Supporting Information

Neodymium-doped Ceria Nanomaterials: Facile Low-Temperature Synthesis and Excellent Electrical Properties for IT-SOFCs

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Experimental

Sample preparation

Chemicals: CeO_2 (99.99%, Sinopharm Chemical Reagent Co. Ltd), $Nd(NO_3)_3 \cdot 6H_2O$, (99.99%, Tianjin Guangfu Chemical Institute), NaOH (analytical grade) and KOH (analytical grade) were used as received without further purification.

Heavily neodymium-doped ceria ($Ce_{0.8}Nd_{0.2}O_{1.9}$) nanowires were prepared by a composite-hydroxide-intermediated (CHM) method. In a typical synthesis, the stoichiometric CeO_2 (3.0293 g, 17.6 mmol) and $Nd(NO_3)_3 \cdot 6H_2O$ (1.9283 g, 4.4 mmol) were first ground and mixed in an agate motar, then added into a 40 mL Teflon beaker as raw materials for reaction, resulting in the mixture of CeO_2 and $Nd(NO_3)_3$, and the molar ratio of Ce/Nd was 4:1. Subsequently, an amount of 20 g of mixed hydroxides (NaOH/KOH = 51.5:48.5 in weight) was placed on the top of the above mixture in the beaker. The beaker was put in the digital oven, then maintained at 240 ^{o}C in ambient air. After the hydroxides were totally molten, the hydroxide solution was stirred by shaking the beaker to ensure the uniformity of the mixed reactants. After 72 h, the beaker was naturally cooled to room temperature. The obtained powder was filtered and washed by deionized water for several times to remove hydroxides on the surface of the particles. Finally, the resulting products were dried in air at 60 ^{o}C. In order to obtain the densified ceramic samples for electrical measurements, the as-prepared powders were uniaxially pressed into cylindrical pellets (diameter in 12 mm) at 200 MPa, and the resulting green pellets were sintered at different temperatures (1200 ^{o}C, 1300 ^{o}C and 1400 ^{o}C) for 12 h in air, employing a

heating and cooling rate of 5 ^{o}C min^{-1}. The apparent densities of sintered pellets were

determined by Archimedes principle using water as immersing medium.

Characterizations

Powder X-ray diffraction (PXRD) patterns of the samples were performed on a

Rigaku D/MAX-2500 diffractometer operating at 40 kV and 150 mA, using Cu Kα

radiation (λ = 1.5406 Å). The data were collected at room temperature over the 2θ

angle range 10-90° with a step size of 0.02^o. A full pattern profile matching

refinement was performed using a strain/size refinement model in Material Studio

(MS4.4) package. The background was presented by a twentieth-order Legendre

polynomial, and the peak shapes were described by a pseudo-Voigt function with 12

parameters. The refinement of peak asymmetry was performed using four

Berar-Baldinozzi parameters. Composition and impurity analyses of the as-prepared

samples were also confirmed using inductively coupled plasma-Mass spectroscopy

analysis (ICP-MS) (Thermal Electron, XSeries II). The product is confirmed as

$Ce_{0.8}Nd_{0.2}O_{1.9}$ with the ratio of Ce/Nd is 18.0:4.6, which is good agreement with the

starting materials. The SiO_2 content of the products is determined to be about 27 ppm.

The microstructures of the powders and sintered pellets were observed using a

field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800 and Philips

XL-30) equipped with energy-dispersive spectroscopy (EDS) for element analysis.

Transmission electron microscopy (TEM), high-resolution transmission electron

microscopic (HRTEM) images and selected area electron diffraction (SAED) patterns

were obtained on a JEOL 2100 microscope operated at 200 kV. A standard carbon-coated (20-30 nm) Formvar film on a copper grid (230 mesh) was used as sample holder. X-ray photoelectron spectroscopy (XPS) measurements were performed with AXIS ULTRA DLD. Before being sent to the chamber, each sample was cleaned carefully. The base pressure of the instrument was 7×10^{-8} Pa. Binding energy was calibrated referenced to the C 1s peak (284.6 eV).

Electrical measurements

Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range from 0.01 Hz to 1 MHz on an Autolab PGStat30 impedance analyzer. The signal amplitude was 50 mV and 0 mV d. c. bias was used. Before measurements, Au paste was painted on two sides of the pellets to form the two-electrode configuration, and the pellets were then dried and fired at 800 $^{\circ}$C for 30 min to erase the solvent. The measurements were conducted in the temperature range from 300 $^{\circ}$C to 800 $^{\circ}$C with an increment of 50 $^{\circ}$C. Oxygen partial pressure was varied from 10^{-4} atm to 1 atm, which was obtained by flowing oxygen-nitrogen mixture through the cell, and controlling the gas flow (total value of 100 sccm) using digital flow-meters (Brooks Instruments). The actual oxygen partial pressure was measured using an electrochemical oxygen sensor (ZDO-102, China). Curve fitting and resistance calculation were done by Zview software. The conductivity (σ) was determined from the corresponding resistances, taking into account the geometric factor $\sigma = L/(AR)$, where R is the resistance obtained from EIS data, L is the pellet

thickness and A is the electrode area of the sample surface. Activation energies (E_a)

were calculated by fitting the conductivity data to the Arrhenius relation for thermally

activated conduction, which is given as $\sigma T = \sigma_0 \exp(-E_a/kT)$, where σ_0, k, T are the

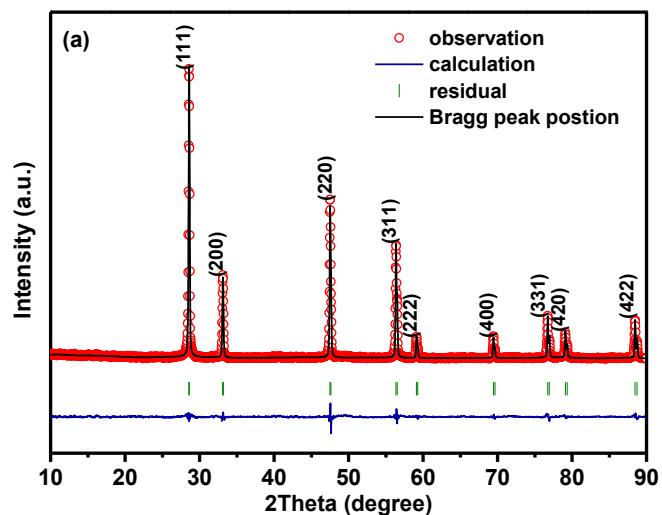pre-exponential factor, Boltzmann constant and absolute temperature, respectively.

Figures

Fig. S1 Rietveld refinement profile for the as-prepared CNO nanomaterials at room temperature using a strain/size refinement model. The observed and calculated profiles, Bragg peak positions, and the residuals between the observed and calculated profiles are shown.
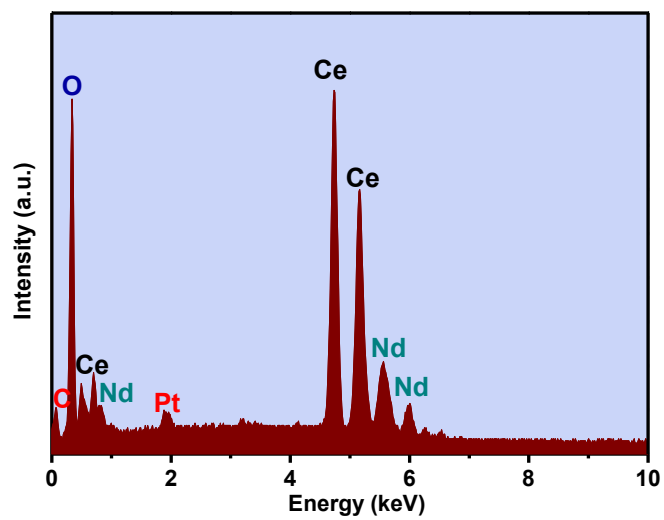
Fig. S2 EDS pattern obtained from the as-prepared products, indicating that the products can be identified as CNO.
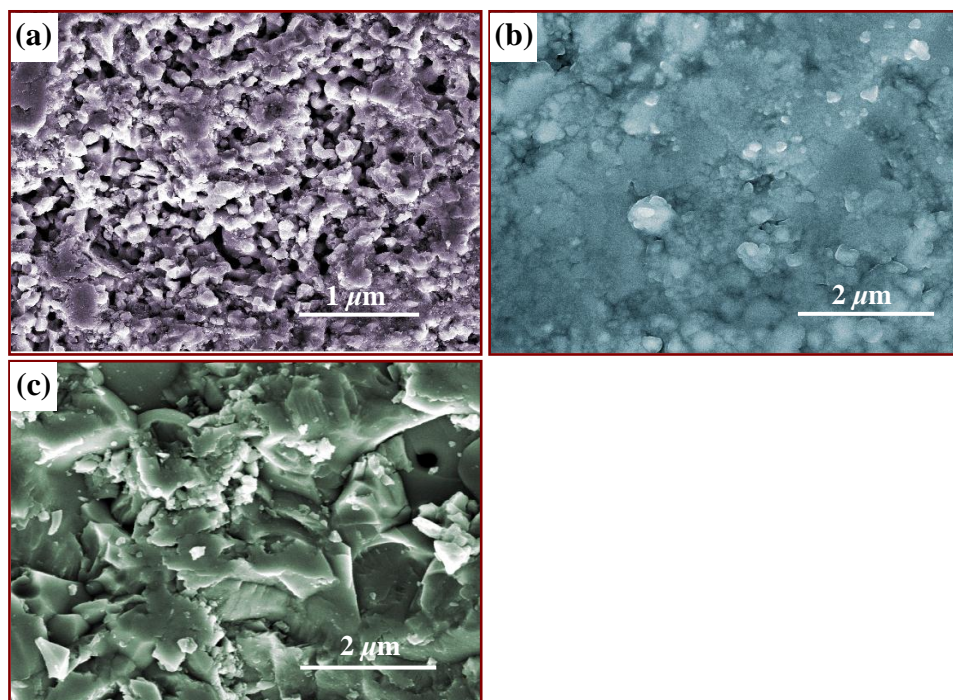
Fig. S3 SEM images of the CNO pellets sintered at (a) 1200 ^{o}C, (b) 1300 ^{o}C and (c)
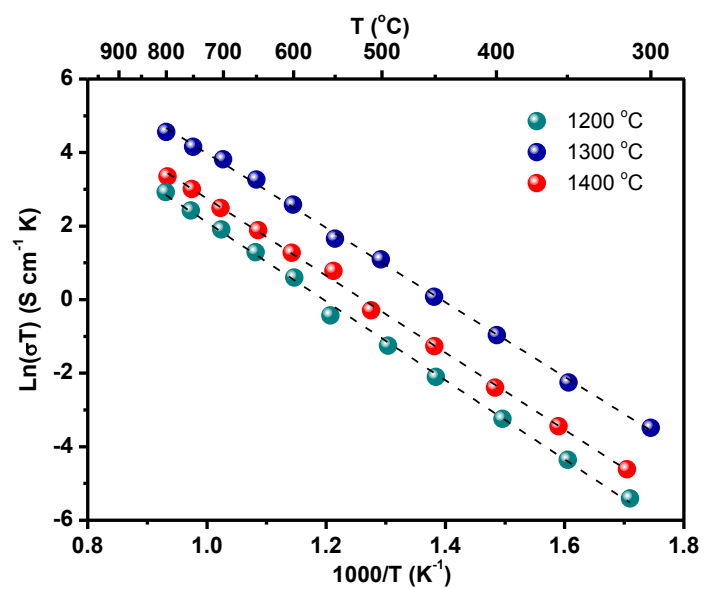
1400 ^{o}C for 12 h.

Fig. S4 Arrhenius plots for the total conductivities of the CNO electrolytes sintered at

1200 ^{o}C, 1300 ^{o}C and 1400 ^{o}C for 12 h.