Supporting Information

Highly Efficient and Robust Oxygen Evolution Catalysts Achieved by Anchoring Nanocrystalline Cobalt Oxides onto Mildly Oxidized Multiwall Carbon Nanotubes

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Experimental

Synthesis of oxidized carbon nanomaterials

Weakly oxidized MWCNT (wMWCNT) was prepared in an alkaline ammonium solution. In this method, 100 mg of MWCNTs was mixed with 10 mL ammonium hydroxide and hydrogen peroxide solution (1:1 (v/v) $NH_3 \cdot H_2O$ (28%) and H_2O_2 (30%)) in a 50 mL round bottom flask. The mixture was stirred gently at 80 ^{o}C with a condenser for 5h, then collected by filtration and washed thoroughly with water and ethanol. The resulting wMWCNT was dried at 40 ^{o}C under vacuum overnight.

Strongly oxidized MWCNT (sMWCNT) was prepared according to the following procedures. 100 mg of MWCNT was mixed with 12 ml 65% HNO_3 and 98% H_2SO_4 mixture (1:1 v/v) in a 50 ml round bottom flask, and stirred at 85 ^{o}C for 2.5 h. The reaction mixture was then diluted with copious amount of water, filtrated and washed thoroughly with water and ethanol. The resulting sMWCNT was collected after drying at 40 ^{o}C under vacuum overnight.

Mildly oxidized graphene oxide (mGO) was prepared using a modified Hummer's method according to a previously published literature.[1] Briefly, 1g of graphite flakes (Sigma-Aldrich) was added in to a 250 ml round bottom flask, followed by the addition of 23 ml 98% H_2SO_4, and stirred at room temperature for 24 h. Then the flask was heated to 40 ^{o}C, and 100 mg $NaNO_3$ was added. After 5 min, 500 mg of $KMnO_4$ was added into the reaction mixture slowly, keeping the reaction temperature below 45 ^{o}C. The solution was allowed to stir for another 30 min. Afterwards, 3 ml of water was added to the flask, followed by 3 ml after 5 min, then 40 ml after another 5 min. The flask was allowed to stir for 15 min, cooled to room temperature, then added with 140 ml H_2O. 10 ml of 30% H_2O_2 was added to the flask to terminate the reaction. mGO was collected by repeated centrifugation and washed with 5% HCl twice followed by copious amount of water.

Synthesis of Co_3O_4 and carbon nanomaterials composites. To synthesize Co_3O_4 and carbon nanomaterials composites, dried carbon nanmaterials were dispersed in absolute ethanol after gentle sonication to form a suspension of 0.33 mg/ml. 0.54 ml of 0.2 M cobalt acetate (($Co(Ac)_2 \cdot 4H_2O$, 98%, Sigma-Aldrich) aqueous solution was added into 10.8 ml of carbon nanomaterial ethanol solution, followed by the addition of 0.54 ml of 28% $NH_3 \cdot H_2O$. The mixture was stirred at 80 ^{o}C in an oil bath for 12 h, then transferred to a 18 mL autoclave for hydrothermal reactions at 150 ^{o}C for 3 h. The resultant composites were collected by centrifugation and washed with ethanol and water subsequently, then dried under vacuum.

Synthesis of Co_3O_4 nanocrystals. 0.54 ml of 0.2 M cobalt acetate (($Co(Ac)_2 \cdot 4H_2O$, 98%, Sigma-Aldrich) aqueous solution was added into 10.8 ml absolute ethanol, followed by the addition of 0.54 ml of 28% $NH_3 \cdot H_2O$. The solution was stirred at 80 ^{o}C in an oil bath for 12 h, then transferred to a 18 mL autoclave for hydrothermal reactions at 150 ^{o}C for 3 h. The resultant particles were collected by centrifugation and washed with ethanol and water subsequently, then dried under vacuum.

Oxygen detection

The catalyst loaded working electrode together with the reference electrode were arranged in one compartment while the Pt counter electrode was placed in another compartment separated by a glass frit. The electrolyte (100 mL 0.1 M KOH) was degassed with high purity N_2 for more than 1 h before electrolysis. The needle probe of the O_2 sensor was positioned in the headspace of the cell through a rubber spectrum, for online monitoring of O_2 concentration at an interval of 1 s. The volume of headspace is 30 mL. The O_2 measurements proceeded with establishment of baseline for 0.5 h for verifying the gas-tightness of the cell, and then followed by 2 h OER. The total amount of O_2 generated was a sum of the O_2 recorded by the sensor directly in the headspace and O_2 dissolved in solution, which was calculated using the Henry's law.[2]

Oxygen reduction reaction (ORR)

The catalytic activity of Co_3O_4/mMWCNT composite for oxygen reduction reactions (ORR) has also been investigated. Figure S6a shows the cyclic voltammograms obtained at a Co_3O_4/mMWCNT-loaded GC electrode in 0.1 M KOH saturated with O_2. The oxygen reduction wave is observed at the onset potential at 0.87 V and the peak potential at 0.75 V, respectively. The RDE voltammograms obtained for oxygen reduction show an increase of current density with the increasing rotating rate owing to the enhanced diffusion (Figure. S6b). The electron number transferred in the ORR is calculated to be 3.8 ~ 3.9 in the potential range of 0.5 V ~ 0.65 V using the Koutecky-Levich equation (inset of Figure. S6b).[3] The parallel and straight fitting lines also demonstrate first-order kinetic for the ORR in 0.1 M KOH.[4] The stability of Co_3O_4/mMWCNT composite for ORR was also investigated by controlled potential electrolysis at 0.7 V for 6 h, the ORR current retains > 90% of its original value after 6h. The above results show that the Co_3O_4/mMWCNT composite is also an efficient and stable bifunctional catalyst for both OER and ORR.

Supplementary Figure S1-S7

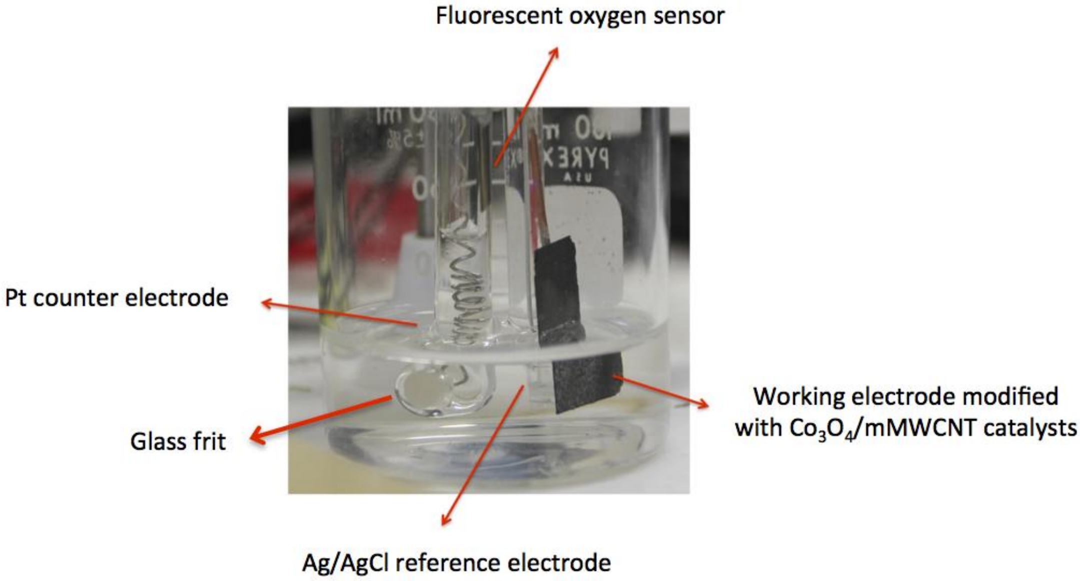

Figure S1. Setup of the electrochemical cell for the detection the generation of oxygen. Counter electrode was placed in a tube separated from the working electrode with glass frit.

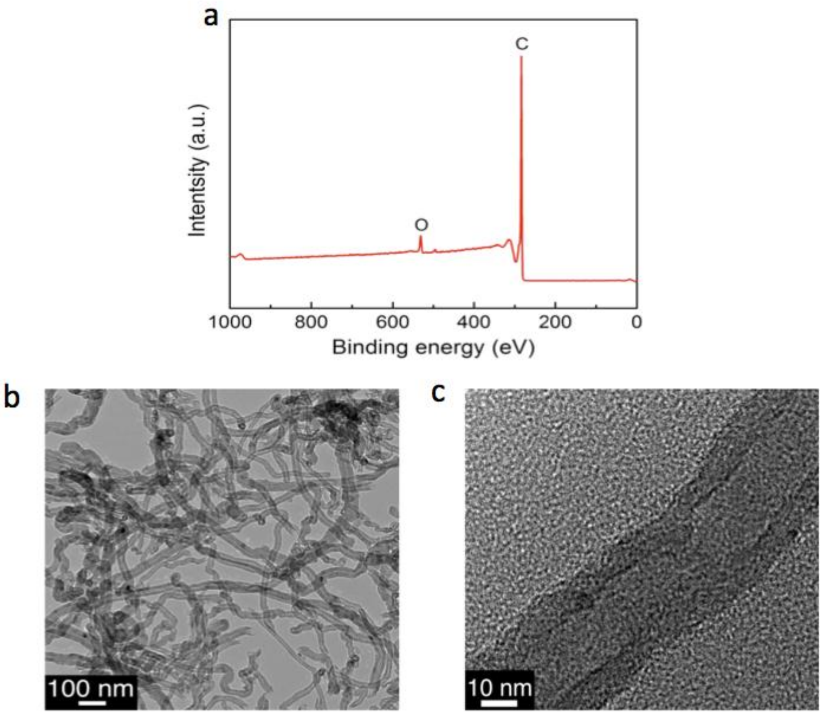

Figure S2. (a) XPS specta of mMWCNT. Only oxygen and carbon can be detected in this spectrum, indicating metal impurities such as Fe and Co, have been removed. TEM images of mMWCNTs at (b) low magnification and (c) high magnification. Most of the CNTs retained their original length and no sidewall breakage was observed. Also, no amorphous carbon was observed in mMWCNTs.

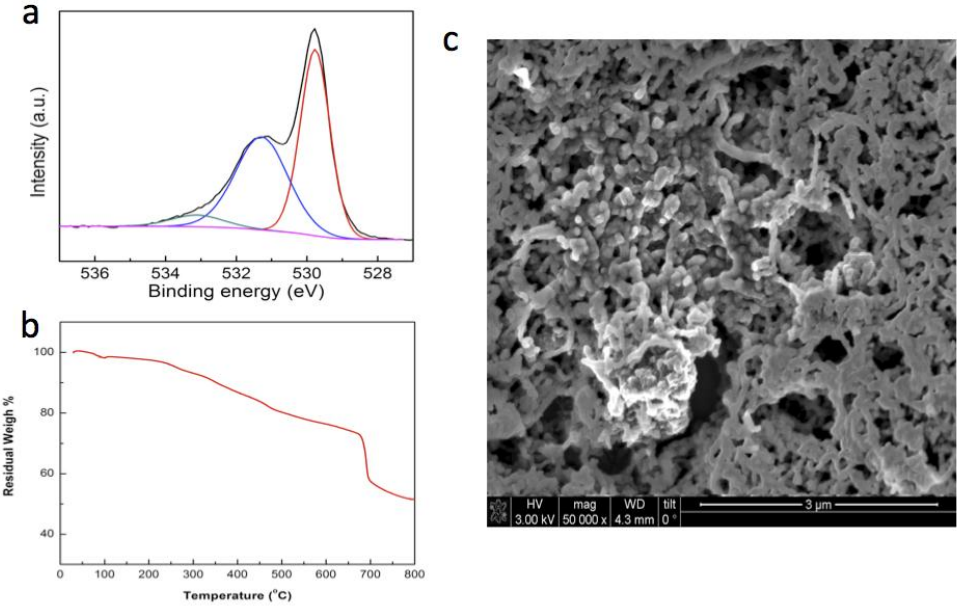

Figure S3. (a) High resolution O1s XPS spectrum of Co_3O_4/mMWCNT, (b) TGA curve of Co_3O_4/mMWCNT composites obtained in N_2 heated from room temperature to 800 ^{o}C and (c) SEM image of Co_3O_4/mMWCNT composite drop-casted onto the surface of an GC electrode. A porous film can be observed.

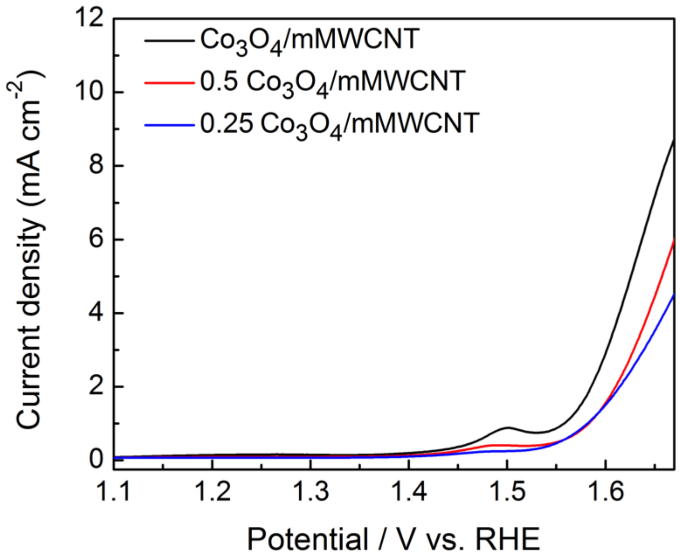

Figure S4. Linear sweep voltammogram curves obtained with glassy carbon electrodes modified with Co_3O_4/mMWCNT, Co_3O_4/mMWCNT with half loading of Co_3O_4 and Co_3O_4/mMWCNT with ¼ loading of Co_3O_4 composites, respectively, at 5 mV s^{-1} in 0.1 M KOH.

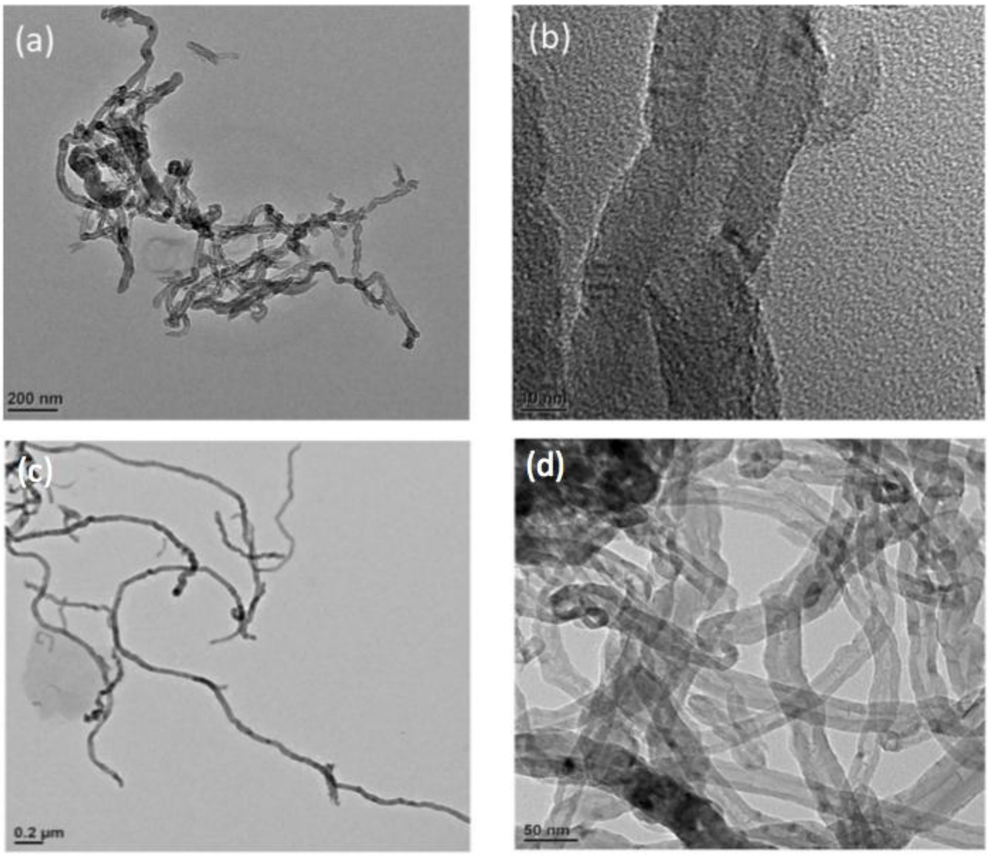

Figure S5. (a) and (b), HRTEM images obtained with sMWCNT at low magnification and high magnification. The length of CNTs was greatly shortened by the "cutting" effect in strong aicds, also, sidewall breakage can be observed. (c) and (d) are TEM images of wMWCNTs at low and high magnifications, respectively. Tube length and sidewall integrity were largely preserved.

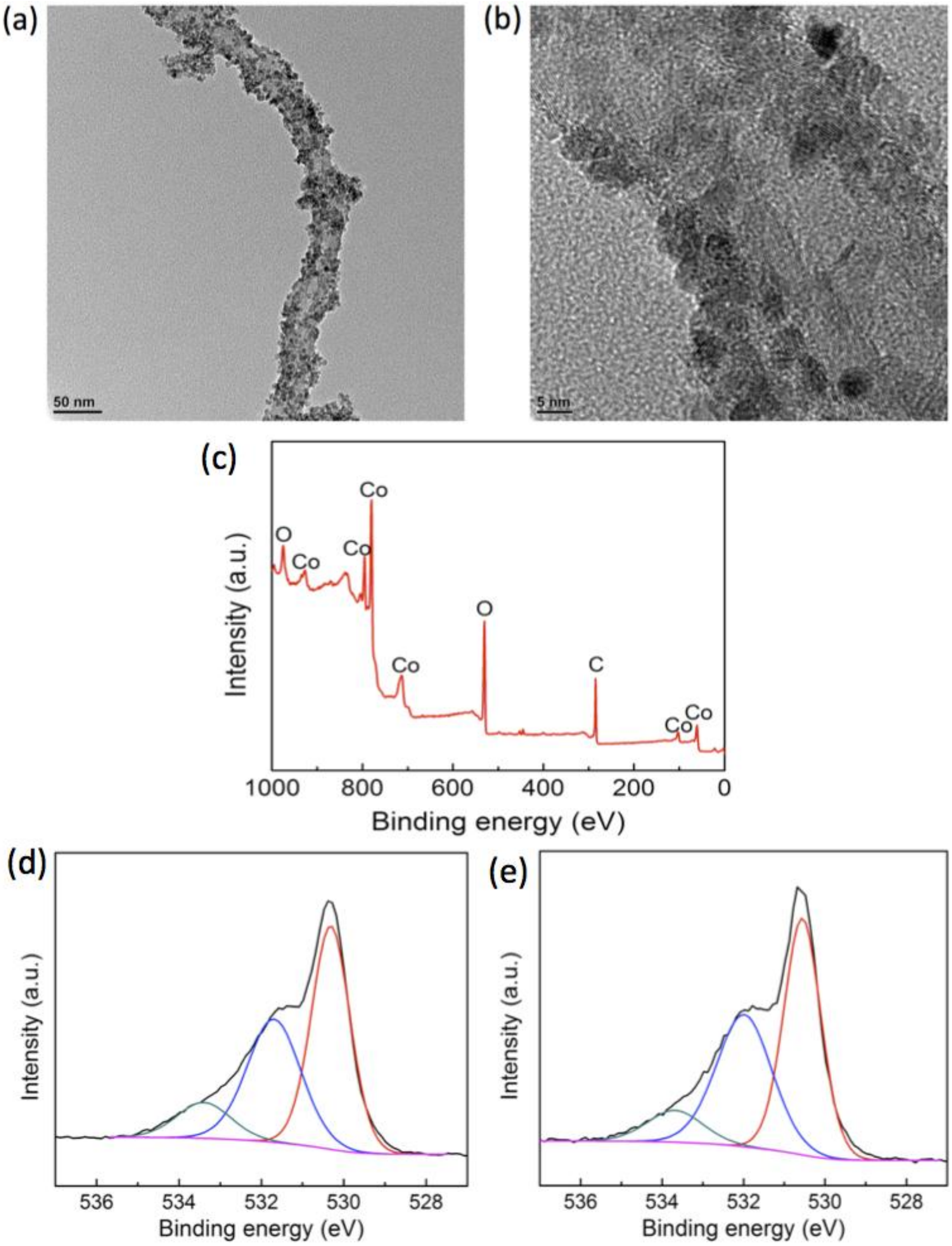

Figure S6. (a),(b), HRTEM images of Co_3O_4/mMWCNT composite after 5h OER at low magnification and high magnification, respectively. (c) XPS spectra of Co_3O_4/mMWCNT after 2h of OER. (d) and (e) are high resolution O1s XPS spectra of Co_3O_4/mMWCNT composite after 2h and 4h of OER, respectively.

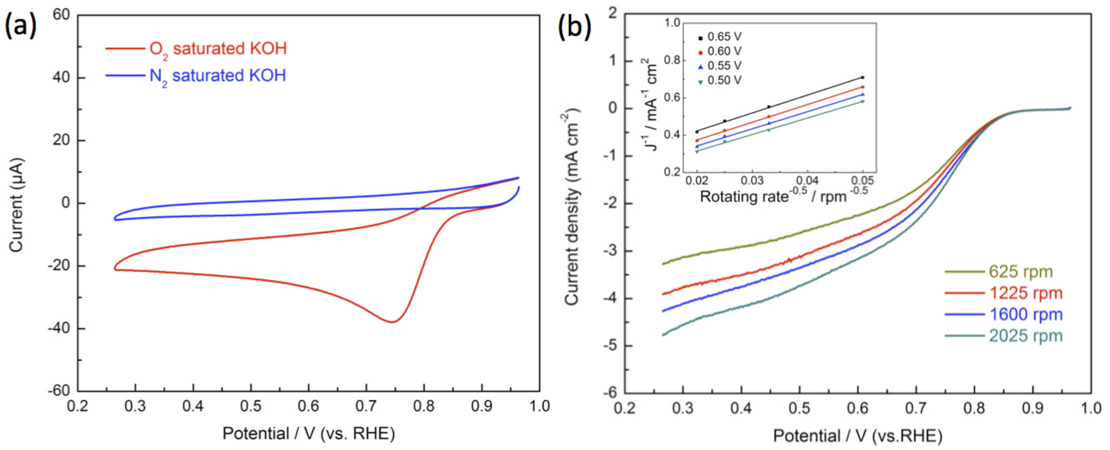

Figure S7. (a) Cyclic voltammograms obtained in 0.1 M KOH at a scan rate of 5 mV s^{-1} with a glassy carbon electrode modified with Co_3O_4/mMWCNT composite with O_2 saturated (red curve) and N_2 saturated (blue curve). (b) RDE voltammograms obtained at 5 mV s^{-1} with Co_3O_4/mMWCNT composite in O_2 saturated 0.1 M KOH with different rotation. The inset shows corresponding Koutecky-Levich plots at different potentials.

References

[1] Y. Y. Liang, Y. G. Li, H. L. Wang, J. G. Zhou, J. Wang, T. Regier and H. J. Dai, *Nat Mater*, 2011, **10**, 780.

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