co<sub>3</sub>O<sub>4</sub>/CNTs showed better electrocatalytic activity for ORR in terms of  $E_{\text{onset}}$ ,  $E_{1/2}$ , and  $j$ . This result highlights the importance of the incorporation of nanocactus-shaped Co<sub>3</sub>O<sub>4</sub> with CNTs that have mesoporous structure and higher SSA. The ORR dynamics at the Co<sub>3</sub>O<sub>4</sub>/CNTs electrode were then investigated by RDE, and the results are shown in Fig. 4b. Figure 4b displays a series of RDE curves for ORR using the Co<sub>3</sub>O<sub>4</sub>/CNTs catalyst at various rotation speeds in same electrolyte at 5 mV s<sup>-1</sup> scan rate. The obtained data were analyzed using Koutecky–Levich (K–L) equation as follows<sup>58–60</sup>:



**Figure 4.** LSV curves for ORR on CNTs,  $\text{Co}_3\text{O}_4/\text{CNTs}$  and Pt/C catalyst in  $\text{O}_2$ -saturated 0.1 M KOH solution at a scan rate of  $5 \text{ mV s}^{-1}$  and at a rotating speed of 1600 rpm (a), LSV curves on  $\text{Co}_3\text{O}_4/\text{CNTs}$  in same electrolyte at various rotating speeds and K–L plots in inset (b), RRDE curves for ORR at 1600 rpm with a constant applied potential of 0.8 V vs. RHE on the ring electrode (c), the transferred electron number and the corresponding  $\text{H}_2\text{O}_2$  synthesis during ORR (d), Tafel plots (e) on CNTs,  $\text{Co}_3\text{O}_4/\text{CNTs}$  and Pt/C electrodes, and LSV curves on  $\text{Co}_3\text{O}_4/\text{CNTs}$  and Pt/C before (solid lines) and after (dotted lines) 3000 cycles (f).

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} \quad (6)$$

$$jL = B\omega^{1/2} = 0.62nFAD_{\text{O}_2}^{2/3}C_{\text{O}_2}v^{-1/6}\omega^{1/2} \quad (7)$$

$$j_k = nFkC_{\text{O}_2} \quad (8)$$

where  $j$ ,  $j_k$ , and  $j_L$  are the measured, kinetic, and diffusion limiting current densities ( $\text{mA cm}^{-2}$ ), respectively;  $n$  is the electron transfer number per  $\text{O}_2$ , and  $A$  is the surface area of the working electrode. Moreover,  $F$  and  $T$  are Faraday constant ( $96485.3 \text{ C mol}^{-1}$ ) and temperature, respectively;  $D_{\text{O}_2}$  and  $C_{\text{O}_2}$  are the oxygen diffusion coefficient ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) and the bulk concentration ( $1.2 \text{ mM L}^{-1}$ ), respectively, in 0.1 M KOH<sup>60</sup>;  $\nu$  is the kinetic viscosity of the electrolyte ( $1 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ );  $\omega$  is the angular velocity of electrode ( $2\pi \cdot \text{rpm}$ ), and  $k$  is the electron-transfer rate constant. Based on the K–L equation, a plot of  $j_k^{-1}$  vs.  $\omega^{-1/2}$  was yielded a straight line and the slopes of those plots reflect the  $B$  factor in equation (7).

However, Fig. 4b inset shows the K–L plots for  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode and the slopes of all K–L plots remain approximately constant over the studied potential range. This result indicates the number of electrons transferred in the ORR remained constant. Based on equations (6) and (7), the average  $n$  value in ORR was estimated to be 4, suggesting a four-electron ( $4e^-$ ) pathway for electrocatalytic ORR<sup>61–63</sup>. The ORR dynamics on the CNTs electrode were also investigated by RDE and the average  $n$  value in ORR was estimated to be 3.6 from corresponding K–L plots (Figure S4). The  $j_k$  obtained from the intercept of the K–L plots for the  $\text{Co}_3\text{O}_4/\text{CNTs}$  ( $16.5 \text{ mA cm}^{-2}$  at 0.8 V) was 3.1-magnitudes larger than that of bare CNTs ( $5.2 \text{ mA cm}^{-2}$ ) catalyst and similar to that of Pt/C ( $17.3 \text{ mA cm}^{-2}$ ). The ORR activities on as-synthesized  $\text{Co}_3\text{O}_4/\text{CNTs}$  at various pH values were also investigated (Figure S5a). Although the  $\text{Co}_3\text{O}_4/\text{CNTs}$  @ pH 12 has the highest  $\text{Co}_3\text{O}_4$  (Table S2), the relatively low  $\text{Co}^{3+}/\text{Co}^{2+}$  might lead to a high charge-transfer (Figure S5b). Hence, a relatively better electrocatalytic activity was observed at  $\text{Co}_3\text{O}_4/\text{CNTs}$  @ pH 10 in based on the higher  $j_k$  among all pH-dependent  $\text{Co}_3\text{O}_4/\text{CNTs}$  (Figure S5a inset).

The rotating ring–disk electrode (RRDE) measurement was performed to further evaluate the ORR pathway on  $\text{Co}_3\text{O}_4/\text{CNTs}$ , bare CNTs, and Pt/C electrodes. The  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode exhibited high disk current density ( $j_d$ ) for ORR and much lower ring current density ( $j_r$ ) than CNTs. The  $j_r$  profiles accompanied with further

reduction of peroxide species synthesized during ORR process are shown in the upper curves. Both  $j_d$  and  $j_r$  from Pt/C are very similar to that of  $\text{Co}_3\text{O}_4/\text{CNTs}$ .

The RRDE data were used to further verify the transferred electron number and monitor the corresponding  $\text{H}_2\text{O}_2$  formation on aforementioned three electrodes during ORR process from equations (9) and (10)<sup>28,64</sup> in Fig. 4d. The average  $n$  value for ORR at the  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode (3.96) was consistently higher than that at the CNTs (3.6) over the tested potential range of 0.7–0.2 V (vs. RHE). The corresponding  $\text{H}_2\text{O}_2$  yields were 3.5% and 9.6% for  $\text{Co}_3\text{O}_4/\text{CNTs}$  and CNTs, respectively, over the same potential range. The calculated  $n$  value (3.98) and  $\text{H}_2\text{O}_2$  (2.9%) yield on Pt/C were slightly higher than the  $\text{Co}_3\text{O}_4/\text{CNTs}$ . The calculated  $n$  values are similar to the result obtained from the K–L plots, signifying that the ORR on  $\text{Co}_3\text{O}_4/\text{CNTs}$  hybrid was mainly by  $4e^-$  involved pathway and the main byproduct was  $\text{H}_2\text{O}$ .

$$n = \frac{4i_d}{i_d + \frac{i_r}{N}} \quad (9)$$

$$\text{H}_2\text{O}_2\% = \frac{200 \frac{i_r}{N}}{i_d + \frac{i_r}{N}} \quad (10)$$

$$N = \frac{-i_r}{i_d} \quad (11)$$

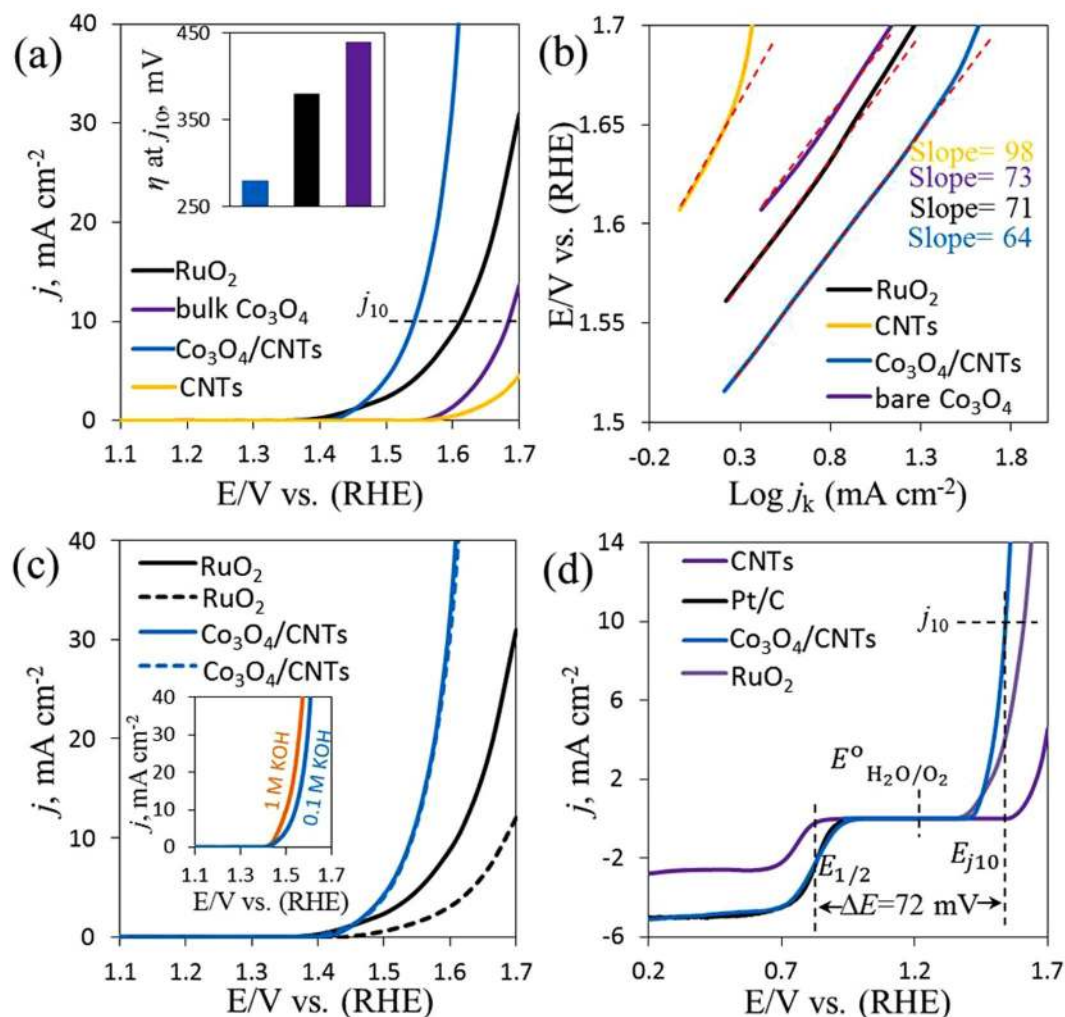
where  $N$  is the collection efficiency of the RRDE (0.37), and  $i_d$  and  $i_r$  are the disk and ring electrode currents, respectively.

The estimated  $j_k$  values were plotted against the electrode potential to investigate the Tafel behavior of  $\text{Co}_3\text{O}_4/\text{CNTs}$ , CNTs and Pt/C (Fig. 4e). The better ORR activity on  $\text{Co}_3\text{O}_4/\text{CNTs}$  was further confirmed by the lower Tafel slope of  $63 \text{ mV dec}^{-1}$  at low overpotential ( $\eta$ ) than the CNTs ( $73 \text{ mV dec}^{-1}$ ) and similar to that of Pt/C ( $61 \text{ mV dec}^{-1}$ ). Furthermore, the LSV curves before and after the accelerated degradation test (ADT) on  $\text{Co}_3\text{O}_4/\text{CNTs}$  and Pt/C in Fig. 4f. It was found that the  $E_{1/2}$  shifted largely at the negative direction (21 mV), and  $j_L$  lost 17.9% on Pt/C after 3000 consecutive cycles. By contrast, the 3.5- and 9-magnitudes lower  $E_{1/2}$  shift (6 mV) and  $j_L$  loss (2%) were observed on the  $\text{Co}_3\text{O}_4/\text{CNTs}$  under the same conditions. Moreover, Figure S6a shows the current density as the function of time by chronoamperometry technique for  $\text{Co}_3\text{O}_4/\text{CNTs}$  and Pt/C at an applied potential of 0.8 V. The  $j$  was maintained up to 93% after 20 h run in real condition, indicating that the catalytic activity on  $\text{Co}_3\text{O}_4/\text{CNTs}$  could be sustained for a long time. For Pt/C, the catalytic activity was then maintained up to 76% with the same period of time. In addition, the  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode demonstrated good methanol tolerance than the Pt/C (Figure S6b). The TEM image of used  $\text{Co}_3\text{O}_4/\text{CNTs}$  displays the decay morphology with the crystalline nature of  $\text{Co}_3\text{O}_4$  after 20 h of real-time continuous monitoring. These results indicate that the  $\text{Co}_3\text{O}_4/\text{CNTs}$  are a competent ORR electrocatalyst because of its better electrocatalytic activity, fuel selectivity, and operational stability than the Pt/C.

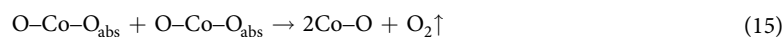
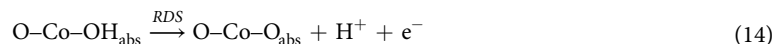
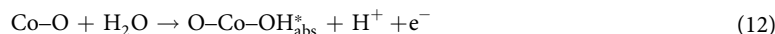
**Electrochemical OER on  $\text{Co}_3\text{O}_4/\text{CNTs}$ .** To evaluate the potential use of our hybrid catalyst, we employed  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode to evaluate the electrocatalytic OER. The OER catalytic activities of all catalysts were studied by LSV at  $5 \text{ mV s}^{-1}$ . The  $\text{Co}_3\text{O}_4/\text{CNTs}$  were used with same mass loading and afforded higher OER activity than either bare bulk  $\text{Co}_3\text{O}_4$ , CNTs or  $\text{RuO}_2$  in Fig. 5. Figure 5a shows that the  $E_{\text{onset}}$  for bulk  $\text{Co}_3\text{O}_4$  was 1.55 V and the maximum  $j$  was  $13.6 \text{ mA cm}^{-2}$  at 1.7 V. The  $E_{\text{onset}}$  for  $\text{RuO}_2$  was 1.36 V with maximum of  $j = 31 \text{ mA cm}^{-2}$  at the same electrode potential. However, considerable negative shifted in the  $E_{\text{onset}}$  was observed at  $\text{Co}_3\text{O}_4/\text{CNTs}$  (1.43 V) with highest  $j = 70.8 \text{ mA cm}^{-2}$  at 1.7 V and the CNTs showed the lowest performance than all electrodes. However, the  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode showed a potential of 1.55 V at the current density of  $10 \text{ mA cm}^{-2}$  ( $E_{j_{10}}$ ), which was lower than that of bulk  $\text{Co}_3\text{O}_4$  (1.68 V) and  $\text{RuO}_2$  (1.61 V). Moreover, as shown in Fig. 5a inset, the  $\eta$  required to drive a  $j_{10}$  for the  $\text{Co}_3\text{O}_4/\text{CNTs}$  was 280 mV, which was also significantly lower than that for the bulk  $\text{Co}_3\text{O}_4$  and  $\text{RuO}_2$  (440 mV and 380 mV, respectively). Thus, the  $\text{Co}_3\text{O}_4/\text{CNTs}$  exhibited higher OER activity than the bulk  $\text{Co}_3\text{O}_4$ , CNTs and  $\text{RuO}_2$  electrodes in respect to the  $\eta$  and  $j$ . This result indicating that the  $\text{Co}_3\text{O}_4/\text{CNTs}$  have higher density of active sites than bulk  $\text{Co}_3\text{O}_4$  and CNTs, and the porous  $\text{Co}_3\text{O}_4$  served as the better active catalytic site for the superior OER even better than benchmark  $\text{RuO}_2$  which resulted in the synergic effect of  $\text{Co}_3\text{O}_4$  and CNTs, the porous nanocactus-like structure, and better  $\text{Co}^{3+}/\text{Co}^{2+}$  ratio. These characteristics allowed improved ability for electron transfer. The poor current densities of bare CNTs and  $\text{Co}_3\text{O}_4$  were probably due to the degradation nature of carbon<sup>32</sup> and aggregation with less conductive nature, respectively<sup>26</sup>.

The Tafel slope of each catalyst beyond the  $E_{\text{onset}}$  was calculated to understand in detail the OER mechanism and the result are shown Fig. 5b. Tafel plots display a lower Tafel slope of  $64 \text{ mV dec}^{-1}$  for  $\text{Co}_3\text{O}_4/\text{CNTs}$  than those of  $\text{RuO}_2$  ( $71 \text{ mV dec}^{-1}$ ), bulk  $\text{Co}_3\text{O}_4$  ( $73 \text{ mV dec}^{-1}$ ) and CNTs ( $98 \text{ mV dec}^{-1}$ ), indicating more favorable kinetics toward OER on the  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode<sup>32,65</sup>. The Tafel slope of  $\text{Co}_3\text{O}_4/\text{CNTs}$  was also comparable to other reported  $\text{Co}_3\text{O}_4$ -based OER catalysts<sup>26,66</sup>. The OER mechanism can be assumed as follows according to the Tafel slope of  $\text{Co}_3\text{O}_4/\text{CNTs}$ . The OER on active Co–O-system<sup>65</sup> in  $\text{Co}_3\text{O}_4/\text{CNTs}$  catalyst was initiated by water adsorption and the formation of adsorbed (ads) reactive intermediate,  $\text{OH}_{\text{abs}}^*$ , by releasing a proton and electron in equation (12). Afterwards, this  $\text{OH}_{\text{abs}}^*$  was converted to another type OH,  $\text{OH}_{\text{abs}}^*$ , in equation (13) (both OH are chemically same but energetically different). In equation (14), a second proton and electron transfer yielded an oxide intermediate, and this step is a rate-determining step (RDS). Recombination of two oxide intermediates completed one reaction turnover in equation (15)<sup>67</sup>.





**Figure 5.** Comparison of the OER activity of CNTs, bulk  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4/\text{CNTs}$  and  $\text{RuO}_2$  electrodes by LSV (a), corresponding Tafel plots of those electrodes (b), LSV curves for the 1<sup>st</sup> and 1000<sup>th</sup> potential cycles (c), bifunctional catalytic activities of CNTs,  $\text{Co}_3\text{O}_4/\text{CNTs}$  and benchmarks Pt/C or  $\text{RuO}_2$  catalysts toward both ORR and OER (d); the overall LSV curves in the potential range of 0.2 to 1.7 V was investigated in argon-saturated 0.1 M KOH solution at  $5 \text{ mV s}^{-1}$  scan rate and at the rotating speed of 1600 rpm. Insets: the comparison of overpotential at  $j_{10}$  (a) and OER activity of  $\text{Co}_3\text{O}_4/\text{CNTs}$  in argon-saturated 0.1 and 1 M KOH solution (c).



Furthermore, the electrochemical stability of  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode was also compared with  $\text{RuO}_2$  under a fixed  $\eta$  and electrolyte conditions. Good stability of  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode was confirmed by the similar LSV curves measured at the 1<sup>st</sup> and 1000<sup>th</sup> potential cycles (Fig. 5c). The used catalyst was characterized by XPS, and the results suggest that amperometric operation did not change significantly in the chemical states except the increase in C-O bond in CNTs and satellite band in cobalt (Figure S7). These results also suggest that  $\text{Co}_3\text{O}_4/\text{CNTs}$  have longer stability in electrochemical process than the  $\text{RuO}_2$ . The OER processes at  $\text{Co}_3\text{O}_4/\text{CNTs}$  electrode in 0.1 and 1 M KOH exhibit the same  $E_{\text{onset}}$  of 1.43 V (Fig. 5c inset). At higher potentials, the more rapid increase in current density was observed for 1 M KOH owing to higher conductivity of the electrolyte. At 270 mV overpotential,  $j = 22 \text{ mA cm}^{-2}$  was obtained in 1 M KOH solution, while it was  $10 \text{ mA cm}^{-2}$  in 0.1 M KOH.

Name	Electrolyte	$E_{1/2}$ (V vs. RHE)	$E_{j_{10}}$ (V vs. RHE)	$\Delta E$ (V)	References
Co <sub>3</sub> O <sub>4</sub> /CNTs	0.1 M KOH	0.83	1.55	0.72	This work
Co-N/G-600	0.1 M KOH	0.764*	1.724*	0.96	21
Co <sub>3</sub> O <sub>4</sub> /N-rmGO	0.1 M KOH	0.83	1.54	0.71	26
Co <sub>3</sub> O <sub>4</sub> /NPC	0.1 M KOH	0.74*	1.63*	0.89	28
Co@Co <sub>3</sub> O <sub>4</sub> /NC-1	0.1 M KOH	0.80	1.65	0.85	30
Co <sub>3</sub> O <sub>4</sub> /CNW-B	0.1 M KOH	0.755*	1.556*	0.801	37
Co <sub>3</sub> O <sub>4</sub> /N-GAs	0.1 M KOH	0.87	1.66	0.79	66
CMO/N-rGO	0.1 M KOH	0.80	1.66	0.86	69
Co <sub>9</sub> S <sub>8</sub> (600)/N,S-GO	0.1 M KOH	0.75	1.63	0.88	70
Co <sub>x</sub> O <sub>y</sub> /NC	0.1 M KOH	0.80	1.66	0.86	71

**Table 1.** The bifunctional catalytic activity of Co<sub>3</sub>O<sub>4</sub>/CNTs catalyst for ORR and OER. \*Converted V vs. RHE.

The overall oxygen activity of the Co<sub>3</sub>O<sub>4</sub>/CNTs as a bifunctional catalyst could be evaluated (Fig. 5d) by the potential difference ( $\Delta E$ ) between the  $E_{j_{10}}$  for OER and  $E_{1/2}$  for ORR<sup>68</sup>. However, the Co<sub>3</sub>O<sub>4</sub>/CNTs catalyst showed the smallest  $\Delta E$  of 0.72 V and this value was markedly lower than the  $\Delta E$  obtained using commercial Pt/C (0.85 V) and many other Co- and Co<sub>3</sub>O<sub>4</sub>-based materials i.e., Co-N/G-600, 0.96 V; Co@Co<sub>3</sub>O<sub>4</sub>/NC-1, 0.85 V; Co<sub>3</sub>O<sub>4</sub>/N-Gas, 0.79 V<sup>21,30,67</sup>. This result signifies better reversible oxygen electrode. The detailed comparison with various Co- and Co<sub>3</sub>O<sub>4</sub>-based materials is shown in Table 1. These results clearly indicate that the Co<sub>3</sub>O<sub>4</sub>/CNTs catalyst is a promising low-cost and efficient catalyst for both ORR and OER.

## Conclusion

We demonstrated an easy and generic method to synthesize a unique nanocactus-like structure of Co<sub>3</sub>O<sub>4</sub> material embedded onto CNTs for bifunctional electrocatalysis. The newly developed Co<sub>3</sub>O<sub>4</sub>/CNTs were an effective bifunctional ORR and OER electrocatalyst with comparatively better activities and stability than the Pt/C or RuO<sub>2</sub> because of their unique architecture with large surface area, rich active sites, and good electron transfer properties. The excellent catalysis and stability of Co<sub>3</sub>O<sub>4</sub>/CNTs with abundant active sites could be attributed to the strong interaction between the nanocactus-shaped Co<sub>3</sub>O<sub>4</sub> and CNTs. Thus, Co<sub>3</sub>O<sub>4</sub>/CNTs are promising alternatives to noble metal-based catalysts for FCs and water splitting applications because of their low-cost, facile synthesis, and excellent catalysis and stability.

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## Author Contributions

M.S. Ahmed performed all electrochemical experiments, wrote the manuscript and analyzed all the results with due discussion with B. Choi and Y.B. Kim.

## Additional Information

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