



Facile Synthesis of Carbon Cloth Supported Cobalt Carbonate Hydroxide Hydrate Nanoarrays for Highly Efficient Oxygen Evolution Reaction

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Developing efficient and low-cost replacements for noble metals as electrocatalysts for the oxygen evolution reaction (OER) remain a great challenge. Herein, we report a needle-like cobalt carbonate hydroxide hydrate ($\text{Co}(\text{CO}_3)_{0.5}\text{OH}\cdot 0.11\text{H}_2\text{O}$) nanoarrays, which *in situ* grown on the surface of carbon cloth through a facile one-step hydrothermal method. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations demonstrate that the $\text{Co}(\text{CO}_3)_{0.5}\text{OH}$ nanoarrays with high porosity is composed of numerous one-dimensional (1D) nanoneedles. Owing to unique needle-like array structure and abundant exposed active sites, the $\text{Co}(\text{CO}_3)_{0.5}\text{OH}@CC$ only requires 317 mV of overpotential to reach a current density of 10 mA cm^{-2} , which is much lower than those of $\text{Co}(\text{OH})_2@CC$ (378 mV), $\text{CoCO}_3@CC$ (465 mV) and $\text{RuO}_2@CC$ (380 mV). For the stability, there is no significant attenuation of current density after continuous operation 27 h. This work paves a facile way to the design and construction of electrocatalysts for the OER.

Keywords: cobalt carbonate hydroxide hydrate, needle-like nanoarrays, porous structure, electrocatalyst, oxygen evolution reaction

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INTRODUCTION

As a key anodic reaction, oxygen evolution reaction (OER) plays an important role in energy-related electrochemical conversion technologies, such as water splitting and rechargeable Zn-air batteries (Song et al., 2020; Wu et al., 2020). However, OER suffers from sluggish kinetics owing to four electron transfer process, which significantly increases the overpotential. (Fu et al., 2018; Xiao et al., 2019; Liu et al., 2020). To facilitate the OER, the noble metal-based materials like IrO_2 and RuO_2 have been regarded as highly active catalysts for the OER. (Xie et al., 2019; Du et al., 2021; Wang et al., 2021). Although they present outstanding activity for the OER, the high cost, scarcity reserves and poor stability are main reasons to limit their practical applications. Therefore, it is highly urgent to explore and develop the cost-effective and earth-abundant electrocatalysts for the OER.

For the past few years, cobalt-based transition metal materials, such as cobalt oxides (CoO_x) (Xu et al., 2016; Li et al., 2018), cobalt phosphides (CoP_x) (Chen et al., 2019; Jin et al., 2019), cobalt sulfide (CoS_x) (Wang et al., 2015; Zhang H. et al., 2020), cobalt nitride (CoN_x) (Chen et al., 2016; Liu et al., 2021), and cobalt hydroxides ($\text{Co}(\text{OH})_2$) Dileep et al. (2020), Qin et al. (2020) have been widely investigated as non-noble metal electrocatalysts for the OER. More recently, cobalt carbonate

hydroxide hydrate [Co(CO₃)_{0.5}OH·0.11H₂O] have received far-reaching attention as the OER catalysts (Zhang et al., 2015; Wang et al., 2017; Zhang S. et al., 2020), and not rather than only as a precursor to produce oxides and phosphides. However, the low conductivity and deficient catalytically active sites of Co(CO₃)_{0.5}OH·0.11H₂O limit its intrinsic OER activity in energy-related electrochemical devices. To address such problems, the introducing carbon support and morphology modulation should be two important strategies for improving the OER activity of transition metal-based materials. Through the introducing carbon support, the electronic contact between the carbon support and the active materials can induce the charge redistribution and the changes in electronic structure of the active materials, probably leading to improve the electronic conductivity and facilitate charge transfer during the OER (Liu et al., 2018; Yang et al., 2020). For the morphology modulation, three-dimensional (3D) porous array structure presents significant advantages among various morphology, including large specific surface area, abundant exposed catalytically active sites, excellent structure stability, which are highly favorable for the mass and charge transfer during electrocatalytic reactions (Xu et al., 2018; Wang et al., 2020). Besides, 1D-nano structure have inherent structural advantages, such as high specific surface area, fast electron and material transport, low solubility and difficult agglomeration, etc. Therefore, 1D-nanostructures are widely used in electrocatalytic applications. However, it still exists a big challenge to realize deliberate control over the above two features in a facile and efficient method.

Herein, we report the anchoring of needle-like Co(CO₃)_{0.5}OH·0.11H₂O nanoarrays on carbon cloth [Co(CO₃)_{0.5}OH@CC] with the assistance of urea and NH₄F through a facile one-step hydrothermal method. Urea and NH₄F serve as both effective agents to help to favor the formation of well-defined needle-like array structure. The geometric and electronic structure are explored in detail by different characterization methods. Benefitted from needle-like array structure and abundant exposed active sites, the developed Co(CO₃)_{0.5}OH@CC displays superior electrocatalytic performance towards OER with a low overpotential of 317 mV at 10 mA cm⁻² and a long-term stability.

EXPERIMENTAL SECTION

Reagents and Chemicals

All reagents and chemicals in the experimental sections were used without further purification. Cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O] was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Urea [CO(NH₂)₂] was brought from Beijing Solarbio Science and Technology Co., Ltd. (Beijing, China). Ammonium fluoride (NH₄F) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cobalt (II) carbonate hydrate (CoCO₃·H₂O), Cobalt (II) hydroxide (Co(OH)₂), commercial ruthenium (IV) oxide (RuO₂) were purchased from Aladdin Ltd. (Shanghai, China).

Synthesis of the Co(CO₃)_{0.5}OH@CC

The Co(CO₃)_{0.5}OH@CC was fabricated by a facile one-step hydrothermal method. In a typical preparation procedure, 1.5 mmol Co(NO₃)₂·6H₂O was dissolved in 30 ml deionized water by magnetic stirring for several minutes to form a homogeneous solution. Then, 0.1 g NH₄F and 0.3 g urea were added to the reactor under vigorous string for 5 min. The obtained clear solution was transferred into a Teflon-lined stainless-steel autoclave and a piece of 2*4 cm² carbon cloth was immersed into the solution vertically. The autoclave was then sealed and placed in an oven at 120 °C for 8 h. After cooled to room temperature, the as-fabricated Co(CO₃)_{0.5}OH@CC was taken out and rinsed with ethanol and deionized water for several times, and dried at 40 °C overnight.

Characterization

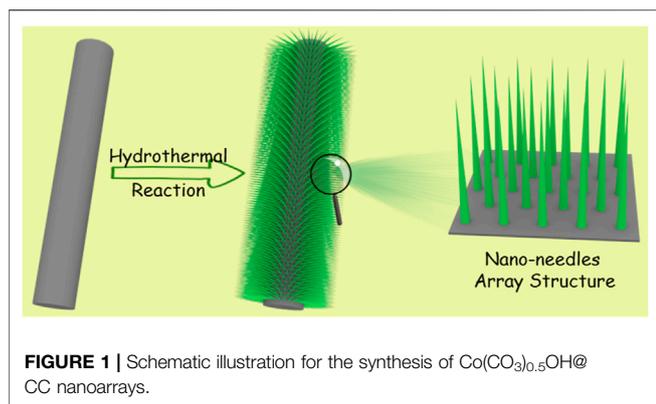
X-ray diffraction (XRD) measurement was performed on X-ray powder diffractometer with a Cu K_α radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) images were collected on Hitachi S5500 scanning electron microscope. Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were collected using a JEOL JEM2100F (accelerating voltage of 200 kV). Element dispersive spectroscopy (EDS) measurements and line scans profiles were performed on FEI Tecnai G2 F20 microscope, an accessory built on the JEOL JEM-2100F. All XPS analyses were carried out with Thermo VG Scientific ESCALAB 250 spectrometer (Al K_α radiator).

Electrochemical Measurement

Electrochemical properties of all catalysts were studied with a standard three-electrode system on CHI 760E electrochemical analyzer (Shanghai Chenchua Co.). A saturated calomel electrode (SCE) and a graphite rod were employed as the reference electrode and the auxiliary electrode, respectively. All the potentials involved in this manuscript were converted to the reversible hydrogen electrode (RHE) scale by following equation: E_{RHE} = E_{SCE} + 0.0592*pH + 0.242. All the potentials involved in this manuscript were not corrected by *iR*-correction. Before the test, 1.0 M KOH was saturated by high-purity O₂. A catalysts-modified carbon cloth (1*1 cm²) was used as working electrode. Linear sweep voltammetry (LSV) measurement was performed with a sweep rate of 5 mV s⁻¹. The C_{dl} value of different catalysts were performed at potential of 1.02 to 1.12 V with the cyclic voltammograms at different sweeping rates from 2 mV s⁻¹–10 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) was collected in a frequency range from 0.01 Hz to 100 kHz at 1.7 V.

RESULTS AND DISCUSSION

The synthesis route of Co(CO₃)_{0.5}OH@CC nanoarrays is illustrated schematically in **Figure 1**. The needle-like Co(CO₃)_{0.5}OH nanoarrays were *in situ* grown on the surface of carbon cloth through a facile one-step hydrothermal method, where the Co(NO₃)₂ aqueous solution were used as precursors

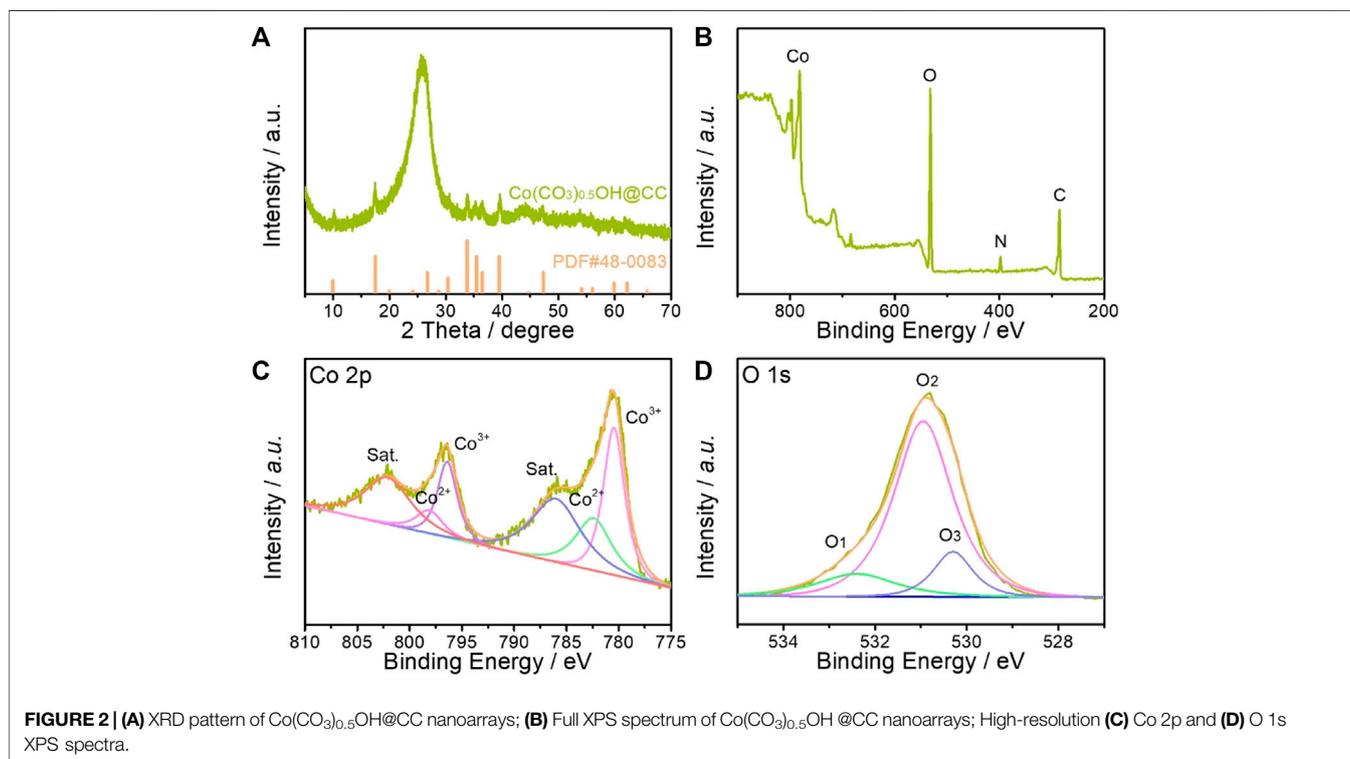


and urea as an alkaline reagent in the presence of NH₄F at 120°C. Urea, a common ammonia-releasing agent, provides hydroxyl ions (OH⁻) and carbonate ions (CO₃²⁻) during the hydrolysis (Wang et al., 2012). NH₄F is a good complexing ligand for Co²⁺ that can serve to reduce the concentration of free Co²⁺ ions, lowering the supersaturation to probably favor the gradual growth of needle-like Co(CO₃)_{0.5}OH nanoarrays (Zhu et al., 2013).

Figure 2A shows the X-ray powder diffraction (XRD) pattern of as-prepared product, which was utilized to investigate the phase and purity of the as-synthesized Co(CO₃)_{0.5}OH@CC catalysts. Except for the peak about 26° derived from carbon cloth, other identified peaks can be matched well with pure orthorhombic Co(CO₃)_{0.5}OH·0.11H₂O (JCPDS No. 48-0,083, *a* = 8.792 Å, *b* = 10.150 Å and *c* = 4.433 Å). The surface composition and valence states

of Co(CO₃)_{0.5}OH@CC nanoarrays were determined by X-ray photoelectron spectroscopy (XPS). Full XPS spectrum demonstrates the co-existence of Co, O, N and C in Co(CO₃)_{0.5}OH@CC nanoarrays (**Figure 2B**). **Figure 2C** shows the high-resolution Co 2p XPS spectrum, which can be best fitted with two spin-orbit doublets and two shakeup satellites. The fitting peaks at 782.40 and 798.10 eV are assigned to Co²⁺ species, whereas the fitting peaks at 780.46 and 796.40 eV are attributed to Co³⁺ species (Li et al., 2020a; Li et al., 2020b). For O 1s XPS spectrum, the peaks located at 530.3, 530.95 and 532.40 eV are associated with metal-oxygen bond, hydroxyl group (OH⁻) and oxygen vacancies (Tang et al., 2020; Li M. et al., 2021). In the as-prepared Co(CO₃)_{0.5}(OH)@CC catalysts, the metal-oxygen bond and hydroxyl group are typical characteristics of carbonate hydroxide hydrates. While the high content oxygen vacancies could also be found in this catalyst, which could offer more efficient active sites and act as oxygen buffer to accelerate the OER kinetics during electrocatalysis process.

The morphology and structure of the product were further characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From typical SEM images (**Figures 3A,B**; **Supplementary Figure S1**), one can see that the as-prepared Co(CO₃)_{0.5}OH·0.11H₂O exhibits a needle-like array structure and grew vertically and densely on the surface of carbon cloth, forming a 3D network structure. The needle-like structure of Co(CO₃)_{0.5}OH·0.11H₂O was clearly observed in TEM images shown in **Figures 3D,E**. The average diameter of Co(CO₃)_{0.5}OH·0.11H₂O of nanoneedle is about 80 nm. 3D porous array structure can facilitate the mass diffusion and the accessibility of the active sites/electrolytes.



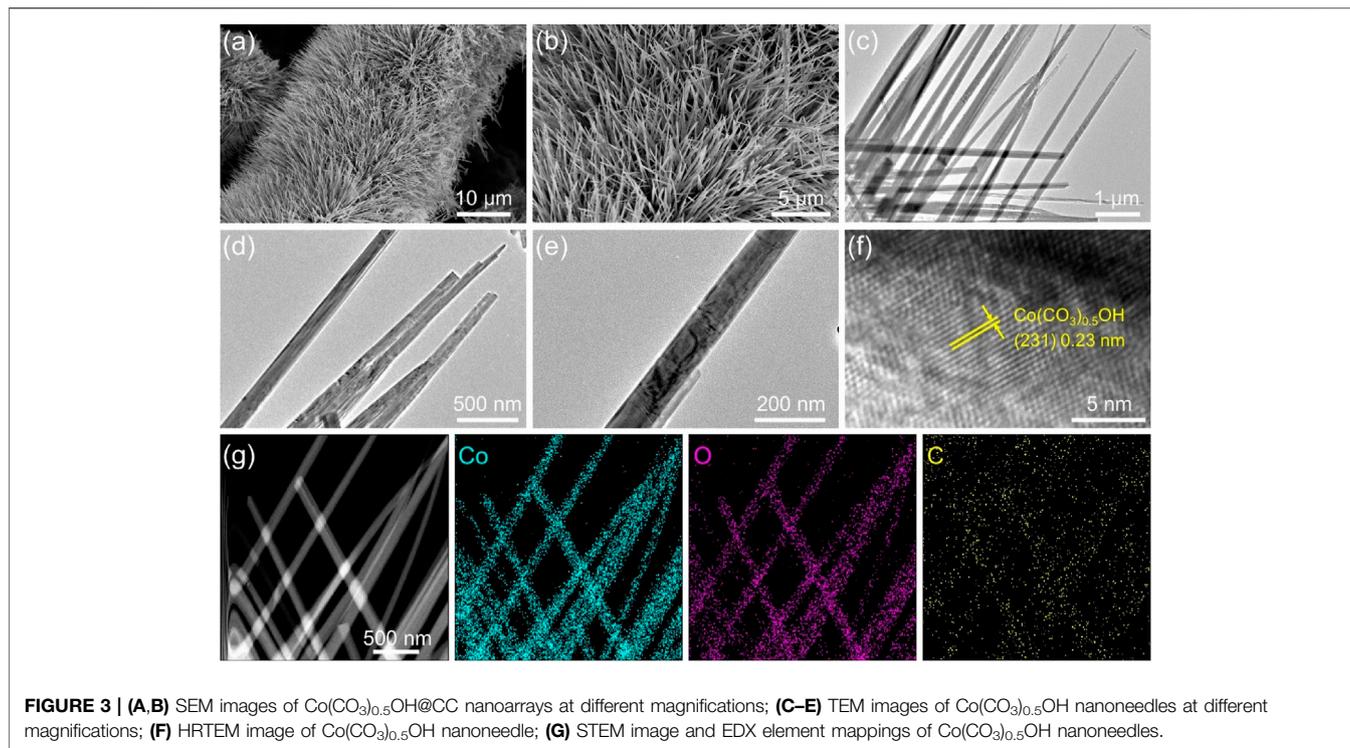


Figure 3F shows the high-resolution TEM (HRTEM) image of Co(CO₃)_{0.5}OH·0.11H₂O of nanoneedle, which presents well-resolved lattice fringes with lattice spacing of about 0.23 nm corresponding to the (231) plane of Co(CO₃)_{0.5}OH·0.11H₂O. Energy dispersive X-ray (EDX) spectrum confirms the presence of Co and O elements (**Supplementary Figure S2**), in accordance with XPS results. The element distribution was further investigated by EDX element mappings (**Figure 3G**; **Supplementary Figure S3**) and EDX line scanning profiles (**Supplementary Figure S4**). It can be seen that the Co, O and C elements are homogeneously distributed throughout the Co(CO₃)_{0.5}OH·0.11H₂O nanoneedles. All the characterizations above prove that Co(CO₃)_{0.5}OH@CC catalyst was successfully synthesized.

The electrocatalytic performance of Co(CO₃)_{0.5}OH@CC nanoarrays for the OER was evaluated using a standard three-electrode configuration in an alkaline medium (1.0 M KOH). For comparison, Co(OH)₂@CC, CoCO₃@CC and RuO₂@CC were also tested under the same condition. **Figure 4A** displays the OER polarization curves of Co(CO₃)_{0.5}OH@CC, Co(OH)₂@CC, CoCO₃@CC and RuO₂@CC. It can be found that Co(CO₃)_{0.5}OH@CC presents the best electrocatalytic activity towards OER as compared with the rest of samples. The Co(CO₃)_{0.5}OH@CC electrode only require 317 mV of overpotential to reach a current density of 10 mA cm⁻² (**Figure 4B**), which is much lower than those of Co(OH)₂@CC (378 mV), CoCO₃@CC (465 mV) and RuO₂@CC (380 mV). The OER reaction kinetics of catalysts was evaluated from the corresponding Tafel plots. As indicated in **Figure 4C**, the Co(CO₃)_{0.5}OH@CC exhibits the smallest Tafel slope of 146.3 mV dec⁻¹, much lower than those of

Co(OH)₂@CC (162.1 mV dec⁻¹), CoCO₃@CC (183.8 mV dec⁻¹) and RuO₂@CC (177.3 mV dec⁻¹), demonstrating a more favorable reaction kinetics of Co(CO₃)_{0.5}OH@CC during the OER. The excellent reaction kinetics of Co(CO₃)_{0.5}OH@CC may be associated with good charge transfer rate (Sun et al., 2018). To confirm this point, the electrochemical impedance spectroscopy (EIS) was performed. The Nyquist plot of Co(CO₃)_{0.5}OH@CC presents the smaller semicircles compared to those of Co(OH)₂@CC and CoCO₃@CC (**Figure 4D**), demonstrating the lower charge-transfer resistance (R_{ct}) and rapid charge transfer rate. The electrochemical double layer capacitance (C_{dl}) was applied to appraise the magnitude of electrochemical active surface area (ECSA) (Li Z. et al., 2021). The measurements were performed at potential of 1.02–1.12 V with the cyclic voltammograms at different sweeping rates from 2 mV s⁻¹ to 10 mV s⁻¹ (**Supplementary Figure S5**). As revealed in **Figure 4E**, the Co(CO₃)_{0.5}OH@CC has a larger C_{dl} value (21.82 mF cm⁻²) than those of Co(OH)₂@CC (14.45 mF cm⁻²) and CoCO₃@CC (0.462 mF cm⁻²), suggesting the presence of higher active surface area on Co(CO₃)_{0.5}OH@CC. The long-term stability is another vital parameter for the practical application of electrocatalysts, which was studied via the chronoamperometric *i-t* test conducted at 1.5 V. After continuous operation 27 h, there is no significant attenuation of current density for the Co(CO₃)_{0.5}OH@CC, indicating good electrocatalytic stability.

The electrocatalytic stability of Co(CO₃)_{0.5}OH@CC is also evidenced by XRD, XPS and SEM characterizations before and after continuous OER operation. From XRD pattern shown in

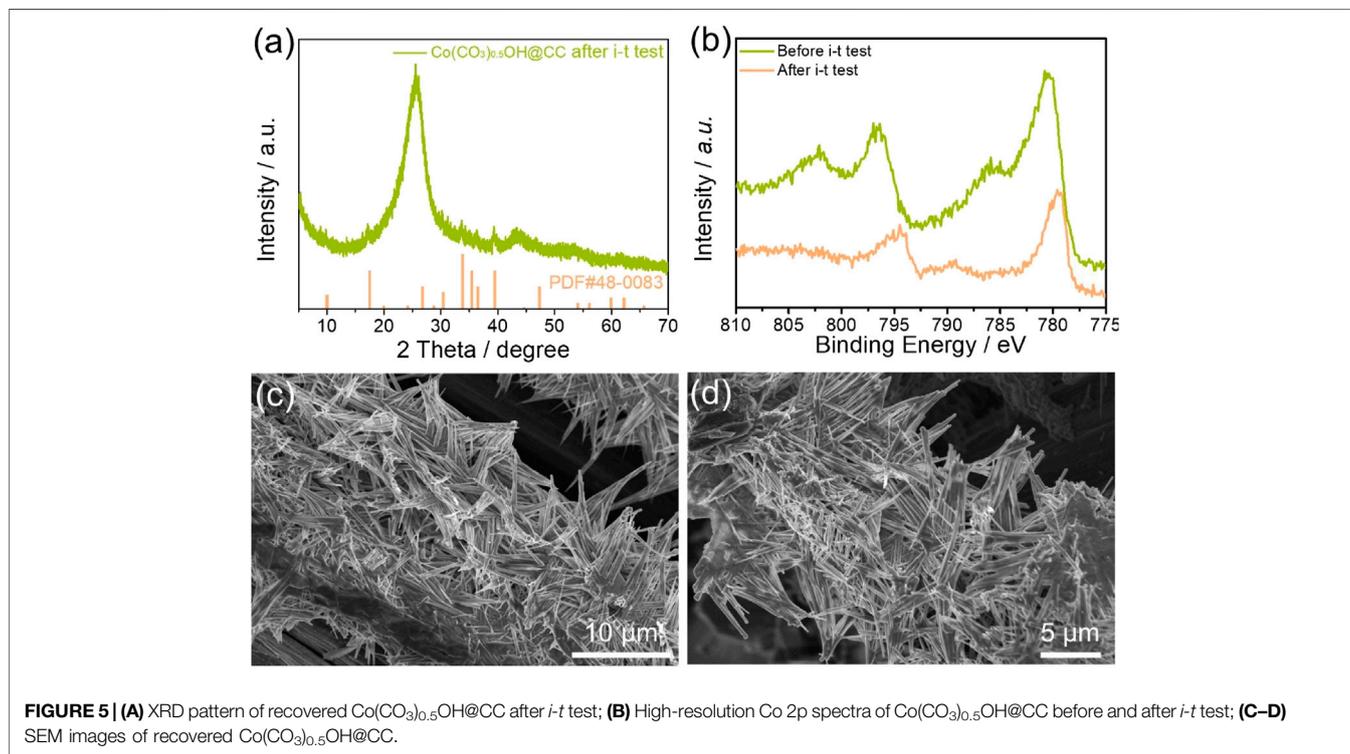
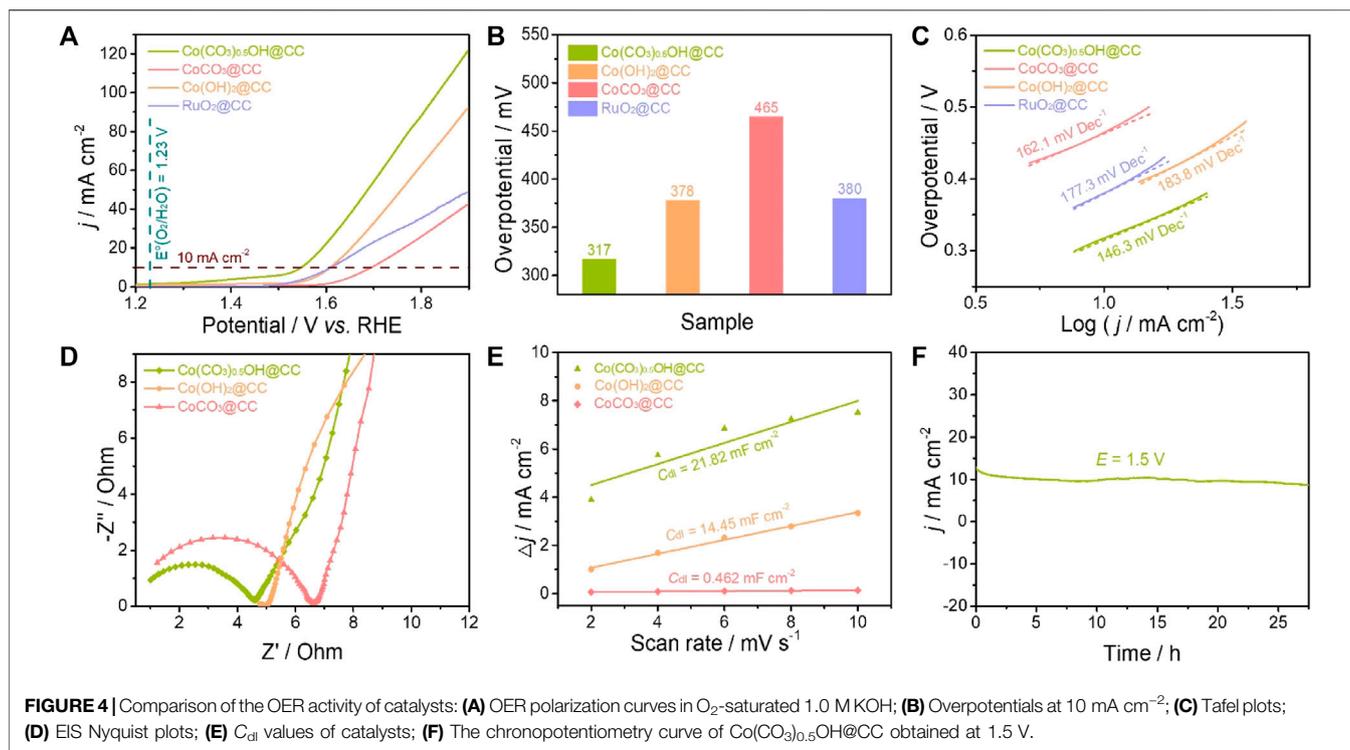


Figure 5A, the diffraction peak of recovered Co(CO₃)_{0.5}OH@CC is the same as that before the OER stability. **Figure 5B** shows the high-resolution Co 2p XPS spectra of Co(CO₃)_{0.5}OH@CC

before and after test. Compared with that before the reaction, the peaks of Co 2p spectrum for Co(CO₃)_{0.5}OH@CC negatively shift, which suggested that Co²⁺ had a tendency to transform

like Co³⁺ during the OER process. The Co³⁺ species may be assigned to the Co species in CoOOH, suggesting CoOOH may serve as active site for the OER (Zhong et al., 2021). Furthermore, the morphology of Co(CO₃)_{0.5}OH@CC is maintained well apart from the slight surface corrosion (Figures 5C,D). According to the above results and data analysis, the Co(CO₃)_{0.5}OH@CC demonstrates outstanding OER activity, which can be its unique needle-like array architecture and surface chemical properties.

CONCLUSION

In summary, we reported a novel catalyst consisting of long-needle like carbonate hydroxide hydrate nanoarrays directly *in situ* growth on carbon cloth substrate by a green and facial one-step hydrothermal strategy. Benefiting from the nanoneedles arrayed architecture and unique active component, the as-prepared Co(CO₃)_{0.5}OH@CC possess abundant accessible active sites, efficient mass/electron transfer channels and robust structure stabilities. Thus, the as-synthesized Co(CO₃)_{0.5}OH@CC exhibits outstanding electrocatalytic performance towards the OER in alkaline medium (1.0 M KOH) with a low overpotential of 317 mV at a current density of 10 mA cm⁻² and could maintained well even after 27 h continuous electrolysis. We believe that such excellent catalytic activity and robust stability of Co(CO₃)_{0.5}OH@CC enables it to be an economical and competent electrocatalyst for large-scale electrochemical applications.

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DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2021.754357/full#supplementary-material>

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