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Abstract

Nano-structured materials demonstrate interesting properties as compared to their bulk counterparts. Porous anodic alumina (PAA) is one of the most exhilarating nanomaterials; it has been used as a template to synthesize nanowires, nanotubes, nanodots, composites for catalysis, emitters and magnetic storage devices.

Structure and morphology of PAA has been mostly characterized by direct imaging techniques. The direct imaging includes Atomic Force Microscopy (AFM) and other techniques such as Scanning Electron Microscopy (SEM), Field Emission Scanning Electron Microscopy (FESEM), and Transmission Electron Microscopy (TEM). These direct imaging techniques have a disadvantage that they encompass only a small surface or cross-sectional area, which may not be the true representation of the sample. On the other hand, Small angle X-ray scattering (SAXS) has the advantage of providing information about the structure of material that is representative of the sample. This technique complements direct imaging and could be used as an alternative for structural characterization of the template. The other advantage of SAXS over the direct imaging in case of PAA is that it is sensitive to density difference of the alumina matrix and void space inside hollow cylindrical pores arrays. Therefore, it not only gives information about the surface of the template but also about its structure deep inside the matrix.

Small angle X-ray scattering (SAXS) has been performed on porous anodic alumina prepared at non-ordering conditions. These were prepared by two-step anodizing to have uniform through-thickness structure. The thickness of the membranes was of the order of 100-200 µm. The scattering has been explained based on structure factor; the magnitude of scattering vectors (**q**) corresponding to well-established peaks being multiples of $2\pi/d$, where d is the inter-pore distance. The usually studied form factor has not been found to play any profound role to determine the scattering response of anodic alumina. The scattering from PAA samples has been extremely anisotropic, where **q** always lies at about 90° with respect to the sample's normal. A deviation from this angle which is limited to about ± 2° has been due to scatter of the pore axis with respect to sample's normal, which is caused by occasional pore turning, branching and

annihilation events. The analysis and methodology adopted in this study has also been suggested as extremely useful for determining the orientation of high-aspect ratio objects in an anisotropic sample along with assessing the degree of misalignment. SAXS studies have provided with the new opening for quantitative determination of pore characteristics, which complement the information obtained from direct imaging method.

Pores in PAA may be hexagonally self-organized, if it is prepared at certain ordering conditions. PAA prepared at non-ordering conditions do not have hexagonally ordered nanoporous structure. The structure factor was theoretically calculated / simulated and successfully fitted to the experimentally measured SAXS intensity of PAA prepared at ordering and non-ordering conditions. These fits revealed information about interpore distance, regularity of interpore distance and structural disorder of the nanoporous structure. The hexagonally ordered PAA samples exhibit SAXS intensity peaks that correspond to two-dimensional hexagonal lattice. This data was theoretically calculated / simulated and fitted sucessfully to the experimentally measured SAXS data. It was found to correspond with dimensional hexagonal lattice that was obtained from the SAXS response. It was also found that hexagonal structure of PAA prepared at ordering voltages for doubly-anodized samples is better than singly anodizing samples. It was also found from SAXS response of these samples that at all of the ordering voltages, long-range hexagonal pore ordering increases with increase in time of anodizing during first-step of anodizing. Based on the SAXS studies, PAA samples prepared at non-ordering voltages do not have hexagonal pore ordering, however, they exhibit regular interpore distance.

Further SAXS studies of ordered PAA samples in different electrolytes and anodizing voltages show that doubly-anodized 40 V sample possesses the best hexagonal nanoporous structure. These samples also show the largest domain size (long-range ordering) among all ordered PAA samples. However, doubly-anodized samples at 27 V have better hexagonal nanoporous structure among the samples anodized in sulfuric acid solution. SAXS analysis on the doubly-anodized samples prepared at ordering voltages reveal that the variation of pore axes in the ordered PAA is smaller than non-ordered PAA. Hence, in ordered PAA extent of parallelism is greater than non-ordered PAA.

Fitting of the simulated 2-D hexagonal lattice to the SAXS spectrum of PAA prepared (by both single-step and two-step) at 60 V reveals that the sample possesses 2-D hexagonal nanoporous structure. Previously, 60 V was presumed as non-ordering voltage on the basis of

direct imaging techniques. Based on the SAXS studies of PAA anodized in oxalic acid it was revealed that hexagonal ordering of pores deteriorates and becomes immeasurably small if the anodizing voltage is increased beyond 60 V.

In addition, it has been shown that direct imaging techniques are complemented by image analysis methods; useful information about the pore nucleation/shape can be obtained for PAA samples prepared under different conditions. This study gave useful insight into the pore nucleation on the different pre-textured surfaces such as electropolished surface and the surface left after anodizing and subsequent dissolution. It was found that nano-stripes formed after these aforementioned treatments determine the shape of the pore tip.