

# Cobalt carbonate hydroxide hydrate nanowires array: a three-dimensional catalyst electrode for effective water oxidation

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The development of Earth-abundant low-cost catalyst materials for effective water oxidation is of critical importance for electrochemical hydrogen production. The first use of hydrothermally in situ grown cobalt carbonate hydroxide hydrate nanowires array on carbon cloth as an effective catalyst electrode for water oxidation in alkaline electrolytes is described. This three-dimensional electrode shows high catalytic activity with the need of overpotential of 323 mV to drive 10 mA cm<sup>-2</sup>, and its activity can be retained for at least 40 h.

**1. Introduction:** Global energy crisis and environmental concerns have attracted considerable and continuous research interest in searching for efficient and environmentally energy carrier alternative to fossil fuels [1]. Hydrogen has been considered as an ideal carbon-free such candidate [2]. Electrochemical splitting of water under alkaline conditions is a simple technique for large-scale production of pure hydrogen. Anodic water oxidation to generate oxygen is a crucial half reaction in water splitting because the oxygen evolution reaction (OER) involves four electrons and suffers from sluggish kinetics during electron transfers, which largely increases overpotential ( $\eta$ ) and impedes the overall water-splitting efficiency [3, 4]. Efficient electrocatalysts are thus needed to drive high current at low overpotential [5–7]. Currently, RuO<sub>2</sub> and IrO<sub>2</sub> are the most active OER catalysts [8], but the scarcity, prohibitive cost, and poor durability of such catalysts severely hinder their widespread industrial uses. Accordingly, it is highly needed to discover Earth-abundant, cost-effective catalyst materials for effective water oxidation.

Cobalt (Co) has emerged as an interesting non-noble metal for its catalytic power toward water oxidation [6] and considerable attention has been paid to design and develop Co-based OER catalysts in alkaline media including oxide [9–14], layered double hydroxide [15–19], chalcogenide [20–23], phosphide [24, 25], nitride [26], and oxalate [27] etc. Co carbonate hydroxide hydrate [Co(CO<sub>3</sub>)<sub>0.5</sub>OH·0.11H<sub>2</sub>O] has also been reported for water oxidation electrolysis using multiwall carbon nanotube [28] and carbon black [29] as conductive supports, with the need of overpotentials of 285 and 509 mV to drive 10 mA cm<sup>-2</sup> in 1.0 M potassium hydroxide (KOH), respectively. From a point of view of practical application, it is highly desired to directly grow the catalyst of interest on the current collector for a polymer binder-free self-supported catalyst electrode because such design not only enables good mechanical adhesion and electrical connection between them, but exposes more sites and improves the conductivity [30]. However, to the best of our knowledge, there is no work reporting on the use of self-supported Co(CO<sub>3</sub>)<sub>0.5</sub>OH·0.11H<sub>2</sub>O-based catalyst electrode for oxygen evolution has been reported before.

In this Letter, for the first time, we demonstrate the utilisation of Co(CO<sub>3</sub>)<sub>0.5</sub>OH·0.11H<sub>2</sub>O nanowires array in situ hydrothermal growth on carbon cloth [Co(CO<sub>3</sub>)<sub>0.5</sub>OH·0.11H<sub>2</sub>O NA/CC] as a three-dimensional (3D) catalyst electrode for water oxidation in alkaline electrolytes. It exhibits high catalytic activity and demands overpotential of 323 mV to afford 10 mA cm<sup>-2</sup>, and its activity can be maintained for at least 40 h. This work offers us an attractive low-cost catalyst material for water-splitting applications.

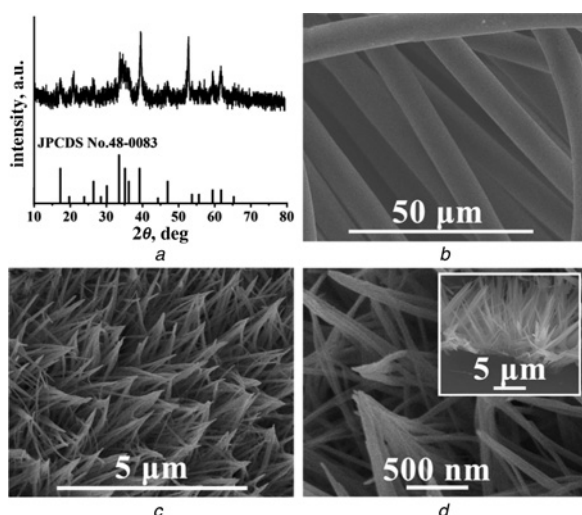
**2. Experimental results:** Co nitrate hexahydrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], ammonium fluoride (NH<sub>4</sub>F), and urea were purchased from Beijing Chemical Corporation. KOH was purchased from Rgent (Tianjin, China). RuCl<sub>3</sub>·3H<sub>2</sub>O and Nafion (5 wt%) were purchased from Sigma-Aldrich (Shanghai) Chemical Reagent Co., Ltd. CC was provided by Hongshan District, Wuhan Instrument Surgical Instruments business, and was pretreated in nitric acid and then cleaned by sonication in water and ethanol for several times to remove surface impurities. The deionised water (DIW) used throughout all experiments was purified through a Millipore system.

Co(CO<sub>3</sub>)<sub>0.5</sub>OH·0.11H<sub>2</sub>O NA/CC was prepared hydrothermally according to the previous report with modifications [31]. In a typical synthesis, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.582 g), NH<sub>4</sub>F (0.186 g), and urea (0.60 g) were dissolved in 40 ml water under vigorous stirring for 30 min. Then, the above pellucid solution and a piece of cleaned CC (2 × 3 cm) were transferred to a 50 ml teflon-lined stainless-steel autoclave and maintained at 120°C for 6 h. After cooling down to room temperature, the substrate was then removed from the solution and washed with DIW thoroughly before vacuum dried.

Powder X-ray diffraction (XRD) data were collected on a RigakuD/MAX 2550 diffractometer with copper K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Scanning electron microscopy (SEM) measurements were carried out on an XL30 field-emission environmental scanning electron microscope (ESEM-FEG) scanning electron microscope at an accelerating voltage of 20 kV.

Electrochemical measurements were performed with a CHI660E electrochemical analyser (CH Instruments, Inc., Shanghai). All electrochemical measurements were conducted in a typical three-electrode setup with an electrolyte solution of 1.0 M KOH at 25°C using Co(CO<sub>3</sub>)<sub>0.5</sub>OH·0.11H<sub>2</sub>O NA/CC as the working electrode, a graphite plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). Linear sweep voltammetry (LSV) measurements were conducted in 1.0 M KOH with scan rate of 5 mV s<sup>-1</sup>.  $E$  (RHE) =  $E$  (SCE) + 1.068 V,  $\eta = E$  (RHE) – 1.23 V. No activation process was involved in all electrochemical tests.

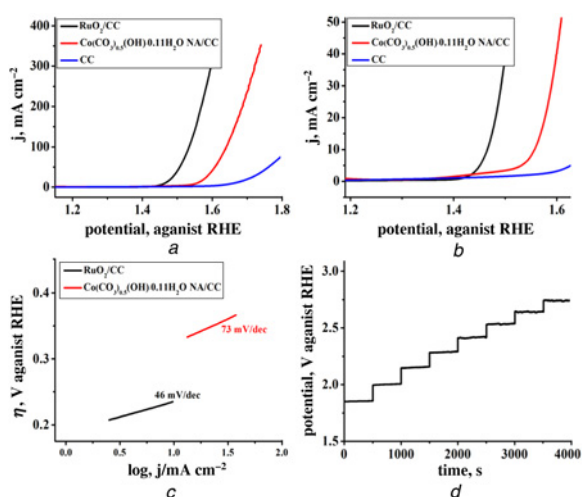
**3. Results and discussion:** Fig. 1a shows the XRD pattern of Co(CO<sub>3</sub>)<sub>0.5</sub>OH·0.11H<sub>2</sub>O in the diffraction angle range of 10–80°, and all diffraction peaks are well matched with the standard diffraction pattern of Co(CO<sub>3</sub>)<sub>0.5</sub>OH·0.11H<sub>2</sub>O (JCPDS Card No. 48-0083). The SEM image of CC substrate (Fig. 1b) indicates that it has smooth surface. The low-magnification SEM image of



**Fig. 1** XRD pattern of  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  in the diffraction angle range of  $10\text{--}80^\circ$   
 a XRD pattern of  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  nanowires scraped from CC  
 b SEM image of CC  
 c Low-magnification SEM images for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC  
 d High-magnification SEM images for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC [inset: cross-section SEM image of  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}/\text{CC}$ ]

$\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC (Fig. 1c) suggests the full coverage of CC by  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  nanowires array after hydrothermal reaction. The high-magnification SEM image further reveals that these  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  nanowires have diameters in the range of  $35\text{--}90\text{ nm}$ , as shown in Fig. 1d. With the assistance of  $\text{NH}_4\text{F}$ , the pink  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  can nucleate preferentially on the outer surface of carbon skeleton and subsequently grow on the carbon cloth substrate on a large scale [32], thereby generating the uniform nanostructures. Cross-section analysis (the inset of Fig. 1d), which can reveal the nucleation sites for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  nanowires on carbon cloth, shows that these nanowires are up to  $8\text{--}10\text{ }\mu\text{m}$  in length.

The  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC (catalyst loading:  $1.12\text{ mg cm}^{-2}$ ) was then tested as an integrated 3D oxygen evolution anode using a typical three-electrode configuration in  $1.0\text{ M KOH}$  with a



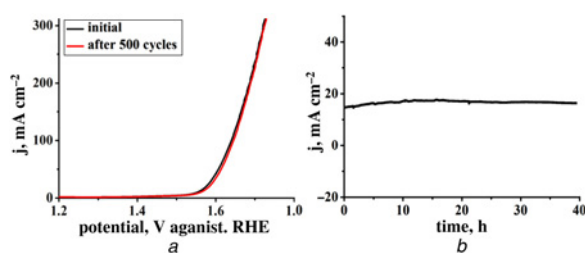
**Fig. 2** LSV curves of CC,  $\text{RuO}_2/\text{CC}$ , and  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC  
 a, b LSV curves for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC,  $\text{RuO}_2/\text{CC}$ , and CC with a scan rate of  $5\text{ mV s}^{-1}$  for OER  
 c Tafel plots for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC and  $\text{RuO}_2/\text{CC}$   
 d Multistep process of  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC (the current density started at  $50\text{ mA cm}^{-2}$  and ended at  $400\text{ mA cm}^{-2}$ , with an increment of  $50\text{ mA cm}^{-2}$  per  $500\text{ s}$  without  $iR$  correction)

**Table 1** Comparison of Co-based OER electrocatalysts in alkaline media

Catalyst	Electrolyte, M KOH	Tafel slope, $\text{mV dec}^{-1}$	$\eta$ at $10\text{ mA cm}^{-2}$ , mV	Reference
$\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$ NA/CC	1.0	73	323	this work
$\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire arrays	1.0	59–64	370	[12]
PNG- $\text{NiCo}_2\text{O}_4$	0.1	156	349	[13]
$\text{Zn}_x\text{Co}_{3-x}\text{O}_4$	0.1	51	320	[14]
NiCo LDHs	1.0	40	367	[18]
Co-S/Ti mesh	1.0	64	361	[21]
$\text{Co}_{1-x}\text{S}/\text{G-glycol}$	0.1	81.3	349	[23]
$\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$	0.1	73	436	[27]
CCHH/MWCNT	0.1	51	285	[28]
CCH/C	0.1	–	509	[29]
ECT-CoO nanosheets	1.0	62	284	[34]
N-doped graphene-CoO	1.0	72	340	[35]
Co-P film	1.0	47	345	[36]
Zn-Co-LDH nanosheets	0.1	101	480	[37]
$\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4$	1.0	88	340	[38]

scan rate of  $5\text{ mV s}^{-1}$ . For comparison, bare CC and  $\text{RuO}_2$  deposited CC ( $\text{RuO}_2/\text{CC}$  with the same loading) were also examined. Given that the measured anodic currents cannot directly reflect the intrinsic behaviour of catalysts due to the effect of ohmic resistance, an  $iR$  ( $R = 3.706\text{ }\Omega$ ) correction was applied to all initial data for further analysis [33]. Figs. 2a and b present the LSV curves of CC,  $\text{RuO}_2/\text{CC}$ , and  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC (all current densities are based on projected geometric area of an electrode). As observed,  $\text{RuO}_2/\text{CC}$  shows excellent OER activity with the need of overpotential of  $235\text{ mV}$  to drive  $10\text{ mA cm}^{-2}$  while bare CC has poor activity.  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC is also efficient for water oxidation electrocatalysis, with the need of overpotential of  $323\text{ mV}$  to achieve  $10\text{ mA cm}^{-2}$ . Although this overpotential is larger than that for CCHH/MWCNT ( $\eta = 285\text{ mV}$ ) [28] and ECT-CoO nanosheets ( $\eta = 284\text{ mV}$ ) [34], it still compares favourably to the behaviour of many reported Co-based OER catalysts in basic media including  $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$  nanowire arrays ( $\eta = 370\text{ mV}$ ) [12], PNG- $\text{NiCo}_2\text{O}_4$  ( $\eta = 349\text{ mV}$ ) [13], NiCo LDHs ( $\eta = 367\text{ mV}$ ) [18], Co-S/Ti mesh ( $\eta = 361\text{ mV}$ ) [21],  $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  ( $\eta = 436\text{ mV}$ ) [27], CCH/C ( $\eta = 509\text{ mV}$ ) [29], N-doped graphene-CoO ( $\eta = 340\text{ mV}$ ) [35], Co-P film ( $\eta = 345\text{ mV}$ ) [36], Zn-Co-LDH nanosheets ( $\eta = 480\text{ mV}$ ) [37], and  $\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4$  ( $\eta = 340\text{ mV}$ ) [38] (Table 1) etc. Fig. 2c shows the Tafel plots of  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC and  $\text{RuO}_2/\text{CC}$ , and the Tafel slopes for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC and  $\text{RuO}_2/\text{CC}$  are  $73$  and  $46\text{ mV dec}^{-1}$ , respectively. Fig. 2d presents a multi-step chronopotentiometric curve for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC in  $1.0\text{ M KOH}$  with the current being increased from  $50$  to  $400\text{ mA cm}^{-2}$  ( $50\text{ mA cm}^{-2}$  per  $500\text{ s}$ ). The potential immediately levels off at  $1.86\text{ V}$  at the start current value and remains unchanged for the rest  $500\text{ s}$ , and the other steps also show similar results, implying the excellent mass transportation, conductivity, and mechanical robustness of the 3D  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC electrode [39].

We further probed the durability for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC electrode by continuous cyclic voltammetry (CV) scanning with a potential between  $+1.368$  and  $+1.768\text{ V}$  (versus RHE) in  $1.0\text{ M KOH}$  at a scan rate of  $30\text{ mV s}^{-1}$ . After  $500$  cycles, the polarisation curve shows negligible difference compared with the initial one (Fig. 3a), suggesting its superior durability. Further bulk electrolysis experiment demonstrates that this electrode can maintain its activity for at least  $40\text{ h}$ . All the results suggest that  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC exhibits remarkable long-term electrochemical durability toward OER in alkaline electrolytes.



**Fig. 3** Polarisation curve

a LSV curves for  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC before and after 500 CV cycles

b Current curve of  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  NA/CC electrode at fixed overpotential of 478 mV in 1.0 M KOH

**4. Conclusion:** In summary,  $\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$  nanowires array has been developed on CC as a non-noble-metal 3D electrode for water oxidation in alkaline electrolytes. This electrode demands overpotential of 323 mV to drive  $10 \text{ mA cm}^{-2}$  with its activity being maintained for at least 40 h in 1.0 M KOH. This work offers us an attractive cost-effective and flexible [40] catalyst electrode with high activity and stability for application in water-splitting devices.

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