Journal of Colloid and Interface Science 426 (2014) 199–205

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Structural characterization of colloidal crystals and inverse opals using transmission X-ray microscopy

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ARTICLE INFO

Article history:
Received 5 December 2013
Accepted 19 March 2014
Available online 2 April 2014

Keywords:
Transmission X-ray microscopy
Colloidal crystal
Inverse opal
Polystyrene microspheres
Electrophoresis

ABSTRACT

A nondestructive tomographic technique was used to determine the crystallographic information of colloidal crystals comprising of polystyrene (PS) microspheres, as well as their silver inverse opals. The properties of the colloidal crystals, such as defects, grain size, grain boundaries, stacking sequence, and grain orientation, were determined using the full field transmission X-ray microscopy (TXM) with a spatial resolution of 50 nm. The PS microspheres (500–750 nm) which underwent a vertical electrophoresis process to form a face-centered cubic (fcc) close-packed structure with an ABCABC packing sequence. In addition, the colloidal crystal exhibited multiple grains, and an orientation variation of 6.1° in the stacking direction between two neighboring grains.

1. Introduction

The concept of photonic crystals was first introduced by Yablonovitch [1] and John [2]. They suggested that a periodic structure with sufficient refractive index contrast can develop a photonic band gap, preventing the transmission of light of a specific wavelength. So far, numerous optical devices based on this unique characteristic have since been demonstrated. In the literatures, photonic crystals are fabricated using either top-down or bottom-up approaches [3,4]. The top-down method involves semiconductor processing, which is often expensive and time-consuming, whereas the bottom-up approach is simple and entails assembling microspheres into a close-packed array by using gravity [5,6], physical confinement [7], solvent evaporation [8,9], and electrophoresis [10]. An assembly of microspheres is known as a colloidal crystal. The filling of the interstitial voids among the microspheres followed by the selective removal of the colloidal template is defined as an inverse opal. Both colloidal crystals and their inverse opals exhibit considerable potential in applications including electrocatalysts [11], photoelectrochemical solar cells [12], electrochemical capacitors [13], and biosensors [14,15].

The crystallographic quality of colloidal crystals and their inverse opals is often diagnosed through planar and cross-sectional images from scanning electron microscopy (SEM) [16]. Due to the limited depth of penetration, SEM images are useful only for surface observations. As a result, the internal structure of the colloidal crystal (packing arrangement of the microspheres) and misorientation between neighboring grains remain unknown. Earlier, two dimensional (2D) images obtained via transmission electron microscopy (TEM) have been utilized by Cai et al. [17] to reveal multiple layers of colloidal crystals. However, a serious limitation arising from employing the TEM is the requirements of a thin sample (less than 100 nm), due to the shallow probing depth, vacuum process, and observation in a small scale. The degree of crystallization of colloidal crystals can be inferred using optical measurements [18] such as infrared (IR) reflection spectroscopy. However, the IR responses are indicative of the aggregate structural effect so localized details are still elusive.

Three-dimensional (3D) structure in a colloidal crystal has been revealed by Hilhorst et al. [19] using tomographic scanning transmission X-ray microscopy (STXM). This technique provides 30 nm spatial resolution for images with 2D absorption contrast utilizing soft X-ray with the energy of about 1.84 keV for silicon K-edge. However, the accuracy and spatial resolution of STXM tomographic reconstruction are degraded owing to the relatively low penetration power of soft X-ray, which limits the azimuthal angle range for 3D tomography data sets with only ±60° [19]. Moreover, the slow acquisition speed and large size of the data set of the STXM also compromises the resolution of tomographic reconstruction because of taking large angle steps, which is 4° in

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http://dx.doi.org/10.1016/j.jcis.2014.03.063
0021-9797/

their work. A full field transmission X-ray microscopy (TXM) imaging of colloidal crystals at 12 keV photon energy was demonstrated by Bosak et al. [20] with improved imaging acquisition speed and penetration depth. The TXM in Bosak's work employed the short-focus compound refractive lenses (CDL) as the objective lens. The spatial resolution is mostly determined by absorption in the lens material, hence, by choosing a more transparent material, such as Be CRL, a resolution of 100 nm is feasible. In this study, we used the full field transmission X-ray microscopy (TXM) [21,22] to investigate the 3D ultra-microstructures of colloidal crystals and their inverse opals. This TXM employs a Fresnel zone plate objective to achieve a spatial resolution of 50 nm, which is dominated by the outmost zone width and the applicable diffraction order of the zone plate, as well as a Zernike phase contrast for low atomic number samples, such as polystyrene (PS) colloidal crystals. Taking advantage of its capability for deep penetration (up to 50 μm when using an 8 keV X-ray), the TXM performs non-destructive observations of internal ultra-microstructures in an ambient environment. Here we demonstrate that the 2D TXM micrography is able to identify crystallization and defect distribution from the surface to the internal structure in colloidal crystals and their inverse opals. The 3D tomography of colloidal crystals and their inverse opals shows a layer-by-layer arrangement of the microspheres and the exact grain orientation. This novel technique allows structural relationships to be analyzed, which is impossible with other analytical instruments, and thus brings valuable insight toward the internal ultra-microstructure of colloidal crystals and inverse opals.

2. Experimental methods

A vertical electrophoresis deposition (EPD) process was adopted to direct the assembly of PS microspheres into colloidal crystals 2 cm × 2 cm × 16 μm in size. The EPD suspension was prepared by mixing 0.5 g of microspheres (500 nm or 750 nm) and 100 mL 99.5 wt% ethanol, followed by ultrasonication for 1 day. In the EPD process, an electric field of 5 V/cm to 20 V/cm was utilized to deposit microspheres onto indium tin oxide (ITO) glass substrates. Subsequently, the samples were dried at 25 °C. The resulting colloidal crystals exhibited impressive surface uniformity and a close-packed structure. A detailed process for synthesizing the PS microspheres and the electrophoretic formation of colloidal crystals were described in our previous studies [10,23]. To fabricate the inverse opals, the colloidal crystal was served as a template, allowing electroplating [24] of silver into the interstitial voids among the PS microspheres. The silver was selected because it provides a strong absorption contrast for the TXM micrograph. 0.2 M $AgNO_3$ (SHOWA) and 0.2 M citric acid (SHOWA) were used to prepare the plating electrolyte. The electroplating process was carried out in a potentiostatic mode, with the range set from 1.1 to 1.5 V. The PS microspheres were then removed using ethyl acetate, producing a silver skeleton with interconnected channels.

The TXM facility [21] of beamline BL01B [22] at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan provides 2D micrograph and 3D tomography at spatial resolutions of 50 nm, with first-order diffraction of a Fresnel zone plate at an X-ray energy of 8 keV. The field of view of the image is 15 × 15 μm^2 for the first-order diffraction of the zone plate. A millimeter-scale field of view of the sample can be generated by stitching images from a series of observation positions. After acquiring a series of 2D micrographs with the sample rotated stepwise azimuthally, the 3D tomography data sets were reconstructed by applying a filtered back-projection algorithm based on 181 sequential image frames taken with the azimuth angle rotating from −90° to +90°. The final 3D tomography structures were generated using Amira 3D software to enhance the visualization.

3. Results and discussion

3.1. SEM imaging analysis of PS colloidal crystals and silver inverse opals

Fig. 1 exhibits the SEM images of the colloidal crystal. Fig. 1a is a top view, showing the assembly of PS microspheres (500 nm in diameter) in grains of 80 μm × 105 μm, along with the presence of grain boundaries and vacancies. Fig. 1b is a cross-sectional view, showing a layer-by-layer structure revealing a close-packed arrangement. Defects such as vacancies and voids were clearly observed, but these might have been produced during the electrophoresis process or were caused simply when breaking the sample for SEM cross-sectional observation. Moreover, the grain orientation and packing sequence were not discernible, which is a persistent problem in the field.

Fig. 2a and b display the top and cross-sectional views of the silver inverse opal fabricated using the colloidal crystal template in Fig. 1. The inverse opal structure consisted of interconnected voids in a hexagonal pattern, and its morphology was similar to that of the colloidal crystal. Both colloidal crystals and inverse opals exhibited excellent crystallinity, and they provided perfect models for structural characterization by TXM.

3.2. Crystallinity and defects characterization by 2D TXM micrograph

Fig. 3a demonstrates the 2D TXM micrograph of a colloidal crystal comprised of PS microspheres with a diameter of 750 nm. The PS microspheres are the areas in dark contrast, owing to their stronger X-ray absorption compared with that of air. Fig. 3b displays the 2D TXM micrograph of an inverse opal generated from

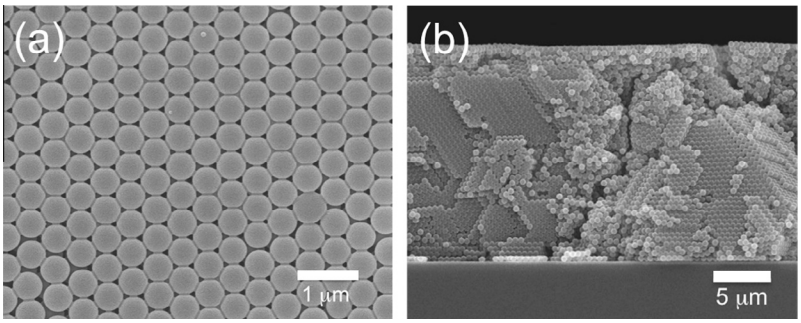

Fig. 1. SEM images of a polystyrene-based (PS) colloidal crystal which underwent a vertical electrophoresis process. (a) Top view, showing the assembly of PS microspheres (500 nm in diameter). (b) Cross-sectional view, showing a layer-by-layer structure in a close-packed arrangement, as well as grain boundaries. These colloidal crystals exhibit excellent crystallinity.