

Development and Characterization of a Hybrid Mesoporous Silica Membrane and Its Application for Fe(II) Analysis

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Development and Characterization of a Hybrid Mesoporous Silica
Membrane and Its Application for Fe(II) Analysis

(メソポーラスシリカハイブリッド膜の開発とキャラクタリゼーション及
び鉄(II)分析への応用)

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論 文 内 容 要 旨

[Chapter 1] An upsurge began in 1992 by Mobil researchers with the development of periodic mesoporous materials (M41 phase) and have opened exciting avenues for designing new classes of nanoporous materials. Among the various preparation methods, a templating method has been most commonly used and extends porous materials to meso-scale with relatively large, uniform and adjustable pore sizes. By utilizing the inherent properties of mesoporous silica materials, extensive studies have been reported in the areas such as adsorption, catalysis etc., Recently, a new hybrid mesoporous membrane (MM) has been developed by our group, which is composed of mesoporous silica within a porous anodic alumina membrane, and the MM has been applied for separation of molecules. Now I develop MM with large pore size using Pluronic F127 (PEO106PPO70PEO106) block copolymers as surfactant template.

[Chapter 2] The preparation of hybrid MM of silica-surfactant nanocomposite in an porous alumina membrane requires a precursor solution. A mixture of F127 (0.92 g), 1 M hydrochloric acid solution (0.20 g), ethanol (17.66 g), and water (1.38 g) was stirred for 1 h at 30°C. Then the silica source TEOS (Tetraethoxy silane) was added and the resultant solution was stirred for 5 hrs at 30°C. Once the precursor solution is ready, the precursor solution was dropped onto the alumina membrane surface, set in a membrane filtration apparatus. Moderate aspiration was applied so that the precursor solution penetrates into the columnar pores of the alumina membrane. The structure of F127-based MM was examined by SEM, TEM, and N₂ adsorption/desorption and the formation of columnar silica-F127 nanocomposite (length = ca. 45 nm) within the alumina pores was confirmed and it had well-ordered pore structures (pore diameter = ca. 12 nm) with circular or concentric three-layer stacked-doughnuts structure. The obtained pore diameter is the largest compared to those reported in the literatures.

[Chapter 3] The F127-based MM was aimed to apply as an analytical chip to detect Fe(II). In this study, one-pot incorporation of bathophenanthroline (Bphen) within the silica-F127 nanocomposites was tried since this method allows simple and rapid incorporation compared to general other methods. The one-pot method relies that the Bphen incorporation is achieved during the formation of the silica-F127 nanocomposite by dropping the precursor solution containing Bphen. In this method, since there is a possibility that the presence of Bphen in the precursor solution may affect the pore structure of the silica-F127 nanocomposite, the effect of Bphen concentration was also examined. Well-ordered pore structure was recognized when the Bphen concentration was between 0 to 15 mM, whereas the excess amount of Bphen (> 20 μM) causes distortion of the pore structure. In the acidic precursor solution, protonated Bphen is distributed on the surface of F127 micelles and catalyze the condensation of TEOS. Hence, the condensation rate at the micellar surface is faster than that without protonated Bphen and would cause the distortion of pore structure. When the F127-based MM with Bphen was immersed in an Fe(II) solution, spontaneous color change, due to formation of $\text{Fe}(\text{Bphen})_3^{2+}$ was observed. After the immersion, the sample membrane was picked up and diffuse reflectance spectra from the sample membrane were measured by using a densitometer. The highest response toward Fe(II) was recognized when the F127-based MM with Bphen was synthesized by using a precursor solution containing 15 mM Bphen, and its detection limit was ca. 20 nM.

[Chapter 4] An observation of solvation dynamics by measuring time-resolved fluorescence (TRF) spectra of a probe dye is a suitable method to study the viscosity of a medium within small pores. In this study, Coumarin 153 (C153) was extracted into F127 micellar phase within the silica-F127 nanocomposite and the fluorescence dynamic Stokes shift of C153 was observed at various temperatures (278 to 298 K). The obtained TRF spectra were quantitatively analyzed using a time-correlation function $[C(t)]$. At 298 K, the decay times are almost consistent with the one obtained for F127 micelles in water, indicating that the viscosity of the F127 micelles does not change by the surrounding within the silica-pores. It has been reported that the solvation dynamics become slower by confinement, inside small pores (<10 nm in diameter) because of the restricted collective motion of molecules. The consistence in decay times found in this study would be due to the larger pore diameter (12 nm). From the plot of decay time vs 1/T, it has been observed that there are two phases for the F127 micelle within the pores, indicating phase transition at

around 288 K (phase I: above 290.5 K, Phase II: 278 to 288 K). The activation energy obtained for phase I is 1.38 kJ/mol and this value is • 6.5 times smaller than that for phase II. In addition, the viscosity for phase I is almost 6 orders smaller than that for phase II. The slow decay time can be ascribed to collective motion of the polymer chain and the relaxation of water molecules. Therefore, the results indicate that the solvation dynamics inside silica-F127 nanocomposite is consistent with the F127 micelle in an aqueous solution at 298 K and there is a sharp phase change around 288 K.

論文審査の結果の要旨

界面活性剤ミセルを鋳型として形成される界面活性剤-シリカナノ複合体は、分子サイズの均一な細孔径と高い吸着容量といった特徴を有し、分離分析への応用が期待されているが、その応用例は限られている。本論文では、新規界面活性剤-シリカナノ複合体の創製と分析場としての応用、さらにはナノ空間における特異物性解明を行うことで、界面活性剤-シリカナノ複合体を利用した新規分離分析システムの構築を目指した。

新規界面活性剤-シリカナノ複合体として、多孔性陽極酸化アルミナ膜のアルミナ細孔中にトリブロクロコポリマーであるPluronic F127 (F127) を鋳型とし、12nmの細孔径を有する規則的細孔が配列した円柱状F127-シリカナノ複合体の形成に成功した。

円柱状F127-シリカナノ複合体が充填されたアルミナ膜（以下、ハイブリッドメソポーラス膜と称す）は、シリカ細孔壁に取り囲まれた疎水的なF127ミセルを微小疎水場とした固相抽出操作に基づく分析チップへの応用が期待された。そこで、Fe(II)の比色試薬であるバスフェナントロリンをF127ミセル相に導入したハイブリッドメソポーラス膜を、one-pot合成により作製し、Fe(II)に対する応答特性について評価した。その結果、F127-シリカナノ複合体の細孔構造を維持したまま、 μM レベルのFe(II)を認識し、それをFe(II)とバスフェナントロリン錯体の色調変化により検出し得る、新規Fe(II)検出チップの作製に成功した。

シリカ細孔壁に取り囲まれた疎水的なF127ミセルでは、通常のパルク水溶液中におけるF127ミセルに比べて粘性が異なることが予想される。粘性は、様々な分離分析操作時間を左右する重要な因子であることから、クマリン153を蛍光プローブとした時間分解蛍光測定によって、シリカ細孔壁に取り囲まれたF127ミセルの粘性の温度変化について検討した。その結果、およそ13°C近傍で急激な相変化が観測され、この温度を境に粘性が大きく変化することが分かった。この相変化は、ミセル中に存在する水分子と高分子鎖との集団運動に起因するミセル内の粘性変化を示唆するものである。

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、Radhakrishnan Logudurai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。