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Monolithic copper oxide aerogel via dispersed inorganic sol–gel method

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To avoid the use of rare copper alkoxides, copper oxide aerogels were prepared using copper chloride, polyacrylic acid and propylene oxide via the dispersed inorganic sol–gel method, a supercritical fluid drying process and a 500 °C thermal treatment. The morphology and composition of the aerogel without thermal treatment (copper-based aerogel) and copper oxide aerogel were both characterized and analyzed. Based on studies of the gelation mechanism, it was demonstrated that polyacrylic acid guides the sol formation including providing a steric effect. Analysis of the thermal treatment process shows that the copper-based aerogel has four primary thermal reactions and the major composition of samples treated above 420 °C is monoclinic copper oxide.

1. Introduction

Aerogels are coherent, porous solids made by the formation of a colloidal gel followed by removal of the liquid from within the pores of the gel [1]. They are highly porous solid materials which consist of typical nanometer-scale pore and skeleton assembled by ultra-micro particles or polymer molecules [2,3]. This results in many interesting properties, such as extremely low thermal conductivity and highly catalytic effectivity [4]. The preparation of various aerogels has been studied for several years for their special properties and wide application prospects [5–10]. A mature and common method is classical sol–gel process which uses metal alkoxides as precursors. This method has been applied successfully to prepare several kinds of aerogels [1,11–13], such as SiO_2, Al_2O_3 and TiO_2. But it is not very suitable for preparing many other kinds of metal oxide aerogels, just like ZrO_2, Nb_2O_5 and RuO_2 [14,15], because many metal alkoxides (the precursor of those aerogels) are rare or difficult to synthesize. It is extremely hard to prepare the monolithic divalent metal (like Cu and Ni) oxide aerogels since these aerogels are difficult to form in a three-dimension network structure. Alexander E. Gash reported a new method to prepare nickel-based aerogel derived from inorganic metal salt solution and epoxide [16].

Nevertheless, the nickel-based aerogel prepared via this method has a loose structure and complex composition. And what is more, this method is not completely suitable for preparing some other metal oxide aerogels based on copper oxide. Thus a novel method, called the ‘dispersed inorganic sol–gel method’ (DIS method), is introduced in this paper. The method is used to prepare monolithic copper-based alcogel using cupric chloride (as inorganic copper resource), PO (propylene oxide) and PAA (polyacrylic acid) instead of the alkoxide. In this case, the well-formed monolithic pure copper oxide aerogel could be obtained only via supercritical fluid dry (SCFD) process and thermal treatment.

Many kinds of metal-based alcogels and aerogels have been prepared via DIS method in our laboratory. The DIS method may provide a new opportunity to prepare other metal oxide aerogels.

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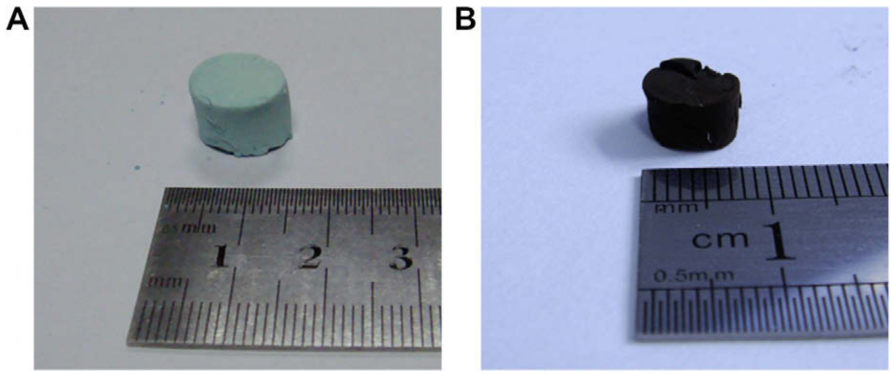

Fig. 1. Photograph of (A) Cu-based aerogel and (B) CuO aerogel.

2. Experimental

2.1. Samples synthesis

2.1.1. Copper-based alcogel

Copper-based (Cu-based) alcogel samples were prepared from cupric chloride ($CuCl_2 \cdot 2H_2O$), PAA (molecular weight is 500–5000) and PO (1,2-epoxypropane) via the DIS method. All the reagents used are analytically pure, and provided by Sinopharm Chemical Reagent Co. Ltd., China.

In the topical procedure, 5 ml of deionized water was added into 12.5 ml of 0.625 M $CuCl_2$ ethanol solution to make the brown solution grass-green. One microliter of PAA was put into the mixture under magnetic stirring to form a bright green Cu-based sol.

After stirring for 10 min, 2 ml of PO was added dropwise. The sol became cyan and opaque immediately and then faded slowly. Finally, the light-cyan Cu-based alcogel was obtained about 2 min later.

2.1.2. Monolithic copper-based aerogel

The alcogel was aged under airtight conditions for two weeks at room temperature and was soaked in ethanol for one week. At last, carbon dioxide (CO_2) SCFD was carried out. The experimental details were as follows: the treated alcogel submerged by ethanol in the SCFD container was replaced by liquid CO_2 below 4 °C for three days. The autoclave was heated to 42 °C with 0.6 °C/min heating speed and dwelled for 4 h. Finally the CO_2 gas was emitted with a decompression speed of about 7 bar/h. The light cyan monolithic Cu-based aerogel, shown in the Fig. 1(A), was prepared after drying was complete. This aerogel was had an easily dislodged, powdery surface texture but it was strong enough to be nipped or pressed by hand under light, uniform pressure.

2.1.3. Monolithic copper oxide aerogel

The black monolithic copper oxide aerogel (CuO aerogel, shown in the Fig. 1(B)) was obtained via heating in air atmosphere from room temperature to 500 °C with a speed of 0.6 °C/min, dwelling for 2 h and natural cooling. This aerogel was more fragile and harder than the Cu-based aerogel. And the shrinkage and decomposition via the thermal treatment almost doubled its density.

2.1.4. Reference sample

The Cu-based green precipitate was prepared by $CuCl_2$ and PO without PAA according to the reaction ratio of Cu-based alcogel as reference sample. It was washed by ethanol for three times and dried in a stove at 50 °C for 3 h. It was then ground for characterization.

The reaction phenomenon and thermal process analysis are discussed in the following text.

2.2. Characterization

The microstructure of the aerogels and the sol was characterized by the scanning electron microscope (SEM, Philips-XL30FEG) and the transmission electron microscope (TEM, JEM 2011), respectively. The composition of the aerogels was tested by the powder X-ray diffraction (XRD, Rigaku D/max2550VB3+/PC) and the Fourier transform infrared spectrometer (FTIR, Bruker-TEN-SoR27). FTIR was performed on films prepared as follow: after adding PO, the Cu-based sol was immediately dropped and spin-coated on the silicon wafer substrate at 2000 rpm for 1 min to prepare a gel films via baked for 2 h at 50 °C. Finally, the thermogravimetry-differential scanning calorimetry (TG-DSC, TA Q600) as well as XRD and FTIR were utilized to analysis the thermal process. The photographs of samples were all taken by Sony CyberShot-T20.

The density was measured by the weighing method, which could be calculated via the following formula:

$$\rho = \frac{4m}{\pi d^2 h}, \tag{1}$$

where ρ is the density of the aerogels, m is the mass which was measured by the precision electronic autobalance, π is the ratio of the circumference, and d and h is the diameter and height of the aerogel cylinder, respectively (measured by the standard straight steel ruler).

The errors from mass measurement are negligible when compared with the errors from diameter and height measurements because of the larger tolerance and reading errors caused by straight steel ruler. Thus the uncertainty of density satisfies the following equation [17] when ignoring the error caused by m

$$\left(\frac{\Delta\rho}{\rho}\right)^2 = 2\left(\frac{\Delta d}{d}\right)^2 + \left(\frac{\Delta h}{h}\right)^2, \tag{2}$$

where ρ, d and h are the mean values of the density, diameter and height respectively. And $\Delta\rho$, Δd and Δh are the respective uncertainties of ρ, d and h. Δd and Δh are calculated by considering both random errors and systematic errors. The random error of a variable (u_a) [18] is the product of the t factor and the mean standard deviation $S_{\bar{x}}$

$$u_a = t \cdot S_{\bar{x}} = t \cdot \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n(n-1)}}, \tag{3}$$

where x_i is the measured value of one time, $\bar{x}$ is the mean, and n is the number of measuring times. The length values in our experiment including d and h were measured for four times ($n = 4$). And t factor has a value of 1.20 considering the four-time measurement and the 68.3% probability with a Gaussian distribution.