



Short communication

Combining scanning electron microscopy and fast Fourier transform for characterizing mesopore and defect structures in mesoporous materials



Yi Zeng, Ziwei Liu, Wei Wu, Fangfang Xu, Jianlin Shi*

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai, 200050, PR China

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ABSTRACT

The mesopore structure is normally determined through Transmission Electron Microscopy (TEM). In this study, a novel technique is proposed for assessing the surface and interior planar pore structures, plane groups of ordered pore arrangements and defect structures in a number of mesoporous materials through a combination of SEM imaging, ion milling and fast Fourier transformation (FFT). This strategy provides a unique and facile approach to characterize the surface and inner pore structures and interior defects of bulky mesoporous materials with varied complex structures.

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1. Introduction

Ever since the invention of M41S family of mesoporous silica in 1992, mesoporous materials have gone on to become one of the most attractive fields of research in materials science [1,2]. Owing to the well-defined mesoporosity, highly ordered pore arrangement, high specific surface area, and tunable pore size and volume of such materials, they show great potential for application in the growing fields of heterogeneous catalysis, adsorption and storage, drug delivery and bio-imaging, nano-synthesis, etc [3–6].

Whatever the application, the decisive factor in determining their effectiveness is their mesoporosity, which is defined by the three-dimensional (surface and interior cross-sectional) structure of their pores. As such, there has been much research focused determining the pore ordering, with a view to gaining a clearer understanding of the self-assembly mechanism during syntheses or to discover new mesoporous materials. To date, determining the pore structure of mesoporous materials has been achieved through TEM (transmission electron microscopy). Although high-resolution SEM (scanning electron microscopy) has been utilized as a supplementary technique for imaging the surface and producing two-

dimensional (2D) projections [7,8], high resolution TEM imaging has become a prevailing approach for the direct observation of a volume of atoms. In this way, this technique has featured in nearly all studies pertaining to the structure and plane group of pores in mesoporous materials, often in combination with small-angle diffraction (SAD). In addition, TEM provides an effective means of visualizing the interior pore interconnectivity [9].

However, despite being a powerful and widely-used technique, TEM still suffers from a number of drawbacks. For example, the images obtained only provide information about the pore structure in two dimensions; the three-dimensional (3D) orientation of the mesopores only were found through a complicated program entailing a series of HR-TEM images and ED patterns taken of the same position at different tilt angles, followed by a computational image reconstruction. Furthermore, the quality of the HR-TEM images obtained is highly subject to the method of sample preparation (e.g., sample thickness) and the condition of the equipment. Finally, but even more importantly, the high-voltage of HR-TEM imaging can quickly destroy the ordered pore structure of a material during observation, so much so, that it may prevent imaging entirely.

Thanks to the recent technical developments, low-voltage SEM has now reached the point at which sub-nanometer scale resolution is possible, thus providing a new opportunity to examine the pore structure of mesoporous materials. Currently, SEM is mainly

* Corresponding author. Tel.: +86 2152412712.

E-mail address: jlshi@mail.sic.ac.cn (J. Shi).

used in the measurement of particle/pore size, as well as for determining the phase composition and morphological features on the material surface. However, it is equally capable of revealing the arrangement of surface or sub-surface pores, and is therefore also commonly used in an auxiliary role to TEM for determining the pore structure of mesoporous materials. What is more, the electron backscattered diffraction (EBSD) of SEM can be used to determine the interplanar spacing and angles of crystallized materials, thereby providing compositional and structural information at an atomic level. Strictly speaking, however, the ordered arrangement of mesopores in silica materials is inherently different from the atomic level ordering of conventional crystals. Consequently, Bragg diffraction does not occur in EBSD patterns for materials with an ordered mesoporosity but disordered framework, *i.e.*, EBSD is not capable of determining the space groups of ordered pore arrangements in mesoporous materials.

Given these limitations, this study presents a simple SEM-based strategy for characterizing both the surface and inner planar pore-structure and interior defects in mesoporous materials. In this, the pore arrangement in cross-sectional SEM images is determined by fast Fourier transform (FFT) analysis to provide information on the pore arrangements, and interior defects in mesoporous materials are revealed by cross-section ion-milling. By combining multiple interior planar images of typical orientations, a three-dimensional reconstruction of the pore structure of mesoporous materials may also be made possible [10,11]. To the best of our knowledge, this is the first such example of pore structure determination by SEM.

2. Materials and methods

2.1. Sample preparation

The SBA-15, KIT-6 and LPSNs (large pore silica nanospheres) mesoporous silica samples used in this study were all synthesized and prepared in accordance with a previously described method [12–16].

2.2. Ar ion cross-sectional polishing

Cross-sectional specimens of each of the mesoporous silica materials were prepared by first uniformly mixing mesoporous powders into a water-soluble carbon paste to a volumetric ratio of 1:1, and then spreading this on-to one side of a 0.1-mm coverslip. After drying, the specimens were polished from the reverse side of the coverslip using an E-3500 Ar ion cross-section polisher (Hitachi Corp., Japan), using an Ar ion acceleration volt-age of 3–4 keV, a discharge beam of 400–500 μA , and slew rate of level 6. A schematic diagram depicting the Ar ion cross-sectional polishing and mesoporous powder sample loading is given in Fig. 1 [17].

2.3. SEM imaging and FFT analysis

The mesoporous molecular sieves produced by Ar ion polishing were examined using a Magellan 400 low-voltage ultra-high resolution field emission scanning electron microscope (FEI Inc., Hillsboro, Oregon, USA). A low acceleration voltage of 1 kV and electron beam current of 3.1 pA were utilized to minimize the damaging effects of the electron beam on the specimens and the charge accumulation resulting from the non-conductive nature of the mesoporous molecular sieves. The SEM images obtained were processed in Image J (version 2.1.4.7, National Institutes of Health, Bethesda, MD, USA) to obtain Fourier diffractogram through FFT analysis. This FFT analysis essentially transforms the grey scale distribution function of an SEM image into a frequency distribution function, from which a diffraction pattern is obtained that can be used to determine the periodicity and symmetry of the pore structure [18]. The lattice plane of pore crystals was determined by FFT of SEM images obtained through continuous tilting of the specimen until the live FFT matched the pattern of the structure of pore crystals or XRD analysis, or the array of pores was edge-on (parallel to the viewing direction, similar to the zone-axis condition in TEM) or evenly distributed.

3. Results and discussion

An SEM image of the surface of a SBA-15 particle is shown in Fig. 2a, revealing a rough texture and apparent ordered arrangement to the pores; the pore size and wall thickness are around 4 and 2 nm, respectively. However, a certain amount of amorphous silica (the white areas in Fig. 2a) is clearly discernible over a number of the oriented pore openings of the sample surface, which is believed to result from excess silica deposition that occurs once the structure directing agents (P123, block copolymer template) are fully consumed in the self-assembly between the silica source and template. Nevertheless, it is still clear that the pore channels are parallel to the incident electron beam but part of pore openings have been covered by excess silica particles. The surface of the SBA-15 also exhibits a certain degree of disorder, which suggests that it is not fully crystalline.

To determine the periodic arrangement of mesopores in the interior of the particles, SEM analysis was performed on cross-sectional specimens of a SBA-15 crystal after electron ion milling. This reveals a perfect periodic pore structure with a hexagonal arrangement, in which all of the pores are fully open along the length of their axis, and without any excess silica deposition observed (Fig. 2b).

To confirm the periodicity of this pore arrangement, FFTs were performed on both SEM images (Fig. 2a and b), with the resulting diffraction patterns shown in the insets of each image. From this, it

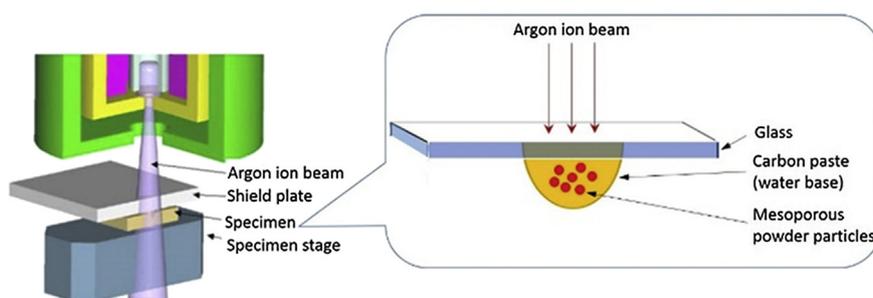


Fig. 1. Schematic diagram demonstrating the Ar ion cross-sectional polishing of a mesoporous powder.

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