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Controlled Formation of Polyamine Crystalline Layers on Glass Surfaces and Successive Fabrication of Hierarchically Structured Silica Thin Films

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Ⓢ *Supporting Information*

ABSTRACT: The formation of silica films on the glass plate whose surface was precoated by crystalline linear poly-(ethylenimine) (LPEI) in advance was systematically investigated via controlling the surface-specific crystallization of the LPEI on the glass plate. Immersing glass substrates into a hot aqueous solution of LPEI containing additives such as transition metal ions and acidic compounds and retaining them on 30 °C for desired periods resulted in the formation of crystalline LPEI layers on the substrates. Subsequently dipping this LPEI-coated glass into silica source solutions afforded successfully hierarchically structured silica film which coated continuously the surface of the substrates. In this two-step process, we found that the formation of hierarchically structured silica films strongly depended on the LPEI layer formed from the LPEI aqueous solutions containing different additives. The LPEI layer formed by changing the kinds of additives and their concentrations provides the differently structured silica films composed of turbine-like structures flatly lying-on and/or vertically standing-on as well as ribbon network structures on the surface of the substrates. Moreover, we functionalized these silica films by the introduction of hydrophobic alkyl chains or emissive Eu(III) complexes and investigated their wettability and emission properties.
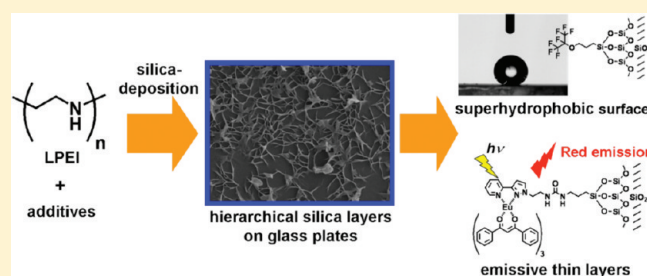
I. INTRODUCTION

In nature, surfaces of living thing are elaborately and precisely constructed to form hierarchical structures and have intrinsic features based on their hierarchy.[1−4] Typically, wettability controls, such as superhydrophobicity with high/low adhesion,[5−7] self-cleaning,[8] water-harvesting,[9] and high adhesive properties,[10,11] originate from scabrous surface patterns in nanometer to micrometer scales and hierarchical alignments of hydrophilic/hydrophobic domains.[1−3] Many efforts have been made on the developments of artificial wettability controls.[12−17] Moreover, the well-known iridescence based on structural color of *Morpho rhetenor* butterflies arises from exquisitely ordered structures on the surface of basements.[3,4]

Construction of silica surfaces with hierarchical structures is fundamentally and practically important.[18] Silica is one of the most widely utilized materials, and up to date, many structured silica in bulk have been created and supposed to various practical usages.[18−33] In these silica structures, mesoporous materials attracted considerable attention and have been widely used for varieties of applications based on their inherent features such as regular porosity and large surface area.[34−54] For preparations of these silica materials, the micelle-template-directing method is commonly used (Scheme 1a). In this method, silica is formed surrounding the hexagonally packed micelle templates with aid of additive

pH regulator which promotes hydrolytic condensation of alkoxysilane in aqueous media.[25−56] This approach is quite useful for construction of inorganic replicas and mesoporous materials.[18,55,56] However, control of mesoporous silica film with special morphology on the surfaces of substrates is not easy, although many techniques were provided for the preparation of mesoporous silica films.[38]
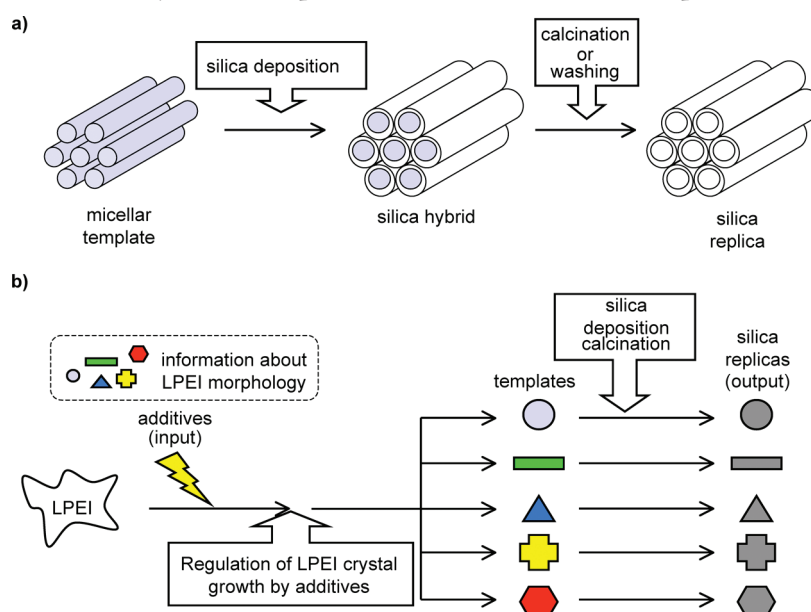
To develop a templating method, we have studied the different approaches to prepare hierarchical silica structures using LPEI as a template, catalyst, and scaffold in silica deposition (Scheme 1b).[57−68] LPEI dissolved in hot water can crystallize rapidly during cooling processes to form aggregates composed of crystalline fibrous structures.[69] The fibrous aggregates show basic properties originating from ethylenimine (EI) units on the surface so that the surface of aggregates itself can effectively promote site-selective hydrolytic condensations of alkoxysilane and deposit silica on the surface. That is, the LPEI aggregates play as catalytic templates for silica duplication. Interestingly, the LPEI crystallization process is effectively controllable by an addition of some molecules that can interact directly/indirectly with ethylenimine (EI) units of LPEI and thus
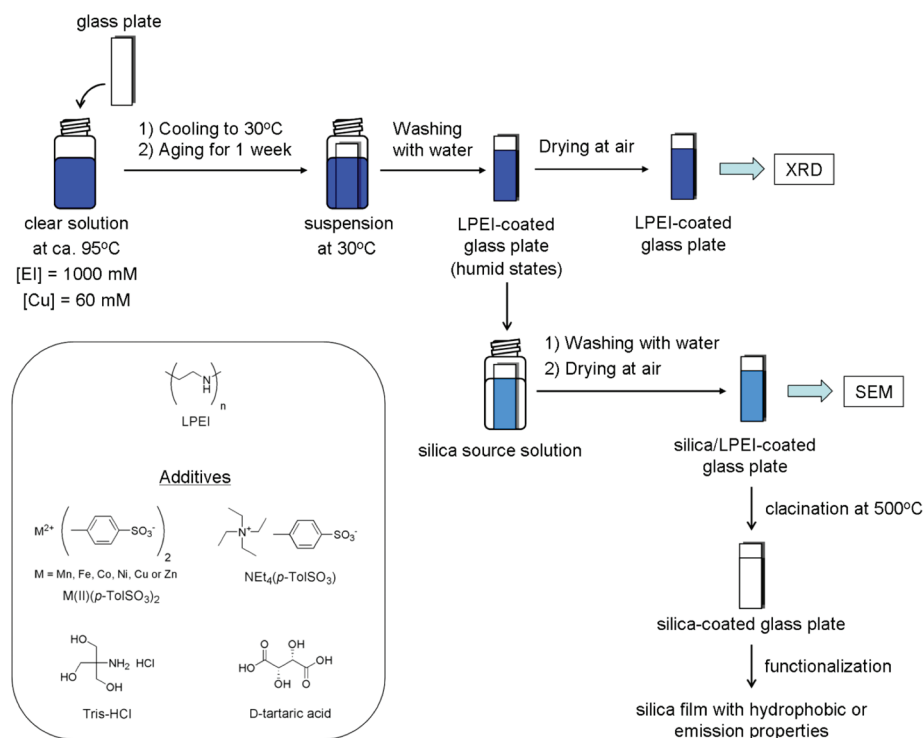
Scheme 1. Concept of Silica Transcription Mediated with Templates: (a) Conventional Mesoporous Silica Transcription; (b) Programmable Control of LPEI Crystalline Templates and Successive Silica Transcription[a]

a)

silica deposition

calcination
or
washing

micellar
template

silica hybrid

silica
replica

b)

information about
LPEI morphology

additives
(input)

silica
deposition
calcination

templates

silica
replicas
(output)

LPEI

Regulation of LPEI crystal
growth by additives

[a] The morphology of LPEI crystalline templates can be regulated by the change in additives.

Scheme 2. Schematic Illustration of the Preparation of Silica Films on the Surface of Glass Plates as Well as Chemical Structures of LPEI and Additives

glass plate

clear solution
at ca. 95°C
[EI] = 1000 mM
[Cu] = 60 mM

1) Cooling to 30°C
2) Aging for 1 week

suspension
at 30°C

Washing
with water

LPEI-coated
glass plate
(humid states)

Drying at air

LPEI-coated
glass plate

XRD

silica source solution

1) Washing with water
2) Drying at air

silica/LPEI-coated
glass plate

SEM

clacination at 500°C

silica-coated glass plate

functionalization

silica film with hydrophobic or
emission properties

LPEI

Additives

M(II)(p-TolSO$_3$)$_2$
M = Mn, Fe, Co, Ni, Cu or Zn

NEt$_4$(p-TolSO$_3$)

Tris-HCl

D-tartaric acid

consequently provide variously shaped LPEI aggregates depending on the species and concentrations of additives, as shown in Scheme 1b.[60−65] Therefore, we can handle these conditions of additives (e.g., species or concentrations) as information source regulating flexible LPEI morphologies by which the successive silica formation is programmable.

Herein, we report two-step process of the fabrications of hierarchically structured silica films on glass substrate which was covered by LPEI crystalline layer under different conditions in advance. In the first step, we performed covering glass substrates with LPEI crystalline layers by immersing the substrate into a series of LPEI aqueous solutions containing different additives

Scheme 3. Fuctionalization of Silica Thin Films on Glass Plates: (a) Chemical Structures of Triethoxysilyl Ligand (L1) and Emissive Eu(III) Complexes (Eu-1 or Eu-2); (b) Modification Procedures of Silica Surfaces[a]
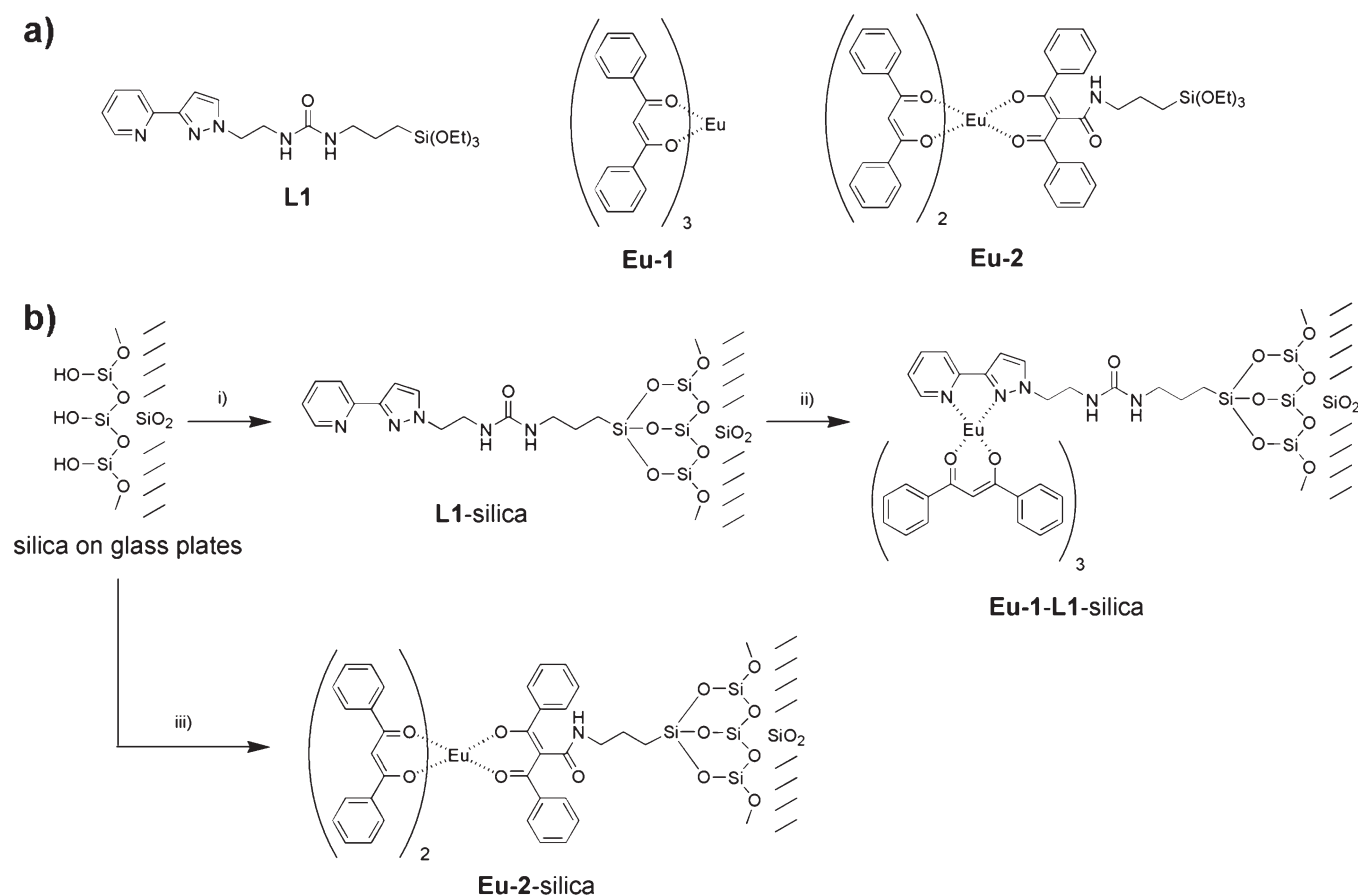
[a] Reagents and conditions: (i) **L1** in toluene, reflux for 6 h in N_2; (ii) **Eu-1** in dichloromethane at rt overnight; (iii) **Eu-2** in dichloromethane/ethanol/NH_3(aq) at rt for 3 days.

such as metal ions, trihydroxymethylaminomethane hydrochloric acid (Tris-HCl), and D-tartaric acid (D-Tart) (see Scheme 2). In the second-step, we fabricated silica film by dipping the substrates covered by LPEI crystalline layers into silica source solution. We found that the final structures of the silica films were dominated by the LPEI crystalline layer formation conditions in the first step. As preliminary attempts, we modified the silica films with hydrophobic moieties or emissive Eu(III) complexes to prepare functional nanosurface films (Scheme 3). Silica film surfaces modified by *n*-decyl or perfluoroalkyl residues showed superhydrophobic properties without losing transparency. Eu-(III)-modified silica films exhibited red emission and sensing ability to respond to methanolic vapors.

II. EXPERIMENTAL SECTION

Reagents and Materials. The poly(2-ethyl-2-oxazoline) (= PEOx, typical M_w = 50 000) was purchased from Aldrich Co., Ltd. Zinc(II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was purchased from Kanto Kagaku Co., Ltd. Tetraethylammonium *p*-toluenesulfonate ($NEt_4(p\text{-}TolSO_3)$) and *p*-toluenesulfonic acid monohydrate were obtained from Tokyo Chemical Industry Co., Ltd. Tris-HCl and D-Tart were purchased from Wako Chemical Co., Ltd., and Tokyo Chemical Industry Co., Ltd., respectively. Alkoxysilyl compounds methyl silicate-51 (MS-51) and tetramethyl orthosilicate (TMOS) were purchased from Meiwa Industry Co., Ltd., and Tokyo Chemical Industry Co., Ltd.,

respectively. These alkoxysilyl compounds were used for the preparation of silica films via the sol–gel reactions on the glass substrates covered by LPEI crystalline layers. Hydrophobic alkoxysilyl compounds *n*-decyltrimethoxysilane (DTMS) and 3-(1,1,1,2,3,3,3-heptafluoroisopropoxy)propyltrimethoxysilane (HFIPPTMS) were purchased from Aldrich Co., Ltd., and utilized for the modification of the surface of silica thin films. Emissive complexes **Eu-1** and **Eu-2** were synthesized partially according to the literature procedure.[73] Details including the synthetic route of triethoxysilyl-modified ligand (**L1**) are described in the Supporting Information. All other reagents and solvents were obtained from commercial sources and used without any purification.

Synthesis of LPEI. LPEI was synthesized by acidic hydrolysis of PEOx according to the methods previously reported.[57–69] The purity of LPEI was confirmed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The contents of water molecules per EI [CH_2CH_2NH] unit were determined to be ca. 2 by X-ray diffraction (XRD) and thermogravimetry (TG) measurements.

Additives. A series of metal *p*-toluenesulfonate salts ($M(II)(p\text{-}TolSO_3)_2$, M = Zn, Mn, Fe, Co, Ni, Cu), $NEt_4(p\text{-}TolSO_3)$, Tris-HCl, and D-Tart were used as additives in preparation of LPEI aqueous solutions. Metal *p*-toluenesulfonate salts were synthesized from the reaction of metal nitrate and *p*-toluenesulfonic acid in water.

Preparation of LPEI Crystalline Layers on Glass Surface. LPEI (316 mg) was dispersed in water (2.0 mL) and heated to ca. 95 °C to form a clear solution ([EI] = 2000 mM). To the solution was added an aqueous solution (2.0 mL) of the additive mentioned above. In the

mixed solution, the concentration of LPEI was fixed at [EI] = 1000 mM while the concentrations of the additives were changed with a certain ratio ([EI] = 1000 mM vs additives). A glass plate washed with ethanol was immersed in the hot solution (at 95 °C) containing LPEI and additive, and then the solution temperature was reduced to 30 °C. The plate immersed in the solution was retained at 30 °C for 1–2 weeks and then taken out, washed by water, and dried in air atmosphere. This procedure resulted in the formation of LPEI crystalline layer on the glass surface.

Preparation of Silica/LPEI Composite Film and Silica Film on Glass Surfaces. The glass plate covered with LPEI crystalline layer obtained from the procedure described above was immersed into silica source solutions (2-propanol/water/MS-51 = 4/2/1 by vol) at ambient temperature for 90 min. Within this period, silica deposition occurred on the LPEI layers to form silica/LPEI composite film on the glass surface. The plate taken out was washed carefully with 2-propanol, dried at air atmosphere, and then subjected to SEM observation. Calcination of the glass plates coated with silica/LPEI film at 500 °C for 3 h under dried air flow resulted in silica-coated glass plate.

Effect of Time Course of LPEI Crystallization on Silica Film Formation. The hydrated LPEI (790 mg, 10 mmol) and Zn(p-TolSO$_3$)$_2$ (310 mg, 0.60 mmol) were dissolved in water (10 mL) at 95 °C, and the solution ([EI] = 1000 mM, [Zn] = 60 mM) was cooled to room temperature (ca. 23 °C) and then divided into 14 portions (ca. 1 mL). After glass plates were immersed in each solution, each aliquot was allowed to stand at room temperature for 60 min. Within this time, precipitations appeared in solution phase. Taking this as starting point, the plates with LPEI layer were taken out by different time and then immersed to a silica source solution (4 mL, ethanol/water/TMOS = 4/2/1 by vol) for 30 min at room temperature. Finally, the plates were washed with ethanol and then dried. The silica-coated plates were subjected to SEM observation.

Preparation of Water Repelling Silica Film. The silica coat prepared on glass plate with LPEI layer (preformed in a LPEI/D-Tart solution, [EI] = 1000 mM, [D-Tart] = 120 mM) was immersed in a solution (10 mL, ethanol/28% NH$_3$(aq) = 50/1 by vol). Then, DTMS dissolved in chloroform (1 mL, 760 mM) was added, and the solution was kept at room temperature for 2 days. The glass plate taken out was washed carefully with ethanol and dried under air conditions. This procedure resulted in n-decyl-modified silica film with water repelling properties.

With the same method, perfluoroalkyl moieties of HFIPPTMS were introduced onto the silica film. For this modification, silica film prepared from LPEI coat preformed in a LPEI/D-Tart solution ([EI] = 1000 mM, [D-Tart] = 125 mM) was used. The glass plate coated with silica film was immersed in a solution (10 mL, ethanol/28% NH$_3$(aq) = 50/1 by vol). Then, HFIPPTMS (ca. 10 mg) dissolved in chloroform (10 mL, 2.87 mM) was added, and the solution was kept at room temperature for 4 days. The glass plate taken out was washed thoroughly with ethanol and dried under air atmosphere.

Synthesis of Eu-1-L1-silica. In this modification, the silica film prepared on LPEI layer preformed in LPEI/D-Tart aqueous solution ([EI] = 1000 mM, [D-Tart] = 100 mM) at 30 °C and calcined at 500 °C was used. The silica film was heated at ca. 180 °C under reduced pressure for 1 h to remove adsorbed water and then immersed in anhydrous toluene solution (50 mL) containing **L1** (20 mg, 0.046 mmol). After the solution was refluxed for 3 h in a N$_2$ atmosphere, the glass plate was taken out and washed thoroughly by methanol and dried under reduced pressure to afford **L1**-modified silica films. The **L1**-modified glass plate was immersed in a dichloromethane solution (20 mL) of **Eu-1** (5 mg, 6 μmol) and allowed to stand overnight at room temperature. After washing the plate with dichloromethane and dried under vacuum for 5 h, the **Eu-1-L1**-silica obtained was used in spectral measurements.
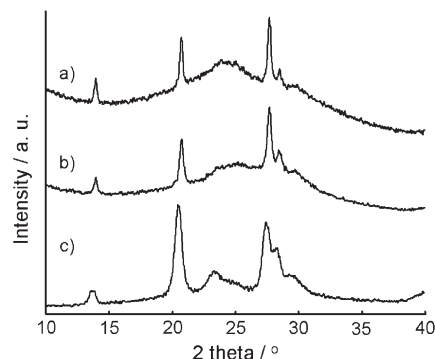

Figure 1. XRD profiles of LPEI layers formed on glass plates. The glass plates were immersed in hot aqueous solutions of LPEI ([EI] = 1000 mM) with (a) Cu(p-TolSO$_3$)$_2$ ([Cu] = 60 mM) or (b) D-Tart (75 mM). (c) LPEI precipitates from aqueous solution of LPEI ([EI] = 1000 mM) with no additives.

Synthesis of Eu-2-silica. The plate with silica film, which was prepared from LPEI layer preformed in LPEI/Tris-HCl aqueous solution ([EI] = 1000 mM, [Tris-HCl] = 350 mM) at 30 °C and calcined at 500 °C, was heated at ca. 180 °C under reduced pressure for 1 h to remove adsorbed water, and then immersed in the solution containing **Eu-2** (11 mg, 0.010 mmol), dichloromethane (1 mL), ethanol (2 mL), and 1% NH$_3$(aq) (0.1 mL) at room temperature for 3 days. The plate taken out was washed carefully with ethanol and dried under vacuum for 5 h.

Characterizations. ^{1}H NMR spectra were recorded on a JEOL NMR spectrometer (300 MHz). Infrared spectroscopy was conducted with a Jasco FT-IR spectrometer FT/IR 4200 using KBr pellets. XRD measurements of LPEI powders were carried out with a Rigaku RX-7 X-ray diffractometer operating Cu Kα radiation (λ = 1.54 Å) at room temperature. TG measurements of LPEI powders were carried out with a Seiko SII TG-DTA 6300 instrument operating at a heating rate of 10 °C min^{-1} in an air flow in the range at 30–800 °C. XRD profiles of film samples on glass plates were recorded on a Rigaku RINT-TTR II diffractometer with Cu Kα radiation (λ = 1.54 Å) at room temperature. Scanning electron microscopy (SEM) observation was performed with a Keyence VE9800 microscope with 8 kV after samples were sputtered-coated with Pt particles. Water-contact angle was measured with a DataPhysics OCA20 optical contact angle meter using 5 μL of water droplet at room temperature. Emission spectra and phosphorescent decay curves were recorded on a Hitachi F4500 fluorescence spectrophotometer at room temperature with a Xe lamp as excitation source. Emission quantum efficiency (η) was calculated according to the literature.[76,78] The equations used for this calculation are shown in the Supporting Information. Emissive properties of silica thin films (**L1**-silica or **Eu-1-L1**-silica) were simply characterized with a handy UV lamp (λ = 375–390 nm). Emission spectroscopy of silica films on glass plates (**Eu-1-L1**-silica or **Eu-2**-silica) was carried out in the front-face detection mode with an incident angle of 45° under an air atmosphere. For **Eu-2**-silica, the sample plate was held in a quartz cell and subjected to emission spectroscopy. The emission spectrum of **Eu-2**-silica under a methanolic atmosphere was recorded after a small volume of methanol was dropped on the bottom of the cell, and the cell was sealed and retained for more than 30 min.

III. RESULTS AND DISCUSSION

Regulation of LPEI Crystalline Aggregates on the Glass Surfaces and Fabrication of Silica Films. We performed the silica film formation on LPEI-coated glass plates via the
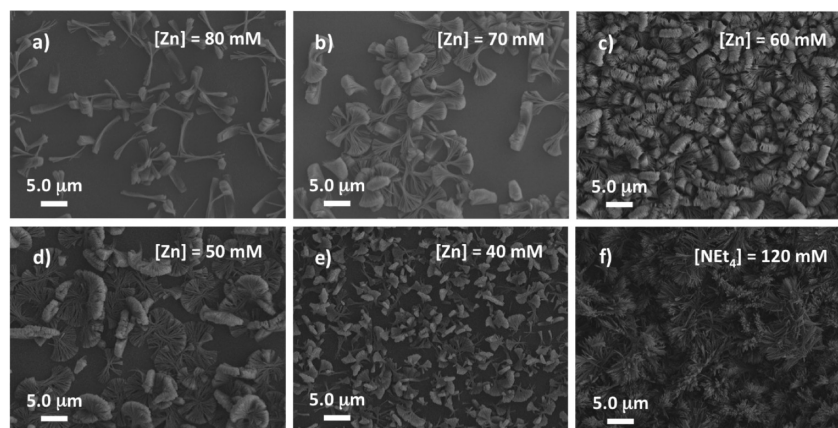
Figure 2. SEM images of the silica/LPEI-coated glass plates. The LPEI coats were prepared from LPEI solution ($[EI]$ = 1000 mM) with $Zn(p\text{-}TolSO_3)_2$ or $NEt_4(p\text{-}TolSO_3)$ and subsequently silicified with MS-51 solutions. Zn(II) concentrations are (a) 80, (b) 70, (c) 60, (d) 50, or (e) 40 mM. (f) $NEt_4(p\text{-}TolSO_3)$ (120 mM) was used as a reference.

procedure shown in Scheme 2 using Cu(II) ions as additives in LPEI solution. A glass plate was immersed in a hot aqueous solution containing LPEI (1000 mM for EI unit) and $Cu(p\text{-}TolSO_3)_2$, (60 mM for Cu(II) ion). When this hot solution was cooled to 30 °C and kept for a few days at the temperature, LPEI precipitates occurred in water phase. At this time, the LPEI crystals grew simultaneously on the glass surface. The glass plate washed with water was covered with pale blue solids, suggesting the presence of LPEI with a subtle amount of Cu(II) ions.[64] Similar covering plates (but color of precipitates is different) were also obtained by the use of other additives. The glass plates covered by LPEI are subjected to XRD measurements for the investigation of the crystalline states of LPEI layers. As a result, the LPEI-coated glass plates, which are formed from hot LPEI aqueous solution containing $Cu(p\text{-}TolSO_3)_2$ or D-Tart, show four diffraction peaks at 2θ of ca. 14.0°, 20.8°, 27.7°, or 28.5° (Figure 1a,b). This diffraction pattern is the same with the usual LPEI precipitates (Figure 1c) which just belong to dihydrate state of LPEI crystals ($[EI]/[H_2O]$ = 1/2).[70,71] This indicates that the layer of LPEI coated on glass surface is composed of dihydrate form of LPEI crystals. Unfortunately, morphology of these LPEI layers cannot be directly characterized by SEM observation because of the structural lability of the hydrated LPEI crystals at vacuum and dried states (Figure S1 in Supporting Information).[67]

We have known that in water LPEI crystallization is easily regulated by metal ions through the formation of coordination bonds between LPEI and metal ions, and the resulting crystalline precipitates readily afforded to the structured silica with well-stacked sheets and turbine-like morphologies when mixed with silica source solution.[63,64] Without any drying processes, we dipped the LPEI-coated glass plates formed in the $LPEI/Zn(p\text{-}TolSO_3)_2$ solution with different concentrations of Zn(II) ion ($[Zn]$ = 40−90 mM) into an aqueous solution containing MS-51 or TMOS for directing silica film via LPEI layer-template procedure. The silica/LPEI films formed on glass surfaces were subjected to SEM observation (Figure 2). In the case of a LPEI solution containing 90 mM of $Zn(p\text{-}TolSO_3)_2$, no precipitation was confirmed either in bulk water phase or on glass plates (data are not shown), indicating that the molar ratio of $[EI]/[Zn]$ = 1000/90 is not suitable for LPEI crystallization. It is conceivable that at the condition of 90 mM of Zn(II) ions a significant

number of EI units were coordinated with Zn(II) ions so that the formation of LPEI crystalline templates was suppressed. Therefore, the usage of less than 90 mM of Zn(II) ions is needed. Actually, precipitation occurred both in water phase and on the surface of the glass plate when the LPEI solution containing 80 mM Zn(II) ions was placed at reduced temperature. By dipping the plate with LPEI layer formed from molar ratio of $[EI]/[Zn]$ = 1000/80 into silica source solution, we successively deposited silica on the surface of glass plate. It can be seen from Figure 2a that well-stacked sheet aggregates are attached on the glass surface but did not form continuous coat. Each sheet in the aggregates features a thickness of less than 100 nm and a length of ca. 5 μm. This morphology is almost same as that of silica which is deposited via mediation of LPEI aggregates pregenerated in water phase (Figure S2 in Supporting Information).

We performed silica film formation by use of an LPEI-coated plate obtained from 70 mM Zn(II) condition and observed that pseudo-turbine-like structures, each edge of which is much branched and radially spread, lied in flat-on modes on the glass surface (Figure 2b). Continuously, we prepared LPEI-coated plate under further reduced Zn(II) concentration (60 mM) and dipped this plate in silica source solution. Interestingly, this processing condition resulted in a specific surface structure where a lot of silica turbines covered continuously the surface of glass plate with vertically standing fashion (Figure 2c). Similar silica structures were also observed in the case of use the other metal ions (Figure S3 in Supporting Information). Although the silica turbines densely covered the glass surface, this plate showed well transparency (Figures S4 and S5 in Supporting Information). It is conclusive that by finely tuning the concentrations of metal ions in LPEI-coating step, we can readily fabricate well-organized nanostructured silica thin film on the glass surface. The plates with silica/LPEI-film slightly colored depending on the kinds of metal ions used, indicating the presence of small amounts of metal ions on the formed film (Figure S5 in Supporting Information). We found that the processing conditions under Zn ions below 60 mM are not suitable for depositing ordered silica film. For example, the processing condition with further decreasing Zn(II) ions to 50 mM allowed to give relatively larger silica turbines which lied sparsely on the surface (Figure 2d). At the condition with 40 mM of Zn(II) ions, the formed turbines became smaller and randomly distributed on the
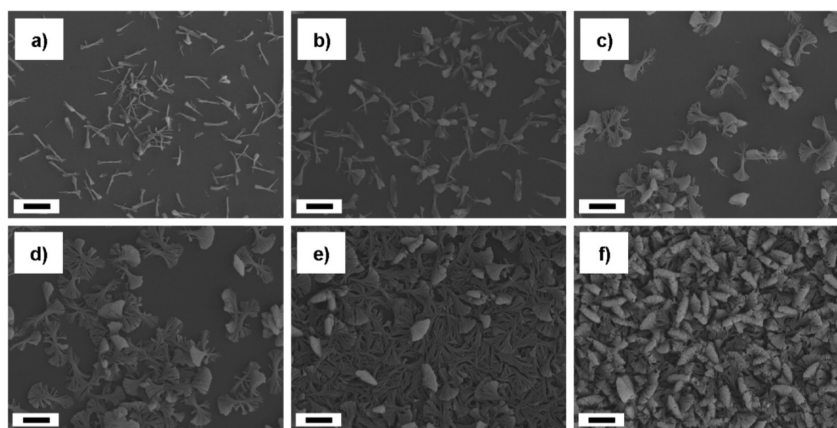
Figure 3. SEM images of the silica layers formed via LPEI layers on the glass plates. The LPEI layers were developed by an immersion of the glass plates in LPEI/Zn(p-TOlSO$_3$)$_2$ solution ([EI] = 1000 mM and [Zn] = 60 mM). Aging periods were (a) 60, (b) 80, (c) 100, (d) 120, (e) 140, or (f) 160 min. Scale bars: 2.0 μm. Each LPEI layer grown by desired times was immersed in the solution of MS-51 to develop silica layers.
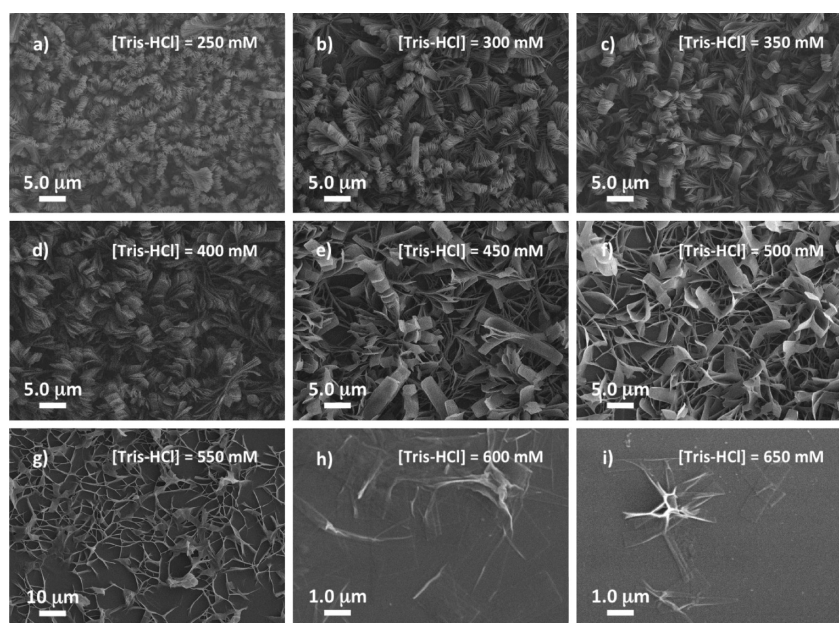

Figure 4. Concentration effects of Tris-HCl on the formation of final silica layers via LPEI crystal growth on the glass surfaces. The LPEI-coated plates were prepared by the dipping of glass plates into LPEI aqueous solutions ([EI] = 1000 mM) with Tris-HCl at different concentrations (250−500 mM) and aging periods (1 or 2 weeks). [Tris-HCl] = (a) 250, (b) 300, (c) 350, (d) 400, (e) 450, (f) 500, (g) 550, (h) 600, or (i) 650 mM. Aging periods: 1 week for (a−f) or 2 weeks for (g−i). The LPEI layers formed on glass surfaces were silicified with MS-51 solutions.

surface (Figure 2e). From the above results, it is obvious that higher concentration of Zn ions prevent the LPEI crystallization while the lower concentration of Zn did not allow to form the ordered LPEI crystalline layer on the substrate. Practically, when the concentration of Zn ions becomes lower, the crystallization of LPEI becomes less inhibited. However, the crystallization of LPEI proceeds dominantly in water phase rather than on the surface of substrate. Therefore, a proper amount of Zn(II) ions is necessary for producing uniformed LPEI layer with surface-specific morphology. Replacing Zn(II) ions with NEt$_4$$^+$, we performed the similar two-step processing for silica deposition. As seen in Figure 2f, the silica formed on the glass surface is randomly bundled fibrous structures, no turbines being observed. This reveals that the induction of the stacked sheet

(turbine) morphologies is related to the formation of coordination bonds between LPEI and Zn(II) ions.

It should be noted that the silica film formed by the ordered turbines standing on the glass surface in edge-on modes is very unique and need further understanding. Therefore, we investigated the effect of the growing time of LPEI crystalline layer on silica formations. As a typical process, glass plates were immersed in LPEI/Zn(p-TolSO$_3$)$_2$ solutions ([EI] = 1000 mM, [Zn] = 60 mM) in a definite period (i.e., pretreatment) and then used for silica formation by putting the LPEI-coated plate into an alkoxysilane solution. Figure 3 exhibits the SEM images of silica formed by use of the plate immersed different time in LPEI/Zn solution. As seen in Figure 3a, on the glass surface, which was pretreated for 60 min in LPEI/Zn solution, smaller silica less than

Scheme 4. Illustration of Crystal Growth of LPEI Regulated by Additives in Water Phase or on the Surface[a]
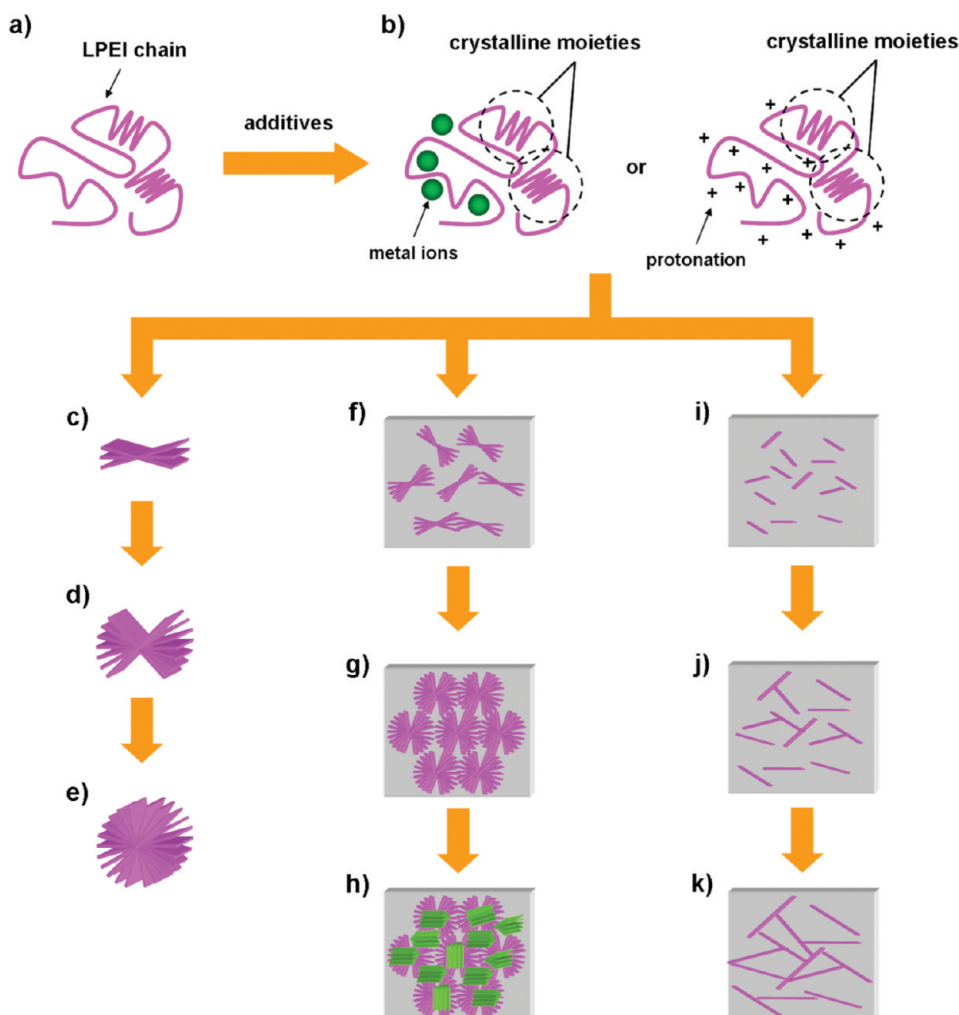
[a] (a) LPEI chain dissolving in hot water. (b) LPEI chains dissolving in water with additives. The LPEI crystallization is inhibited by partial interactions of EI with additives through coordination bonds (left) or protonation of EI (right). (c−e) Stepwise LPEI crystal growth in water. From sheets to turbine-like structures are produced depending on crystallization conditions. (f−k) Stepwise crystallization processes on the surface of substrates. (f−h) Rapid crystallization leads to comparable branched sheets, which results in the surfaces covered with turbine-like structures or vertically growing sheets (grass-like surface). (i−k) Slow crystallization affords large monosheet structures with fewer branches on edge-on modes, which combine each other during further crystal growth periods to form network structures.

100 nm in width with nanosheet-stacked structures were generated. The stacked-nanosheet silica attached on the plate grew larger with branching and spreading their edge when the LPEI-coated plate obtained via longer immersion times in LPEI/Zn solution was used for silica deposition (Figure 3b,c). On the glass plate which was pretreated in LPEI/Zn solution by 120 min, a large number of turbine-like structures were formed in flat-on styles (Figure 3d). On the LPEI-treated glass plate by 140 min, turbine-like silica structures densely covered the glass surface with one layered flat-on form (Figure 3e). Further elongation of the pretreatment time of the plate in LPEI/Zn solution to 160 min allowed to promote the formation of hierarchically structured silica film where the turbines densely covered the surface with vertically standing fashion (Figure 3f). Evidently, the LPEI layer formed via longer time in LPEI/Zn solution is effective to promote the formation of hierarchically structured silica film.

To investigate the effect of organic additives in LPEI solution on the formation of final silica film, we performed the similar experiments with above replacing metal ions by Tris-HCl. Figure 4 shows SEM images of silica deposited on the LPEI-coated glass plates. On the plates treated in LPEI solution with association of different Tris-HCl concentrations (250−500 mM), complexly ordered silica films were generated (Figure 4a−f). In these silica films, nanosheet-like components closely stand to form densely covered hierarchical structures. However, the density of the sheet-covered structures on the plates became lower evidently as the concentrations of Tris-HCl for pretreatment of the plates increased from 250 to 500 mM. The further increase of Tris-HCl to 550 mM for the pretreatment of the plate allowed to generate many compartmented areas by nanosheet networks (Figure 4g). Such morphological structures were not observable in bulk water phase (Figure S6 in Supporting Information).

When D-Tart was used as an additive, the same behavior was observed (see Figure S7 in Supporting Information). Since D-Tart has stronger acidity than Tris-HCl, smaller amounts of
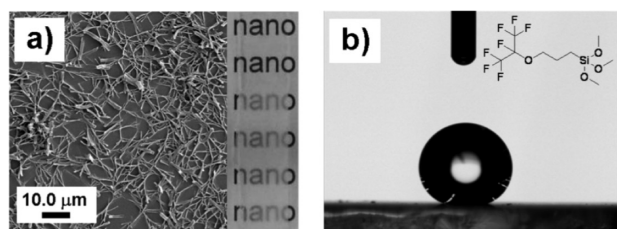
Figure 5. Characterization of hydrophobic silica surfaces. (a) SEM images of silica layers modified with DTMS. Inset: photograph of the silica layers after DTMS reaction. (b) Superhydrophobic properties of silica layers reacted with the PFIPPTMS. The structure of PFIPPTMS is depicted in inset. These silica surfaces were prepared from LPEI layers preliminarily formed from LPEI/D-Tart acid solution ([EI] = 1000 mM, [D-Tart] = 100 mM) after silicification and calcination.

D-Tart can regulate the crystal growth of LPEI on glass surface and promote the formation of specially structured silica films. To precisely characterize the development of sheet-based hierarchical silica structure, stepwise observation was performed. The glass plates pretreated by immersing in LPEI solutions ([EI] = 1000 mM) with association of 120 mM of D-Tart at 30 °C for different times were dipped in silica source solution and the obtained silica was subjected to SEM observation (see Figure S8 in Supporting Information). On the pretreated glass plate by 3 days, silica with short sheet-like structures were afforded, many of which were flatly dispersed through the surface (Figure S8a). This surface structure is similar to those observed at the conditions of 600−650 mM of Tris-HCl (Figure 4h−i). On the plate treated for further longer times in LPEI/D-Tart solution, the quantities of silica sheet deposited on the glass surface increased and trended to form network structures with compartmented area (Figure S8b−d). In this structure, interestingly, many silica sheets were standing in edge-on modes. These results lead us to the conclusion that longer pretreatment terms of glass substrate by LPEI solution associated with additives is essential for producing large nucleus of sheets and developing compartmented areas which covered densely the substrates to form hierarchically structured silica films.

On the basis of the above results, we can draw a plausible mechanism of induction of the silica film with two typical structures of LPEI crystalline layers (Scheme 4). One is as shown in Scheme 4f−h, in which the crystalline LPEI grow up to turbines that cover the substrates by vertical fashion. This structure formation is dependent on the optimized concentrations of the additives, too high or too low concentrations of the additives being out of the structure. The other is as shown in Scheme 4i−k, in which the crystalline LPEI grow up to sheet compartmented areas that cover the substrate. This structure is easily developed in the LPEI solution associated with proton donating additives such as This-HCl and D-tart.

Functionalization of Hierarchically Structured Silica Films. Calcination of the silica films mentioned above at 500 °C for 3 h can remove the organic fractions (LPEI templates and subtle amounts of additives) to give silica alone films. From the TG analysis, it was proved that organic components such as LPEI and additives were fully removed from silica/LPEI composites after calcined at 500 °C.[65] The calcined silica films with high transparency were used in chemical modification for developing their potential applications. We modified silica film with hydrophobic alkoxysilyl compounds or emissive Eu(III) complexes. The silica

sheets-coated glass plate with compartmented network structures (as seen in Figure 5a) was immersed into an ethanolic solution of DTMS and allowed to stand for more than 2 days at room temperature. We confirmed that network-like morphology and transparency still remained after the plate was modified with DTMS for long times. It should be noted that before DTMS treatment the water contact angle on this film was 0°. This is due to the capillary effect of the nanosheet compartment network structure on the plate. However, the DTMS-modified silica film showed a contact angle of ca. 137° for water droplets. On the other hand, when HIPPTMS was used to modify the same surface structures, the water contact angle increased to 179 ± 0.1° (Figure 5b), showing superhydrophobicity. Thus, the silica nanosheet compartmented network structure with transparency on the plate can be the promising candidate for superhydrophobic materials.

For the construction of emissive silica films, we selected tris(1,3-diphenyl-1,3-propanedionato)Eu(III) complex (**Eu-1**) as a fluorophore. This β-diketonato-Eu(III) complex is widely used as highly emissive core in various materials.[72−82] The introduction was performed by the modification of silica with pyridyl-pyrazole ligands bearing triethoxysilyl groups (**L1**), followed by coordination of **Eu-1** with **L1** to afford **Eu-1-L1**-silica (Scheme 3). As seen in Figure 6b, no destruction of silica structures was observed in the **Eu-L1**-modified glass plate. The plate had a good transparency showed a bright red emission under irradiation of a UV lamp (Figure 6a). This strong red emission is typical for Eu(III) ions, originating from the intra f−f transition of lanthanide species.[72−82] The emission spectrum as shown in Figure 6c mainly shows three peaks at 578, 590, and 610 nm, which are assigned to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, or $^5D_0 \rightarrow {}^7F_2$ transitions, respectively. The $^5D_0 \rightarrow {}^7F_3$ transition also appeared at 650 nm with weak intensity while the $^5D_0 \rightarrow {}^7F_4$ transition peak was not observed. The well-defined single $^5D_0 \rightarrow {}^7F_0$ transition indicates the presence of only one coordination site of Eu(III) ions.[75,77] The $^5D_0 \rightarrow {}^7F_1$ transition is induced by the partially allowed magnetic dipole transition and independent of Eu(III) coordination environments.[72−82] The $^5D_0 \rightarrow {}^7F_2$ transition is intensively stronger than others. This transition is an electronic dipole transition and significantly sensitive to Eu(III) coordination environments. This spectrum is quite similar to that of other Eu(III) complexes with a low symmetry,[72−82] suggesting the maintenance of the coordination with three β-diketonato ligands. We confirmed that few Eu(III) ions were loaded onto silica thin films without **L1** modification (data are not shown). Therefore, it is appropriate that **Eu-1** was introduced into silica surfaces via coordination with one **L1** ligand. Phosphorescent lifetime of the Eu(III) complexes incorporated in the silica layers was also characterized (Figure 6d). A single-exponential curve was obtained, and the phosphorescent lifetime (τ) was calculated to be ca. 0.57 ms. This value is typical of the tris(β-diketonate)Eu(III) complexes modified on the silica walls.[76,77,80] The emission quantum efficiency (η) is calculated to be ca. 56%, which is also the same degree as those reported.[75,77]

We expect that the silica nanosheet-coated glass plate with attaching emissive Eu(III) complexes would be useful in sensing chemicals. Therefore, we investigated sensing properties of the plate of **Eu-2** attached/sheet surface by monitoring its emissive changes at 610 nm under air and methanolic atmospheres. The methanol vapors were generated by the dropping methanol in the bottom of cell and sealed the cell (Figure 7a). As shown in Figure 7b, the emission intensity of **Eu-2** attached plate in an air condition decreased dramatically as the plate was exposed in methanol vapors. As the plate was re-exposed to air, the emission
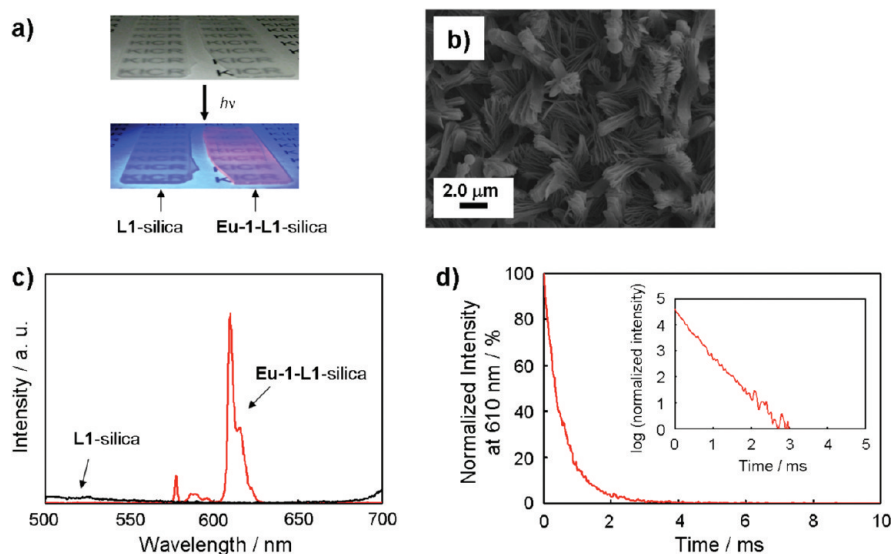
Figure 6. (a) Photographs of **L1**-silica (left) or **Eu-1-L1**-silica on glass plates (right) without irradiation (upper) or with irradiation (bottom) by a UV lamp (λ = 375−390 nm). (b) The SEM image of hierarchical surfaces of **Eu-1-L1**-silica. (c) Emission spectra of silica films on glass plates. Red line: **Eu-1-L1**-silica. Black line: **L1**-silica (without Eu(III)). λ_{ex} = 360 nm. (d) Phosphorescent decay curve at 610 nm of **Eu-1-L1**-silica films. λ_{ex} = 360 nm. Inset: ln(normalized intensity) vs time plots.
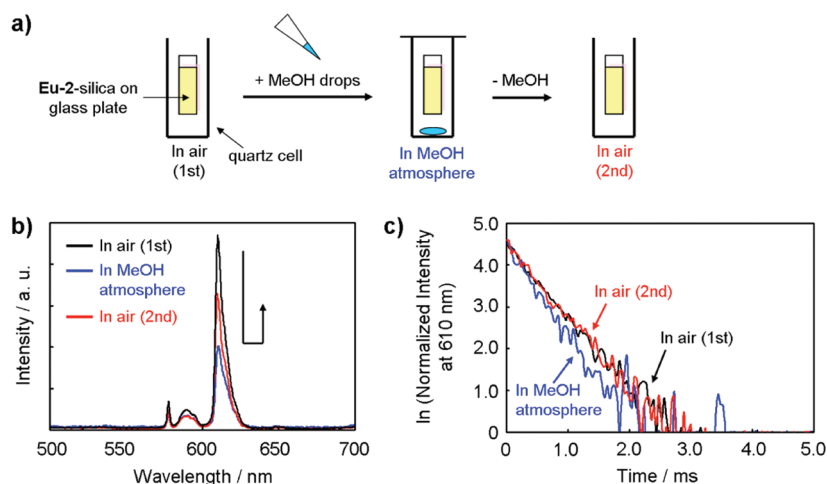

Figure 7. (a) Schematic illustration of methanol sensing experiments with **Eu-2**-silica formed on the glass plate. (b) Emission spectra and (c) phosphorescent decay curves at 610 nm of **Eu-2**-silica in the first, second air or methanol vapor conditions. Black: in an air atmosphere (first, before exposure to methanol vapor). Blue: in a methanol atmosphere. Red: in an air atmosphere (second, re-exposure to air). λ_{ex} = 360 nm.

intensity trended to return to original state. This methanol vapor-induced quenching should be attributed to the coordination interactions of hydroxyl group in methanol with Eu(III) ion; such hydroxyl-based interactions hinder strongly the f−f transition of Eu(III) ions, and thus the emission is weakened.[72,76,83] We also found that τ of **Eu-2** attached film was changed from ca. 0.59 to ca. 0.46 ms after methanol vapor was purged in the cell and returned when exposed again in air (Figure 7c). This result revealed that the Eu(III)-modified nanosurface silica film is capable of sensing methanol vapor in the atmosphere.

IV. CONCLUSIONS

In this paper, we investigated the developments of controllable silica coats with hierarchically structured fashion on glass plates.

These structures can be produced simply via sol−gel reaction of alkoxysilane on the LPEI crystalline layers which were generated by immersing glass substrate into the aqueous solutions of LPEI associated with additives such as metal ions and proton donating compounds. The additives that can interact with LPEI by coordination and protonation play quite important roles in the morphological evolution of LPEI crystalline layers on the surface of glass substrate. A plausible mechanism of LPEI crystalline layers on substrate is summarized in Scheme 4. A large excess of additives cannot afford precipitation of LPEI on the substrate so that silica deposition is not available. When the concentrations of additives are adjusted to proper values to keep the molar ratio balance between ethylenimine (EI) unit and the additives, the free EI units that not interacted with the additives aggregate each other to form precipitates of LPEI from which the formations of

crystalline layers are promoted. By association of LPEI with additives, we can prepare various hierarchical LPEI crystalline structures not only in bulk water phase but also on the surface of substrate. Once the hierarchical LPEI crystalline layers formed on the substrate, the silica thin film with hierarchical structures could be systematically constructed. Especially, association with small amounts of additives leads to grass-like silica structure on glass plates while association with large amounts of additives leads to unique surface composed of turbine-like structures flatly lying on the surface. Moreover, controlled conditions of growing LPEI layers on substrate such as molar ratios of LPEI to additives, solution temperature, and immersing time of substrates in LPEI solution allow to produce compartmented network structures consisting of silica nanosheets with well-transparency on the surfaces of substrate. Modifying the hierarchically structured silica thin films, we succeeded in preparing superhydrophobic or emissive nanosurfaces. Potential applications of these films as functional materials are now under way.

■ ASSOCIATED CONTENT

S **Supporting Information.** Description of the material. This material is available free of charge via the Internet at http://pubs.acs.org.

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