Colloids and Surfaces A: Physicochem. Eng. Aspects 441 (2014) 354–359

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Stabilization of monodispersed spherical silica particles and their alignment with reduced crack density

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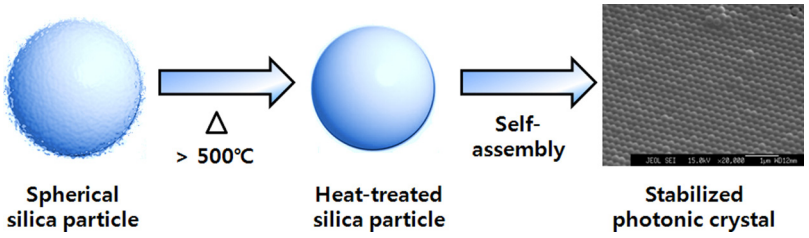
HIGHLIGHTS

- A facile technique to stabilize spherical silica particles was suggested.
- The effect of heat treatment on silica particles was carefully examined.
- Photonic crystals with reduced crack density were obtained.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 July 2013
Received in revised form
16 September 2013
Accepted 19 September 2013
Available online 27 September 2013

Keywords:
Monodispersed spherical silica
Photonic crystal
Heat treatment
Crack density
Alignment

ABSTRACT

Monodispersed spherical silica nanoparticles synthesized by the Stöber process contain large amounts of impurities and adsorbed- and structural water which cause structural and thermal instability of the microspheres. Proper heat treatment was applied to remove the impurities and water endowing the particles with high thermal and structural stability suitable for post-processes. Intrinsic changes of as-prepared silica particles during heat treatment at 550 °C were thoroughly examined by TGA, FT-IR, SAXS, TEM and SEM characterization. The annealed silica particles became much more reliable building blocks for a self-assembled thin film, as evidenced by low crack/defect density in the fabricated film. In this paper, we provide a method of stabilizing silica particles and thereby aligning them into a close packed structure without macroscopic defects. This method is potentially useful for the delicate silica alignment for patterning and fabrication of high-quality photonic crystals adequate for optical switches, waveguides, lasers and antireflective films for solar cells.

1. Introduction

Monodispersed spherical oxide particles play an important role as raw materials in the preparation of functional ceramic materials [1]. In particular, monodispersed spherical silica particles have been widely used for optical materials, by virtue of their characteristics exhibiting different optical, crystalline, and spectroscopic properties depending on their crystallographic orientations by their periodical arrangements [2,3]. For example, a self-assembled silica array having a hexagonally closed pack structure has been applied as photonic crystals [4] and lithographic masks [5]. In the field of optical communication, the silica photonic crystals are used for novel switching and wave-guiding media [6]. Accordingly, the techniques of controlling such silica particles to arrange periodically in one-, two-, and three-dimensional manners with long range order are very important in utilizing them for various purposes of photonic crystals.

Various methods for preparing monodispersed spherical silica particles have been developed. Among them, the Stöber synthesis is the most well known and has been widely applied [7,8]. This method allows for the preparation of monodispersed silica particles of varying sizes within the range of 10–2000 nm in diameter. Uniformity of silica particles in size and shape is crucial in producing high quality photonic crystals since either non-sphericity

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http://dx.doi.org/10.1016/j.colsurfa.2013.09.025

or poly-dispersity of silica particles leads to poorly ordered silica particle arrays [9]. In order to align silica particles with long range order, indirect methods using lithography and holography, and self-assembly methods such as sedimentation [4,10], vertical deposition [11–13], spin coating [14,15], slide coating [16], etc., have been developed. There are several methods that are promising for the fabrication of high quality photonic crystals, however, it is still difficult to make defect-free photonic crystals in large size.

In this study, we found that thermal and structural stability of silica particles significantly affects the quality of silica photonic crystals. Silica particles synthesized by the Stöber method contain large amounts of moisture and organic by-products inside of their micropores and on their surface. We conclude that proper heat treatment can remove those impurities and thereby stabilize the silica particles. Precise comparison of as-synthesized and heat-treated silica particles in their physical characteristics is provided and differences in their alignment are clearly presented in the text.

2. Experimental

2.1. Materials

Monodispersed spherical silica particles of 300 nm and 425 nm in average diameters were prepared with the Stöber method [7,8] (see Supplementary material) and those of 1.0 μm in average diameter were purchased from Polysciences, Inc. Absolute ethanol was purchased from Acros Organic and used as received and sodium chloride was purchased from Dea Jung Chemical (99%). Silicon wafer ((1 1 1) surface, 3 inch in diameter) were purchased from Sigma–Aldrich and cut into pieces of 10 mm × 50 mm. The cut silicon slides were soaked in a 7:3 volumetric mixture of 98% H_2SO_4 and 30% H_2O_2 for 20 min under boiling and rinsed with deionized water and absolute ethanol several times in sequence.

2.2. Instruments

Thermogravimetric analysis (TGA) was performed with thermogravimetric analyzer (TA Instruments, Inc., model Q600 SDT). Specific surface areas of the respective silica were determined by the BET (Brunauer, Emmet, and Teller) method using a surface area analyzer (BEL Japan, Inc., model BELSORP-max) after evacuation at 100 °C for 1 h. Particle size analysis was performed with an aerodynamic particle sizer (APS, TSI model 3321). Scanning electron microscope images were obtained by FEI-ESEM with acceleration voltage of 15 kV without coating (model XL-30 FEG; observed in environmental SEM mode) and transmission electron microscopy images were obtained by FEI Tecnai G^2 TEM with acceleration voltage of 200 kV (TEM images were recorded on an Ultrascan 2 K × 2 K CCD camera). Fourier transform infrared (FT-IR) spectroscopic analysis was conducted with KBr pellets of silica powders using a Mattson FT-IR spectrometer (IR300). Small angle X-ray scattering (SAXS) data were obtained with dry silica powders by Anton Paar, SAXSess mc^2 to determine the internal structures of silica particles. Optical microscopy images of colloidal crystals were taken by a Carl Zeiss optical microscope (Axiovert 100A) and reflectance spectra were obtained using a microspectrometer CRAIC (QDI 302) coupled to the microscope. The light beam has a spot size of 25 μm × 25 μm.

2.3. Heat treatment of silica particles

Monodispersed spherical silica particles were isolated from water by centrifugation (model = Hanil Supra 22 K, centrifugal condition = 12,000 rpm for 5 min) and re-dispersed in DI water to make a 1-wt% colloidal solution (10 mL). To the solution was added NaCl up to its saturation and the solution was quickly frozen by liquid nitrogen and dried by freeze dryer (Ilshin Bondiro®). The dried sample was obtained as white powder which was calcined in a muffle furnace along a three-step heating profile – (i) ramping to 550 °C at a rate of 2 °C/min, (ii) holding at 550 °C for 4 h, and (iii) cooling to 25 °C over at a rate of 2 °C/min. The heat-treated sample was then washed with DI water for four times (10 mL 4×) and dispersed in DI water (10 mL) by sonication (Bransonic® ultrasonic cleaner) to make a silica colloidal solution. Surface potential of the colloidal solution (0.05 wt%) was measured by zeta analyzer (Photal Otsuka Electronics ELSZ-1000) to see any change of surface charge upon the heat treatment but it showed little change compared to that of as-synthesized silica: −46.1 mV (heat-treated) vs. −48.7 mV (as-synthesized). It may indicate that the heat treatment temperature was low enough to avoid the formation of sodium silicate on the silica surface.

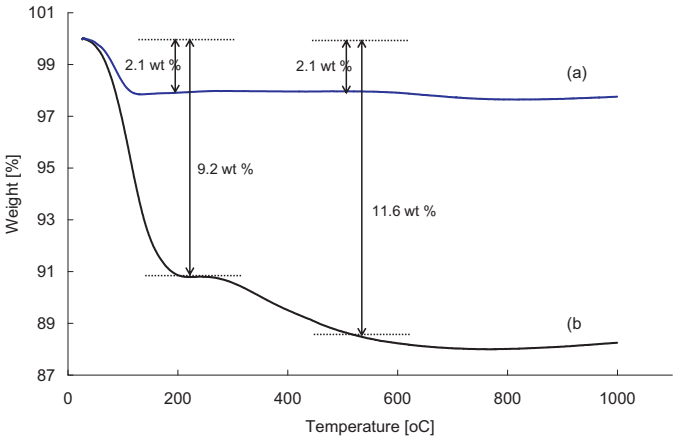

Fig. 1. Thermogravimetric analysis curves of 425-nm silica particles: (a) as-synthesized and (b) heat-treated at 550 °C.

2.4. Vertical deposition of silica particles by self-assembly method

In a 20-mL vial, silica particles (0.1 g) were mixed with deionized water (10 ml) to make a 1-wt% colloidal suspension and then treated in an ultrasonic bath for 1 h in order to disperse the particles. A silicon wafer slide (1 cm × 5 cm) was dipped vertically in the vial filled with white colloidal suspension of silica particles, after which the vial was placed in an oven kept at 60 °C so as to allow water to slowly evaporate, leading to deposition of silica particles on the surface of the silicon wafer. After keeping it in the oven for 18 h, the slide was taken out from the solution, dried at room temperature for 1 h, and then placed in an oven at 60 °C for 24 h.

3. Results and discussion

3.1. Physical properties of as-synthesized and heat-treated silica particles

3.1.1. Thermal and surface area analysis

In order to determine the physical changes of silica particles during heat treatment, the weight changes of the heat-treated silica were examined by TGA analysis and compared with those of the as-synthesized one. With the as-synthesized silica particles of 425 nm in diameter, ~9.2% reduction in weight was observed at the temperature range of 210–280 °C (Fig. 1(a)), while only ~2.1% reduction in weight was found with the heat-treated silica particles in the same range (Fig. 1(b)). In addition, at temperature above 280 °C, the weight of as-synthesized silica continued to decrease, reaching 11.6% reduction in weight at 550 °C. On the other hand, in the same range the heat-treated silica showed no additional