

Color manipulation of silica aerogel by copper incorporation during sol-gel process

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Copper (Cu)-incorporated silica aerogel was synthesized by a sol-gel process with two-step drying process for color modification. The microstructure of the silica aerogel was not affected significantly by the Cu concentration and an amorphous structure was maintained without any crystalline impurity phases. The textural properties of the silica aerogels investigated by using N₂ adsorption-desorption isotherms exhibited the typical features of mesoporous materials. The pore size and porosity were not changed significantly even with the incorporation of Cu up to 1.5 M, which indicates negligible variation of thermal insulating properties. However, the color of the aerogel changed from white and light greenish to dark greenish with increasing Cu content. The color change of the silica aerogel was due to the modification of the electron energy band structure of silica by the Cu atomic levels. Therefore, the color of the silica aerogel powders could be manipulated by incorporating Cu without degrading the thermal insulating properties.

Key words: Aerogel, Color manipulation, Cu doping, Silica, Thermal insulation.

Introduction

Recently, eco-friendly and energy-efficient technologies for a wide variety of industrial applications have attracted great attention due to the global warming problem. So the green energy industry and enterprise activity's paradigm are changing. Therefore, insulation technology for maximizing the energy efficiency of the next generation automobiles and buildings has been attracting great attention. Many countries are enforcing green certification of public buildings, doubling the insulation performance standard of new buildings, and mandating the display of energy consumption. Accordingly, there is a growing interest in high-efficiency thermal insulation materials.

Aerogel has been regarded as a good candidate material for thermal insulation because of its porous nature [1-4]. Especially, silica aerogels have received much attention due to their attractive properties such as low thermal conductivities (~ 0.02 W/mK) and low bulk densities (< 0.15 g/cm³) [5-8]. At the same time, their high specific surface area (> 500 m²/g) and high porosity ($> 90\%$) result in lightness and hydrophobicity [5-8]. Therefore, they also could be good materials for sound-absorbing, ship construction, and aerospace applications [1-8]. However, their commercialization has been limited by their low productivity and expensive processing coming from the supercritical drying process [1-8]. Therefore, most efforts have focused on the fabrication of highly porous aerogel

materials based on new and cost-effective synthetic ways [1-8]. In this case, the color of silica aerogels remains inherently white-based. However, successful manipulation of the color of the aerogel materials without degrading the insulating properties will enable a wider variety of applications and additional advantages. In this study, we report on improving esthetics by color manipulation of silica aerogels by Cu incorporation during the sol-gel based wet process at low temperature.

Experimental Procedure

Synthesis

The copper (Cu)-incorporated silica aerogels were synthesized by combining the sol-gel process and two-step drying from the metal alkoxide solution, as shown in Fig. 1. Firstly, the alkoxide solution was prepared by diluting a 4.35 wt % solution of commercial SiO₂ water glass into deionized (DI) water at room temperature. For the ion-exchange process, the diluted SiO₂ water glass was filled and passed through the ion-exchange column to remove the Na⁺ ions. Next, 10 ml of 0.1 M HCl and various amounts of Cu nitrate (Cu(NO₃)₂) were added into this solution, followed by stirring for 5 min to afford a sol state. The amount of Cu nitrate was set at 0, 0.5, 1.0, and 1.5 M. The gelation of these sol solutions was induced by adding 40 ml of methanol and stirring for 10 min. In order for the gel to become hydrophobic and induce surface modification, 180 ml of a mixed solution of isopropyl alcohol, *n*-hexane, and trimethylchlorosilane with a ratio of 1:1:1 was added. The gels were filtered by using a funnel and filter paper, and washed by flowing DI water to remove impurities such as NaCl. The washed gels were

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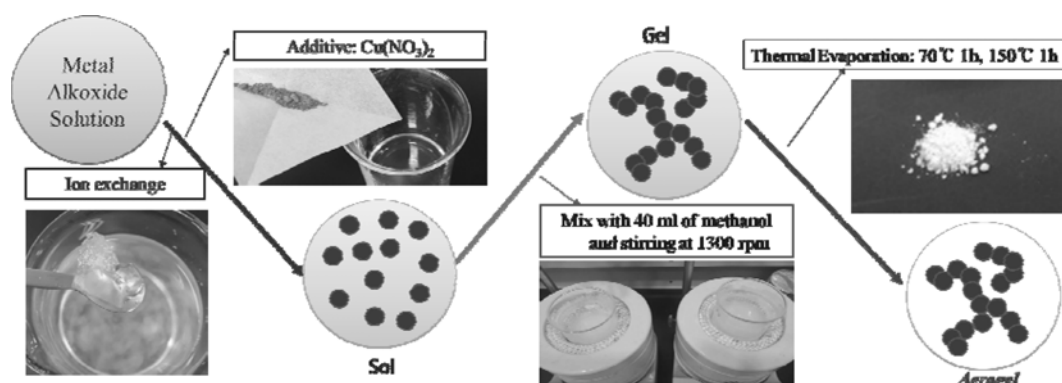


Fig. 1. Schematic of processing steps for the fabrication of Cu-incorporated silica aerogel by sol-gel method.

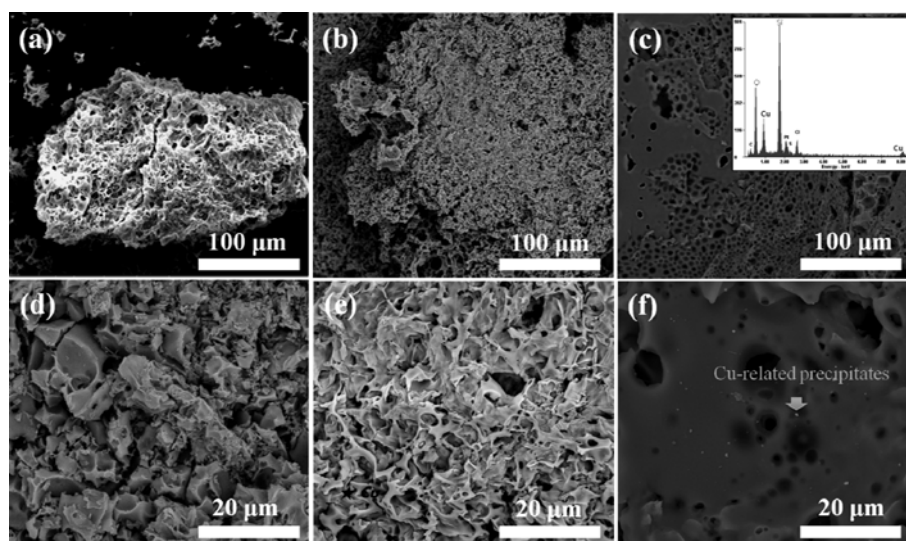


Fig. 2. FE-SEM images of the Cu-incorporated silica aerogel by secondary drying at (a) and (d) 150 °C, (b) and (e) 215 °C, and (c) and (f) 230 °C. The inset shows the EDX results for the silica aerogel dried at 230 °C.

primarily dried at 70 °C for 1 hr and secondarily dried at a temperature between 150 and 230 °C for 1 hr to obtain the final aerogel powder. To investigate the effect of the second drying temperature on the morphologies of silica aerogel, we varied the temperature from 150 to 230 °C with the amount of Cu nitrate fixed at 0.1 M.

Characterization

Structural investigations for Cu-incorporated silica aerogel were performed by using field emission scanning electron microscopy (FE-SEM; Hitachi S-4700) and X-ray diffraction (XRD, Rigaku D/Max-2500 diffractometer equipped with a Cu K α source). The aerogel was chemically analyzed by energy dispersive X-ray (EDX) spectroscopy attached to the FE-SEM. The textural properties of the silica aerogels were measured by porosity analyzer (NOVA4200e, Quantachrome Instruments, FL, USA). The N₂ adsorption-desorption isotherms were obtained at 77 K. The porosity of the aerogel was calculated using the

Brunauer-Emmett-Teller (BET) method.

Results and Discussion

The microstructural evolution of the silica aerogel with variation of the secondary dry temperature was observed by using FE-SEM, as shown in Fig. 2. The molar content of the Cu nitrate was 0.1 M for all samples. Even with Cu incorporation, all the samples exhibited a porous structure with pores of various sizes. As the second drying temperature was increased up to 230 °C, the pore size increases drastically and their microstructure became flattened. Following drying at 230 °C, small particles were found on the surface. These were identified as Cu-related precipitates from the EDX measurement, as shown in the inset of Fig. 2(c). As shown in Figs. 2(b) and (e), the silica aerogel showed uniform pores when dried at 215 °C. Therefore, we fixed the second drying temperature at 215 °C. Before this ambient pressure drying process, the surface of the alcogel was organically modified by

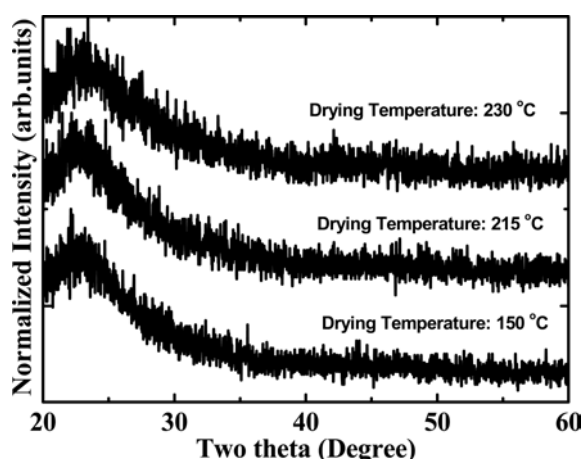
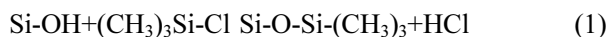


Fig. 3. Normalized θ - 2θ XRD patterns of aerogels prepared by drying at various temperatures.

trimethyl groups present in the trimethylchlorosilane. This surface modification process prohibits the formation of new siloxane bonds between the adjacent silica clusters. The surface of the alcogel is modified by the trimethylchlorosilane according to the following chemical reaction [9]:



To investigate the crystalline structure of the fabricated porous structures, XRD measurements were taken and the results are shown in Fig. 3. The XRD patterns for all samples showed a broad peak between 20 and 30°. These patterns are typical characteristics of the amorphous structure of silica (SiO_2) [10]. Because amorphous materials do not possess long range order compared to crystalline materials and have order only few atomic or molecular dimensions, the incident X-rays were scattered in many directions, leading to the broad peak distributed over a wide angle instead of

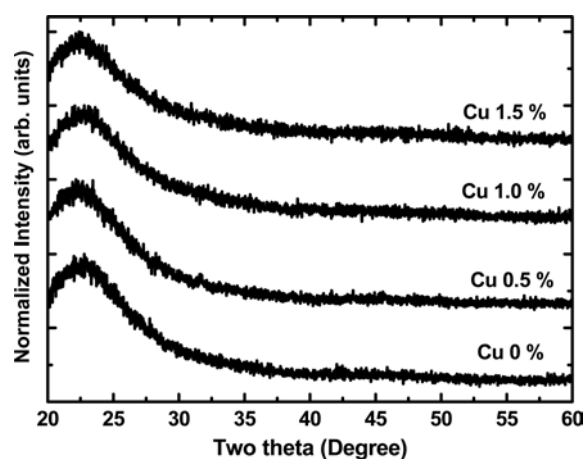


Fig. 5. Normalized θ - 2θ XRD patterns of aerogels prepared with different doping concentrations.

narrower high-intensity peaks. The non-detection of diffraction peaks for any other chemical species, such as Cu oxide or other impurities, indicates that the Cu ions were successfully incorporated into the silica aerogel without forming unintentional precipitates.

To investigate the microstructural evolution of the silica aerogel according to the Cu molar concentration, we fabricated the silica aerogel with various Cu concentrations at the fixed second drying temperature of 215 °C. Fig. 4 shows the morphological evolution of the silica aerogel according to the range of Cu concentration from 0 to 1.5 M. Even as the Cu incorporation content increases up to 1.5 M, there is no significant variation of the porous microstructures. As the Cu concentration increases up to 1.0 and 1.5 M, many small aggregates are found, as shown in Figs. 4(g) and (h). The EDX measurements (data not shown here) were used to identify these small particles as Cu-related precipitates because a large amount of Cu incorporation causes precipitation of the salts. To

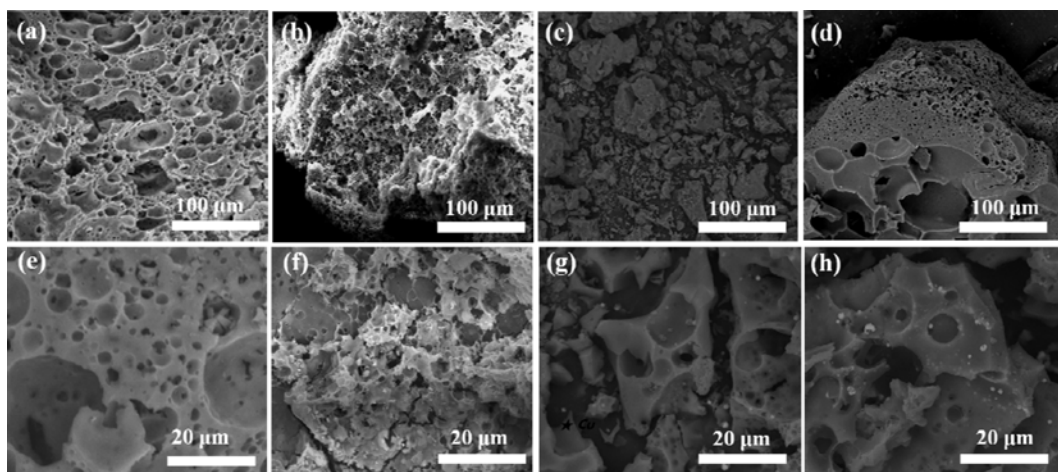


Fig. 4. FE-SEM images of the Cu-incorporated silica aerogel with Cu content: (a) and (e) 0 M, (b) and (f) 0.5 M, (c) and (g) 1.0 M, and (d) and (h) 1.5 M.

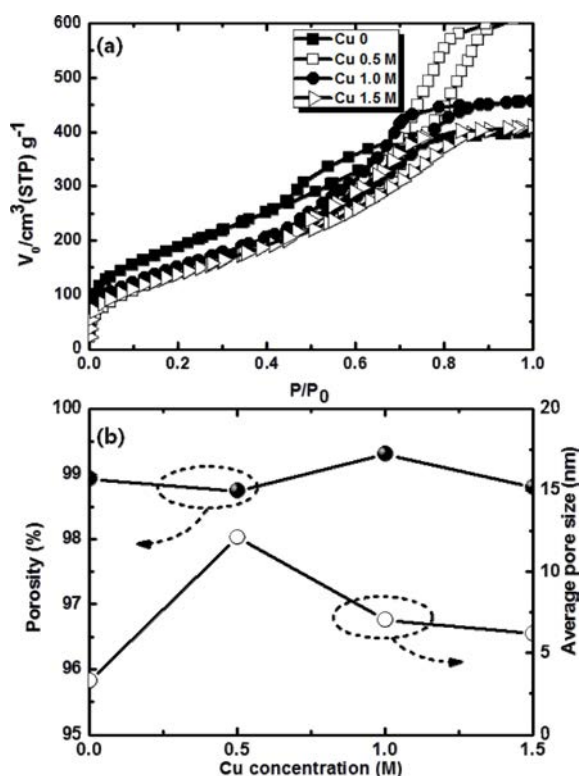


Fig. 6. (a) N₂ adsorption-desorption isotherms of the silica aerogel obtained by using different Cu content. (b) Porosity and average pore size of silica aerogels according to Cu content.

investigate the crystalline structure of the silica aerogel according to the Cu content, XRD measurements were taken and the results are shown in Fig. 5. The XRD patterns for all samples showed a broad peak between 20 and 30° without any additional peaks, similar with the previous data shown in Fig. 3. This confirmed that the amorphous structure of silica gel was maintained regardless of the Cu content.

The Cu-incorporated silica aerogels showed similar microstructures to those described above. To investigate the textural properties of these structures, pore size and porosity were measured. Fig. 6(a) shows the measured N₂ adsorption-desorption isotherms, which indicate the

amount of the gas adsorbed at equilibrium as a function of the partial pressure (P/P_0) at 77 K. The N₂ physisorption isotherms obtained for all samples exhibited Type IV hysteresis loops, which is a typical feature of mesoporous materials [11]. The desorption cycles for all samples exhibited a hysteresis loop that also showed typical features originating from the capillary condensation that occurred in the mesopores inside of the silica aerogels. The porosity and pore size of the samples according to the Cu content were estimated from the BET measurements. The porosity of the aerogels was calculated as follows :

$$\text{Porosity}(\%) = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100 \quad (2)$$

where, ρ_s is the skeletal density and ρ_b is the bulk density of the silica aerogel [12]. As shown in Fig. 6(b), there was no significant change in the porosity or average pore size with increasing Cu molar content. One of the most important factors to be considered for the application of the aerogel is thermal insulating property. The thermal conductivity depends on the porosity and pore size in the aerogel [13]. Therefore, we can assume that the thermal insulation properties of the aerogel were not affected by the Cu incorporation.

The color of the silica aerogel powder showed systematic change according to the Cu content, as shown in Fig. 7. The pure silica aerogel is a white powder due to scattering of all visible light from the porous microstructures. However, as the Cu element is incorporated and its content increases, the color of the powder materials changes from white and light greenish to dark greenish. The numbers in the figure shows RGB values (color coordination numbers) indicated in the monitors. The change in color of the aerogel originated from the modification of the electron energy band structure of silica by the Cu atomic levels, as shown in Fig. 7. The band gap of silica (SiO₂) is about 9 eV [14]. Therefore, the silica itself is intrinsically transparent to all visible wavelength light and becomes white due to the scattering of all visible wavelength lights by its porous structure. However, as Cu is

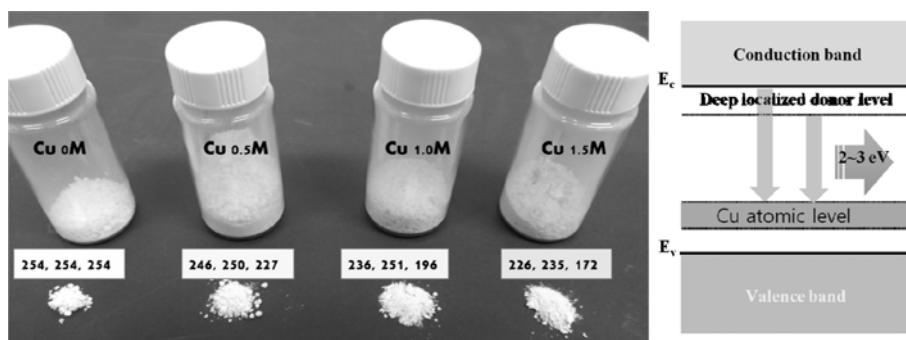


Fig. 7. Images of synthesized Cu-incorporated silica aerogel powders showing different colors (The numbers in the box indicate the color coordination numbers) and schematic electron energy band structure of Cu-incorporated silica materials.

incorporated into the silica, it forms atomic levels inside of the energy band gap of the silica matrix, which can alter the absorption and emission properties of the silica aerogel and changes the color. Therefore, the color of the silica aerogel can be controlled by incorporating Cu without degrading the thermal insulating properties.

Conclusions

Cu-incorporated silica aerogel was synthesized based on a sol-gel process with two-step drying process. The microstructure of the silica aerogel was affected by the secondary dry temperature and drying at 215 °C produced pores of the most uniform shape. The microstructure of the silica aerogel was not affected significantly by the Cu concentration and an amorphous structure was maintained without any crystalline phases. The textural properties of the silica aerogels investigated by using N₂ adsorption-desorption isotherms exhibited the typical features of mesoporous materials. The pore size and porosity were not changed significantly even with incorporation of Cu up to 1.5 M. Thus, the thermal insulating properties were maintained even with Cu incorporation. However, the color of the aerogel changed from white and light greenish to dark greenish, due to the modification of the electron energy band structure of silica by the Cu atomic levels. Therefore, we could manipulate the color of the silica aerogel powders by incorporating Cu without degrading the thermal insulating properties. The proposed approach is expected to provide a viable method for controlling the color of insulating aerogels with potential for wide

industrial applications.

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