we investigated the coating process of mesostructured triblock copolymer-tetraethoxysilane (P123-TEOS) and mesoporous silica (MPS) films on a bioinert poly(dimethylsiloxane) (PDMS) with the different cross-linker concentrations through an oxygen-plasma treatment to evaluate the mesostructure formation and adsorption ability of proteins (albumin, fibrinogen, γ-globulin, fetal bovine serum). In the PDMS preparation, the cross-linker concentration affected the polymer network formation and the siliceous layer was formed on the most-surfaces by the plasma treatment. The transparent siliceous films of P123-TEOS and MPS were successfully covered on the cross-linked PDMS without voiding and the coating film thicknesses were ca. 100 nm. The FT-IR spectra indicated that the change from P123-TEOS to MPS occurred with preserving the PDMS chemical bonds by the calcination. Especially, the XRD patterns and nitrogen adsorption and desorption isotherms of the MPS on PDMS indicated the mesostructured film formation with preserving the ordered nanopore structures (BJH pore sizes: 1.6–4.2 nm, BET surface areas: 394–602 m²/g). The hydrophobic PDMS surfaces became more wettable by the coating. The adsorption amounts of acidic proteins (albumin, fibrinogen) were changed by the coating. For the fibrinogen, the P123-TEOS on PDMS exhibited the most adsorption sites. Therefore, the bio-interactive properties of the PDMS surfaces were demonstrated based on the coating processes. [DOI: 10.1380/ejssnt.2018.41]

Keywords: Surface chemical reaction; Biological compounds; Nano structure chemistry, processing and fabrication; Biological aspects of nano-structures; Mesoporous silicas; Poly(dimethylsiloxane); Protein adsorption

I. INTRODUCTION

Poly(dimethylsiloxane) (PDMS) has been widely used as a bioinert material in the medical devices such as catheter, medical tube and contact lens, and has been applied to the bio-interfaces with living body tissues. PDMS has a backbone of siloxane bonding (Si–O–Si) and an end group of methyl group (–CH₃) [1]. These several biomedical applications are based on the chemically stable and highly heat resistant siloxane backbone [2], which is related with the low toxicity [3]. In the implantation of PDMS into biological fluid, the proteins are adsorbed on the surface to be denatured and the protein covering state would affect the bio-interface properties. Thus, the hydrophobic solid surfaces rearrange the adsorbed protein structures to be favorable states [4]. For example, the denaturation of some proteins (e.g., lysozyme [5]) may cause aggregation or can trigger immune reactions on the PDMS surfaces [6], which are often occurred on the contact lens in tear fluid [7]. The sediments cloud the contact lens surfaces and cause the human’s wearer discomfort, and can be responsible for the variety of inflammatory reactions [8]. Therefore, the bio-interface modifications of the PDMS surfaces are important for the applications.

The chemical modification of the PDMS surface is difficult due to the hydrophobic methylsilyl group. Thus, the researches have focused on oxygen-plasma treatment [9], chemical reforming by ultraviolet rays and ozone treatment [10]. The modifications cause the hydrophilic Si–OH on PDMS surface, and the characteristic surfaces gradually recover the hydrophobicity with the time (e.g., ca. 3 days) [11, 12]. The process would results from the initial diffusion of low molecular weight PDMS chains and subsequent overturning of the polar hydrophilic groups from the surface to inner bulk [13, 14]. The surface wettability that can be used for a long term is important. From the viewpoints, the UV/ozone photodeactivation and subsequently chemical modification such as self-assembled monolayer formation of (tridecafluorooctyl)triethoxysilane [15] and polymeric grafting of 2-hydroxymethyl methacrylate [16] have been investigated. Although there is organic-inorganic hybrid polymer of Ti–O–Si network modified with 2-phenylphenoxyethyl acrylate has been reported [17], the modification of nanostructured siliceous layer on PDMS towards the bio-interface applications has not been reported.

The silica-surfactant mesostructures (SSM) and mesoporous silica (MPS) films have extensively been studied [18] because of their ordered mesostructure arrangements, which can be applied for separation membranes [19], gas sensors and insulating films [20]. The mesostructure formation depends on the supramolecular templating by surfactant micellar systems [21]. The coating method is often used by spin-coating [22] and dip coating [23]. In the spin-coating for uniform thin film formation, the film thickness can be controlled by the silica source concentration as well as the solvent species [24, 25]. The spin-coated SSM and MPS films for biomedical applications has not been reported, and can enhance the bio-interface properties as bioactive materials if the transparent films can be formed on the PDMS surface. Therefore, the study on the transparent and mesostructured siliceous layer on PDMS based on organic/inorganic interfacial design is necessary for the application.

In this study, the coating process of mesostructured triblock copolymer-tetraethoxysilane (TEOS) and MPS films on the bioinert PDMS were investigated through an oxygen-plasma treatment technique to evaluate the mesostructured formation and adsorption ability of pro-

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Scheme 1. Illustration of the preparation process of this study containing (a) formation mechanism of cross-linked PDMS and (b) O$_2$-plasma exposure and P123-TEOS coating processes. Here, the chemical structures of TEOS and P123 were shown in (c).

II. EXPERIMENTAL

A. Materials and preparation

A cross-linked PDMS film was prepared by the mixture of liquid PDMS (Sylgard 184A, Dow Corning Co., Ltd.) and cross-linker (Sylgard 184B, Dow Corning Co., Ltd.). The mixture weight ratio of the liquid PDMS to cross-linker was 10:0.4, 10:0.7 and 10:1.0. The mixture was diluted by chloroform (Wako Chemical Co., Ltd.) at the concentration of 0.1 g of mixture in 1 ml of chloroform. The diluted mixtures were spin-coated (3000 rpm, 20 s) on a glass plate or silicon (100) wafer to be baked and cross-linked at 65°C for 12 h. Before the coat, the substrates were cleaned by an exposure to UV/OZONE (ASUMI GIKEN, Limited, ASM401N) for 5 min. The thermally cross-link reaction occurred based on the hydrosilation, and the schematic illustration of the siloxane base oligomer having vinyl groups with the siloxane cross-linker in the presence of the proprietary platinum-based catalyst was shown in Scheme 1(a). The cross-linked PDMS film prepared by the ratio of the liquid PDMS to cross-linker at 10:χ was denoted as χPDMS (χ = 0.4, 0.7, 1.0).

The cross-linked PDMS films were irradiated by an oxygen (O$_2$-) plasma treatment (Yamato Scientific Co., Ltd., PMI100) under the condition of output power of 49 W, pressure of 1.73 kPa, O$_2$ flow rate of 30 ml/min, and irradiation time for 600 s. The irradiation time for the SSM and MPS film formation was 60 s, and the film was denoted as PlasχPDMS (χ = 0.4, 0.7, 1.0).

The SSM and MPS films were synthesized based on the previous reports [18, 26]. 252 mg of non-ionic surfactant (Pluronic P-123, (PEO)$_{20}$-(PPO)$_{70}$-(PEO)$_{20}$, Sigma-Aldrich) in Scheme 1(b) was dispersed in 415 µL of 0.01 N-hydrochloric acid aqueous solution (Wako Chemical Co., Ltd, HCl). The polymerization was carried out by mixing 1118 µL of tetraethoxysilane (Si(OCH$_2$CH$_3$)$_4$, Tokyo Chemical Industry Co., Ltd., TEOS) in Scheme 1(b), 1121 µL of ethanol (Wako Chemical Co., Ltd), 130 µL of ultrapure water and 29 µL of 1 N-hydrochloric acid at 40°C for 30 min. Then, the siliceous solution was cooled and added into the surfactant solution at the molar ratio of TEOS:water:ethanol:HCl:P123=1:1.5:4:0.006:0.009. The resulting solution was spin-coated (6000 rpm, 10 s) on a glass plate, silicon (100) wafer, or PlasχPDMS and dried at 40°C for 18 h and the hybrid film was abbreviated as P123-TEOS/χPDMS (χ = 0.4, 0.7, 1.0). The supramolecular template was removed by the calcination at 350°C for 6 h and the calcined films were denoted as MPS/χPDMS (χ = 0.4, 0.7, 1.0). These preparation processes were summarized in Scheme 1(c).

B. Protein adsorption

The protein adsorption of bovine serum albumin (Ab: Waco Chemical Co., Ltd., 66 kDa), fibrinogen (Fgn: Merck KgaA Co., Ltd., 340 kDa), γ-immunoglobulin (Glo: Waco Chemical Co., Ltd., 150 kDa) and Fetal bovine serum (FBS; Sigma-Aldrich Co., Ltd.) was carried out on 1.0PDMS, Plas1.0PDMS, P123-TEOS/1.0PDMS and MPS/1.0PDMS. The proteins of Ab, Fgn and Glo were dispersed in phosphate buffer saline (PBS; DS Pharma Biomedical Co., Ltd) with the ions (K$^+$:4.15 mM, Na$^+$:153 mM, HPO$_4^{2-}$:9.57 mM, Cl$^-$:139.57 mM) to prepare Ab/PBS, Fgn/PBS and Ig/PBS liquid at the con-
centrations of 100 μg/mL. The film was immersed in 4 mL of each protein liquid at the room temperature for 6 h and the adsorption amount was determined by the absorbance changes at 279 nm in UV-visible adsorption spectra. FBS was dispersed in Minimum Essential Medium Alpha(1X) (αMEM; Life Technologies Corporation) to prepare 10 vol% of FBS in αMEM (FBS/αMEM). The film was immersed in 4 mL of FBS/αMEM at the room temperature for 6 h, and the absorbance changes at 595 nm of the supernatant solution stained with the solution (Takara Bio. Inc., TaKaRa Bradford Protein Assay Kit T9310A) was measured by the UV-visible adsorption spectra to obtain the protein adsorption amount.

C. Characterization

Infrared spectra were recorded on a Fourier transform infrared spectrometer (FT-IR; JASCO Co., Ltd., FT/IR-4600) as the background of silicon (100) wafer in the range between 500–4000 cm\(^{-1}\) with the accumulation times of 64. In order to understand the unreacted vinyl group in liquid PDMS, the ratios of the absorption band area of CH\(_2\) group in =Si–CH–CH\(_2\) at the wavenumber between 1380–1438 cm\(^{-1}\) (\(A(CH_2)\)) to that of Si–H group in cross-linker at the wavenumber between 2111–2200 cm\(^{-1}\) (\(A(Si–H)\)) were calculated. In order to understand the silicaceous layer formation on the cross-linked PDMS, the ratios of the absorption band area of =Si–O–Si= in silicaceous layer at the wavenumber between 976–1136 cm\(^{-1}\) (\(A(Si–O–Si)\)) to that of =Si–CH\(_2\) in PDMS at the wavenumber between 1243–1278 cm\(^{-1}\) (\(A(–CH_2)\)) were calculated with the plasma exposure time. The surface wettability was recorded with a contact-angle meter (Excimer. Inc., Smart Contact 100) with the drop volume of 3.1 μL under the static condition. The dynamic contact angles at the advance and sweepback states were measured by an extension/contraction method. The optical microscope images of the interface between P123-TEOS and PDMS for P123-TEOS/0.4PDMS and the most-top MPS/PDMS surfaces were taken using the inverted microscope (Olympus Co., Ltd., CKX41) with color camera (Olympus Co., Ltd., DP72). The cross-section of the hybrid films was observed through a field emission scanning electron microscope (FE-SEM; Hitachi, Ltd., S-4800) at an accelerating voltage of 5.0 kV and an emission current of 10.5 pA. X-ray diffraction (XRD) patterns were determined by X-ray diffractometer (Rigaku Co., Ltd., Smart Lab). The XRD patterns were measured with the X-ray source of CuKα line (λ = 1.5418 Å) and voltage/current of 40 kV/30 mA. The specific surface area and pore size distributions were determined through nitrogen (N\(_2\)) adsorption and desorption instrument (MicrotracBEL Co., Ltd., BELSORP-mini). The Brunauer-Emmett-Teller (BET) [27] surface areas and Barrett-Joyner-Halenda (BJH) [28] pore sizes were calculated. The UV-Visible adsorption spectra were measured by a UV-Visible spectrophotometer (JASCO Co., Ltd, V-750).

III. RESULTS AND DISCUSSION

Figure 1 showed the FT-IR spectra of the PDMS films with the different cross-linker concentrations. The summary of the characteristic PDMS band assignments was tabulated in Table I, which are associated with –CH\(_3\) rocking and =Si–C= stretching, =Si–OH stretching, CH\(_2\) in =Si–(CH\(_2\))\(_2–\)Si= and =Si–CH\(_2–\)Si= wagging, asymmetric and symmetric =Si–O–Si= stretching, sym-
metric CH₃ vendoing, in-plane CH₂ scissoring, =Si–H stretching, and C–H stretching [10, 29, 30]. The spectral changes due to =Si–H stretching in cross-linker and those due to =CH₂ scissoring of =Si–CH=CH₂ in liquid PDMS were shown in Fig. 1(b) and (c), respectively. As shown in the ratio changes of A(CH₂) to A(Si–H)) were shown in Fig. 1(d). With increasing the cross-linker concentration, the unreacted vinyl group decreased, indicating that the cross-linking degree depends on the cross-linker concentration [31]. The cross-linker owns three =Si–H bonding per one molecule, and the breaking of the double bond of the vinyl group in liquid PDMS occurred to form =Si–CH₂–CH₂–Si= bridge with one =Si–H segment in cross-linker [32]. Therefore, the cross-linker concentration affected the PDMS network formation.

Figure 2 showed the contact angle changes with the exposure time to O₂-plasma. The angles of all the PDMS films decreased from 120° to 20° for the exposure time of 60 s. Therefore, the PDMS film surfaces were changed to be hydrophilic by the exposure.

The chemical bond changes of the PDMS films with the exposure time to O₂-plasma for 480 s were measured by FT-IR as shown in Fig. 3. The exposure clearly caused the decrease in the absorbance bands derived from in-plane CH₃ rocking, Si–C stretching and symmetric CH₃ vendoing in =Si–CH₃ segments. In constant, the symmet-

| Wavenumber/cm⁻¹ | Assignment | Vibration state |
|-----------------|------------|----------------|
| 805             | CH₃ in ⇔Si–CH₃ | In-plane rocking |
| 870             | Si–C ⇔ in ⇔Si–CH₃ | Stretching |
| 1015–1150       | CH₃ in ⇔Si–(CH₂)₂–Si= and ⇔Si–CH₂–Si= | Out-of-plane wagging |
| 1089            | =Si–O–Si= | Symmetric stretching |
| 1261            | =CH₃ in ⇔SiCH₃ | Vending |
| 1370            | =CH₃ and -(CH₃)– of P123 | Vending |
| 1410            | CH₃ in ⇔Si–CH=CH₂ | In-plane scissoring |
| 2161            | =Si–H | Stretching |
| 2808            | C–H in ⇔C–CH₃ (PO in P123) | Symmetric stretching |
| 2962            | C–H in -(CH₂)– and -CH₃ of PDMS | Stretching |
| 2970            | C–H in -(CH₂)– in PPO and PEO (P123) | Asymmetric stretching |
| 3050–3700       | O–H in ⇔Si–OH and ⇔C–OH | Stretching |

Figure 3. FT-IR spectral changes of (a) 0.4PDMS, (b) 0.7PDMS and (c) 1.0PDMS with the plasma exposure time at 0, 30, 60, 120, 180, 300 and 480 s. The absorbance was ascending or descending with the exposure time, which were indicated by the arrows in the figure.
FIG. 4. FT-IR spectral band area ratios of $A(\text{Si–O–Si})$ at 976–1136 cm$^{-1}$ to $A(–\text{CH}_3)$ at 1243–1278 cm$^{-1}$ of 0.4PDMS ($\Delta$), 0.7PDMS ($\bigcirc$) and 1.0PDMS ($\Box$) with the plasma exposure time. (b): illustration of the possible mechanism of siliceous layer formation on PDMS by the plasma exposure. 

FIG. 5. FT-IR spectra of (a) 1.0PDMS and calcined 1.0PDMS and (b) P123-TEOS and MPS films on Si (100). 

calcination, the characteristic silicate band due to symmetric Si–O–Si stretching at 1030 cm$^{-1}$ increased and that due to asymmetric Si–O–Si stretching at 1089 cm$^{-1}$ decreased. The several bands due to −CH$_3$ and −CH$_2$–vending at 1370 cm$^{-1}$, symmetric C–H stretching at 2898 cm$^{-1}$ and asymmetric C–H stretching in −CH$_2$− at 2970 cm$^{-1}$ clearly disappeared, indicating the complete removal of the surfactant P123 template [34]. Therefore, silica phases due to MPS were generated with preserving the PDMS chemical bonds by the calcination at 350°C. Furthermore, the detected bands of the hybrid films before and after the calcination in Fig. 6 indicated that the change from P123-TEOS to MPS phases successfully occurred with preserving PDMS chemical bonds by the calcination.

Figure 7 showed the optical microscope photographs of the hybrid films before and after the calculation at the transmittance states. In the P123-TEOS/0.4PDMS (Fig. 7(a)), there were the cracks at the most-top surfaces of the P123-TEOS/0.4PDMS film, indicating the alligatoring of the siliceous layer formed by O$_2$-plasma treatment. It was suggested that the cross-linker concentration affected the lower cross-linking degree to form the brittle siliceous layers on the 0.4PDMS. In the other P123-TEOS/PDMS films, there were no cracks on the surfaces. After the calcination, the MPS/0PDMS films exhibited the cracks on the most-top surfaces, indicating that the stress difference between the MPS and PDMS layers by the heat shrinkage induced the cracks of the MPS layers.

Figure 8 showed the cross-sectional SEM images of the hybrid films before and after the calculation. The P123-TEOS and MPS layers were tightly covered on the PDMS surfaces without voiding. These siliceous film thicknesses (P123-TEOS and MPS) were ca. 100 nm.

Figure 9 showed the XRD patterns of the hybrid films before and after the calcination. Figure 9 (inset) showed the photographs of the hybrid films on glass substrate, indicating the high transparency of the films. The sharp reflections of the hybrid films indexed as (1 0 0), (1 1 0) and (2 0 0) of a hexagonal structure due to mesostruc-
FIG. 8. Cross-sectional SEM images of (a) P123-TEOS/0.4PDMS, (b) P123-TEOS/0.7PDMS, (c) P123-TEOS/1.0PDMS, (a') MPS/0.4PDMS, (b') MPS/0.7PDMS and (c') MPS/1.0PDMS at higher magnifications, and the representative lower magnification images of (d) P123-TEOS/1.0PDMS and (d') MPS/1.0PDMS.

FIG. 9. Out-of-plane XRD patterns of P123-TEOS/0.4PDMS and MPS/0.4PDMS, P123-TEOS/0.7PDMS and MPS/0.7PDMS, and P123-TEOS/1.0PDMS and MPS/1.0PDMS. (Inset): their photographs on a glass substrate (scale bar: 1 cm).

FIG. 10. (a–c) Nitrogen adsorption (○) and desorption (●) isotherms and (d–f) BJH pore size distributions of (a, d) MPS/0.4PDMS, (b, e) MPS/0.7PDMS, (c, f) MPS/1.0PDMS.

FIG. 11. Contact angles of water on 1.0PDMS, Plas1.0PDMS, P123-TEOS/1.0PDMS and MPS/1.0PDMS. By coating of P123-TEOS and MPS, the cross-linked PDMS became more wettable. MPS/1.0PDMS showed the hydrophobic, indicating the mixed surfaces between PDMS and MPS because of the crack formation (Fig. 7(f)). The difference between the advancing and receding angles was largest in P123-TEOS/1.0PDMS, indicating the preferential protein dynamics on the surfaces for the subsequent protein-surface interaction changes [35]. Since the wettability of the films was related with the protein adsorption properties [36], the wettability of the films, which was varied by the coating of the mesostructured films, would affect the protein adsorption ability.

FIG. 12 showed the adsorption amounts of Ab, Fgn, Glo and FBS on the films. The averaged adsorption amount of Ab was determined in the order of P123-TEOS/PDMS (13.8 μg/cm²) > Plas1.0PDMS (8.4 μg/cm²) > MPS/1.0PDMS (6.7 μg/cm²) > 1.0PDMS (4.6 μg/cm²). The adsorption amount of Fgn was determined in the order of P123-TEOS/PDMS (29 μg/cm²) > Plas1.0PDMS (23 μg/cm²) > 1.0PDMS (17 μg/cm²) > MPS/1.0PDMS (12 μg/cm²). P123-TEOS/1.0PDMS exhibited the largest adsorption amounts. The Ab (iso-
For the adsorption amount of FBS proteins, there was no difference between the films. The serum proteins cause “Vroman effect” that is a phenomenon in which adsorbed protein on surfaces is replaced with the other abundant proteins [44], implying the complex adsorption mechanism. Thus, the adsorption amount of the FBS proteins was dominated by the abundant proteins of Ab and Glo as well as the cell-binding proteins [45]. Therefore, the serum protein adsorption amounts were varied by the siliceous layer coating. In particular, the Fgn adsorption properties on the films were clearly changed by the coating to exhibit the characteristic bio-interactive features.

IV. CONCLUSIONS

We investigated the coating process of P123-TEOS and MPS films on the bioinert PDMS with the different cross-linker concentrations through the oxygen-plasma treatment to evaluate the mesostructure formation and adsorption ability of proteins (Ab, Fgn, Glo, FBS proteins). In the PDMS preparation, the cross-linker concentration affected the polymer network formation, and the siliceous layer was formed on the most-surfaces by the plasma treatment. The transparent siliceous films of P123-TEOS and MPS were successfully covered on the cross-linked PDMS without voiding and the coating film thicknesses were ca. 100 nm. The FT-IR spectra indicated that the change from P123-TEOS to MPS occurred with preserving the PDMS chemical bonds by the calcination. Especially, the XRD patterns and N2 adsorption and desorption isotherms on MPS/PDMS indicated the mesostructured film formation with preserving the ordered nanopore structures (BJH pore sizes: 1.6–4.2 nm, BET surface areas: 394–602 m²/g). The hydrophobic PDMS surfaces became more wettable by the coating. The adsorption amounts of acidic proteins (Ab, Fgn) were changed by the coating. For the Fgn, P123-TEOS/PDMS exhibited the most adsorption sites. Therefore, the bio-interactive properties of the PDMS surfaces were elucidated by the coating processes.

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[1] G. C. Lisensky, D. J. Campbell, K. J. Beckman, C. E. Calderon, P. W. Doolan, R. M. Ottosen, and A. B. Ellis, J. Chem. Educ. 76, 537 (1999).
[2] G. Camino, S. M. Lomakin, M. Lazzari, Polymer 42, 2395 (2001).
[3] A. Mata, A. J. Fleischman, and S. Roy, Biomed. Microdevices 7, 281 (2005).
[4] P. Roach, D. Farrar, C. C. Perry, J. Am. Chem. Soc. 127, 8168 (2005).
[5] M. Yari, S. S. Sharijimi, and O. Moradi, J. Phys. & Theo. Chem. I. A. U. Iran 1, 169 (2004).
[6] D. Luensmann and L. Jones, Contact Lens Anterior Eye. 35, 53 (2012).
[7] J. L. Bohnert, T. A. Horbett, B. D. Ratner, and F. H. Royce, Invest. Ophthalmol. Vis. Sci. 29, 362 (1988).
[8] M. J. Miller, L. A. Wilson, and D. G. Ahearn, J. Clin. Microbiol. 26, 513 (1988).
[9] H. Hillborg, J. F. Anker, U. W. Gedde, G. D. Smith, H. K. Yawata, and K. Wikström, Polymer 41, 6851 (2000).
[10] K. Elimenko, W. E. Wallace, and J. Genzer, J. Colloid Interface Sci. 254, 306 (2002).
[11] V. Jokinen, P. Suvanto, and S. Franssila, Biomicrofluidics. 6, 016501 (2012).
[12] D. T. Eddington, J. P. Puccinelli, and D. J. Beebe, Sens. Actuators B Chem. 114, 170 (2006).
[13] Y. Berdichevsky, J. Khandurina, A. Guttman, and Y.-H. Lo, Sens. Actuators B Chem. 97, 402 (2004).
[14] H. Hillborg and U. W. Gedde, Polymer 39, 016501 (2012).
[15] D. T. Eddington, J. P. Puccinelli, and D. J. Beebe, Sens. Actuators B Chem. 114, 170 (2006).
[16] Y. Berdichevsky, J. Khandurina, A. Guttman, and Y.-H. Lo, Sens. Actuators B Chem. 97, 402 (2004).
[17] H.-Y. Ma, T.-L. Wang, P.-Y. Chang, and C.-H. Yang, Nanomaterials 6, 44 (2016).
[18] M. Tagaya, K. Kobayashi, and M. Nishikawa, Mater. Lett. 164, 651 (2016).
[19] Y. Wu, C. Wu, Y. Li, T. Xu, and Y. Fu, J. Memb. Sci. 350, 322 (2010).
[20] A. Walcarius, Comptes Rendus Chim. 8, 693 (2005).
[21] G. J. de A. S.-lllia, E. L. Crepaldi, D. Grosso, and C. Sanchez, Curr. Opin. Colloid Interface Sci. 8, 109 (2003).
[22] J. M. Gomez-Vega, M. Iyoshi, K. Y. Kim, A. Hozumi, H. Sugimura, and O. Takai, Thin Solid Films. 398-399, 615 (2001).
[23] D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, and G. D. Stucky, Adv. Mater. 10, 1380 (1998).
[24] M. D. Tyona, Adv. Mater. Res. 2, 195 (2013).
[25] N. Nishiyama, S. Tanaka, Y. Egashira, Y. Oku, and K. Ueyama, Chem. Mater. 14, 4229 (2002).
[26] M. Tagaya, M. Okuda, S. W. Jones, and T. Kobayashi, Trans. GIGAKU 1, 01012 (2012).
[27] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. 60, 309 (1938).
[28] E. P. Barrett, L. G. Joyner, and P. P. Halenda, J. Am. Chem. Soc. 73, 373 (1951).