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Highly transparent silica aerogel thick films with hierarchical porosity from water glass via ambient pressure drying

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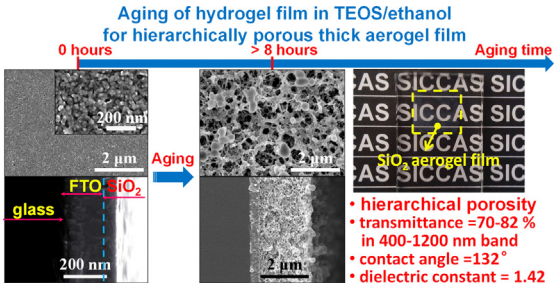
HIGHLIGHTS

- SiO_2 aerogel films with hierarchical porosity.
- A facile method to prepare ambient dried SiO_2 aerogel films from water glass.
- Highly transparent and porous SiO_2 films up to 2–3.6 μm thick.
- Good hydrophobicity and low dielectric constant were achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Highly transparent silica aerogel films of 2–3.6 μm thick and with the hierarchical porosity were deposited on fluorine doped tin oxide (FTO) conductive glass substrate via the sol–gel and ambient drying processes, by using water glass as the silicic source. An innovative aging process was developed by immersing the hydrogel film in large volume of tetraethoxysilane (TEOS)–ethanol solution. Obtained aerogel films possessed both the mesopores and the submicron pores, with the average pore size of 19.1 nm, the specific surface area of 530 $m^2\ g^{-1}$, and the pore volume of 2.96 $cm^3\ g^{-1}$. The leaching of silicic acid molecules from the hydrogel film into the bulk aging solution was responsible for the formation of submicron pores. The aging of the hydrogel film in TEOS–ethanol solution could greatly enhance the silica skeleton and resist the film shrinkage during the ambient drying process, and an aging time longer than 8 h was appropriate to obtain thick aerogel films without obvious structure collapse. The SiO_2 content in the precursor should be kept at medium level, to avoid nonuniform film thickness or lower surface area. In addition, the aerogel film synthesized at optimal condition possessed good hydrophobicity (contact angle: 132°), high transparency (70–82% in 400–1200 nm band), and low dielectric constant ($k = 1.42$). The work demonstrates a facile and low-cost route toward transparent silica aerogel films with hierarchical pore structures, which can be used as the intermetal dielectrics or the template to synthesize novel functional materials requiring high transmittance, high surface area and effective mass transport.

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1. Introduction

Silica aerogel has been gaining extensive research interest in recent years due to its remarkable physical properties and vast applications in the superthermal insulation, acoustic insulation, and catalyst carriers etc [1–5]. In particular, the aerogels with interconnected networks of small and large pores are desirable in some areas such as catalysis, sensing, and liquid-electrolyte based electrodes, because of their ability to provide a functional balance of high activity with effective mass transport through a porous material [6–8]. Thus, the preparation technique of aerogel powders or monolith with hierarchical porosity and the strategies to finely tailor the hierarchical pore structure of aerogel are both fundamentally and technically important, having received increasing attention recently.

The silica aerogel in the film state is an attractive form of aerogel, which can be easily integrated into the silicon-based integrated circuits and many photo and/or electrical devices, and used as the humid sensors [9], photoanodes of dye-sensitized solar cells [10], internal dielectrics (IMD) [11], or window glazing [12], etc. The aerogel films can be broadly classified into two types according to the film thickness, the thin film (around 50 nm to several hundred nanometers) and the thick film (>1 μm). While extensive studies have focused on the thin aerogel films in the last two decades, researches on the thick aerogel films are relatively less, which, however, are especially attractive as the high-surface-area template to fabricate the electrodes in dye-sensitized solar cells or lithium batteries [10], internal dielectrics (IMD) [11], and catalyst carriers films [13]. In some cases such as the photoanode in dye-sensitized solar cells, and electrode in Li-batteries or supercapacitors, both the high surface area and effective electrolyte transport are desired [14–16]. However, up to now there is no report on the aerogel film with hierarchical pore structures.

Typically the supercritical drying and the ambient drying are two commonly used strategies to prepare silica aerogel films. In view of the expensive, labor intensive and time-consuming nature of the supercritical drying process, it is greatly valuable to develop novel methods to prepare high-quality SiO_2 aerogel films via the simple and cheap ambient drying process [17,18]. The preparation of the thick aerogel films via the ambient drying process is usually more difficult than that of the thinner ones because of their much more severe shrinkage during the solvent evaporation and extraction process, which may easily result in the film cracking or peeling off from the substrate. While the large surface tension in the numerous nanopores of aerogel film occurred in the solvent evaporating and extracting processes is the underlying reason of the shrinkage, it is usually hampered by using such following measures: (1) In the early film deposition stage (i.e., the gelling process), an alcohol-saturated atmosphere is applied to prevent the rapid evaporation of alcohol solvent [19]. For the SiO_2 aerogel films using silicon alkoxides and low-surface-tension solvent (e.g., ethanol, isopropyl alcohol), the atmosphere saturated with ethanol or isopropyl alcohol is required. (2) After the gelling of the wet gel film, an aging process is applied to strengthen the as-formed SiO_2 framework, rendering it strong enough to resist the surface tension originating from the solvent extraction [20]. A typical aging practice is to immerse the as-deposited wet gel films in the pure alcohol solvent [12], or expose to the alcohol atmosphere for a certain period of time [21–23]. While predominant studies have focused on the silicon alkoxides based aerogel films using the low-surface-tension alcohol solvent, researches on SiO_2 aerogel films originating from the high-surface-tension aqueous water glass precursor were scare. Here we would like to stress that the preparation of water glass based SiO_2 aerogel film is not only low-cost and simple (requiring no the solvent-saturating atmosphere in the gelling stage), but also expected to provide an efficient aging route to strengthen the SiO_2 framework due to the considerable presence of water in the aerogel films.

In this work, we report a novel method to deposit ambient-dried SiO_2 aerogel films with hierarchical porosity using water glass as the silicic precursor. The significant effects of the aging process on the formation of the hierarchical pore structure and on the reduction of the film shrinkage during the ambient drying process were stressed. By optimizing the aging time and the silica content of the precursor, we obtained an optimal strategy to prepare thick SiO_2 aerogel films on fluorine doped tin oxide (FTO) substrate via the ambient drying process. The aging mechanism of the hydrogel film in TEOS/ethanol solution and the typical chemical and physical properties (including the hydrophilicity, optical transmittance, and dielectric properties) were discussed and investigated. To the best of our knowledge, this is the first demonstration of transparent SiO_2 aerogel films possessing the hierarchical porosity. The facile strategy to create the hierarchical pore structure in aerogel film, and the in-depth exploration of the microstructure evolution of the aerogel film with the aging process will broaden our knowledge on the controllable deposition of the aerogel film via the ambient drying route.

2. Experimental

2.1. Materials

Water glass (SiO_2, 26 wt. %) was purchased from Shanghai Qingfeng Chem. Inc. Tetraethoxysilane (TEOS, >98.0%) was purchased from Shanghai Lingfeng chemical regent. Co., Ltd. Trimethylchlorosilane (TMCS, >98.0%), cyclohexane (C_6H_{12}, >99.5%), and ammonia ($NH_3 \cdot H_2O$, 25.0–28.0%) were supplied by Sinopharm Chemical Reagent Co., Ltd. Ion exchange resin (HL-120 strong acidic styrene cation exchange resin) was purchased from Shanghai Hualing Resin Co., Ltd. Fluorine doped Tin Oxide (FTO, SnO_2:F) was provided by Dalian HeptaChroma SolarTech Co., Ltd. All chemicals were used as received without further purification.

2.2. Preparation of silicic acid sol using water glass

The water glass solution was diluted with distilled water at different H_2O/water glass volume ratios (dilution ratio, briefed as 'r'), forming the sodium silicate solutions with different SiO_2 contents, which were mixed with equal volume of ion exchange for about 10 min to get the final silicic acid solution with a pH value of 2.0–3.0. Afterward, the silicic acids were catalyzed by diluted ammonia (1 mol L^{-1}) and maintained the pH value of 5.0–6.0. The solution would gelate within 4.5–15 min, depending on the precursor concentration.

2.3. Deposition of SiO_2 hydrogel films

FTO glass was selected as the substrate for its high hydrophilicity, which ensured good spread of the aqueous silicic acid drop. Prior to use, the substrate was ultrasonically cleaned in distilled water and ethanol for 5 min in sequence. The hydrogel film was deposited on FTO substrate via doctor-blade method. In brief, a strip of adhesive tape (Scotch Magic #810) was applied on four sides of the substrate respectively, forming a very shallow cavity with an area of 1.0 × 1.0 cm^2 and a height of 100 μm. The silicic acid sol of 2 μL was dropped using a pipette into the cavity, and was

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