

## Synthesis and Structural Characterization of $\text{Co}_3\text{O}_4$ Electrocatalysts on Carbon Fiber Cloth with Tunable Morphologies and Electrochemical Properties

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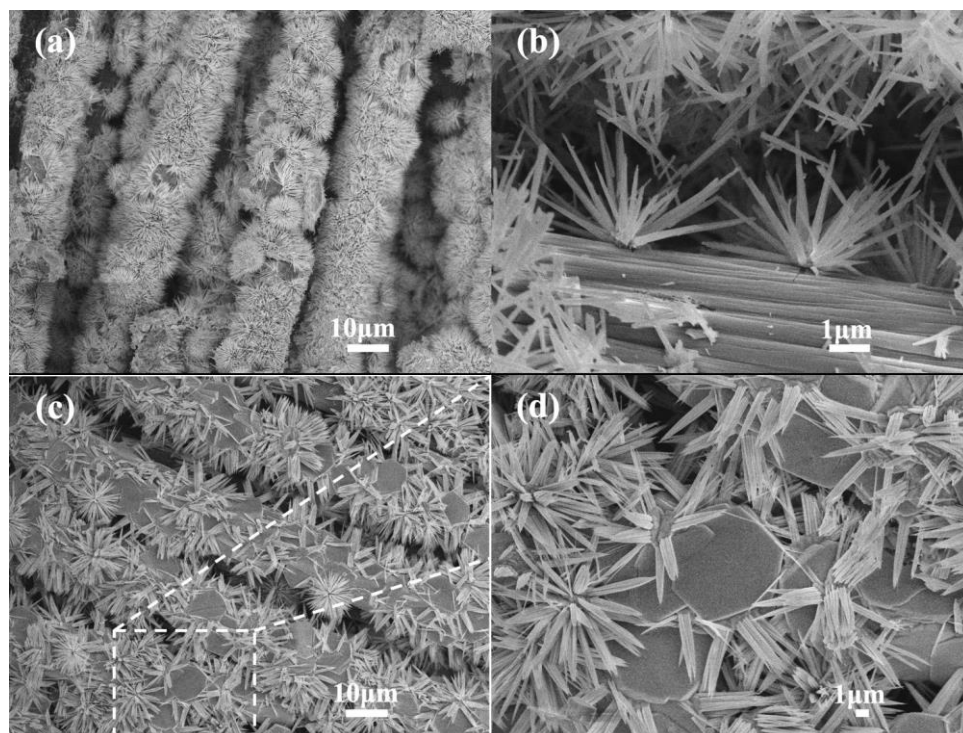
Along with the advance of electric vehicles and portable electronic devices, insufficient capacity and environmental problems have drawn more attention on energy storage systems, especially rechargeable metal-air batteries because of their remarkable theoretical capacity, low cost, and environmental-friendly. However, the fabrication process and efficiency of gas diffusion electrode has limited their large-scale applications [1-2]. Herein, a simple method is developed to directly synthesize electrocatalytic materials (e.g.  $\text{Co}_3\text{O}_4$ ) on carbon fiber cloth without additives, which shall not only simplify the assembly process of gas diffusion electrode but also improve electrocatalytic activity for oxygen reduction reactions.

In our experiments, pretreated carbon fiber clothes were used as substrates, acicular clusters or sheets of  $\text{Co}_3\text{O}_4$  precursor were obtained by hydrothermal reaction with different concentrations of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , ammonium fluoride and urea in distilled water for 8 or 5 h, respectively. The precursor was rinsed several times with distilled water, dried at  $60^\circ\text{C}$  for 12 h, and then annealed at  $330^\circ\text{C}$  for 2 h in air. The morphology and electrochemical properties of the samples were characterized by field emission scanning electron microscopy (FESEM, JEOL, JSM-6700F) and electrochemical workstation (Chenhua, CHI 760E), respectively.

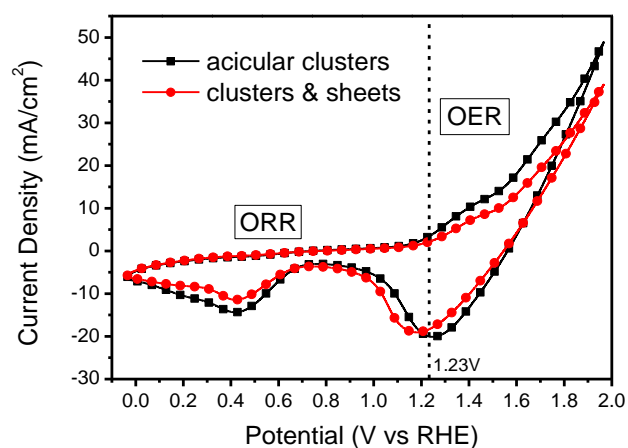
It is challenging to synthesize  $\text{Co}_3\text{O}_4$  materials on the surface of carbon fibers owing to their smooth and graphitic surface. While in this study, a simple hydrothermal reaction is developed to obtain uniform  $\text{Co}_3\text{O}_4$  acicular clusters and sheets on carbon fiber surfaces. As given in Figure.1a-b. acicular  $\text{Co}_3\text{O}_4$  clusters are formed on the substrate surface with a diameter from 100 to 200 nm and a length in several  $\mu\text{m}$ . Different morphologies of  $\text{Co}_3\text{O}_4$  can be synthesized by varying concentrations of the solution and reaction time. For instance, Figure 1c-d. displays that the surface of carbon fiber is uniformly covered with a mixture of  $\text{Co}_3\text{O}_4$  sheets and acicular clusters. Figure 2 shows electrochemical properties of these two types of  $\text{Co}_3\text{O}_4$  structures in oxygen saturated 0.1M KOH solution. As for oxygen reduction reactions (ORRs),  $\text{Co}_3\text{O}_4$  acicular clusters have lower onset potential and higher current density than the mixture of acicular clusters and sheets. In the oxygen evolution reaction (OER) region, the acicular cluster also exhibits lower potential at the same current density of  $10 \text{ mA cm}^{-2}$  than the sheets. The results above clearly demonstrate that acicular  $\text{Co}_3\text{O}_4$  clusters have better catalytic performances of both ORR and OER electrocatalytic activities. Therefore,  $\text{Co}_3\text{O}_4$  with different morphologies and electrochemical properties can be directly synthesized on the surface of carbon fibers as electrode materials for metal-air batteries.

## References:

- [1] X. Chen *et al*, *Small* **14** (2018), p. 1801929.  
 [2] Z. Cui *et al*, *ECS Journal of Solid State Science and Technology* **7** (2018) p. M161.  
 [3] This work was financially supported by the National Natural Science Foundation of China (21776147, 61604086 and 21606140), the International Science & Technology Cooperation Program of China (2014DFA60150), the Department of Science and Technology of Shandong Province (ZR2018BB066), and the Department of Education of Shandong Province (J16LA14 and J17KA013). L. F. Dong also thanks financial support from the Malmstrom Endowment Fund at Hamline University.



**Figure 1.** SEM images of (a-b)  $\text{Co}_3\text{O}_4$  acicular clusters obtained from 0.16 M  $\text{Co}^{2+}$  solution for 8 h and (c-d)  $\text{Co}_3\text{O}_4$  clusters & sheets obtained from 0.125 M  $\text{Co}^{2+}$  solution for 5 h.



**Figure 2.** Cyclic voltammetry (CV) curves of two types of  $\text{Co}_3\text{O}_4$  structures at a scan rate of  $50 \text{ mV} \cdot \text{s}^{-1}$ .