Solvent-assisted synthesis of dendritic cerium hexacyanocobaltate and derived porous dendritic Co₃O₄/CeO₂ as supercapacitor electrode materials

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Experimental

Synthesis of Ce-Co PBA precursor

Firstly, solution A: 2 mmol of Ce(NO₃⁻)₃ were added into a mixture of ethanol (100 mL) and deionized (DI) water (x mL). Solution B: 5 mL, 0.2 M K₃Co(CN)₆ aqueous solution was injected into the above solution A with stirring for 5 min. Then the mixture solution was put at room temperature for 12 h. As shown in Table S1, The volume ratios of mixed solvent (ethanol and DI water; 100 mL/(x+5) mL) were 1:1, 2:1, 3:1 and 4:1, respectively. The products were centrifuged, and rinsed with ethanol 3 times, which were denoted as "Ce-Co PBA-1", "Ce-Co PBA-2", "Ce-Co PBA-3"and "Ce-Co PBA-4", respectively. The precipitates were dried under vacuum at 60 °C overnight. Synthesis of porous Co₃O₄/CeO₂-H and Co₃O₄/CeO₂-D

Ce-Co PBA-1 with hexagonal bipyramidal microcrystals and Ce-Co PBA-4 with dendritic microcrystals were heated to 500°C under air for 2 h (with a ramp 5°C/min), which were denoted as " Co_3O_4/CeO_2 -H", and " Co_3O_4/CeO_2 -D", respectively.

Characterizations

The morphology of products was observed by scanning electron microscope (SEM, Japan, Hitachi JSM-7500F) and transmission electron microscope (TEM, FEI TECNAI G2 F20). Thermogravimetric analysis (TGA) was conducted on a Switzerland METTLER TOLEDO thermal analyzer from 50 to 700°C under air. Transmission Electron Microscope (TEM) using an accelerating voltage of 20 kV. Raman spectroscopy was collected on a Renishaw in Via confocal Raman system. The Brunauer–Emmett–Teller (BET) surface area was measured using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry System in a N₂ atmosphere. EPR spectroscopy was recorded on A300-9.5/12 electron paramagnetic resonance spectrometer. X–ray diffraction (XRD) was performed on Shimadzu XRD-6100 X-ray diffractometer from 10-70°. Nitrogen adsorption desorption analyses were conducted on Quantachrome Instruments at 77K. X-ray photoelectron spectroscopy (XPS) was collected on ThermoFischer, ESCALAB Xi+.

Electrochemical measurements

The as-prepared active materials, acetylene black and poly(vinylidene fluoride) at the weight ratio of 8:1:1 with a suitable amount of N-Methyl pyrrolidone were mixed under vigorous stirring for 2 h to prepare the slurry to fabricate working electrode. Then the slurry was drop-dried into several pieces of Ni foam and dried at 80 °C under vacuum

for 12 h. The mass loading of active materials was about 2-2.5 mg/cm². CHI 660E electrochemical workstation were used to explore the electrochemical properties in 6.0 M KOH solution. In a three-electrode system, platinum and Hg/HgO electrode were used for the counter electrode and the reference electrode.

The specific capacitances of the electrodes in the three-electrode two-electrode system were calculated by from the following equation (1).

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where I is response current, Δt is discharge time, m is mass of active materials and ΔV is potential window, respectively. The energy density (E) and power density (P) in twoelectrode system were obtained from the following equations (2) and (3).

$$E = \frac{1}{2}CV^{2}$$
(2)
$$P = \frac{E * 3600}{\Delta t}$$
(3)

Where C is specific capacitance, V is potential window and Δt is discharge time in the two-electrode system, respectively.

Sample	Solution A		Solution B
	EtOH (mL)	H ₂ O (mL)	$H_2O(mL)$
Ce-Co PBA-1	100	95	5
Ce-Co PBA-2	100	45	5
Ce-Co PBA-3	100	28.3	5
Ce-Co PBA-4	100	20	5

Table S1. The volume of the solvent in the mixed solvent for the samples



Fig. S1. Low-magnification SEM image of Ce-Co PBA with different radio of ethanol and water:

(a) 1:1, (b) 2:1, (c) 3:1, (d) 4:1.



Fig. S2. Schematic crystal structure of Ce-Co PBA.



Fig. S3. The pore size distributions of Ce-Co-PBA-1, Ce-Co-PBA-2, Ce-Co-PBA-3, and Ce-Co-PBA-4.



Fig. S4. (a) Low-magnification and (b) high-magnification SEM images of Ce-Co PBA after the solution was diluted 3-fold



Fig. S5. TGA of Ce-Co PBA under air



Fig. S6. (a) Low-magnification and (b) high-magnification SEM images of Co_3O_4/CeO_2 -H



Fig. S7. (a) SAED image of Co₃O₄/CeO₂-D.



Fig. S8. (a) N_2 adsorption–desorption isotherms and (b) corresponding pore size distributions of Co_3O_4/CeO_2 -H and Co_3O_4/CeO_2 -D.



Fig. S9. XPS spectra of Co_3O_4/CeO_2 -H and Co_3O_4/CeO_2 -D.



Fig. S10. EPR spectra of Co_3O_4/CeO_2 -H and Co_3O_4/CeO_2 -D.



Fig. S11. CV curves at different scan rates of Co₃O₄/CeO₂-H electrodes.



Fig. S12. (a) CV curves of AC and Co₃O₄/CeO₂-D electrodes measured in three-electrode system at 10 mV/s; (b) CV curves of the Co₃O₄/CeO₂-D//AC ACS at 50 mV/s at various potential windows; (c) GCD curves and(d) corresponding specific capacity of the Co₃O₄/CeO₂-D//AC ACS at various current densities; (e) Cycling stability of the Co₃O₄/CeO₂-D//AC ASC at 3 A/g. (f) Ragone plot of the Co₃O₄/CeO₂-D//AC ASC. (the inset: the digital image of a LED lit by the devices)



Fig. S13. CV curves (a) and GCD curves (b) at different potential window of Co_3O_4/CeO_2 -D//AC ASC.

Table S2. The relative ratios of the surface concentration of Ce^{3+} and O_Vs based on XPS analysis

Samples	Ce^{3+} (%)	O _V S (%)
Co ₃ O ₄ /CeO ₂ -H	14.7	6.5
Co ₃ O ₄ /CeO ₂ -D	15.9	7.6