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Preparation of zirconia aerogel with L-glutamic acid

Yangyang Wu[1], Shouquan Zhang[1], Gangling Chen[1]*, Xiaohui Tian[2]* & Xiaoqing Wang[1]*

[1]College of Materials and Chemical Engineering, Chuzhou University, Huifeng West Road 1#, Chuzhou 239000, China
[2]Suzhou Woshi Digital Technology Co., LTD, Xinhu Street 328#, Suzhou Industrial Park, Suzhou, 21500, China

*E-mail: xiaoqingwang2013@chzu.edu.cn (XW), tianxiaohui@zju.edu.cn (XT), chengangd@126.com (GC)

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In preparation of zirconia aerogel, propylene oxide (PO) is generally used as gel accelerator. PO is toxic and harmful to the environment. So in this article, green, environmental protection, safe and non-toxic L-glutamic acid (LGA) and L-aspartic acid (LAA) have been applied as gelators to replace PO. Series of ZrO_2 aerogels have been synthesized with sol-gel method by ethanol supercritical drying and characterized by XRD, SEM and TEM techniques. Nitrogen adsorption-desorption measurements have been used to characterize the specific surface area. The effect of H^+ concentration on the crystallinity of zirconia has also been studied. The prepared ZrO_2 aerogels with low density, low thermal conductivity, and high specific area can make them promising candidates for a wide array of multifunctional applications, e.g., catalyst support, energy conversion, and thermal insulation.

Keywords: Green and environmental protection, L-glutamic acid, Sol-gel, ZrO_2 aerogel

Introduction

Aerogel materials with large specific surface area, high melting point, low density and low thermal conductivity, have some advantages over other materials and have a very good application prospect in the fields of catalyst, catalyst carrier, high temperature insulation material, 3D printing, medical loading, ultra-low sound speed, photothermal conversion and so on [1-9]. The melting point of ZrO_2 blocks is about 2700 °C and the thermal conductivity at room temperature is about 2.4 W/mK [10, 11]. These advantages make ZrO_2 aerogel materials the first choice for a new generation of lightweight and efficient thermal insulation materials [12].

At present, two methods dominated the preparation of zirconium dioxide aerogel: one was the sol-gel method with organic zirconium source as raw material, and the other was sol-gel method with inorganic zirconium source as raw material and propylene oxide as gel accelerator [13-19]. Sui reported ZrO_2 aerogels using zirconium alkoxide hydrolysis in acetic acid [20]. Liu synthesized zirconia aerogels by hydrolysis of polyacetylacetonatozirconium applying ammonia hydroxide as the gel initiator [21]. Due to the high cost of metal alkoxides and their sensitivity to moisture, inorganic zirconium salts were applied to replace zirconia alkoxides using propylene oxide (PO) as gelators. Zhong synthesized ZrO_2 aerogels with well-developed mesoporous structure and a high specific surface area of 454 m^2/g by adjusting the ratio of HNO_3 to H_2O [22]. Chervin obtained Y_2O_3-stabilized ZrO_2 aerogels using $ZrCl_4$ as zirconium source [23]. However, consider the need for green environmental protection and cheap price, we developed an environmentally friendly sol-gel method to prepare zirconia aerogel using inorganic zirconium source as raw materials and amino acids as gel promoters [24, 25].

In this experiment, different volume of the acid amino acid L-glutamic acid (LGA) and L-aspartic acid (LAA) were used as gel accelerators, $ZrOCl_2{\cdot}8H_2O$ was used as zirconia source, for preparing ZrO_2 aerogels.

Experimental Section

Materials and reagents

All chemical reagents were analytically pure and used as received without further purification, including zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, 99.9%, Aladdin, China), L-glutamic acid (LGA, 99%, Aladdin, China), L-aspartic acid (LAA, 99%, Aladdin, China) and HCl solution, absolute ethanol (Sinopharm Chemical Reagent Co, Ltd (SCRC)).

Preparation of ZrO_2 aerogel

Firstly, 27.6 mmol of $ZrOCl_2{\cdot}8H_2O$ was dissolved in 60 mL of ethanol solution and 0.8 mol/L of LGA solution was prepared using a mixture ethanol and

HCl as solvent (volume ratio of 4:1). Then the LGA solution (2-8 mL) was rapidly fed into the zirconium salt solution. The mixed solution was mixed thoroughly. At last, the mixed solution was transferred to sealed strain bottles at 60 °C to form the wet gels. The wet gels were kept 2 h for Wald ripening at 60 °C. Subsequently, the wet gels were aged and dried in EtOH. The detailed steps and conditions were followed as per our previous reports[26]. The detailed experimental parameters of the preparation of ZrO_2 aerogels was given in Table 1.

Characterisation

Morphologies of the aerogels were characterized by both field emission scanning electron microscope (FE-SEM) (Gemini 450, Zeiss) and transmission electron microscopy (TEM) (JEOL-2100F). X-ray diffraction (XRD) measurement was performed in a X-ray diffractometer (JSM-6510LV) with Cu K_α radiation (λ = 1.5418 Å) at 10°/min scanning speed in the 2θ range from 10° to 70°. The porous properties of ZrO_2 aerogels were clarified by nitrogen adsorption and desorption isotherms measured at 77 K (3Flex, Micromeritics). The surface areas were calculated in the relative pressure (P/P_0) range from 0.01 to 0.1 using the Brunauer-Emmett-Teller (BET) method. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms applying the Barrett-Joyner-Halenda (BJH) model.

Results and Discussion

Material preparation

In this paper, zirconia wet gels were prepared by sol-gel method with environment-friendly amino acids LAA and LGA as gel accelerators and $ZrOCl_2{\cdot}8H_2O$ as inorganic zirconia source. Zirconia aerogels were obtained by supercritical drying. The reaction diagram was shown in Fig. 1.

From Table 1, it can be seen that the gelation time of zirconia was gradually shortened as the volume of acidic amino acids was increased. When the volume of $ZrOCl_2{\cdot}8H_2O$ and the concentration of acidic amino acid were immobilized, the larger the volume of acidic amino acid added, the shorter of the gelation time. It can be simply understood as: the more acidic amino acid content was added, the more -NH_2 and -COOH groups were around Zr^{4+}, so the gelation time was shortened. The possible gel mechanism of acidic amino acids and Zr^{4+} was shown in Scheme 1 [23,27,28]. Taking LGA as an example, $ZrOCl_2{\cdot}8H_2O$ hydrolyzed to $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ in Reaction (1) as shown in Scheme 1 [23,27,28]. Then Zr^{4+} and -NH_2 and -COOH groups in LGA formed covalent bonds and coordination bonds to form wet gels, which was shown in Reaction (4) in Scheme 1[27]. At the same time, there may be hydrogen bond interaction between -COOH and -NH_2 in LGA, as shown in

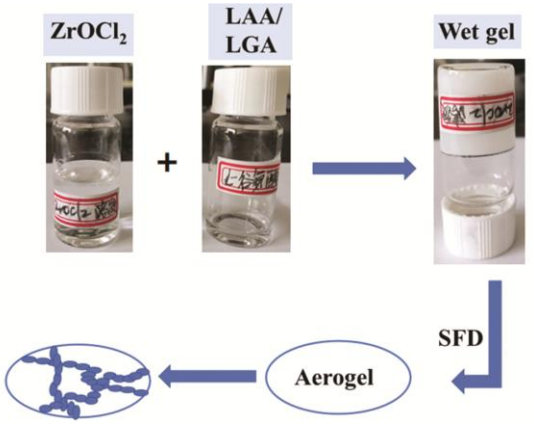
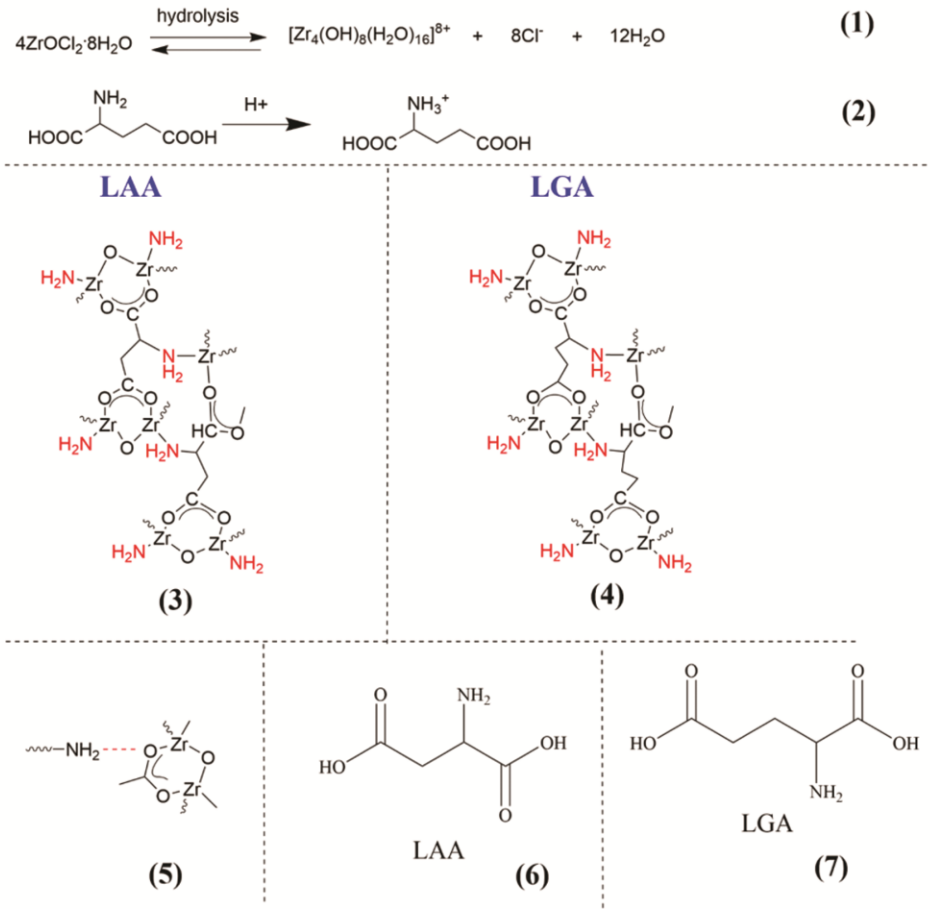


Fig. 1 — Formation process of the preparation of ZrO_2 aerogels

Table — Experimental parameters of the preparation of ZrO_2 aerogels

Sample series	V_{LGA} (mL)	Gelation time (min)	V_{HCl} (mL)	Colour of the gel	Gelation temperature (°C)	Aerogel
LAA-2	2	80	0	white	60	√
LAA-4	4	10	0	white	60	√
LAA-6	6	7	0	white	60	√
LAA-8	8	1	0	white	60	√
LGA-2 [a]	2	60	0	white	60	√
LGA-4	4	4	0	white	60	√
LGA-6	6	0.5	0	white	60	√
LGA-8	8	immediately	0	white	60	√
ZrO_2-0 HCl	6	0.5	0	white	60	xerogel
ZrO_2-0.5HCl	6	1.5	0.5	white	60	xerogel
ZrO_2-1HCl	6	3.5	1	white	60	xerogel
ZrO_2-1.5HCl	6	7	1.5	white	60	xerogel
ZrO_2-2HCl	6	10	2	white	60	xerogel

[a]LGA-2 means the volume of the gelation accelerator is 2 mL of LGA



Scheme 1 — Schematic representation of the reaction routes between the organic acid and the Zr^{4+} ions

Reaction (5) in Scheme 1. This complex interaction promoted the formation of three-dimensional gel network structure, and the same gel formation mechanism was also applicable to LAA system.

The influence of H^+ content on gelation time was also investigated. From Table 1, it can be easily seen that the gelation time increased as the volume of HCl increased. This result can be explained as more the amount of H^+, the slower hydrolysis rate of LGA, resulting the slower combination rate of LGA and $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. The gelation time was prolonged, which was consistent with our experimental results. However, when the volume of H^+ was more than 2 mL, the gelation cannot be obtained. The reason was that strong acidic conditions severely inhibit the condensation process and a network cannot be formed[29].

SEM analysis

The white bulk ZrO_2 aerogels were obtained after the supercritical drying. Our previous article gave the apparent photographs of wet gel and aerogel of LAA-4, respectively[31]. As can be seen, the wet gels can remain basically intact after supercritical drying process, and the aerogel with a diameter of about 4 cm can be obtained. This was because the low capillary force of supercritical fluid inhibited the collapse of nanopores in wet gels during drying process.

The surface morphology of the samples was characterized by SEM, as shown in Fig. 2. It can be seen that ZrO_2 aerogels were formed by a large number of accumulated nanoparticles, and mesoporous existed between nanoparticles. The surface morphology of ZrO_2 aerogels obtained by this method was basically no different from that obtained by the other two common methods of preparing aerogels, namely "inorganic salt method" and "propylene oxide method" [30, 31].

BET analysis

The specific surface area and pore structure of LGA series aerogels were studied by N_2 adsorption-desorption characterizations. Fig. 3a showed the

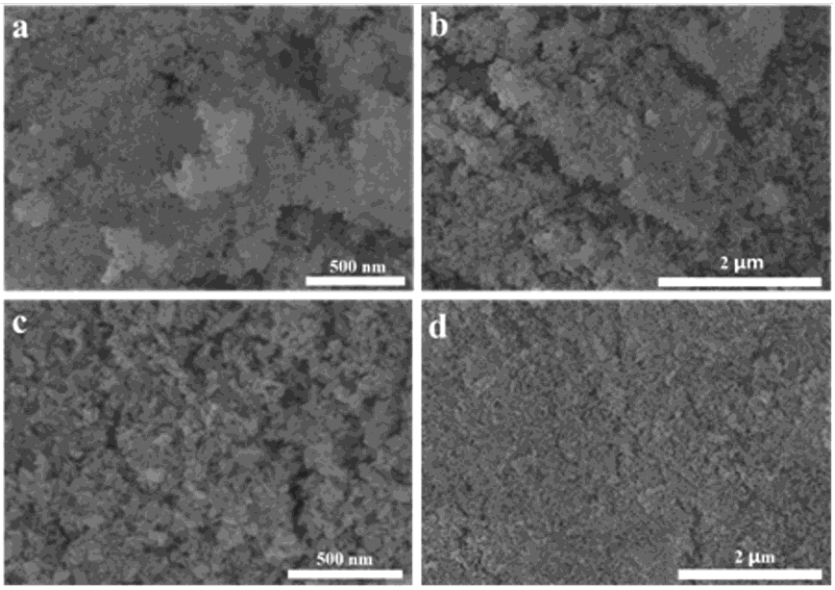


Fig. 2 — SEM images of (a, b) LGA-2 and (c, d) LGA-8 aerogels

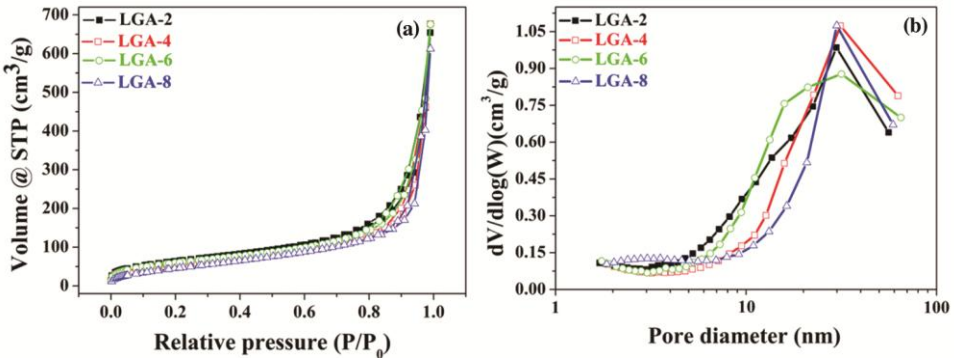


Fig. 3 — (a) Nitrogen adsorption-desorption isotherms and (b) the pore size distributions for the aerogel samples LGA-X (X = 2, 4, 6, 8)

isotherm curves of aerogel with different LGA supplemental amounts, which can be seen as type II curves, indicating the existence of large pores in the samples. The specific surface area and pore volume calculated by this method were shown in Table 2. It can be concluded that the specific surface areas of LGA-2, LGA-4, LGA-6 and LGA-8 aerogels were 233, 208, 219 and 186 m^2/g, respectively, and the pore volumes were 1.01, 1.05, 1.05 and 0.95 cm^3/g, respectively. This was similar to the specific surface area of ZrO_2 aerogels reported in other literatures [32, 33].

The above results showed that the specific surface area of ZrO_2 nanoporous aerogel materials prepared with organic acids as gel accelerators and $ZrOCl_2$ as zirconium source was equivalent to that of ZrO_2 nanoporous aerogel materials prepared with organic alcohols as zirconium source, which fully proved the value of this method. The pore size distribution of the corresponding aerogels can be seen in Fig. 3b.

Table 2 —Comparison of surface area, pore volume and pore diameter of LGA-X(X= 2, 4, 6, 8) aerogels as-prepared

Samples	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
LGA-2	233	1.01	29.8
LGA-4	208	1.05	31.2
LGA-6	219	1.05	31.7
LGA-8	186	0.95	30.1

LGA-X aerogels had a large number of pores with average pore size ranging from 20-30 nm, belonging to the mesoporous range, which was consistent with the ZrO_2 aerogel samples reported previously [34, 35].

TEM analysis

Fig. 4 (a, b) showed the microstructures of zirconia aerogel sample LGA-2 characterized by TEM. As can be seen from the images, zirconia aerogels were composed of a large number of irregular spherical particles. The average size of nanoparticles was about 3 nm. The boundary between the nanoparticles

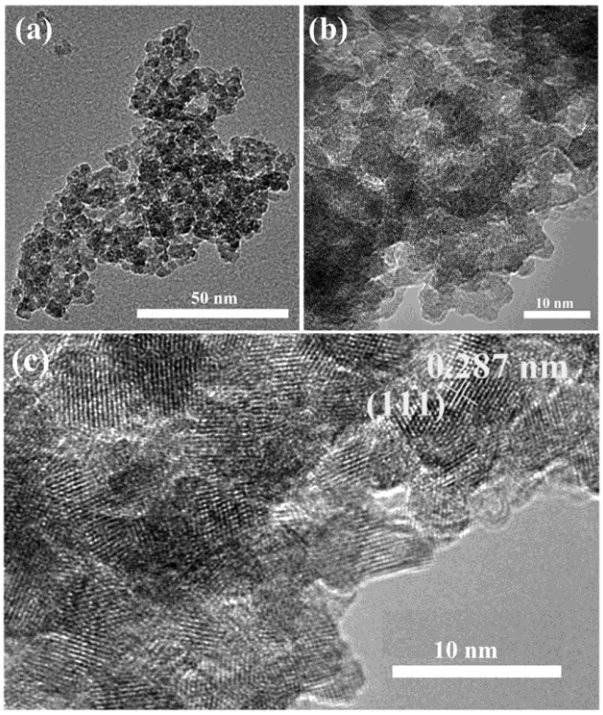


Fig. 4 — (a, b) TEM images and (c) HRTEM image of synthesized LGA-2 aerogel

was not clear and there were porous particles between them. At the same time, the lattice fringe of the monoclinic phase (111) plane can be clearly distinguished from the HRTEM atlas of high resolution transmission electron microscopy (Fig. 4c), and its width was 0.287 nm, indicating that the sample LGA-2 obtained after supercritical drying was crystalline, which was also consistent with the XRD results discussed later.

XRD analysis

The samples obtained by supercritical drying were not very crystalline, which can be verified by XRD results in Fig. 5(a). The curves showed that sample LGA-6 had wide diffraction peaks at 28.17°, 31.47° and 34.16°, respectively, which was corresponding to the monoclinic phase ZrO_2 of No. 37-1484 in the standard card [36]. After heat treatment at 400°C and 600°C, agglomeration occurred between particles, which increased the size of nanoparticles and enhanced the crystallinity of ZrO_2 aerogel samples, which was also consistent with the results previously reported [27, 37, 38].

We also investigated the effect of H^+ concentration on crystallization of ZrO_2. Take LGA-6 as an

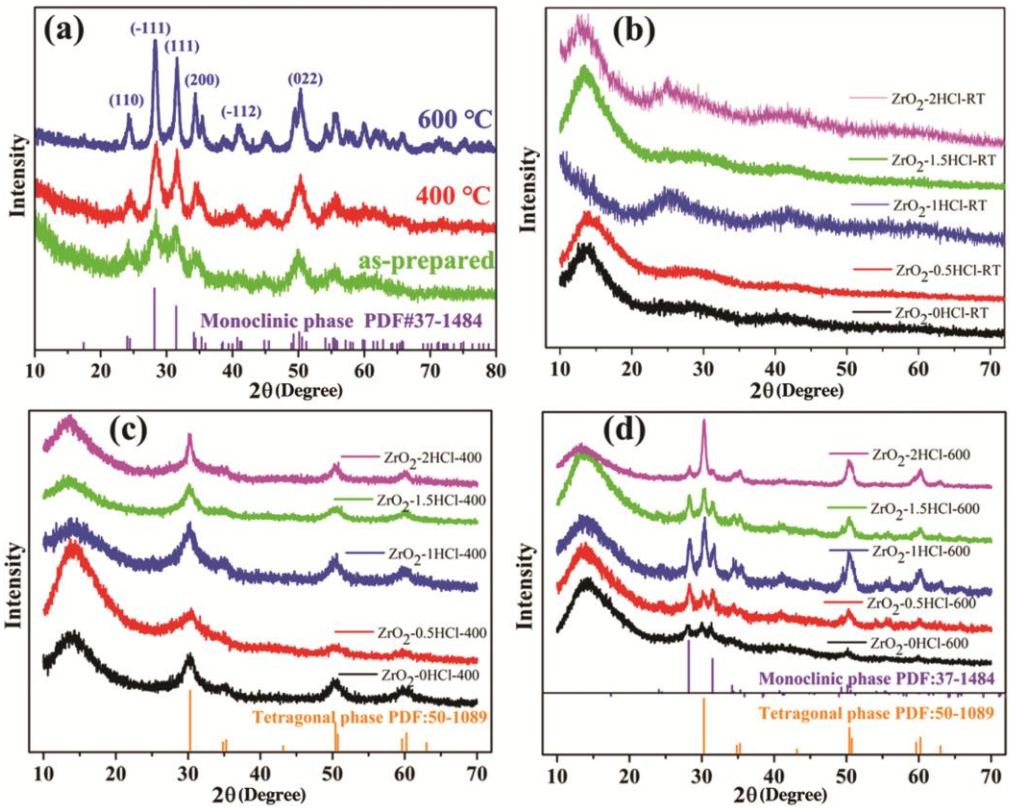


Fig. 5 — XRD plots of (a) LGA-6-aerogel, (b) ZrO_2-XHCl-RT xerogels, (c) ZrO_2-XHCl-400 xerogels treated with 400 °C and (d) ZrO_2-XHCl-600 xerogels treated with 600 °C (X = 0, 0.5, 1, 1.5, 2 mL)

example. In the process of the preparation of wet gels, the different volume of HCl of 1 mol/L was additional added. The gels were dried at atmospheric pressure after aging. Then the dried gels were heated at 400 °C and 600 °C. As shown in Fig. 5(b), the xerogels ZrO_2-XHCl-RT (X = 0, 0.5, 1, 1.5, 2 mL) were almost amorphous phase. While the as-prepared sample LGA-6-aerogel was weak crystal, which can be explained that the environment such as high temperature 260 °C and high pressure was helpful to crystallization. The results also showed that the samples ZrO_2-XHCl-400 (X = 0, 0.5, 1, 1.5, 2 mL) were tetragonal phase, belonging to the PDF card of ZrO_2 of 50-1089. While the samples ZrO_2-XHCl-600 (X = 0, 0.5, 1, 1.5, 2 mL) were mixed of tetragonal phase and monoclinic phase, belonging to the PDF card of ZrO_2 of 50-1089 and 37-1484, which were showed in Fig. 5(c) and (d). Furthermore, with the increase of H^+, tetragonal phase can be well maintained at 600 °C. The observed effect of the acid-to-Zr^{4+} ratio on the formation of zirconia gels was in agreement with other studies [39, 40].

Conclusion

In this paper, ZrO_2 aerogels were prepared by sol-gel method with the aid of acid amino acid as the gel promoter, $ZrOCl_2$ as the inorganic zirconium source, ethanol as the solvent. The raw materials of ZrO_2 aerogels prepared by this method were not only safe and non-toxic, but also environmentally friendly. The ZrO_2 aerogels obtained by supercritical ethanol drying were composed of nanoparticles, and its crystallinity was weak, and its specific surface area was about 233 m^2/g. The crystallinity of ZrO_2 aerogel was enhanced after heat treatment at 400 and 600 °C. The effect of H^+ concentration on the crystallinity of zirconia was studied. It was found tetragonal phase can be well maintained accompanied by an increase of H^+ at 600 °C.

Acknowledgement

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