



# Hierarchical cerium oxide derived from metal-organic frameworks for high performance supercapacitor electrodes



Guojin Zeng<sup>a,b</sup>, Ying Chen<sup>a,b</sup>, Lin Chen<sup>a,b</sup>, Peixun Xiong<sup>a,b</sup>, Mingdeng Wei<sup>a,b,\*</sup>

<sup>a</sup> State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, Fujian 350002, China

<sup>b</sup> Institute of Advanced Energy Materials, Fuzhou University, Fuzhou, Fujian 350002, China

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## ABSTRACT

Presented in this report is a new, simple and effective method for synthesizing hierarchical dumbbell-shaped CeO<sub>2</sub> derived from a Ce-BTC MOF at room temperature. The product was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopic measurements. When used as an electrode in a supercapacitor with a KOH electrolyte and a K<sub>4</sub>Fe(CN)<sub>6</sub> redox-active additive, the capacitor exhibited large a specific capacitance, high rate capability and good cycling stability. Capacitances of 779 and 501 F g<sup>-1</sup> were achieved at rates of 1 and 15 A g<sup>-1</sup>. Simultaneously, the capacity retention was maintained at nearly 91% after 10000 cycles.

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## 1. Introduction

Electrochemical supercapacitors exhibit high power density, long cycle life and balanced rate performance, which has generated great research interest [1]. According to their relative charge storage mechanism, supercapacitors can be classified into two categories. The first is the electrostatic double-layer capacitor that stores energy on the internal surfaces of the carbon-based active materials [2]. The second is the pseudo-capacitor that is centered on fast and reversible redox electrochemical reactions on the surface of active materials [3]. A large number of electrode materials including carbon [4–6], transition metal oxides [7–9] and conducting polymers [10,11] have been developed to increase performance, but none can meet the standards for supercapacitors due to their low capacitance, high cost and poor stability. Thus, it is necessary to develop new electrode materials for supercapacitors with higher energy densities, better rate capabilities and longer cycling lifetimes.

Metal-organic frameworks (MOFs), with large surface areas, adjustable pore sizes and incorporated redox metal centers represent a promising electrode material for supercapacitors

[12]. Previously, our group reported on a layered structural Ni-based MOF electrode [13], which exhibited a capacitance of 1127 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>. Doping of this Ni-based MOF with Zn ions [14], resulted in a higher capacitance of 1620 F g<sup>-1</sup> at 0.25 A g<sup>-1</sup>. Moreover, Wang et al. [15] investigated Co-based layered MOF as a supercapacitor electrode, which achieved a specific capacitance of 2474 F g<sup>-1</sup> at 1 A g<sup>-1</sup>. Unfortunately, MOFs have poor electronic conductivity, low steric hindrance and bad electrolyte compatibility, which restricts their application in supercapacitors.

Recently, MOF-derived transition metal oxides have also proven to be useful for supercapacitors, because of their large, accessible internal surface areas, which can facilitate diffusion of ions through their highly porous substructure [12]. Zhang et al. [16] obtained a hierarchical Co<sub>3</sub>O<sub>4</sub> material by heating a Co-based MOF in air which exhibited an initial specific capacitance of 208 F g<sup>-1</sup> at 1 A g<sup>-1</sup>. Guo et al. [17] prepared porous Co<sub>3</sub>O<sub>4</sub> materials using the same method, which exhibited a capacitance of 150 F g<sup>-1</sup> at 1 A g<sup>-1</sup>. Moreover, other derivations from ZIF-67 [18], Co-MOF [19] and Fe-MOF [20] also exhibited good cycling stability. In general, the charge storage in MOFs-derived metal oxides is based on the surface faradic processes which are strongly affected by the diffusion of ions.

To date, CeO<sub>2</sub>, a low-cost, rare earth metal oxide with a dynamic redox couple and eco-friendly features, has been investigated in a very limited fashion as a supercapacitor electrode

\* Corresponding author at: State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, Fujian 350002, China.  
E-mail address: [wei-mingdeng@fzu.edu.cn](mailto:wei-mingdeng@fzu.edu.cn) (M. Wei).

material. Gopalan et al. [21] achieved a capacitance of  $523 \text{ F g}^{-1}$  at  $2 \text{ mV s}^{-1}$  using hexagonal  $\text{CeO}_2$  nanoparticles. Wang et al. [22] prepared a  $\text{CeO}_2$ -graphene composite, which exhibited a capacitance of  $208 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$ . In particular, Padmanathan et al. [23] reported on carbon-supported  $\text{CeO}_2$  nanorods, which showed a high capacitance of  $644 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$ . Although their specific surface areas are relatively small,  $\text{CeO}_2$  can also be expected to be a potential electrode material for supercapacitors. Traditionally, the electrolytes used in supercapacitors are aqueous or organic solutions or liquid salts (commonly known as ionic liquids) [24]. Aqueous solutions are the most common electrolyte used in supercapacitors by virtue of their high ionic conductivity. Examples include, KOH, LiOH,  $\text{Na}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$  and so on. At present, reports on the modification of the electrolyte to further improve the supercapacitor performance are relatively rare. Recently, Sandipan et al. [25] demonstrated that addition of  $\text{K}_4\text{Fe}(\text{CN})_6$  into KOH solution significantly influenced the pseudo-capacitive performance of  $\text{MnO}_2$ . Adopting a similar strategy, a dramatic improvement for MOF derived  $\text{CeO}_2$  was also achieved [26]. These results encouraged us to initiate considerable study to the use of  $\text{K}_4\text{Fe}(\text{CN})_6$  in supercapacitor electrolytes.

Herein, we proposed a facile synthesis of a hierarchical, dumbbell-shaped  $\text{CeO}_2$  architectures at room temperature using Ce-BTC MOF as a sacrificial template. In addition, this material was then used as an electrode in a supercapacitor, with  $\text{K}_4\text{Fe}(\text{CN})_6$  as a redox-active additive in a KOH solution, which exhibited good electrochemical performance.

## 2. Experimental

### 2.1. Materials synthesis

All the reagents in the experiments were analytical grade and used without any further purification.

#### 2.1.1. Synthesis of Ce-BTC MOF

In a typical synthesis of the Ce-BTC MOF dumbbell-shaped architectures [27], 1 ml of 0.5 mol/l  $\text{Ce}(\text{NO}_3)_3$  aqueous solution was slowly added to 1,3,5- $\text{H}_3\text{BTC}$  (0.5 mmol/l) water-ethanol solution (40 ml, v/v=3:1) dropwise with vigorous stirring at room temperature and a large quantity of white precipitate occurred immediately. After stirring for 10 min, the precipitate was collected by centrifugation and thoroughly washed several times with ethanol and water. Finally, the white product was dried at  $70^\circ\text{C}$  for 12 h in air.

#### 2.1.2. Synthesis of $\text{CeO}_2$

Briefly,  $\text{CeO}_2$  was synthesized via treatment of Ce-BTC MOF in 2 mol/l KOH at room temperature for 2 h. And then the precipitate was collected by centrifugation and thoroughly washed several times with ethanol and water. Finally, the product was dried at  $70^\circ\text{C}$  for 12 h in air. The resulting powder was straw yellow in color.

### 2.2. Materials characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray diffractometer by using the Cu-K $\alpha$  radiation. Scanning electron microscopy (SEM) and transmission electron microscopy observations (TEM) were obtained using an Hitachi S4800 instrument and a FEI F20 S-TWIN instrument. The surface area of the product was determined using the Brunauer–Emmett–Teller (BET) method employing a ASAP2020 instrument from Quanta Chrome. Initially, the sample was vacuum degassed for 6 h at  $150^\circ\text{C}$  under flowing nitrogen before the BET measurement. Fourier transform infrared (FTIR) transmission spectra of the products were obtained using a BRUKER-EQUINOX-55 IR

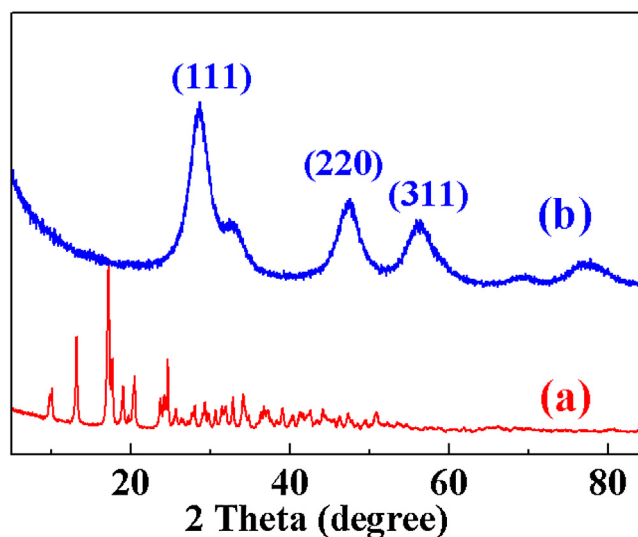


Fig. 1. XRD patterns of (a) Ce-BTC MOF and (b)  $\text{CeO}_2$ .

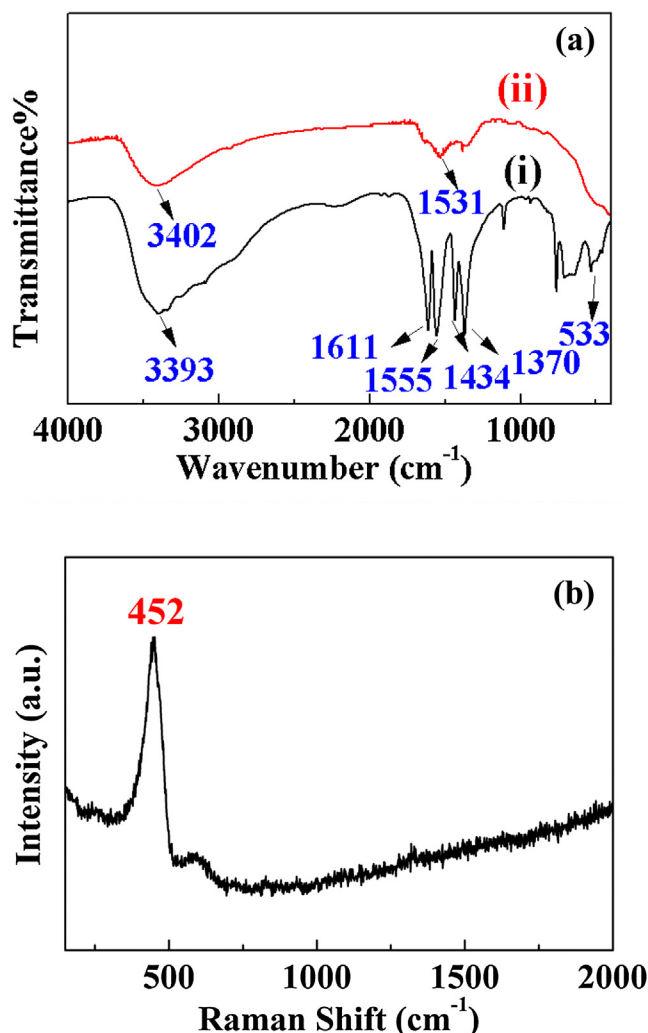


Fig. 2. (a) FTIR spectra of (i) Ce-BTC MOF, (ii)  $\text{CeO}_2$ ; (b) Raman spectrum of  $\text{CeO}_2$ .

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