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A Facile preparation of CoFe$_2$O$_4$ nanoparticles on Polyaniline-Functioned Carbon Nanotubes as Enhanced Catalysts for Oxygen Evolution Reaction

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Designing and preparing high efficient non-precious metal electrocatalyst for the oxygen evolution reaction (OER) is extremely urgent but still remains a challenge. In this study, a polyaniline-multiwalled carbon nanotubes (PANI-MWCNTs) supported, high performance CoFe$_2$O$_4$ nanoparticles (NPs) loading electrocatalyst (CoFe$_2$O$_4$/PANI-MWCNTs) is synthesized through a novel and simple in-situ process at modest condition. It is found that the introduction of PANI improves the synergistic effect between CoFe$_2$O$_4$ NPs and MWCNTs, so as to promote the electrical conductivity and stability of the catalyst. Meanwhile, PANI provides more active sites to attach CoFe$_2$O$_4$ NPs uniformly and tightly. By electrochemical measurement, the electrocatalyst displays excellent OER activities at a low overpotential of 314 mV for 10 mA cm$^{-2}$ current density and a small Tafel slope 30.69 mV dec$^{-1}$ in 1 M KOH at a scan rate of 5 mV s$^{-1}$. Furthermore, this electrocatalyst exhibits remarkably long durability evaluated by continuously cycling 1000 cycles and stably working at 0.54 V (vs. Ag/AgCl) for at least 40 h. The achieved results confirm that CoFe$_2$O$_4$/PANI-MWCNTs hybrid is an earth-abundant and cheap fabricated anode material for OER.

Introduction

With gradual depletion of non-renewable energy resources, renewable energy resources now attract widely attention. Hydrogen (H$_2$), as an important renewable energy resource, can be obtained by water splitting which is considered as an effective and environmentally friendly method. The water splitting reaction is composed of two half reactions: the oxygen evolution reaction (OER, 4OH$^{-}$ $\rightarrow$ 2H$_2$O + 4e$^{-}$ + O$_2$ in base) and the hydrogen evolution reaction (HER, 2H$^+$ + 2e$^{-}$ $\rightarrow$ H$_2$ in acid). However, the efficiency of H$_2$ production from water splitting is subject to the OER because of the sluggish kinetics of the OER at the anode. Thus, an efficient catalyst is needed to promote the 4-electron oxidation process and make OER proceed at low overpotential to lower the water splitting reaction energy barrier. The oxides such as ruthenium (IrO$_2$) and iridium (RuO$_2$) are known to be the most active electrocatalysts for the OER owing to the low overpotential and small Tafel slope. However, the high cost and scarcity of IrO$_2$ and RuO$_2$ hinder the widespread commercialization of fuel cells and metal-air batteries.

As is well-known, mixed transition metal oxides with spinel structure, due to their diverse advantages such as strong super paramagnetic property, good biocompatibility, high electronic conductivity, abundant resources, low cost and environmental friendliness, have attracted much attention. Therefore, numerous kinds of transition oxide catalysts can be used as superior OER electrocatalysts, such as Co$_3$O$_4$/N-doped graphene hybrid, Co–Fe–O/rGO, Ni$_2$Co$_{1-x}$O$_4$, Ni–Fe oxide and M$_x$Mn$_{1-x}$O$_4$ (M=divalent metals). Among the transition metal oxides, the spinel-type compounds with the general formula of AB$_2$X$_4$ (A, B=metal, X=chalcogen) have been shown as promising electrocatalysts for the OER. Li et al. have reported that MFe$_2$O$_4$ (M = Co, Ni, Cu, Mn, etc.) nanofibers (NFs) synthesized by electrospinning and subsequent thermal treatment processes exhibited considerable catalytic activities for both OER and H$_2$O$_2$ reduction/detection in alkaline media. Meanwhile, CoFe$_2$O$_4$ NFs have shown the highest catalytic activities among the MFe$_2$O$_4$ NFs. Bian et al. have also demonstrated the superior electrocatalytic activities of CoFe$_2$O$_4$ materials for the OER and Oxygen Reduction Reaction (ORR). Multiwalled carbon nanotubes (MWCNTs) are ideal electrocatalyst support owing to their high accessible surface area, good electronic conductivity and chemical stability. However, both size and high distributions of metal nanoparticles (NPs) directly deposited on MWCNTs are usually
not uniform to ascribe to their inert surface. Wrapping carbon nanotubes with conducting polymers is a good way to solve this issue. Among conducting polymers, polyaniline (PANI) is one of the most widely studied conducting polymers on account of its unique π-conjugated structures, which lead to good environmental stability and unique redox properties. Moreover, PANI has numerous amino groups as anchor sites for metal ions, preventing metal NPs from aggregating. Spinel-type oxides are usually synthesized through solid-state method, hydrothermal technique, co-precipitation, microemulsion route and sol-gel process. And in general, these traditional methods need grinding or firing the mixtures of the corresponding metal precursors, which call for elevated temperature and prolonged time to overcome the reaction energy barriers. Therefore, it remains challenging to synthesize homogenous and ultrasmall nanocrystalline spinels under facile conditions. In this work, a novel and simple in-situ method has been reported to prepare monodisperse CoFe$_2$O$_4$ NPs on the PANI-covered multiwalled carbon nanotubes (CoFe$_2$O$_4$/PANI-MWCNTs) at mild temperature and room atmosphere. The synthesis of the procedure is illustrated in Scheme 1. The aniline monomer was firstly selectively adsorbed onto the carbon surface via preferential π-π conjugation between the aniline and acid-treatment MWCNTs surface and then polymerized in situ on the carbon surface via ammonium peroxydisulfate (APS) and FeSO$_4$ oxidation in acidic solution. Subsequently, the aqueous solution containing a fixed ratio of 2:1 Fe$^{3+}$/Co$^{2+}$ precursors and hydrazine hydrate was heated at 120°C for 4 hours to obtain CoFe$_2$O$_4$ NPs. The as-synthesized CoFe$_2$O$_4$/PANI-MWCNTs hybrid performed remarkable catalytic activity and long-term stability towards OER in alkaline solution, exceeding CoFe$_2$O$_4$ NPs and CoFe$_2$O$_4$/MWCNTs hybrid. The results further demonstrated PANI in this hybrid played a crucial role in mediated functionalization. It not only improved the catalytic performance for the OER, but also led to homogeneous distribution of CoFe$_2$O$_4$ NPs.

### Experimental

**Materials**

Multi-walled carbon nanotubes were purchased from Shenzhen Nanotech Port Co. Ltd. sulfuric acid (95%~98% w/w), nitric acid (65%~68% w/w), hydrazine chloride (36%~38% w/w), ammonium peroxydisulfate ((NH$_4$)$_2$S$_2$O$_8$ ≥98% w/w), iron (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O ≥99% w/w), Iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O ≥99% w/w), Cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O ≥99% w/w), Ruthenium(IV) oxide (99.95% metal basis), Iridium(IV) oxide (99.9% metal basis), Hydrazine monohydrate (≥80% w/w), deionized water (18.2 Ω cm) were commercially available and used throughout the experiments. All the commercialized chemicals used in this study were of analytical grade and not further purified.

**Acid-treatment of MWCNTs**

The MWCNTs were treated with an acid mixture in the presence of sonication for their functionalization. Specifically, 200 mg MWCNTs were mixed in a 500 mL round bottle flask with 150 mL HNO$_3$ and 50 mL H$_2$SO$_4$ (3:1(v/v)) at 75 °C for 4 h. After reaction, the obtained black powder was separated by suction filtration and washed with deionized water until its pH value became approximately 7 before drying at 70 °C.

**Preparation of PANI-MWCNTs**

The PANI-MWCNTs were prepared by the in-situ polymerization of aniline in the presence of a carbon nanotube suspension. To synthesize the PANI-MWCNTs composite (e.g., aniline monomer: MWCNTs = 1:20 (w:w)), 100 mg acid-treatment MWCNTs and 10 mL of 2 M HCl aqueous solution was sonicated at room temperature for about an hour and then mixed with 5 μL aniline monomer to sonicate for another half an hour. 5 mL of 2 M HCl aqueous solution containing 100 mg (NH$_4$)$_2$S$_2$O$_8$ and 5 mg FeSO$_4$·7H$_2$O which served as the oxidant was later added dropwise with vigorous stirring. The reaction mixture was constantly stirred in an ice bath (< 5 °C) for 1 h and then reacted at room temperature for 3 h. The products were purified by centrifugation with ethanol and deionized water and then dried in vacuum freezing dryer to constant weight (101 mg, 96.2%). PANI-MWCNTs composites with weight ratios of 1:1, 1:2, 1:5, 1:10, 1:35, 1:50 (w:w) were also prepared by the similar method. The product amounts and yield of PANI-MWCNTs composites were provided in Table S1.

**Preparation of CoFe$_2$O$_4$/PANI-MWCNTs$_{1:20}$(40 wt.%) composites**

The PANI-MWCNT$_{1:20}$ (10 mg) was suspended in 10 mL of EtOH/H$_2$O (1:1, v:v) with ultrasonic treatment for 30 min to form a homogeneous solution. After sonication, designated amounts of FeCl$_3$·6H$_2$O (15.34 mg) and Co(NO$_3$)$_2$·6H$_2$O (8.26 mg) with 2:1 molar ratio were added to the above solution and the mixed solution was sonicated for another 10 min. Then, 20 mL of hydrazine hydrate were added to the mixture and stirred for half an hour. Afterwards, the above mixture was heating at 120 °C for 4 h. The product (14.7 mg, 88.0%) was collected by centrifugation and washed with deionized water and ethanol.
and then dried at 50 °C for 12 h. Other composites with different CoFe₂O₄ loading amounts (20 wt.%, 30 wt.%, 50 wt.%, 60 wt.%) and without support were also prepared with the same procedure. The product amounts and yield of CoFe₂O₄/PANI-MWCNTs₁:₂₀ were shown in Table S2.

Characterization

The morphologies and microstructures of CoFe₂O₄/PANI-MWCNTs₁:₂₀ (40 wt.%) composites were observed by a FEI-TECNAI G2 transmission electron microscope operating at 200 kV. TEM (FEI company). Elemental composition data was collected by Energy dispersive X-ray (EDX) performed using a TECNAI G2 microscope. The crystal structure of the sample was examined by X-ray diffraction (XRD) which was performed on Rigaku D/max-2400 diffractometer, using Cu-Kα radiation as the X-ray source in the 2θ range of 10–90°. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument.

Electrochemical measurements

Electrochemical measurements were carried out in the electrochemical workstation (CHI 660E, shanghai chenhua) with a standard three-electrode system at room temperature. The three-electrode system used glassy carbon electrode (GCE) with 3 mm diameter (catalyst loading 0.285 mg cm⁻²) as working electrode, a platinum wire as the counter electrode and an Ag/AgCl (3 M KCl) electrode as the reference. The working electrode was polished mechanically with Al₂O₃ powders (Aldrich, 0.05 mm) and then cleaned with ethanol and deionized water, respectively. The catalyst ink was formed with 4 mg catalysts and 30 μL Nafion solutions (0.5 wt.%) dispersed in 1 mL water-ethanol solution with volume ratio of 1:1, followed by sonicating for at least 30 min. Then, 5 μL well-dispersed suspension (containing 20 μg catalyst) was loaded onto working electrode and dried at room temperature. The working electrodes were scanned several times until the signals were stabilized and then data were collected.

The electrolyte was 1 M KOH solution prepared from deionized water. Linear sweep voltammetry (LSV) worked from 0 to 1.0 V vs. Ag/AgCl at a scan rate of 5 mV s⁻¹ in a N₂-saturated electrolyte. The electrochemical impedance spectroscopy (EIS) measurements were carried out in the same configuration at 0.50 V vs. Ag/AgCl from 10⁵ to 0.01 Hz with an AC voltage of 5 mV. The durability test for OER was performed on the catalysts by cycling the electrode potential between 0 and 0.8 V vs. Ag/AgCl at 200 mV s⁻¹ for 1000 cycles, after which the polarization curves for the OER was measured. The electrical double layer capacitor (Cdl) were measured from double-layer charging curves using cyclic voltammograms (CVs) in a small potential range of 1.22–1.28 V vs. RHE at different scan rates (2–10 mV s⁻¹). Working electrodes were scanned for several potential cycles until the signals were stabilized, and then the CV data were collected. The plot of current density (at 1.25 V vs. RHE) against scan rate has a linear relationship and its slope is the Cdl. The current density was normalized to the geometrical surface area. All the potentials reported in our work were against reversible hydrogen electrode (RHE) through RHE calibration. For conversion of the obtained potential (vs. Ag/AgCl) to RHE, eq 1 was used

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times pH \] (1)

Result and discussion

Fig. 1A illustrates the morphologies of MWCNTs, we can obviously observe that the surface of the nanotubes is smooth. However, there is an amorphous component wrapping the outside of the tube perimeter in Fig. 1B, demonstrating that the PANI is successfully covered on MWCNTs. Fig. 1C-D shows TEM micrographs of CoFe₂O₄/MWCNTs (40 wt.%) hybrid and CoFe₂O₄/PANI-MWCNTs₁:₂₀ (40 wt.%) hybrid. On the bare MWCNTs support, CoFe₂O₄ metal particles prone to cluster, but when supported on MWCNTs with PANI functionalization, CoFe₂O₄ NPs are more evenly separated and well dispersed in the range of 3.28–10.59 nm with an average particle size of 6.22 nm. The Scanning electron microscopy (SEM) and TEM images of CoFe₂O₄/PANI-MWCNTs₁:₂₀ (20 wt.%, 30 wt.%, 50 wt.%, and 60 wt.%) are also provided in Fig. S1. The EDX pattern in the insert of Fig. 1F reveals that Co, Fe, C, O and N are main elements and Cu element arising from copper grid is also detected. The existence of the N element further indicates that the MWCNTs have been functionalized by PANI. Fig. 1G-
H show high-resolution transmission electron microscopy (HRTEM) images of the catalyst samples. The lattice planes with an interlayer distance of 0.291 nm correspond to CoFe$_2$O$_4$ (220) crystal planes. The X-ray diffraction (XRD) patterns of samples are shown in Fig. 2A. The diffraction peaks at 26.0°, 43.2° are assigned to (002) and (100) planes of hexagonal graphite. And the appearance of these peaks with high intensity suggests that MWCNTs have a high graphic structure. For PANIMWCNTs, the diffraction peaks with lower intensity are similar to MWCNTs, which indicates that an extremely thin PANI film is covered on the MWCNTs. The XRD patterns of CoFe$_2$O$_4$/PANI-MWCNTs$_{1:20}$ (40 wt.%) hybrid at 2θ = 18.4°, 30.2°, 35.4°, 42.9°, 56.9° and 62.4° correspond to (111), (220), (311), (400), (511) and (440) crystal planes of CoFe$_2$O$_4$ (PDF#22-1086), while the peak at around 26° is attributed to (002) planes of MWCNTs. The results of XRD patterns prove that the CoFe$_2$O$_4$ NPs are efficiently immobilized on PANIMWCNTs and have a highly crystalline fcc phase.

To obtain the oxidation state and the surface chemical composition of CoFe$_2$O$_4$/PANI-MWCNTs$_{1:20}$ (40 wt.%) hybrid, X-ray photoelectron spectroscopy (XPS) measurements are the composite in the Co 2p region is shown in Fig. 2C. It can be deconvoluted into four peaks. The peaks with binding energies (BE) of about 780.4 and 786.1 eV are in accord with Co 2p$_{3/2}$ and its shakeup satellites, while the higher BE peaks around 796.1 and 802.7 eV correspond to Co 2p$_{1/2}$ and its shakeup satellites, respectively. The existence of Co 2p$_{1/2}$ and Co 2p$_{3/2}$ main peaks and shake-up satellite peaks indicates the presence of Co$^{3+}$ in the high-spin state. For the high-resolution XPS spectrum of Fe 2p (Fig. 2D), all the deconvoluted Fe 2p spectra generally show two main peaks for Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ at a BE of around 710.7 and 724.2 eV, and Fe 2p$_{1/2}$ accompanied by a satellite line visible at a BE of around 718.3 eV, only indicative of the presence of Fe$^{3+}$ cations. Meanwhile, the presence of the peak around 713.3 eV implies that the Fe$^{2+}$ species exist in more than one coordination environment. This could ascribe to the high affinity of Co$^{3+}$ ions in octahedral sites of inverse spinel structure, demonstrating the existence of CoFe$_2$O$_4$. According to the C 1s XPS spectra of the catalyst as shown in Fig. 2E, the peaks at 284.6, 285.2, 286.6, 288.7 and 290.6 eV corresponding to the oxygen and carbon atoms in the forms C=C, C=O, O=C and O=C=O, respectively. The C 1s XPS spectrum of Fe 2p (Fig. 2D), all the deconvoluted Fe 2p spectra display the XPS spectrum of N 1s, which is composed of three peaks at about 398.8 eV (N–), 400.0 eV (N=), and 401.2 eV (–N=), which indicates the acid-treatment MWCNTs were successfully decorated by PANI. The highest BE peak observed in N$^+$ is due to the protonated amine units.

The electrochemical activity of the support materials for OER has been evaluated with polarization curves. The polarization curves for a series of MWCNTs which are decorated with different mass ratios of PANI are measured in N$_2$-saturated 1M KOH solution with a scan rate of 5 mV s$^{-1}$ at room temperature. It is well-known that MWCNTs is a poor OER catalyst with a slight current density. However, decorating MWCNTs with PANI can promote the electrochemical activity. As is shown in Fig. 3, PANI-MWCNTs$_{1:20}$ hybrid is considered as the best support material for OER due to the most negative onset potential and highest current density. Meanwhile, other
PANI-MWCNTs hybrids also exhibit better OER catalytic activity than pure MWCNTs, assuring that the PANI-MWCNTs material has a high effective surface area which is beneficial for electronic transmission. Generally speaking, MWCNTs functioned with PANI is available for promoting synergistically the OER.

According to the polarization curves in Fig. 4A, the PANI-MWCNT_{1:20} hybrid with different loading amounts of CoFe_{2}O_{4} is evaluated in the same condition. The contents of CoFe_{2}O_{4} on the PANI-MWCNT_{1:20} is identified by atomic absorption spectroscopy (AAS) as 18.95 wt.% 28.14 wt.% 38.78 wt.% 47.33 wt.% 58.64 wt.%, which are close to theoretical value (Table S3). As we all know, the overpotential for different catalysts to deliver a 10.0 mA cm^{-2} current density is a metric related to solar fuel synthesis. The overpotential at a current density of 10.0 mA cm^{-2} of these CoFe_{2}O_{4}/PANI-MWCNT_{1:20} samples with various CoFe_{2}O_{4} loadings (20 wt.% 30 wt.% 40 wt.% 50 wt. and 60 wt.%) are estimated to be 353, 342, 314, 324 and 344 mV, respectively, which show a volcanic type trending. With the increase of CoFe_{2}O_{4} content, the OER activity increases firstly and reaches the maximum value when the CoFe_{2}O_{4} content is 40 wt.%. Then it declines sharply, indicating that the synergistic effect is not apparent when the loading amount of CoFe_{2}O_{4} is too low or too high. Meanwhile, the Tafel plots of these catalysts which derive from the polarization curves fit well with the Tafel equation \eta = a + blog(j), where \eta is the over-potential, b is the Tafel slope and j is the current density] at different overpotential ranges, and only the linear portions were selected to obtain a clear comparison. As is shown in Fig. 5B, the Tafel slopes of all the catalysts are between ~30.69 and ~57.87 mV dec^{-1}. A smaller Tafel slope means a faster increase of the OER rate with increasing potential. Above all, CoFe_{2}O_{4}/PANI-MWCNT_{1:20} (40 wt.%) hybrid is the relatively optimal electrocatalyst for its low overpotential (314 mV) and small Tafel slope (~30.69 mV dec^{-1}). Furthermore, a detailed comparison of different highly active spinel-type OER catalysts was shown in Table S4, and further confirming the outstanding catalytic behavior of CoFe_{2}O_{4}/PANI-MWCNT_{1:20} (40 wt.%) hybrid.

Moreover, the catalytic activity of CoFe_{2}O_{4}/PANI-MWCNT_{1:20} (40 wt.%) hybrid is compared with CoFe_{2}O/MWCNTs (40 wt.%) hybrid, pure CoFe_{2}O NPs and PANI-MWCNTs in the same condition. As is shown in Fig. 5, the PANI-MWCNTs hybrid possesses relatively negligible catalytic activity due to the low current density and high Tafel slope (126.39 mV dec^{-1}). The OER onset potential of the CoFe_{2}O/PANI-MWCNT_{1:20} (40 wt.%) hybrid is about 1.50 V (vs. RHE) in 1 M KOH (an overpotential only about 270 mV, at pH 13.6), which is much more negative than that of the CoFe_{2}O/PANI-MWCNTs (40 wt.%) composite and pure CoFe_{2}O NPs electrodes. Particularly, the Tafel slope of CoFe_{2}O/PANI-MWCNT_{1:20} (40 wt.%) hybrid (~30.69 mV dec^{-1}) is much smaller than those of CoFe_{2}O/PANI-MWCNTs (40 wt.%) hybrid (~38.06 mV dec^{-1}) and pure CoFe_{2}O NPs (~54.73 mV dec^{-1}). The results strongly demonstrate that the CoFe_{2}O/PANI-MWCNT_{1:20} (40 wt.%) hybrid has excellent OER catalytic activities in alkaline solution in comparison to pure CoFe_{2}O NPs and CoFe_{2}O/PANI-MWCNTs (40 wt.%) hybrid. This is probably contributed to PANI which could promote the synergistic effect between CoFe_{2}O NPs and MWCNTs components.

In addition, by comparing CoFe_{2}O/PANI-MWCNT_{1:20} (40 wt.%) hybrid with commercial IrO_{2} and RuO_{2} in Fig. S2, the catalyst yielded lower overpotential at current density of 10 mA cm^{-2}, whereas it displayed higher overpotential at current density of 20 mA cm^{-2} for IrO_{2} and 50 mA cm^{-2} for RuO_{2}. As
also observed, the Tafel slope of the catalyst is much lower thanIrO₂ (62.50 mV dec⁻¹) andRuO₂ (91.89 mV dec⁻¹).

We also estimated the electrochemically active surface area
by the electrochemical double-layer capacitances (Cₐ) using a
simple cyclic voltammetry (CV) method. Current response in
the potential window used for the CV (1.22–1.28 V vs. RHE) at
different scan rates (2–10 mV s⁻¹) should be due only to the
charging of the double-layer (Fig. 6A, B and C). The Cₑg for
each sample, which should be directly proportional to the
surface area, are extracted by plotting the Δj= j–jₑg at a given
potential (1.25 V vs. RHE) against the CV scan rates (Fig. 6D)
47, 48. By calculating the slope from the linear relationship of
the current density against the scan rate, Cₑg of the CoFe₂O₄/PANI-
MWCNTs₁:2₀ (40 wt.%) hybrid is confirmed to be ~30 mF cm⁻²,
which is much higher than that of CoFe₂O₄/MWCNTs (40 wt.%) hybrid (~22 mF cm⁻²) and pure CoFe₂O₄ NPs (~11 mF cm⁻²). The results demonstrated that the CoFe₂O₄/PANI-
MWCNTs₁:2₀ (40 wt.%) hybrid has relatively larger active
surface area. Meanwhile, this increase in Cₑg indicates better
exposure and enhanced utilization of electroactive sites, which
certainly ascribe to the introduction of PANI and contribute to
the improved catalytic performance.

Additionally, we used electrochemical impedance
spectroscopy (EIS) to investigate the electrode kinetics under
the catalytic OER operating conditions. The EIS data of
CoFe₂O₄/PANI-MWCNTs₁:2₀ (40 wt.%) hybrid, CoFe₂O₄/
MWCNTs (40 wt.%) hybrid and pure CoFe₂O₄ NPs have been
detected and compared at an operating potential of 0.50 V vs.
Ag/AgCl in Fig. 7A. It is revealed that the CoFe₂O₄/PANI-
MWCNTs₁:2₀ (40 wt.%) hybrid shows a much smaller radius of
the semicircle in the Nyquist plots compared with
CoFe₂O₄/MWCNTs (40 wt.%) hybrid and pure CoFe₂O₄ NPs,
indicating that the reaction sites of the electrode increased,
which leads to facile transfer of charge species (electron and
ions OH⁻). The reason can be attribute to the presence of the
PANI, which makes the CoFe₂O₄ NPs attach to MWCNTs closely.
Also, the smaller Tafel slope and lower resistance correspond
to a more favorable OER kinetics of the CoFe₂O₄/PANI-MWCNTs₁:2₀ (40 wt.%) hybrid.

The stabilities of catalysts for the OER were appraised with
the chronoamperometric method in Fig. 7B. It can be observed
that the Current-time (i–t) curves of the CoFe₂O₄/PANI-
MWCNTs₁:2₀ (40 wt.%) hybrid worked at a potential of 0.54 V
(vs. Ag/AgCl) for at least 40 h. In the initial period, the decay
current density decreases rapidly. However, during the whole
time, the larger residual current is nearly constant. Furthermore,
the durability test was also carried out by cycling catalyst
continuously for 1000 cycles (the inset of Fig. 7B). At the end
of the cycling, it afforded similar i-V curves as initial test.
Demonstrating the high stability of CoFe₂O₄/PANI-
MWCNTs₁:2₀ (40 wt.%) in alkaline. Moreover, the stability of
the CoFe₂O₄/PANI-MWCNTs₁:2₀ (40 wt.%) hybrid has been compared with CoFe₂O₄/MWCNTs (40 wt.%) hybrid by i–t curves at the same condition in Fig. S3. Obviously, the
CoFe₂O₄/PANI-MWCNTs₁:2₀ (40 wt.%) hybrid has higher
current density, indicating that the introduction of PANI to this
electrocatalyst can improve the synergistic effect between
CoFe₂O₄ NPs and MWCNTs to promote stability of the
catalyst.

Conclusion

In conclusion, we have developed a novel in-situ synthetic
method to prepare CoFe₂O₄ NPs on the as-prepared
polyaniline-multiwalled carbon nanotubes at mild temperature
(120 °C) and room atmosphere. The mass ratios of PANI-
MWCNTs and the loading amounts of CoFe₂O₄ are explored in
this paper. Our study shows that the introduction of PANI could
improve the synergistic effect between CoFe₂O₄ NPs and
MWCNTs, so as to promote the electrical conductivity and
stability of the catalyst. Meanwhile, PANI provides more active
sites to result in a homogeneous distribution of CoFe₂O₄ NPs.
The OER activities of the CoFe₂O₄/PANI-MWCNTs₁:2₀ (40 wt.%) hybrid were further compared with the
CoFe₂O₄/MWCNTs (40 wt.%) and pure CoFe₂O₄ NPs. By
comparison, we found that the CoFe₂O₄/PANI-MWCNTs₁:2₀ (40 wt.%) hybrid exhibits the most superior oxygen evolution
activity and strong durability as a promising alternative to noble
metal catalysts in OER. It is believed that this simple
preparation method paved a possible way to fabricate a range of
spinel-type oxide/PANI-MWCNTs based composite as an
outstanding OER electrocatalyst.

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A Facile preparation of $\text{CoFe}_2\text{O}_4$ nanoparticles on
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