論文の内容の要旨

論文題目 Ion Transport in Oedered Nanoporous Structures

（規則性ナノ細孔内部のイオン移動に関する研究）

氏　　　名 黄 畯浩

Transport of ions and molecules in nanochannels/nanopores has attracted great interest and been extensively investigated to understand the various functions of ion channels. Nanofludic system with dimensions ranging from 1 to 100 nm, which is comparable to the Debye length that characterizes the range of electrostatic interactions in aqueous solution, exhibit surface charge governed ion transport phenomenon which is not observed in microfluidic system. So far, the majority of studies have been performed in nanofludic channels with dimensions larger than ~10 nm, since it is fairly challenging to fabricate nanochannels whose dimensions are less than 10 nm by means of approaches that utilize conventional nanolithography. In this thesis, we suggest a new possibility of developing nanofludic devices using mesoporous silica with well-ordered nanoporous structures synthesized bybottom-up nanofabrication technique and focuses on phenomena that arise in sub-10 nm nanochannel. First, we synthesized mesoporous silica SBA-16 thin films with highly ordered three-dimensional cubic structures on a Si substrate via the dip-coating method based on evaporation-induced self-assembly and demonstrated ion transport phenomena in nanofludic device fabricated using those films. When the Debye length of the aqueous solution clearly exceeded the spherical pore radius (~9.5 nm), the measured ionic current exhibited nonlinear behavior with increasing an electric potential bias applied. The nonlinear behavior of ionic currents at low concentration can be reasonably attributed to the electric potential barrier created in pores measuring a few nanometers in diameter (~2.3 nm). To quantitatively discuss nonlinear ionic current behavior due to the electric potential barrier, we established the modified Poisson-Nernst-Plank equation, which was applied to express the discreteness of molecules in nanopors, as the governing equation to describe ion transport in nanopores below ~5nm in diameter and successfully analyzed by means of continuum dynamics instead of stochastic or molecular dynamics. In addition, proton transport behavior through mesopores of SBA-16 showed considerably different result compared to conventional nanofluidic system. When proton current was measured in surface-governed regime, the conductance generally decreases with increasing concentrations of aqueous solution because the surface charge density on the inner surface of mesopores decreases by protonation of silanol groups. However, in the case of nanopores with a few nanometers in diameter, the conductance increases in spite of active protonation. Since the dissociated proton and silanol groups were very close to each other, proton close to silanol sites also became charge carriers and might transport by hopping between silanol sites. The electric potential barrier was therefore lowered, but the density of proton did not decrease appreciably, thus increasing the conductance.Finally, we developed nanofludic devices embedded mesoporous silica SBA-15 thin films with two-dimensional hexagonal mesoporous silica SBA-15 thin film with dimensions ranging of 5-10 nm. Since mesoporous silica SBA-16 has limitations such as complex three-dimensional geometry and too small sized nanopores close to ~2 nm, it is somewhat difficult to apply commonly general conditions. Therefore, sub-10 nm nanofludic devices with more simple geometry was required to investigate ion or water transport phenomena of aqueous solution confined in mesopores. Before fabricating nanofludic devices, we investigated to find the best synthesis condition of SBA-15 thin films suitable for transport studies, because thickness and hexagonal pore-array dimensions of film depends on dip-coating rate. As a result, we found that SBA-15 films produced at a withdrawal speed of 3.0 mm s^{-1} featured the most perfect pore structure of the global one-dimensional pore alignment and local two-dimensional hexagonal pore array because a thin film of dilute solution was formed uniformly and the micelle self-assembly proceeded slowly.