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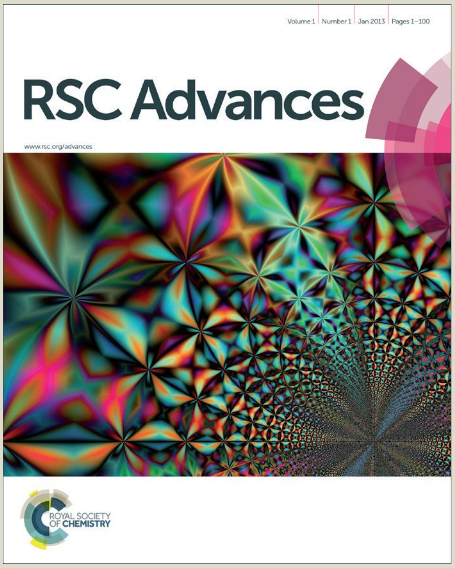

Journal Name

COMMUNICATION

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

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A facile and general strategy for the synthesis of yttria-stabilized zirconia (YSZ) aerogels was developed by using citric acid as gelation accelerator. This is a low-cost, nontoxic approach to prepare zirconia based aerogels which have very critical prospects of application in catalysis and insulation materials.

Aerogels with high surface area, low density and highly porous microstructure are greatly beneficial for various purposes, including absorbing and filtration media, heterogeneous catalysis, thermal insulators, and electrodes for batteries and capacitors.[1-6] Zirconia aerogels have attracted widespread interest in recent years because of its wide potential applications in catalyst-supports, chemical sensors, separation media, and thermal insulation materials.[7-13]

During recent years, great effort has been made on the synthesis of zirconia aerogel. Acid-catalyzed sol-gel method using zirconium alkoxide as precursors was firstly adopted to synthesize zirconia aerogel.[14-18] The resulted uncalcined zirconia aerogels have high surface areas up to 500 $m^2 g^{-1}$ and narrow pore size distribution.[14,19] However, the common zirconium alkoxide precursors such as zirconium n-propoxide,[14-21] zirconium iso-propoxide[22] and zirconium n-butoxide[23] have drawbacks such as high cost and high toxic. In addition, the fast hydrolyze rate of the alkoxide required the prevention of partial hydrolysis prior to the desired hydrolysis reaction, which limits the practicability of the synthesis procedures. [24,25]

Another method to prepare metal oxide aerogel was firstly proposed by Gash and co-workers, which adopts organ epoxide as the proton scavenger and inorganic metal salt as the precursor. [26-28] In such method, epoxide aids the hydrolysis and condensation reactions of the hydrate metal salt in water and other polar solvent, and various sol-gel materials can be formed.[28-30] Yttria-stabilized zirconia aerogels with high surface area (409 $m^2 g^{-1}$) were prepared from $ZrCl_4$ and $YCl_3•6H_2O$ by this method.[31] Zhong et al. also prepared monolithic zirconia aerogels via the epoxide assisted method from $ZrOCl_2•8H_2O$. The transparency of gel can changed by adjusting molar ratio of acid to zirconium and water to zirconium.[32] However, the epoxide holds the disadvantages such as toxic, flammable and explosive.

In this communication, we report a facile and environmental friendly method for the preparation of monolithic yttria-stabilized zirconia (YSZ) aerogel using citric acid as t gelation accelerator. The citric acid was used to control the hydrolysis rate of $ZrOCl_2•8H_2O$ in ethanol solvent. The COO^- functional group helped to build a rigid zirconia nanoparticles based framework as the building blocks of aerogel. YSZ aerogels can be obtained from wet gels by ethanol supercritical drying. The gelation time, the density, and the specific surface area of YSZ aerogels can be effectively adjusted by changing the ratio of citric acid to Zr^{4+}. The as-prepared YSZ aerogels could retain its tetragonal phase at different annealing temperature up to 1000°C.

Experimental details for the preparation of the YSZ aerogels are given in the ESI†. Addition of citric acid solution to ethanol solution of $ZrOCl_2$ resulted in the formation of monolithic gels (in closed containers at 60°C) The colour of the wet gel and the gelation time was found to be sensitive to the amount of the citric acid, as shown in Table S1. Such finding indicates th the initial gel formation reaction should be closely related to the citric acid. A control experiment was also carried out to further examine the role of the citric acid in the gel formation proce, as shown in the Supplementary Information Figure S1. It wa found that monolithic gel could only form when citric acid ar $ZrOCl_2$ were mixed together as gelation accelerator a zirconium source, respectively. Other acid such as formic acid

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Electronic Supplementary Information (ESI) available: Experimental details, preparation parameters, surface area, and pore volume of the yttria-stabilized zirconia (YSZ) aerogels, and photographs of wet gels. See DOI: 10.1039/b000000x/

acetic acid as well as oxalic acid were also used as the gelation accelerator but no stable wet gel were formed in current investigation. The mechanism of the gel formation can be explained based on the reactions between the zirconyl complex and the citric acid. As reported by Clearfield et al,[33] $[Zr_4(OH)_8 \bullet 16H_2O]^{8+}$ complex was believed to be the main form of Zr^{4+} ions in ethanol solution. When citric acid and $ZrOCl_2$ were mixed at 60°C in ethanol, a series of reactions are proposed as below to give the gel:

$C_6H_8O_7 \rightarrow R(COO^-)_3 + 3H^+$ (R1)

$n[Zr_4(OH)_8(H_2O)_{16}]^{8+} + R(COO^-)_3 \rightarrow$
$\{[Zr_4(OH)_7(H_2O)_{16}]_n(-OOC)_nR(COO^-)_{3-n}\}^{(9n-3)+} + nOH^-$ (R2)

$\{[Zr_4(OH)_7(H_2O)_{16}]_n(-OOC)_nR(COO^-)_{3-n}\}^{(9n-3)+} +$
$\{[Zr_4(OH)_7(H_2O)_{16}]_m(-OOC)_mR(COO^-)_{3-m}\}^{(9m-3)+} \rightarrow$
$\{[(H_2O)_{16}(OH)_7Zr_4\text{-}O\text{-}Zr_4(OH)_7(H_2O)_{16}]_x[Zr_4(OH)_7(H_2O)_{16}]_{(n+m-2x)}(-OOC)_{n+m}R(COO^-)_{6-n-m)}\}^{[9(n+m)-6]+} + xH_2O$ (R3)

The hydrolysis and complexion of the citric acid by R1 gives a lot of $R(COO^-)_3$ ionized agent. The tetramer $[Zr_4(OH)_8(H2O)16]^{8+}$ reacts with such $R(COO^-)_3$ to produce larger complex $\{[Zr_4(OH)_7(H_2O)16]_n\ (-OOC)_nR(COO\text{-})_{3-n}\}^{(9n-3)+}$ as shown in R2. Subsequently, as shown in R3, the complex $\{[Zr_4(OH)_7(H_2O)_{16}]_n\ (-OOC)_nR(COO\text{-})_{3-n}\}^{(9n-3)+}$ tends to form more complex molecules, mainly in the form of $\{[(H_2O)_{16}(OH)_7Zr_4\text{-}O\text{-}Zr_4(OH)_7(H_2O)_{16}]_x[Zr_4(OH)_7(H_2O)_{16}]_{(n+m-2x)}(-OOC)_{n+m}R(COO\text{-})_{6-n-m})\}^{[9(n+m)-6]+}$. Such complex molecules build a continuous and rigid network backbone for the aerogel. When the citric acid solution volume increased from 1 mL to 9 mL, the gelation time decreased from 1200 min to 1min as well as the wet gels varied from translucent white to opaque (as shown in Figure S2). This may be due to the increased amount of the citric acid altered the gel formation reaction kinetics and the condensation of the zirconyl complex species was more complete.

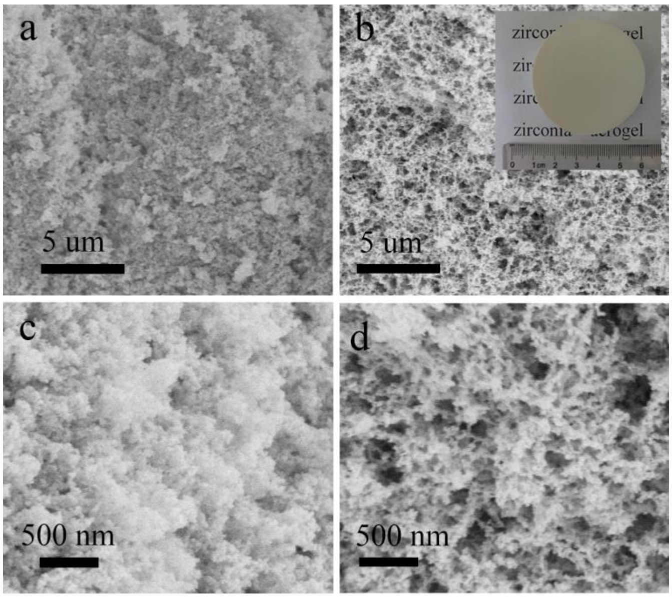

Figure 1. SEM images of A1 (a and c) and A5 (b and d)

Aerogel was obtained after supercritical drying. Figure 1 shows the SEM images of sample A1 and A5, for which the lowest and the highest amount of citric acid was used. It is obvious that the surface of A5 has more macropores (larger than 50 nm) than A1, indicating a better development of the backbone (Figure 1 (a) and (b)). This again proves that citric acid played a vital role in the aerogel formation. The insert image in Figure 1 (b) shows monolithic aerogel can be obtained by such method and the diameter of the aerogel was larger than 5 cm, which is one of the largest sizes ever reported.[8,32,34-38]

A further investigation of aerogel microstructure was achieved by TEM, which reveals the particle size and the pores in the aerogel. Figure 2 shows the TEM images of the as prepared sample A5 and the samples after calcination at different temperatures (at 300 ℃, 400 ℃, 600 ℃, 800 ℃ and 1000 ℃). Before calcination, most of the particles were agglomerated to clusters and the boundaries of the particles were not clearly indentified. The pores in the irregular shaped clusters varied from several nm to 50 nm. The particles were about 2 nm after calcinations at 300 ℃, and increased to about 5 nm after calcinations at 400 ℃. When the calcinations temperature further increased, the particle size increased dramatically. The particle size of the sample calcined at 600 ℃, 800 ℃ and 1000 ℃ were 15 nm, 25 nm and 50 nm, respectively. Such particle size is comparable with the aerogel samples prepared by other methods. For instance, Chervin et al. prepared YSZ aerogels using zirconium oxychloride and yttrium nitrate as the precursor by the epoxide assisted method and the particles sizes were about 10 nm and 40 nm after calcination at 550℃ and 1000 ℃, respectively.[31] Sui et al. synthesized zirconia aerogels using zirconium alkoxide as the precursor by a sol-gel method, and crystallite size of the zirconia aerogels is 10 nm after calcination at 500 ℃.[39]

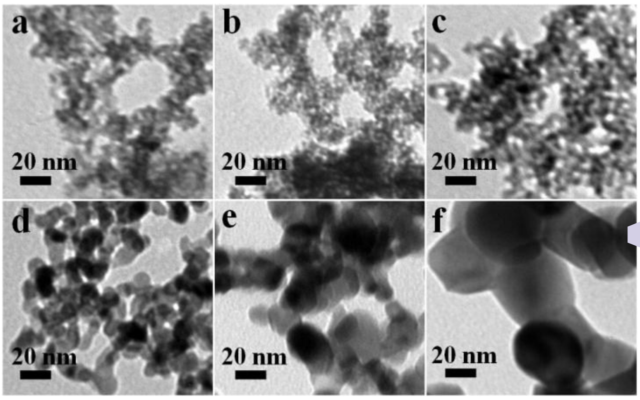

Figure 2. TEM images of samples A5 (a is the as-prepared sample and b,c,d,e,f are the samples calcined at 300 ℃, 400 ℃, 600℃, 800 ℃ and 1000 ℃ for 2 hour, respectively.)

The surface area of the aerogel was examined by N_2 adsorption-desorption. Figure 3(a) is the isothermal curves for the samples from A1 to A5. All samples showed similar Type II behavior, which indicates that there were macro-pores existed in the samples. The surface area and the pore volume are summarized in Table S2 (ESI). The surface area increased with the increased citric acid. Aerogel A5 has the largest surface area of 490 m^2 g^{-1} and pore volume of 1.928 cm^3 g^{-1}, which is superior to other zirconia aerogels reported before. For examples, the surface area of zirconia aerogels prepared by an alkoxide sol-gel method is 399 m^2 g^{-1}.[15] and 454 m^2 g^{-1} by adding epoxide into zirconium oxychloride.[33] It should be noticed that the surface area of the A5 reduced to 315 m^2 g^{-1} and 63 m^2 g^{-1} after calcination at 400 ℃ and 1000℃, respectively. Such values are also comparable to ref 7 and 14. The analysis of the meso-pore size distribution was completed by BJH method, as shown in Figure 3(b). The majority of the mesopores for all the samples lies below 30 nm.

The peak size shifted to smaller pore size when the citric acid amount was increased. When the average pore size of A1 is larger than 30 nm (beyond the calculation limit of BJH method), smaller pore size distribution was observed in A5 (less than 10 nm). It is obvious that with the increased citric acid amount, the pore size distribution became narrower. As proposed above, citric acid played the role as the gelation accelerator for the aerogel. When the concentration of citric acid is higher, the hydrolysis rate of $ZrOCl_2•6H_2O$ is faster and more zirconium complex molecules would connect to each other to form the aerogel.

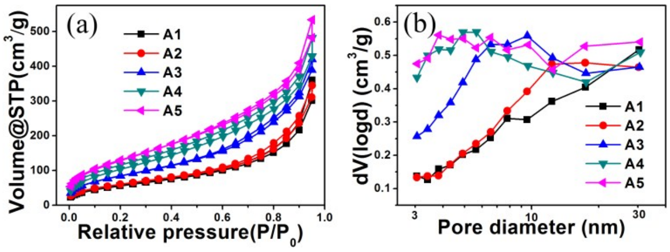

Figure 3. Nitrogen adsorption–desorption isotherms for the samples (a), and the pore size distributions (b).

The XRD patterns of sample A5 calcined at different temperatures are depicted in Figure 4. The XRD pattern of the as-prepared sample in Figure 4 (top inset) shows that the as-prepared YSZ aerogel has broaden diffraction peaks, which indicate the aerogel is amorphous. Such amorphous nature kept the same up to 300 ℃. The crystallite size calculated from Scherrer equation is ~ 3-5 nm, which is close to the TEM results. Upon heating at 350 ℃ the intensity of the diffraction peaks increased due to the increased crystalline degree, and the FWHM (full width at half maximum) of the peaks narrowed since the grain growth at high temperature. The broaden peaks at ~ 80^o (2θ) are due to the overlapping of the (114) (222) and (130) peaks of the tetragonal phase. All the patterns can be indexed as the tetragonal phase zirconia (JCPDS card No. 50-1089). It should be noted that the small crystallite size and the high surface area of the YSZ aerogel are desired for the applications of catalyst and oxide support.

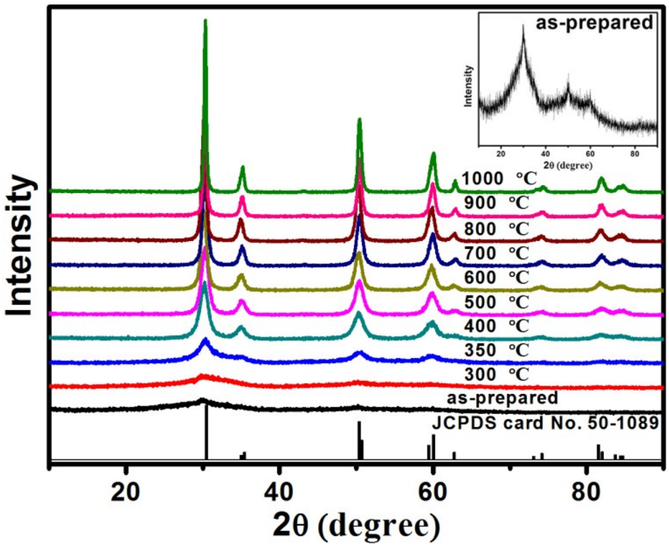

Figure 4. XRD patterns of the A5 (for the as prepared sample and samples after calcination at different temperature for 2 hours)

Conclusions

In summary, we have demonstrated a facile route for the preparation of yttria-stabilized zirconia aerogels by using citric acid as the gelation accelerator. The densities and the gelation time of as-synthesized aerogels are can be tuned, and the surface area of the YSZ aerogels varies from 214 to 490 m^2 g-1. The crystallite size of YSZ aerogels was less than 5 nm when the calcination temperature is below 400 ℃. Considerable surface area can be retained even when the aerogel was calcined at high temperature, which makes it suitable for catalysis in future. The ability to prepare zircinia-based porous materials through such simple and cost-effective sol–gel method presents great significance and implications for the future preparation of aerogels.

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