

Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2015

A Facile Citric Acid Assisted Sol-gel Method for Preparing Monolithic Yttria-Stabilized Zirconia Aerogel

Zhiyi Zhang,^a Qiuyue Gao,^a Yi Liu,^a Chunmei Zhou,^a Mingjia Zhi,^{*a} Zhanglian Hong,^{*a}

Fan Zhang^b and Bin Liu^b

^a State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

^b Aerospace Research Institute of Special Material and Processing Technology, Beijing 100074, PR China

* To whom correspondence should be addressed. E-mail:

hong_zhanglian@zju.edu.cn (Zhanglian Hong); mingjia_zhi@zju.edu.cn

(Mingjia Zhi)

1. Experimental

Materials: All the analytically pure chemical reagents, including the zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) and ethanol (EtOH), were purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC), and were used as received without further purification.

Preparation of yttria-stabilized zirconia aerogels: Typically, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were completely dissolved in 60 ml ethanol in the molar ratio of 92:16 and stirred to give a clear colorless solution. The ion concentrations of Zr^{4+} and Y^{3+} were 0.46 and 0.08 mol/L, respectively. A given volume (1-9 ml) of citric acid ethanol solution (1 mol/L) was then quickly added into the above solution under continuous stirring. The solution was then transferred to a sealed glass containers at 60 °C and gel monoliths was formed (the sols no longer flow when the reaction containers were steeply tilted). The wet gels were then aged for 24 h at 40 °C in ethanol in closed containers. Finally the aged wet gel was subjected to supercritical drying in ethanol at 260 °C for 1 hour to give YSZ aerogel. The experimental parameters for the as prepared YSZ aerogels are listed in Table 1. The samples were denoted as A1, A2, A3, A4 and A5 based on the amount of citric acid used.

Characterization: The morphology of the aerogel was observed by using HITACHI S-4800 scanning electron microscope (SEM).

Transmission electron microscopy (TEM) was performed on Philips CM-120 microscope. X-ray diffraction (XRD) measurements were performed in a X-ray diffractometer (XRD-6000, Shimadzu) with the use of Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 4°/min scanning speed in the 2 θ range from 10° to 90°. A Nitrogen adsorption–desorption measurements (Quantachrome Instrument Corp) was used to obtain the nitrogen physisorption isotherms at 77 K. Surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method from the adsorption branch of the isotherm. The pore-size distributions were calculated according the Barrett-Joyner-Halenda (BJH) model, and the average pore diameters and cumulative pore volumes were calculated using the desorption branch of the isotherm.

Table 1 The preparation parameters of the YSZ aerogels

Sample ID	Citric acid solution (ml)	Color of the wet gel	Gelation time(min)	Color of the aerogel	Aerogel density (g/cm³)
A1	1	transparent	1200	white	0.264
A2	3	white	30	white	0.222
A3	4.5	white	10	white	0.166
A4	6	white	5	white	0.105
A5	9	white	1	white	0.097

Table 2 The surface area, pore volume of the aerogel A1 to A5.

Sample ID	Surface area (m ² /g)	Pore Volume (cm ³ /g)
A1	213	2.058
A2	225	1.688
A3	317	1.702
A4	400	1.855
A5	490	1.928

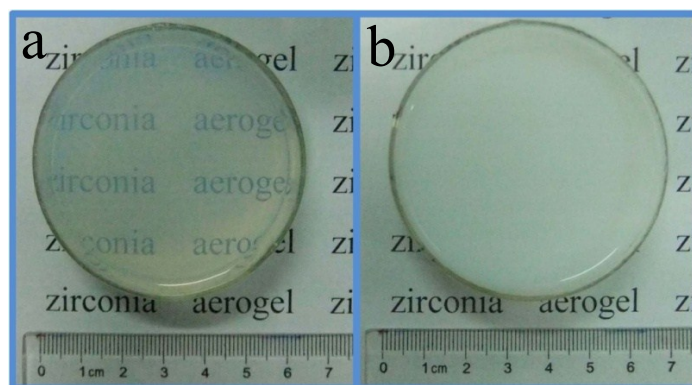


Figure S1 wet gel of A1 (a) and A5 (b).



Figure S2 (a) citric acid/ethanol solution; (b) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} + \text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ethanol solution; (c) mixture of 1 ml citric acid ethanol solution and 10 ml $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} + \text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ethanol solution (d) mixture of 9 ml citric acid ethanol solution and 10 ml $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} + \text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ethanol solution .

The concentrations of citric acid, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ are 1mol/L, 0.46mol/L and 0.08mol/L, respectively.