

Fabrication and Application of Silica Nanochannels in Anodic Alumina Membrane

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論 文 内 容 要 旨

Introduction and Background

Mesoporous silica materials that have been fabricated in many forms like powders, monoliths, and films have attracted considerable attentions in the last two decades. Due to their uniform pores ranging from a few to tens nm and stability in organic and inorganic solution phases, they have been considered as candidates for many promising future applications such as size-exclusive separation, enzymatic nanoreactors, catalysis, sensors, and nanofluidic devices. In our group a new method to fabricate silica nanochannels within the pores of anodic alumina membrane (AAM) has been developed using surfactant templated method.¹ In this work, diffusivities of different charged metal complexes inside the 1D silica-surfactant (SS) nanochannels incorporated alumina membrane (NAM) fabricated using cetyltrimethylammonium bromide (CTAB) as a template was studied. Moreover, different Brij type template surfactants with different alkyl and/or ethylene oxide (EO) groups have been used to fabricate 3D silica nanochannels inside the 1D nanopores of AAM. Characterization of the mesoporosity, geometry and morphology of the fabricated nanochannels carried out using different tools like N₂-isotherm, SEM, TEM, and many others. Grafting of the inner walls of the silica nanochannels using hydrophobic trimethylchlorosilane (TMS) carried out to increase the hydrophobicity inside the nanochannels and give better stability to silica nanochannels against organic phases. Size-exclusive separation of silver nanoparticles (AgNPs) carried out using TMS-modified silica nanochannels to control size, crystallinity, and monodispersity of the AgNPs.

Fabrication and Characterization of Silica Nanochannels using Brij Template Surfactants

For the preparation of silica nanochannels inside the pores of AAM, a precursor solution composed of Brij surfactant, ethanol, tetraethylorthosilicate (TEOS), and HCl was mixed under hydrothermal condensation

reaction for 150 min. at 30 °C. The AAM was set in an ordinary filtration system, and the precursor solution was introduced to its pores under moderate aspiration. The membrane was allowed to dry and then calcined under air at 600 °C for 2 hours to remove the template surfactant. The mesoporosity, geometry, and morphology of the fabricated silica nanochannels were characterized using N₂-isotherm, SEM, and TEM. All N₂ isotherm results show type IV isotherm with H₂ hysteresis which indicates the formation of mesoporous silica materials with tunable pore diameters varied from 3.7 to 5.1 nm. The pore diameter was found to be dependent of the length of the alkyl group (core region) as well as the EO group (corona region) of the template surfactant. All BET surface areas are within the same range except the BET surface area of the Brij30-based hybrid membrane has the lowest BET surface area. This refers to the presence of small number of EO group which participating mainly in the formation of the silica wall at the expense of the pore diameter leading to small BET surface area.

SEM images show the morphology of the fabricated silica nanochannels which indicated the fabrication of columnar and tubular silica nanorods within the 1D pore of AAM. On the other hand TEM images were recorded to check the geometry of the fabricated mesostructures. TEM patterns indicated the successful fabrication of long range, uniform, and well ordered 3D silica nanochannels within the 1D pore of AAM.

Diffusivities of Metal Complexes inside 1D Silica-Surfactant Nanochannels Hybrid Membrane CTAB was used as a template surfactant to fabricate 1D silica-surfactant (SS) nanochannels incorporated alumina membrane. Hereafter we will name it as nanochannelled incorporated alumina membrane (NAM). Different metal complexes varied between cationic, anionic, and neutral were used to study the diffusivity inside NAM and to check the diffusion and extraction mechanisms inside the SS-nanochannels. The NAM was imbedded between feed phase which contains the metal complex and KCl and receiver phase which has only KCl. The amount of the metal complex diffused across the NAM was detected electrochemically using 3-electrodes system set inside the receiver phase.

The time dependent mass transport profile of different metal complexes across the NAM and alumina membrane examined. In the NAM system, I can recognize remarkable lag-time that is defined as the time required for the molecule to diffuse through the membrane, and the lag-time is independent on the concentration of the metal complex in the feed phase (C_{feed}). In contrast, no remarkable lag-time is observed for the alumina membrane. These results indicate that the lag-time is due to the diffusion of metal complex inside the SS-nanochannel. Hence, I tried to estimate the apparent diffusion coefficient of different metal complexes inside the SS-nanochannel from the observed lag-time under the same experimental conditions. The apparent diffusion coefficient values are found to be 5 orders of magnitude lower than those in bulk aqueous solution. These results reveal also that the neutral metal complexes have faster diffusivities than charged ones. It was proposed that the SS-nanochannel is composed of three regions, silica framework, hydrophobic interior of the surfactant micelles, and the ionic interface containing the head group of the surfactant with its counter anion. By considering this mesostructure, the charged metal complexes are electrostatically interacting with the ionic species at the ionic interface, whereas the electrostatic interaction between the neutral metal complexes with the ionic interface is weak. The weak electrostatic interaction is suggested to be responsible for the faster diffusivities of neutral metal complexes inside the SS-nanochannels.

2 Size-Exclusive Separation of Ag Nanoparticles

The control of the shape, size, crystallinity, and dimensionality of metal nanocrystals (or

nanoparticles: NP) has been paid great interest in materials science. Difficulties in the synthesis of nanocrystals with control their shapes and crystallinity is a hard task up to date.

Mesoporous silica nanochannels fabricated inside the AAM can be considered as the best simple candidate to regulate and control the shape and crystallinity of the polycrystalline and polydispersed nanoparticles. In this study, 3D silica nanochannels have been used for size-exclusive separation of AgNPs in a trial to get Ag nanocrystals with uniform, spherical, and monodispersed. For that goal, grafting of the inner walls of the silica nanochannels with TMS carried out via hydrothermal condensation reaction to increase the hydrophobicity inside the nanochannels and give better stability to silica nanochannels against organic phases. After grafting, the N₂ isotherm was measured and the results revealed that there is no meso-structural deformation, both samples have 3D mesostructure, and the pore diameter reduced from 4.4 to 3.9 nm due to the intact of the hydrophobic TMS group to the inner walls of the silica nanochannels. Moreover, the small angle XRD patterns were recorded for both as made and TMS-grafted silica nanochannels hybrid membranes. The results reveal the fabrication of highly ordered 3D silica nanochannels with body centered cubic mesostructure.

AgNPs has been synthesized by using sodium laureate and sodium borohydrate as a capping / reducing agent TEM images of the as made AgNPs show that the NP's size varies between 1-16 nm with polydispersed, and nonuniform shaped nanocrystals. For the separation experiments, the TMS-grafted hybrid membrane (pore diameter 3.9 nm) was set in an ordinary filtration system and the AgNPs solution was introduced to its 3D TMS-silica nanochannels.

Experimental results reveal that the grafting of the inner walls of the silica nanochannels lead to facile size-exclusive separation across the 3D nanochannels without non-aggregated yield and this refers to the increase of the hydrophobic atmosphere inside the nanochannels. Moreover, the AgNPs yield was detected by Uv-Vis spectrophotometer and TEM.

Results indicated that well ordered and monodispersed nanocrystals of AgNPs were formed with pore diameter less than 4.0 nm which is in a complete matching with the pore diameter of the TMS-grafted silica nanochannels.

Reusability and efficiency of the 3D TMS-silica hybrid membrane was also examined. For this purpose, the hybrid membrane was used for more than one separation cycles, after each cycle, the hybrid membrane was washed thoroughly and then used for the other cycle and so-on. Detecting the lag time for each cycle and the N₂ isotherm, the results show that the BET surface area, mesoporosity, and the pore size distribution decrease with a remarkable increase in the macroporosity because of the long intact time of the silica nanochannels with the AgNPs organic solution phase which causes deterioration of the fabricated mesostructure. Moreover, there was no recorded lag time after the fifth cycle this may refer to the complete destroy of the mesostructure of the TMS-silica hybrid membrane. From here we can conclude that the 3D TMS grafted silica nanochannels hybrid membranes can be used for size-exclusive separation of AgNPs or others effectively even for 5 cycles.

Summary and Conclusions

Fabrication and characterization of long range, well ordered, and uniform 3D silica nanochannels within the pores of AAM successfully carried out using Brij surfactants as template surfactants. These fabricated materials show promising application in size-exclusive separation of AgNPs to control their crystallinity, and shape for better future usability. I believe that these Brij based silica nanochannels will play an excellent role in applications in the near future.

論文審査の結果の要旨

陽極酸化アルミナ膜内の円柱状アルミナ細孔内部に、界面活性剤ミセルを鋳型として均一な高規則性シリカナノチャンネル集合体であるメソポーラスシリカを形成させた複合メソポーラス膜は、均一ナノチャンネルに由来する分子ふるい効果、閉じ込め効果による溶媒・溶質分子の特異的拡散、といった特徴を利用した新たな分離分析手法への適用が期待されている。本論文では、一連の Brij 系界面活性剤ミセルを鋳型としたシリカナノチャンネル集合体作製手法について検討すると共に、シリカナノチャンネル内部における溶質拡散挙動の解明、分子ふるい効果を実証した。

Brij 系界面活性剤ミセルを鋳型とするシリカナノチャンネル集合体作製においては、前駆体溶液内の界面活性剤とシリカ源である TEOS (Tetraethoxysilane) のモル比、pH、水/エタノール混合比、および前駆体溶液の熟成時間と温度、といったパラメーターを適正化することで、広範囲に規則性均一メソ細孔を有するシリカナノチャンネル集合体 (メソポーラスシリカ) を作製可能であることを見出した。作製したメソポーラスシリカの微細構造は TEM や SEM、XRD、窒素吸脱着、電子線回折などによって複合的に評価し、主として cubic 型細孔構造であることを確認した。

また、サイズの異なる Brij 系界面活性剤ミセルを鋳型とすることで細孔径が 3~5 nm の範囲で調製できることが分かった。

シリカナノチャンネル集合体内部における溶質分子の拡散挙動解明においては、複合メソポーラス膜の形状を活かした膜透過実験系を独自に組み上げ、電気化学検出による金属錯体の膜透過挙動ダイナミクス計測を行った。その結果、見かけの拡散係数がバルク溶液中に比べて 4~5 桁低下することを確認し、拡散係数の低下に対してシリカナノチャンネル内部におけるイオン性界面と溶質分子間の静電相互作用が重要であることを見出した。

分子ふるい効果の実証においては、溶液内還元法によって作製した銀ナノ微粒子溶液を複合メソポーラス膜によってろ過し、ろ液内の銀ナノ微粒子サイズ分布を計測した。ここでは、ラウリン酸単分子層で覆われた銀ナノ微粒子のトルエン溶液を作製し、実験に用いた。また、Brij97 界面活性剤ミセルを鋳型としたシリカナノチャンネル集合体を含む複合メソポーラス膜をろ過膜として用いた。なお、シリカナノチャンネル内壁をトリメチルシリル化することで、シリカ内壁への銀ナノ微粒子の吸着を抑えている。ろ過実験の結果、ろ液にはシリカナノチャンネルの直径 (3.9nm) 以上の銀ナノ微粒子が観測されず、複合メソポーラス膜がシャープな分子ふるい特性を有することを実証した。

以上の研究成果は論文提出者が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、Moataz Mahmoud Mekawy 君提出の博士論文は博士 (理学) の学位論文として合格と認める。