RSC Advances



View Article Online

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Cite this: RSC Adv., 2015, 5, 27823

Reduction-induced surface amorphization enhances the oxygen evolution activity in Co_3O_4 †

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Received 17th January 2015 Accepted 13th March 2015

DOI: 10.1039/c5ra00995b

www.rsc.org/advances

Modifying crystalline Co_3O_4 by thermal H_2 annealing and air exposure produced an amorphous surface layer consisting of mixed hydrated cobalt hydroxide/carbonate species and remarkably enhanced the oxygen evolution activity.

The increasing public concern about global climate change and the energy crisis demands more efficient sustainable technologies for renewable carbon-neutral energy. The oxygen evolution reaction (OER) plays a pivotal role in a number of energy conversion and storage processes and devices, such as watersplitting and rechargeable metal–air batteries.^{1–5} Taking the anodic reaction in water splitting for instance, one dioxygen molecule is generated from two water molecules through a fourelectron transfer reaction coupled with the formation of four protons (eqn (1)).^{6,7}

$$2H_2O \leftrightarrow O_2\uparrow + 4e^- + 4H^+ E = 1.23 \text{ V vs. RHE}$$
 (1)

In practical operation, overpotential (η) is required to overcome the sluggish reaction kinetics. Overpotential requires the input of extra energy which often reduces the conversion efficiency from electrical energy to chemical energy. How to reduce the OER overpotential in order to improve the energy efficiency remains a great challenge. Precious noble metal-based materials, such as IrO₂ or RuO₂, are the most active OER electrocatalysts that have shown the best energy efficiency.⁸ However, due to the scarcity and high cost of precious metals, their scaleup application has been impeded to some extent. Therefore searching for non-noble active OER electrocatalysts is of paramount importance.

First-row transition metal oxides, such as spinel oxides and perovskites, have received increasing interest for their great potentials as alternative low-cost OER electrocatalysts. Among them, spinel oxide Co₃O₄ has shown good activity and stability in OER.9-11 By reducing the particle size or increasing the porosity of Co₃O₄, more active sites can be generated. As a result, porous Co3O4 nanoparticles exhibited superior OER activity.12,13 Lattice substitution with Li, Ni, or Cu for Co also enhanced the OER activity.11,14-17 Au-decorated Co3O4 showed enhanced OER activity,18-20 which is attributed to the facilitated oxidation of Co(2+) and Co(3+) in Co₃O₄. Gerken et al. suggested that the surface of Co₃O₄ is reformed into a layered structure during the OER process which is accompanied by the oxidation of Co species.²¹ This is supported by the phase transformation of Co₃O₄ to layered CoOOH during OER according to in situ Raman spectroscopy and X-ray diffraction (XRD).19,22,23 Recently, it has been reported that mesoporous Co3O4 nanowires treated with NaBH₄ exhibited excellent OER activity. And this superior performance was attributed to the large surface area and the oxygen vacancies which lead to higher conductivity and electrocatalytic activity.24 Obviously the OER activity of Co3O4 depends on many factors such as morphology, phase structure, crystallinity, composition, co-catalyst, and surface properties.

Amorphous OER electrocatalysts have shown great interest recently. Amorphous Co_3O_4 film occupied more active sites and hence displayed superior OER activity compared to the crystalline film at low overpotentials.²⁵ An amorphous CoPi or CoBi film synthesized by electrodeposition has attracted intensive study due to its application in mild environment (neutral pH, room temperature).^{6,26–29} Its superior performance is attributed to the small size of CoO_x fragments. Besides cobalt, other metal based amorphous materials also show promising performance towards OER. Electrodeposited amorphous FeOOH film exhibits OER activity comparable to that of CoBi film.³⁰ Berlinguette *et al.* reported that the OER catalytic properties of amorphous Fe₂O₃ is superior to those of crystalline Fe₂O₃ and they synthesized an amorphous oxides Fe_{100-y-z}Co_yNi_zO_x with OER activity comparable to those of noble metal oxides.³¹

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[†] Electronic supplementary information (ESI) available: Experimental section, XPS fitting parameters, scheme of surface transformation, working principle of RRDE, TOF calculation, and stability test. See DOI: 10.1039/c5ra00995b

OER activity of carbon-supported amorphous nanoparticles $Ni_{0.69}Fe_{0.31}O_x$ outperformed the commercial noble Ir/C catalyst.³² Even for the crystalline perovskites, surface amorphization contributes to the improvement of OER catalytic activity.³³ It is perceived that the number of active sites in amorphous materials is higher than that in crystals due to the small clusters in amorphous phase.

It has been reported that the thermal H_2 treatment introduced a disordered layer on the surface of TiO₂ which facilitated the photocatalytic activities substantially.³⁴ It is speculated that OER activity of Co₃O₄ may be improved by H₂-reductioninduced surface amorphization. In this work, we report the surface amorphization of Co₃O₄ crystals caused by thermal H₂ reduction and stabilization in air. We demonstrate the largely improved OER activity which is facilitated by the amorphous surfaces. The crystal structure and the surface properties of the modified Co₃O₄ crystals were studied by using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The results suggested that the mixed hydrated cobalt hydroxide/carbonate species in the surface amorphous layer are essential to the performance improvement.

Fig. 1a shows the thermal gravimetric (TG) curve for the thermal reduction of as-prepared Co₃O₄ (Co₃O₄-AP) under flow of 5 vol% H₂ + N₂. Before 130 °C, the 1.6% weight loss is attributed to the removal of the absorbed species on the surface, such as water. In the range of 130 °C and 600 °C, the total weight loss is 26.6% which corresponds to the theoretical mass loss (26.5%) for complete transformation of Co_3O_4 into Co metal. The reduction proceeds in two steps: a 6.9% weight loss occurs at the first step ranging from 130 °C to 320 °C, while the second step from 350 °C to 600 °C has a 19.7% weight loss. No obvious weight loss is observed between 320 °C and 350 °C. The Co₃O₄-AP sample was reduced at 320 °C for 1 h; otherwise the longterm reduction at higher temperature could result in pure Co metal. The reduced sample was stored in ambient air without particular protection (denoted as Co₃O₄-R). We show later that the surface of Co₃O₄-R became an amorphous layer containing different Co(+2, +3) species after the ambient storage. X-ray diffraction (XRD) was adopted to study the phase evolution from Co₃O₄-AP to Co₃O₄-R. Fig. 1b reveals that Co₃O₄-AP is pure Co₃O₄ while additional reducing species (CoO and Co) exist in Co₃O₄-R. Peaks related to CoO and Co are broad, indicating their low crystallinity. Crystal sizes of Co₃O₄ are estimated to be 21 nm for Co₃O₄-AP and 17 nm for Co₃O₄-R by using the Scherrer equation.

XPS was used to analyze the surface chemical species on the original and reformed samples. The fitted XPS profiles are shown in Fig. 2 and the fitting parameters are listed in Table S1.[†] As shown in Fig. 2a, Co_3O_4 -AP exhibited typical Co $2p_{3/2}$ spectrum.^{35–37} The principle peak was fitted by three sub-peaks: one at 779.5 eV represents Co(3+); the other two at 781 eV and 782.5 eV are assigned to Co(2+). Co(2+) is characteristic of higher binding energy and broad principle peak.³⁷ Peaks S1 and S2 are assigned to shake-up satellites. What is interesting is that the Co $2p_{3/2}$ spectrum of Co_3O_4 -R is almost the same with that of Co_3O_4 -AP, containing peaks related to Co(3+) and Co(2+) with



Fig. 1 (a) Thermal gravimetric curve of the reduction of Co_3O_4 -AP recorded at the heating rate of 2 °C min⁻¹ under reducing environment of mixture 5 vol% H₂ + N₂. (b) XRD profiles of Co_3O_4 -AP (blue) and Co_3O_4 -R (red).

similar ratios. This result is consistent with the result of thermal-H₂-treated TiO₂ which showed similar Ti 2p spectrum to that of pristine TiO₂.^{34,38} But it is different from the XPS results of NaBH₄-reduced TiO₂ and Co₃O₄ which exhibited negative shift in the Ti 2p and stronger Co(2+) signal in Co 2p respectively.^{24,39} This confirms the re-oxidation of the reduced sample on exposure to air which is reasonable considering that Co and CoO are thermodynamically unstable in atmospheric condition. It has been known widely that CoO is easily oxidized to Co₃O₄ under mild ambient condition.^{35,40} The surface of Co metal is oxidized to hydrated cobalt oxide or cobalt (oxy) hydroxide upon exposure to air at room temperature.^{41,42} Nonetheless the XRD results reveal Co and CoO phases in the bulk of Co₃O₄-R sample, which could imply that the oxidation of Co₃O₄-R is likely limited to the surface.

To elaborate the detailed surface chemical structure, the O 1s and C 1s spectra of Co_3O_4 -R were recorded and compared



Fig. 2 XPS high resolution spectra of Co_3O_4 -AP (a-c) and Co_3O_4 -R (d-f): Co $2p_{3/2}$ (a and d), O 1s (b and e) and C 1s (c and f).

with those of Co₃O₄-AP. The fitting parameters are listed in Table S1.[†] O 1s spectrum of Co₃O₄-AP is fitted by three components which are assigned to stoichiometric O²⁻ bonded to Co, non-stoichiometric O⁻ compensating for deficiencies in the subsurface and weakly absorbed species.35 The O 1s spectrum for Co₃O₄-R is quite different. Aside from the peak corresponding to O^{2-} , there are three peaks at higher binding energy that are assigned to oxygen in OH⁻, CO₃²⁻ and H₂O, respectively, which indicate the formation of hydrated/carbonated Co(OH)₂. TiO₂ annealed under H₂ also displayed additional peak related to OH⁻ in the O 1s spectrum.^{34,38} C 1s spectrum of Co_3O_4 -R also confirmed the presence of CO_3^{2-} while all C 1s signal of Co₃O₄-AP is only related to the carbon contamination. CO32- and H2O could come from air and may exist in the interlayer space of Co(OH)₂ so that a hydrotalcite-like layered structure is formed. XPS results suggest that the surface of Co₃O₄-R is chemically different from that of Co₃O₄-AP. The new surface contains Co(2+), Co(3+), OH⁻, CO₃²⁻ and H₂O, which form a material with a formula of $Co(2+, 3+)(OH)_r(CO_3)_v \cdot H_2O$. This surface layer should be very thin, or the crystallinity is low, so that no corresponding peaks are observed in XRD.

Transmission electron microscopy (TEM) and highresolution TEM (HRTEM) were used to identify the morphological change and the atomic structures of the surfaces of Co₃O₄-R and Co₃O₄-AP samples, as shown in Fig. 3. Co₃O₄-AP consists of truncated octahedral single-crystal nanoparticles with size from 15 to 25 nm (Fig. 3a). HRTEM image in Fig. 3b shows the lattice fringes that are assigned to spinel Co₃O₄, in consistence with the XRD results. Fig. 3c displays the irregular particles of Co₃O₄-R. The larger particle size and the shape change indicate the fusing of the nanoparticles during the thermal reduction. The BET specific surface area of Co₃O₄-AP is 48 m² g⁻¹ while that of Co_3O_4 -R is reduced to 22 m² g⁻¹, which again suggests the particle agglomeration. In HRTEM image of Co₃O₄-R (Fig. 3d), an amorphous layer with thickness of around 1-2 nm (indicated by dashed line) was observed. This amorphous layer should be the hydrated/carbonated cobalt



Fig. 3 TEM images of Co₃O₄-AP (a and b) and Co₃O₄-R (c and d). Insets in (d) are FFT from ~15 nm \times ~15 nm areas labelled by squares A1 and A2, respectively.

hydroxide. Different types of lattice fringes were observed in a single particle of Co_3O_4 -R comparing to that of Co_3O_4 -AP. The fast Fourier transformation (FFT) of area A1 can be indexed consistently to spinel Co_3O_4 .^{43,44} The FFT of A2 could be assigned to (311) planes of Co_3O_4 or (111) planes of CoO. This morphological transformation occurred simultaneously with the partial reduction of Co_3O_4 to CoO and Co, which may be related to the higher atomic mobility because of the bond breakage during phase transformation.^{45,46} Combining all the above results, we propose Scheme S1† to describe the surface reformation of the Co_3O_4 nanoparticles during thermal reduction and ambient stabilization. In summary, a novel structure with crystalline Co_3O_4 inside and amorphous layer on the surface was formed by thermal hydrogen reduction and the following stabilization in air.

To measure the OER activity, linear sweep voltammograms (LSVs) of Co₃O₄-AP and Co₃O₄-R were recorded on a rotating ring-disk electrode (RRDE). In Fig. 4a, the disk current of Co₃O₄-R and Co₃O₄-AP starts to rise sharply at around 1.55 V. This current rise is dominated by OER, which is confirmed by the ring current in Fig. 4b since ring current is an indicator of oxygen produced at the disk electrode according to the working principle of RRDE (Scheme S2[†]). Apparently, Co₃O₄-R exhibited higher OER activity relative to Co3O4-AP. An overpotential $\eta = 580 \text{ mV}$ is required to attain 10 mA cm⁻² on Co₃O₄-AP. Co₃O₄-R showed a much lower overpotential of 490 mV to obtain the same current density of 10 mA cm^{-2} . An important parameter and benchmarking of the catalytic activity is the onset potential. However, as shown in the inset of Fig. 4a, the disk current around the onset potential was interfered by another Faradaic process which is attributed to the oxidation of



Fig. 4 Electrochemical performance of Co_3O_4 -AP and Co_3O_4 -R in 0.1 M KOH. LSVs collected on a rotating ring-disk electrode with a rotating speed of 1600 rpm: (a) disk current densities (inset is the enlarged view of the disk current densities showing the sample oxidation prior to OER), (b) ring current densities (inset is the enlarged view of the ring current densities around the onset potential region). (c) Tafel plots recorded at potential descending with steps of 20 mV. (d) CVs collected at 30 mV s⁻¹.

Co in the catalysts (Fig. 4d). Since the current at ring is merely related to the oxygen evolution, the onset potential of OER could be decided unequivocally from the ring current. The onset potential of Co_3O_4 -R is 1.50 V ($\eta = 270$ mV) according to ring current, which is 50 mV lower than that of Co_3O_4 -AP. The onset potential and potential at current density of 10 mA cm⁻² for Co_3O_4 -R are 35 mV and 60 mV lower respectively than those for mesoporous Co_3O_4 tested under similar conditions.¹³ The onset potential is even 30 mV lower than that of mesoporous Co_3O_4 embedded with Au nanoparticles.²⁰

Tafel plots of Co₃O₄-AP and Co₃O₄-R are shown in Fig. 4c. The Tafel slope is related to the reaction mechanism and the exchange current density is a measure of the catalytic activity at the equilibrium potential. At low overpotential region, Co₃O₄-R and Co₃O₄-AP showed Tafel slopes of 61 mV dec⁻¹ and 66 mV dec⁻¹, respectively. These values are comparable to those of Cobased spinels¹¹ and perovskites,^{47,48} cobalt oxyhydroxides,⁴⁹ and amorphous CoPi film,⁵⁰ and are in the range of 60 mV dec⁻¹ $(2.3RT/\alpha F)$, indicating the rate determining step on either sample is the activation controlled process involving one electron transfer.^{11,51} The exchange current densities of Co₃O₄-R and Co_3O_4 -AP are 2 × 10⁻⁹ A cm⁻² and 4 × 10⁻⁹ A cm⁻², respectively, one order of magnitude larger than the reported value of electrodeposited cobalt oxides25 and CoPi films,50 and in the same order of magnitude with that of Co₃O₄.⁴⁹ Although the exchange current density of Co₃O₄-R is lower than that of Co₃O₄-AP, Co3O4-R exhibited lower Tafel slope and thus still had higher OER activity than Co₃O₄-AP at high overpotential. This is consistent with the consideration that evaluation of electrocatalytic activity should be based not only on the exchange current density, but also on the Tafel slope.52 At higher overpotential region, Tafel slope of Co3O4-R and Co3O4-AP increased to 90 mV dec $^{-1}$ and 117 mV dec $^{-1}$, respectively. This Tafel slope increase may result from the change in the coverage of OH species,⁴⁷ or the porous structure of the catalysts,⁵³ or the evolving bubbles blocking part of the active surface area.⁵¹

Turn-over frequency (TOF) was calculated (refer to ESI[†] for TOF calculation) to evaluate the activity of OER. TOF was calculated from the OER current density at an overpotential of 400 mV, assuming 100% faradaic efficiency and all Co sites are involved in OER (a lower bound on activity). Co_3O_4 -R shows a TOF of 0.006 S⁻¹, much larger than that of Co_3O_4 -AP (0.0023 S⁻¹). TOF of Co_3O_4 -R is slightly larger than that of mesoporous Co_3O_4 ,¹³ but lower than that of Co_3O_4 nanoparticles reported by Esswein *et al.*¹²

Cyclic voltammograms (CVs) in Fig. 4d compare the redox properties of Co_3O_4 -AP and Co_3O_4 -R. Two redox couples (A1, C1) and (A2, C2) are observed in CV of Co_3O_4 -AP. Redox couple (A1, C1) centred at 1.49 V with peak separation of 75 mV is related to the transformation between Co(2+) and Co(3+). Redox couple (A2, C2) centred at 1.28 V with peak separation of 30 mV is assigned to the oxidation of Co(3+) to Co(4+) and its reverse.^{54,55} In contrast to the defined peaks in Co_3O_4 -AP, the redox peaks in CV of Co_3O_4 -R are too diffused to be distinguished. This peak broadness is connected with the heterogeneity of Co atoms in the amorphous phase. The lattice disorder in amorphous phase affects the energy distribution of the active sites, and thus broadens the CV peaks. It has been suggested that the special energy status of the active sites in amorphous materials is promising for catalysis.⁵⁶ In this study, the special energy status of Co sites in the amorphous layer may be one of the factors that facilitate OER. The anodic current in CV of Co₃O₄-R results from the oxidation of hydrated Co(2+) species to Co(3+) and Co(4+)species, while the cathodic current is caused by the reverse processes.^{57,58} Therefore Co(4+) in Co₃O₄-R exists in a more hydrous form which probably possesses a layered structure. This structure benefits the electron and proton transportation and thus the OER process.²¹ Integration of the cathodic current allows the estimation of cobalt ions that changed oxidation states.^{28,59} The cathodic charge estimated by this method is 8 mC cm⁻² for Co₃O₄-R and 5.7 mC cm⁻² for Co₃O₄-AP. Therefore, Co₃O₄-R has more oxidisable cobalt ions and thus more Co(4+) ions were obtained during the cobalt oxidation process. Since Co(4+) are considered as active sites for OER,^{19,20,60} it is reasonable that Co₃O₄-R has higher OER activity due to the larger number of Co(4+). In mesoporous Co_3O_4 nanowires reduced by NaBH₄, authors attributed the enhanced OER activity to the oxygen vacancies which enhance electrocatalytic performance and improve the conductivity. The existence of the oxygen vacancies was confirmed by the stronger Co(2+) signal in XPS data than that in the pristine sample.²⁴ But in our surface-engineered sample Co3O4-R, surface atoms reduced by thermal hydrogen treatment were re-oxidized on exposure to air, and no additional or stronger signal related to Co metal or Co(2+) was observed in XPS in Fig. 2d. Therefore, we correlate the enhanced OER activity with the layered surface amorphous structure which provides more active sites. The stability of Co₃O₄-R for OER was assessed by polarizing the electrode at 1.63 V (overpotential of 400 mV) for different duration. In Fig. S1,[†] the OER current of Co₃O₄-R keeps almost constant after oxidation for 10 min, 20 min and 70 min, which indicates good stability of Co₃O₄-R.

Conclusions

We reported the improved OER activity of surface reformed Co_3O_4 . The amorphous surface contains hydrated/carbonated cobalt hydroxide species and is more active compared to the highly crystalline surface of pristine Co_3O_4 nanoparticles. Through cyclic voltammetry, we show that the Co(4+) active sites in the amorphous layer exist in special environment and agglomerate. The amorphous surface layer also exhibited good stability after prolonged anodic oxidation. This work demonstrates a new avenue towards the development of more efficient OER catalyst through surface engineering.

Acknowledgements

We acknowledge the financial support from UNSW Australia, The University of Queensland and Australian Research Council Discovery Project (DP110100550). D.W.W. acknowledges the support from UNSW FRG/ECR scheme. The authors acknowledge the facilities, and the scientific and technical assistance, of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy and Microanalysis, The University of Queensland.

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