

*Electronic Supplementary Information for*

**Nanostructured organosilicas constructed by homopolycondensation of a transesterified bulky precursor and their potential in laser desorption/ionization**

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## 1. Experimental section

### 1.1 Materials and methods

All reagents and solvents were purchased from Aldrich, Wako, Gelest, and Tokyo Chemical Industry and used without further purification. Surfactant **1** was synthesized according to the literature.<sup>1</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured using a JEOL JNM-ECX400P spectrometer.  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker Avance 400 spectrometer using 7-mm zirconia rotors. For solid-state  $^{29}\text{Si}$  MAS NMR measurements, single 4.5- $\mu\text{s}$   $\pi/2$  pulses were applied with proton decoupling during detection, 80-s recycle delays, and 900 scans in order to ensure complete relaxation of  $^{29}\text{Si}$  magnetization for all silicate species between each signal acquisition. The sample spinning frequency was set to 4 kHz. The chemical shifts for all spectra were referenced to tetramethylsilane at 0 ppm. Infrared measurements were conducted with a Thermo Nicolet Avatar 360 FT-IR spectrometer using an attenuated total reflection (ATR) attachment. Scanning electron microscopy (SEM) observations were conducted on a Hitachi SU3500 with an accelerating voltage of 15 kV. Scanning transmission electron microscopy (STEM) observations were conducted on a Hitachi S-5500 with an accelerating voltage of 30 kV. Transmission electron microscopy (TEM) observations were conducted on a JEOL JEM-2100F with an accelerating voltage of 200 kV. Measurements of nitrogen adsorption–desorption isotherms were conducted on a Quantachrome Autosorb-1 sorptometer at  $-196\text{ }^\circ\text{C}$ . All samples were outgassed at  $100\text{ }^\circ\text{C}$  for 2 h before measurements. Brunauer–Emmett–Teller (BET) surface areas were calculated from the linear section of the BET plot ( $P/P_0 = 0.05\text{--}0.2$ ). Pore size distributions were determined by the density functional theory (DFT) method (DFT kernel:  $\text{N}_2$  at 77 K on silica, cylindrical pore, NLDFT adsorption branch model). Pore volumes attributable to surfactant-templated mesopores were estimated by the  $t$ -plot method ( $P/P_0 = 0.6\text{--}0.8$ ). UV-vis absorption spectra were measured using a JASCO V-670 spectrometer. Powder samples were dispersed in  $\text{BaSO}_4$  and their absorption spectra were measured by a diffusion reflectance method. Fluorescence spectra were obtained with a JASCO FP-6500 spectrometer. Fluorescence quantum yields (within an error margin of  $\pm 3\%$ ) were determined using a photoluminescence quantum yield measurement system equipped with a calibrated integrating sphere (Hamamatsu Photonics, C9920-02). LDI time-of-flight (TOF) mass spectra were recorded on a Bruker Daltonics autoflex maX mass spectrometer (laser wavelength: 355 nm).

## 1.2 Synthesis of NI derivatives

### Synthesis of ethylene bis(1,8-naphthalimide) (NI-d)

A mixture of 1,8-naphthalic anhydride (7.93 g, 40.0 mmol), ethylenediamine (1.20 g, 20.0 mmol), and pyridine (80 mL) was stirred at 110 °C for 72 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into water (150 mL) and the resulting precipitate was collected by suction filtration. The residual material was dispersed in ethanol (60 mL) and stirred at 60 °C for 10 min. The solid material was collected by suction filtration, washed with ethanol, and dried under reduced pressure to produce a pale yellow solid of 82% yield (6.87 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): 4.68 (s, 4H), 7.68 (dd, *J* = 7.2, 8.3 Hz, 4H), 8.17 (d, *J* = 8.3 Hz, 4H), 8.45 (d, *J* = 7.2 Hz, 4H).

### Synthesis of ethylene bis{2,7-bis[2-(triisopropoxysilyl)ethyl]-1,8-naphthalimide} (NI-d-Si(IP))

A mixture of NI-d (2.52 g, 6.00 mmol), RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> (331 mg, 0.36 mmol), triisopropoxyvinylsilane (11.62 g, 50.0 mmol), and mesitylene (70 mL) was stirred at 160 °C for 8 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was purified using silica gel column chromatography (eluent: chloroform/hexane (1/1, v/v), then chloroform/ethanol (10/1, v/v)). The corresponding fractions with a purple color were collected and the solvents were removed using a rotary evaporator. The crude material was dissolved in chloroform (200 mL) and a commercially available scavenger SiliCycle SiliaMetS<sup>®</sup> DMT (20 g) was added to the solution. The mixture was stirred at room temperature for 72 h. After the removal of the scavenger by suction filtration, the solvents were removed from the filtrate using a rotary evaporator. The residue was recrystallized from cold acetonitrile to produce a white solid of 95% yield (7.71 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): 0.89 (m, 8H), 1.11 (d, *J* = 6.0 Hz, 72H), 3.24 (m, 8H), 4.13 (m, 12H), 4.62 (s, 4H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.94 (d, *J* = 8.2 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ in ppm): 13.3, 25.5, 29.9, 39.8, 64.8, 118.5, 129.2, 130.3, 130.5, 133.0, 153.1, 164.1. IR (ATR):  $\nu$  = 750, 768, 870, 957, 1028, 1117, 1173, 1335, 1367, 1379, 1448, 1556, 1655, 1689, 2891, 2933, 2970 cm<sup>-1</sup>. MS (MALDI) *m/z*: [M-H]<sup>+</sup> calcd for C<sub>70</sub>H<sub>112</sub>N<sub>2</sub>O<sub>16</sub>Si<sub>4</sub>, 1347.70; found 1347.70 (Unexpected [M-H]<sup>+</sup> species was detected as a main parent peak for this compound).<sup>2</sup>

## 1.3 Synthesis of organosilicas

### Transesterification of NI-d-Si(IP)

In a typical procedure, NI-d-Si(IP) (0.10 g) and *p*-TsOH·H<sub>2</sub>O (2.0 mg) were added to 1.0 mL of alcohols, ME or MEE. The mixture in a sealed vessel was heated on a hot plate at 130 °C for 30–300 min, resulting in homogeneous solutions of NI-d-Si(ME) or

NI-d-Si(MEE). After cooling to room temperature, the alcohol solutions were used as organosilane sources.

### **Synthesis of nanospheres**

The synthesis of organosilica nanoparticles was carried out by adding an MEE solution of NI-d-Si(MEE) prepared by the transesterification treatment (reaction time: 5 h) to an aqueous solution containing acid or base catalysts. As a typical procedure, the naphthalimide-silica nanospheres were prepared as follows. An MEE solution of NI-d-Si(MEE) (3.0 mL) prepared by the transesterification of NI-d-Si(IP) (0.3 g) was added to a 0.3-wt% aqueous solution of triethanolamine (300 mL) and stirred at 70 °C for 18 h, and then at 100 °C for 1 h, resulting in a homogeneous dispersion. The naphthalimide-silica nanospheres were collected by centrifugation (3200 rpm, 1 h) and washed with ethanol using centrifugation (3200 rpm, 1 h × 3). The nanospheres were obtained as a 2.0-wt% dispersion in ethanol (9.0 g).

### **Synthesis of microparticles with a wrinkled surface**

An ME solution of NI-d-Si(ME) (1.0 mL) prepared by transesterification (reaction time: 30 min) of NI-d-Si(IP) (0.1 g) was added to water (10 mL) under stirring. The resulting dispersion was aged at room temperature for 24 h. A white precipitate consisting of naphthalimide-silica microparticles with a wrinkled surface was collected by suction filtration and dried under a reduced pressure.

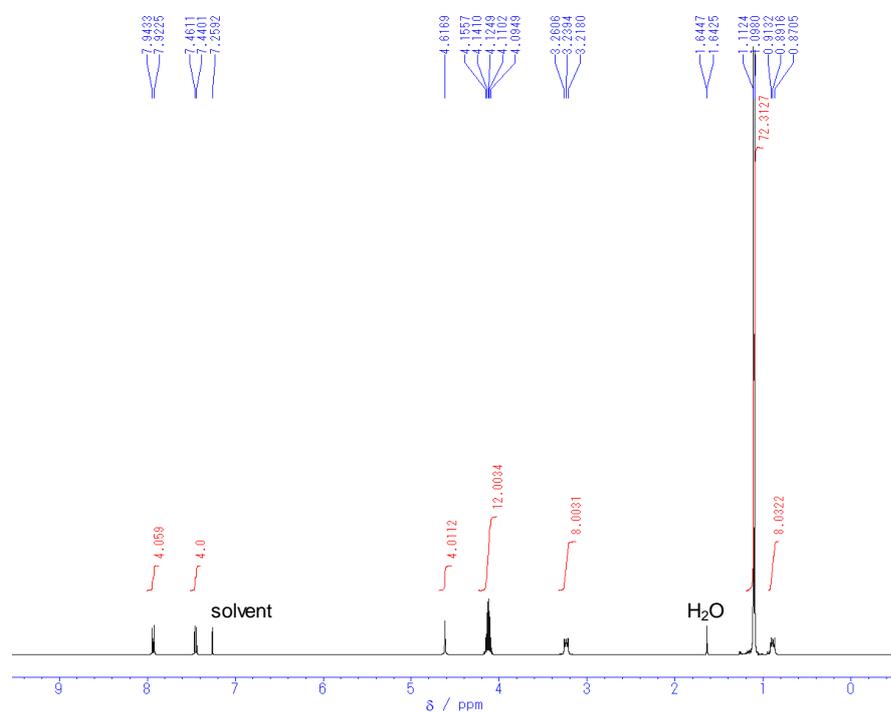
### **Synthesis of PMOs**

The PMOs were prepared by hydrolysis and condensation of NI-d-Si(MEE) in an aqueous solution of a surfactant. The reaction mixtures were stirred at room temperature for 24 h, and then heated at 95 °C for 24 h. The resultant as-prepared organosilicas containing surfactants were washed with a mixture of ethanol and HCl aq. and dried to produce the PMO materials. As a typical example, the synthetic procedure of PMO-B1 is described. An MEE solution of NI-d-Si(MEE) prepared by transesterification (reaction time: 30 min) of NI-d-Si(IP) (0.3 g) with MEE (1.5 mL) and *p*-toluenesulfonic acid monohydrate (3.0 mg) was added to a mixture of **1** (0.8 g) and water (12 mL). After adding a 6.0-M NaOH aq. (0.5 mL), the reaction mixture was stirred at room temperature for 24 h and then heated at 95 °C for 24 h. The resultant material containing **1** was collected by suction filtration and dried. The as-prepared organosilica was dispersed in a mixture of ethanol and 35% HCl aq. (200/1 (v/v), 20 mL) and heated at 60 °C for 12 h to extract the template surfactant **1**. The solid material was collected by suction filtration, washed with ethanol, and dried under reduced pressure to produce an NI-PMO (PMO-B1).

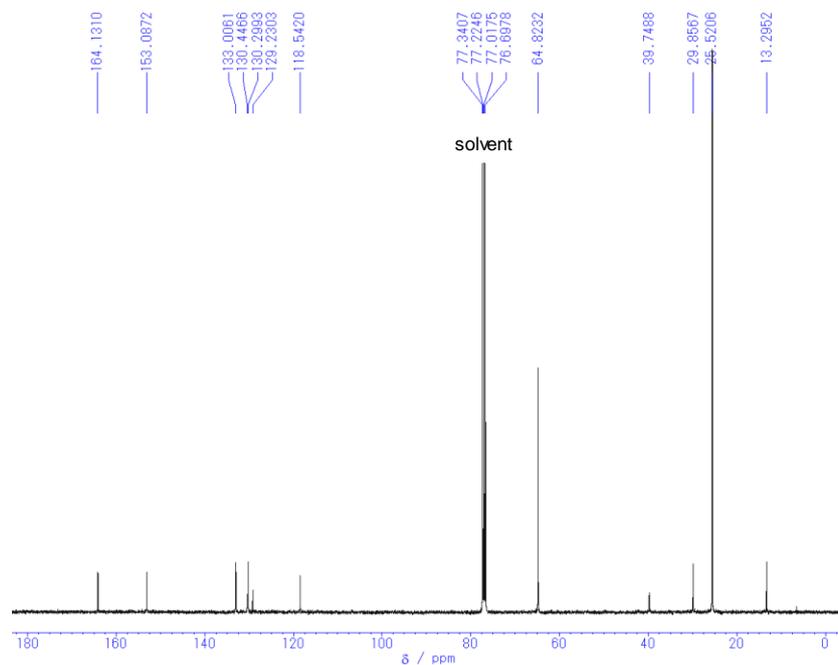
#### 1.4 LDI-MS measurements

The NI-silica particles were treated with trimethylethoxysilane to cap the residual surface silanols with a TMS group. For NI-silica spheres, trimethylethoxysilane (0.5 mL) was added to dispersions of the NI-silica spheres in ethanol (5 mL, for microspheres) or toluene (5 mL, for nanospheres) and the mixture was stirred at 80 °C for 6 h. After removal of the solvent and trimethylethoxysilane under reduced pressure, the residual particles were dispersed in acetonitrile at a concentration of 20 mg mL<sup>-1</sup>. For wrinkled microparticles and PMOs, the powders were exposed to a vapor of trimethylethoxysilane in a sealed vessel at 100 °C for 3 h. The TMS-capped powders were dried under reduced pressure and then dispersed in acetonitrile at a concentration of 20 mg mL<sup>-1</sup>. The dispersions of the nanostructured NI-silica materials in acetonitrile (25 μL) were mixed with an aqueous solution of angiotensin I (10 μM, 25 μL) containing 0.1-vol% CF<sub>3</sub>COOH. The mixtures were drop-cast on a silicon wafer and dried moderately at room temperature. The LDI-MS measurements were operated in a reflector mode. All the spectra were measured in a positive ion mode. In a standard measurement condition, 50 laser shots were summed at each location to yield one spectrum, and five spectra from different locations of each sample spot were averaged.

## 2. NMR spectra of NI-d-Si(IP)



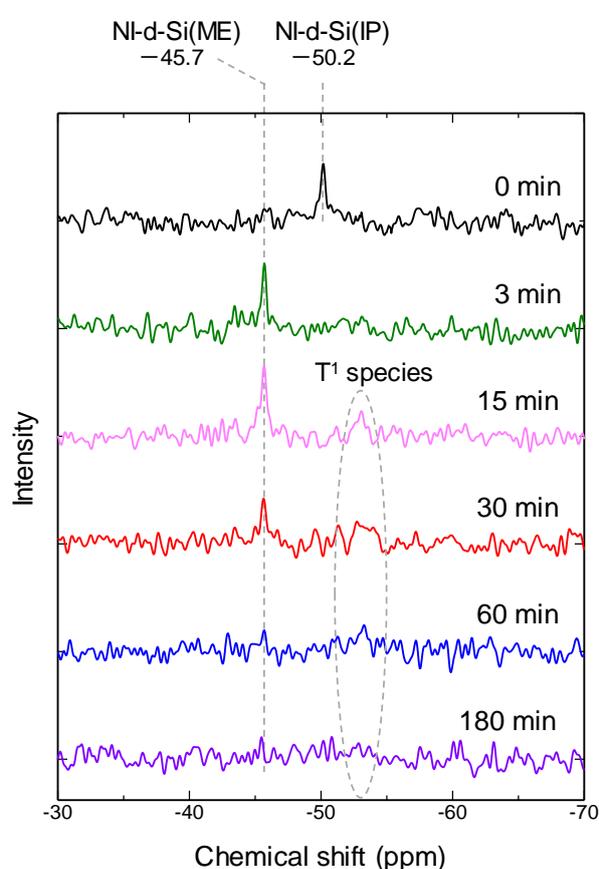
**Fig. S1** <sup>1</sup>H NMR spectrum of NI-d-Si(IP) (in CDCl<sub>3</sub>).



**Fig. S2** <sup>13</sup>C NMR spectrum of NI-d-Si(IP) (in CDCl<sub>3</sub>).

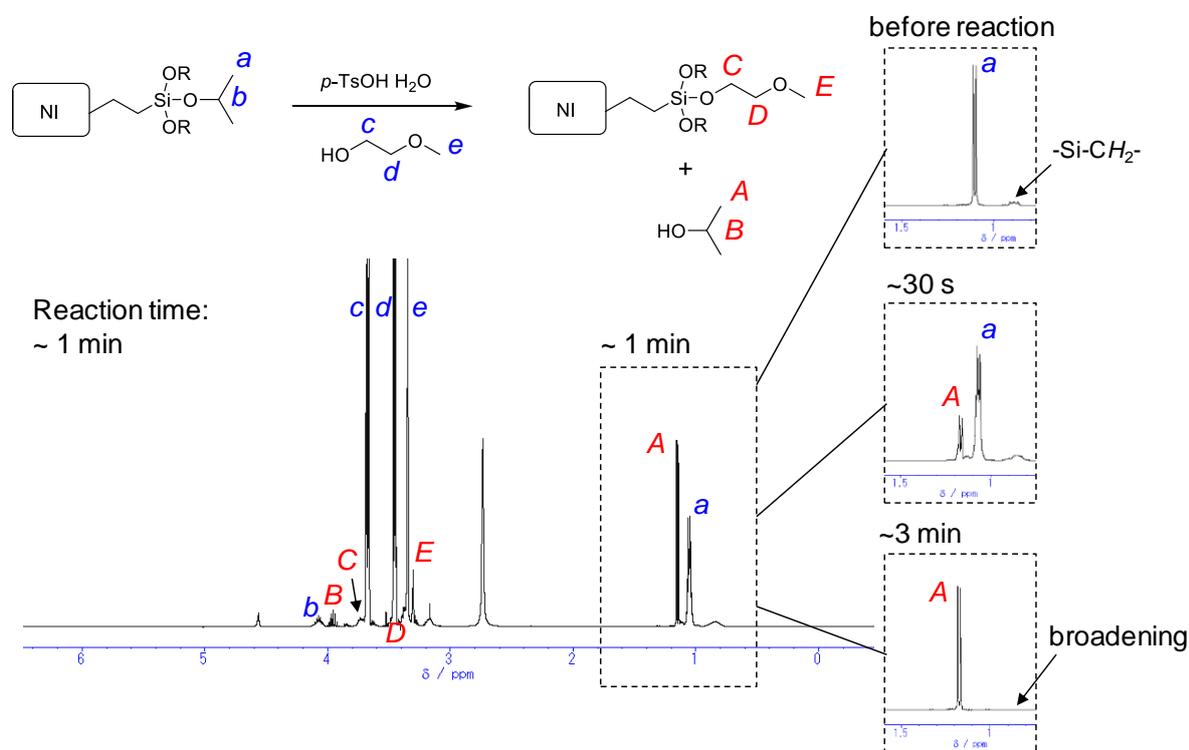
### 3. Observation of transesterification reaction using $^{29}\text{Si}$ and $^1\text{H}$ NMR measurements

Fig. S3 shows  $^{29}\text{Si}$  NMR spectra of the transesterification reaction mixtures of NI-d-Si(IP) in ME at a reaction time of 0–180 min. The original signal at  $-50.2$  ppm attributed to triisopropoxysilyl groups of NI-d-Si(IP) disappeared in 3 min and a new signal corresponding to NI-d-Si(ME) appeared at  $-45.7$  ppm. The new signal was observed for reaction times of 3–30 min. However, the signal was weakened and broad signal attributed to  $\text{T}^1$  species appeared for elongated reaction times. This indicates that hydrolysis and polycondensation of the precursor gradually proceeded in the ME solution, probably due to a trace amount of water included in the catalyst, solvents, and atmosphere.



**Fig. S3**  $^{29}\text{Si}$  NMR spectra of the transesterification reaction mixtures of NI-d-Si(IP) in ME at a reaction time of 0–180 min.

The transesterification reaction was also examined using  $^1\text{H}$  NMR measurements. A part of the reaction mixtures based on ME were collected at different reaction times and dissolved (diluted) in deuterated chloroform to follow the reaction states and components. Fig. S4 shows an example of  $^1\text{H}$  NMR spectrum of the reaction mixture (reaction time:  $\sim 1$  min). The  $^1\text{H}$  NMR analysis revealed that elimination of isopropanol from the  $\text{Si}(\text{O}^i\text{Pr})$  group occurred rapidly and efficiently in the reaction mixture (signals *a* and *A*). The introduction of ME into silyl group was also confirmed by an appearance of new NMR signals (signals *C–E*). The ratio of the integral value of the signal *A* (eliminated isopropanol) to that of signal *E* (introduced ME group) in Fig. S4 is 6H/2.8H. This means that the molar ratio is 3.0/2.8, and more than 90% of the reacted  $\text{Si}(\text{O}^i\text{Pr})$  sites were replaced with ME at this stage, but not 100%. After 3 min, the  $\text{Si}(\text{O}^i\text{Pr})$  structure (signal *a*) disappeared, but the signals derived from the NI precursor showed remarkable broadening. This indicates that oligomerization of the precursor by partial hydrolysis and condensation gradually occurs in the reaction mixtures, although the condensation reaction may be accelerated by mixing with chloroform. These results are consistent with those of  $^{29}\text{Si}$  NMR measurements (Fig. S3). From these observations, the NI derivatives after the transesterification treatments are not pure compounds but probably mixtures of transesterified and partially hydrolyzed species.



**Fig. S4**  $^1\text{H}$  NMR spectrum of a reaction mixture for transesterification from NI-d-Si(IP) to NI-d-Si(ME) (reaction time:  $\sim 1$  min; diluted with  $\text{CDCl}_3$ ) and tracking of the conversion of the  $\text{Si}(\text{O}^i\text{Pr})$  group.

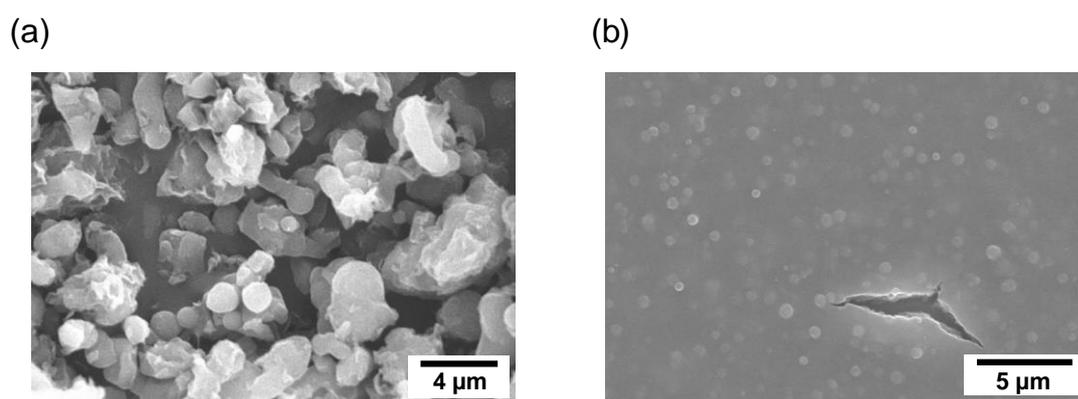
#### 4. Syntheses of NI-silica particles from NI-d-Si(MEE) in various conditions

Table S1 lists synthetic conditions of NI-silicas from NI-d-Si(MEE) and the results. Fig. S5 shows SEM images of samples A3 and B1.

Table S1. Synthetic conditions of NI-silicas from NI-d-Si(MEE)<sup>a</sup>

Sample	Solvent	Catalyst	Reaction condition	Result
A1	H <sub>2</sub> O (50 mL)	2 M HCl aq. (1 mL)	25 °C (24 h)	Figure 3a
A2	EtOH (50 mL)	2 M HCl aq. (1 mL)	25 °C (24 h), 70 °C (24 h)	Deposition of films
A3	H <sub>2</sub> O (50 mL)	—	25 °C (24 h)	Figure S5a
B1	H <sub>2</sub> O (10 mL)	28% NH <sub>3</sub> aq. (1 mL)	25 °C (24 h)	Figure S5b
B2	H <sub>2</sub> O (50 mL)	28% NH <sub>3</sub> aq. (5 mL)	70 °C (7 h)	Similar to B1
B3	H <sub>2</sub> O (17 mL)	28% NH <sub>3</sub> aq. (1.7 mL)	70 °C (2 h)	Figure 3b
B4	H <sub>2</sub> O (50 mL)	6 M NaOH aq. (0.5 mL)	70 °C (2 h)	Similar to B3
B5	H <sub>2</sub> O (10 mL), EtOH (40 mL)	28% NH <sub>3</sub> aq. (5 mL)	70 °C (2 h)	Similar to B3
B6	H <sub>2</sub> O (50 mL)	Triethanolamine (0.15 g)	70 °C (2 h)	EtOH-soluble particles
B7	H <sub>2</sub> O (50 mL)	Triethanolamine (0.15 g)	70 °C (18 h), 100 °C (0.5 h)	Figure 3c
B8	H <sub>2</sub> O (100 mL)	Triethanolamine (0.30 g)	70 °C (18 h), 100 °C (0.5 h)	Figure 3d

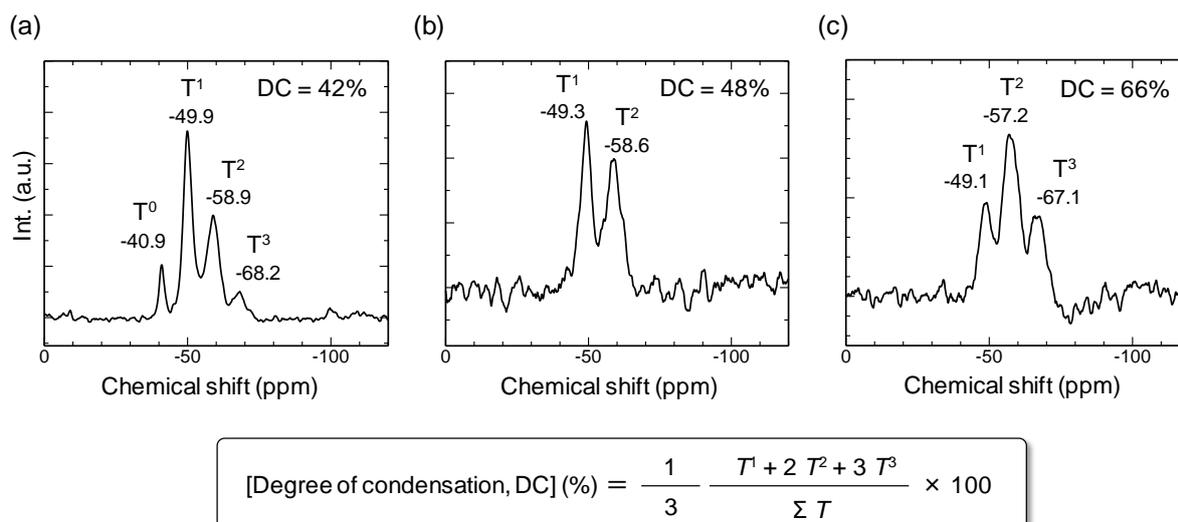
<sup>a</sup> A solution prepared using NI-d-Si (0.1 g), MEE (1.0 mL), and *p*-TsOH·H<sub>2</sub>O (2 mg) was used as an organosilane source.



**Fig. S5** SEM images of NI-silicas obtained by the polycondensation of NI-d-Si(MEE) in aqueous mixtures using (a) *p*-TsOH (trace, A3 in Table S1) and (b) 2.8 wt% NH<sub>3</sub> aq. (B1 in Table S1) as a catalyst.

## 5. $^{29}\text{Si}$ MAS NMR spectra

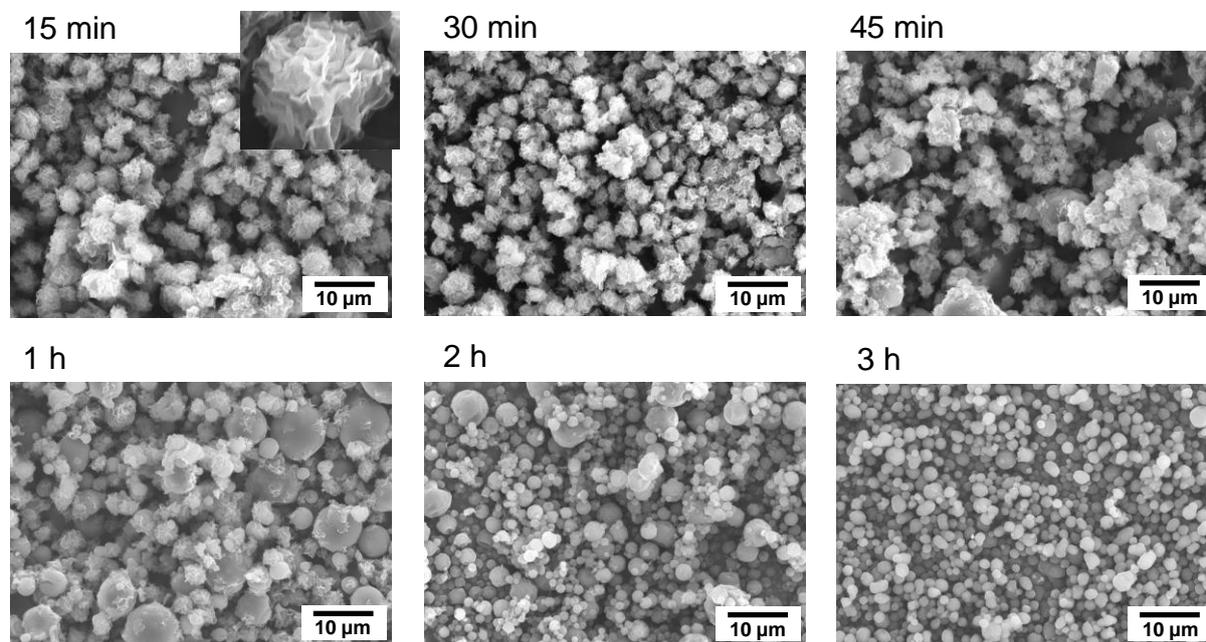
Fig. S6 shows  $^{29}\text{Si}$  MAS NMR spectra of the nanostructured NI-silica hybrid particles. These spectra indicate that crosslinking reaction of organosilica framework sufficiently proceeded in each organosilica particle.



**Fig. S6**  $^{29}\text{Si}$  MAS NMR spectra of (a) NI-silica nanosphere, (b) NI-silica particle with a wrinkled surface, and (c) PMO-B1, and calculation of the degree of condensation (DC) ( $T^n$  indicates the peak area of the signal  $T^n$ ).

## 6. Yield of NI-silica microparticles with a wrinkled surface

The yield of the NI-silica microparticles with a wrinkled surface was found to depend on the reaction times of the transesterification for the precursor.  $^{29}\text{Si}$  NMR measurements for NI-d-Si(ME) indicate that hydrolysis and polycondensation of the precursor gradually progress in the ME solution when the transesterification treatment is continued for more than 1 h (Fig. S3). This is probably due to a trace amount of water included in the catalyst, solvents, and atmosphere. Fig. S7 shows the supplementary SEM images of the microparticles obtained using the precursors with different transesterification reaction times. The aqueous dispersion of NI-d-Si(ME) prepared by the transesterification treatment for 30 min or less gave only microparticles with a surface wrinkle structure. For transesterification time of 1 h, both nanostructured particles and spherical particles were generated from the dispersion. For transesterification times of more than 2 h, spherical particles with no surface nanostructure were produced. These results indicate that the precursor subjected to hydrolysis and polycondensation exhibits the fast growth and crosslinking reaction of the organosilica framework in water, whereby fine particles having a near spherical shape are formed. In contrast, when non-hydrolyzed monomeric NI-d-Si(ME) is mixed with water, it is thought that the precursor reacts slowly in the turbid aqueous dispersion to yield the wrinkled particles.



**Fig. S7** SEM images of NI-silica hybrid materials obtained from aqueous dispersions of NI-d-Si(ME) with different transesterification reaction times.

## 7. Trial for PMO synthesis

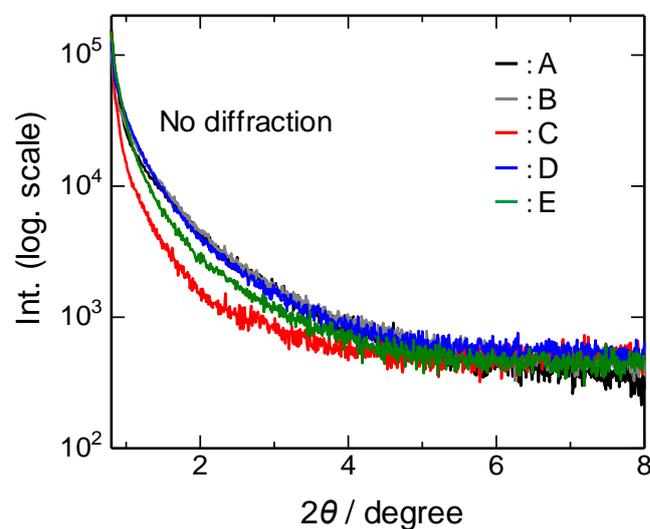
Synthesis of PMO from NI-d-Si(IP) or NI-d-Si(ME) was attempted using reaction conditions shown in Table S2. However, none of the resulting NI-silica particles had periodic mesostructures (Fig. S8).

Table S2. Synthetic conditions<sup>a,b</sup> of samples A–E

Sample	Precursor	Template	Catalyst
A	NI-d-Si(IP)	<b>2</b> (0.5 g)	HCl (0.84 M)
B	NI-d-Si(IP)	<b>3</b> (0.5 g)	HCl (0.84 M)
C	NI-d-Si(IP)	<b>2</b> (0.3 g)	NaOH (0.19 M)
D	NI-d-Si(ME)	<b>2</b> (0.3 g)	NaOH (0.21 M)
E	NI-d-Si(ME)	<b>1</b> (0.8 g)	NaOH (0.21 M)

<sup>a</sup> The precursors were prepared by transesterification of NI-d-Si(IP) (0.3 g).

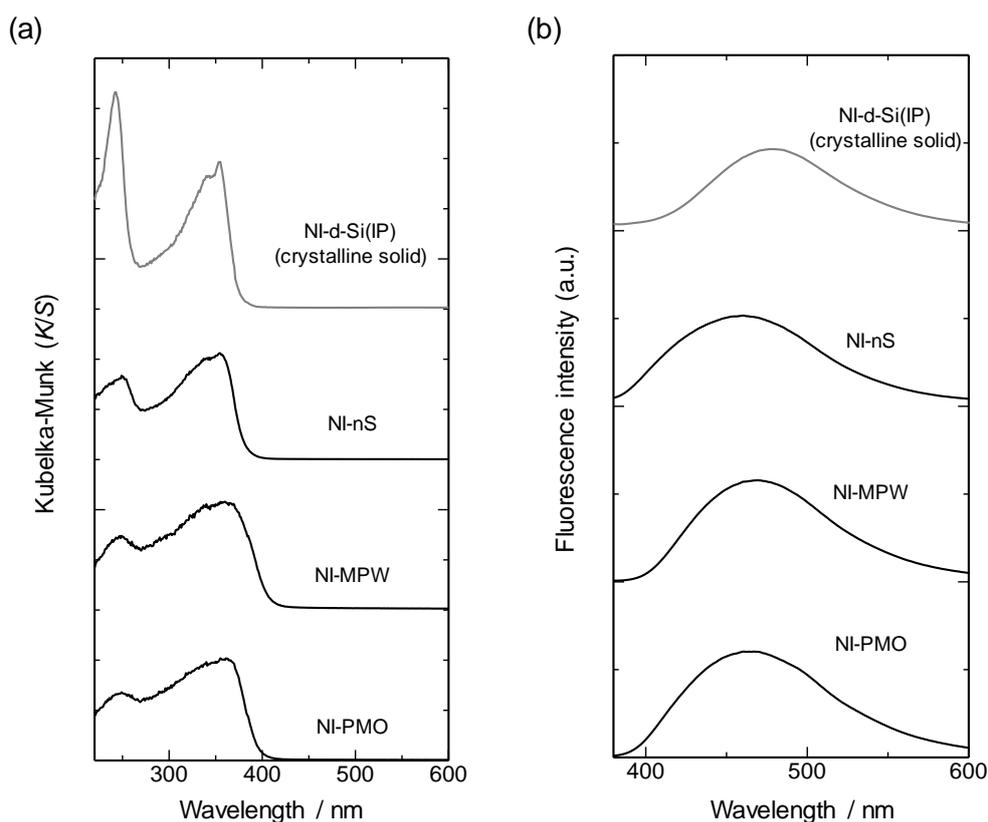
<sup>b</sup> The reaction mixtures (13-15 mL) were stirred at 25 °C for 24 h, followed by heating at 95 °C.



**Fig. S8** XRD patterns of NI-silicas obtained under synthetic conditions of Table S2.

## 8. Optical properties of nanostructured NI-silica particles

Fig. S9 shows UV-vis absorption and fluorescence emission spectra of the NI-silica particles. The absorption maximum wavelength ( $\lambda_{\text{abs}}$ ), fluorescence emission wavelength ( $\lambda_{\text{em}}$ ) and fluorescence quantum yield upon excitation at  $\lambda = 340$  nm ( $\Phi_{340}$ ) are listed in Table S3. The nanostructured NI-silica particles exhibit similar optical properties, because all the particles consist of an amorphous NI-silica framework (NI- $\mu$ S and NI-nS exhibited almost the same optical properties). Slight differences in the optical properties are probably due to those in DCs and the reaction conditions. For example, the UV-vis absorption spectrum of NI-MPW is slightly broader than those of NI-nS and NI-PMO. Also, the  $\lambda_{\text{em}}$  is a little longer and the  $\Phi_{340}$  is a little higher. This may reflect the difference in the reaction conditions that NI-nS, NI- $\mu$ S and NI-PMO are synthesized under heating conditions, while NI-MPW is obtained at room temperature.



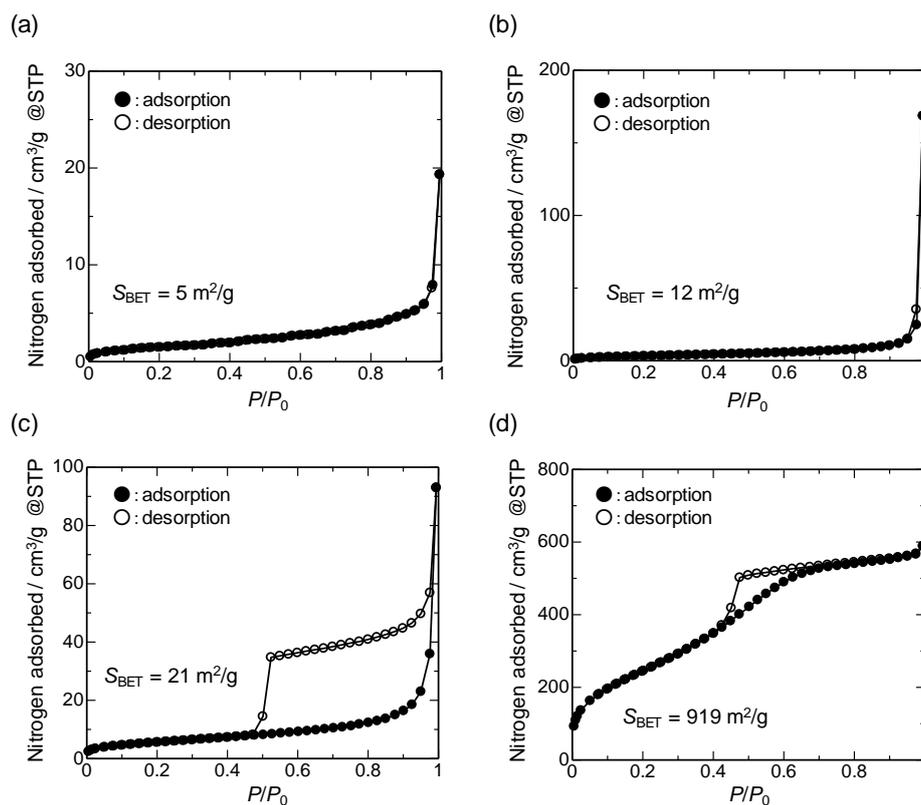
**Fig. S9** (a) UV-vis absorption and (b) fluorescence emission spectra (excited at  $\lambda = 340$  nm) of NI-d-Si(IP) (crystalline solid), NI-nS, NI-MPW and NI-PMO.

Table S3. Optical properties of Ni-d-Si(IP) and Ni-silica particles

Sample	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\Phi_{340}$
Ni-d-Si(IP) (solution in CH <sub>2</sub> Cl <sub>2</sub> )	246, 353	391	0.003
Ni-d-Si(IP) (crystalline solid)	242, 354	478	0.029
Ni- $\mu$ S	355	460	0.019
Ni-nS	355	460	0.019
Ni-MPW	360	469	0.040
Ni-PMO	361	464	0.028

## 9. Nitrogen adsorption–desorption isotherms

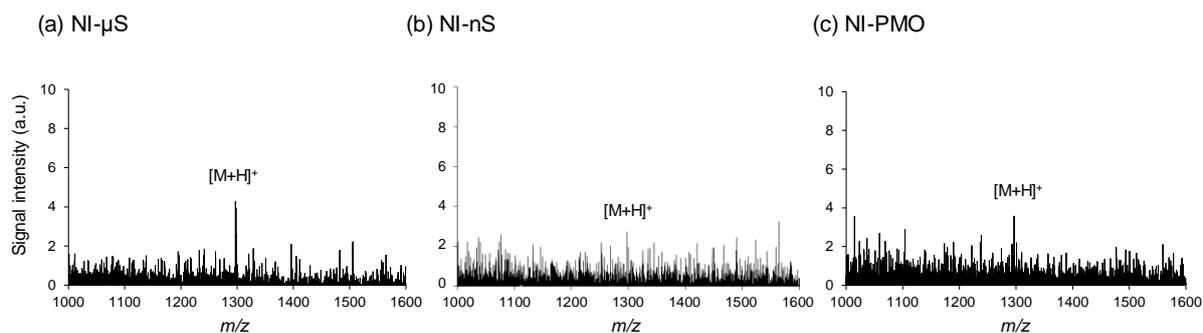
Fig. S10 shows nitrogen adsorption–desorption isotherms of TMS-modified NI-silica particles used for LDI-MS measurements. NI- $\mu$ S, NI-nS, and NI-MPW exhibited sharp increases in the amounts of nitrogen adsorbed at  $P/P_0 > 0.9$ , which are attributable to their interparticle voids. A large hysteresis observed for NI-MPW is probably due to nitrogen adsorption to the slit-shaped microspace formed by the accumulated folds.



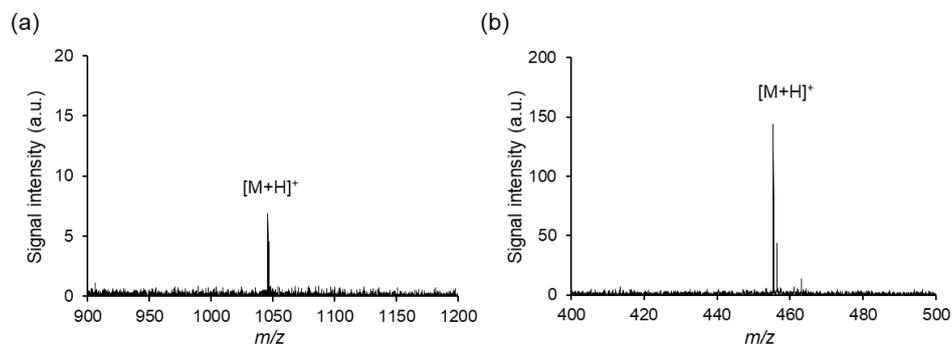
**Fig. S10** Nitrogen adsorption–desorption isotherms of TMS-modified NI-silica particles: (a) NI- $\mu$ S; (b) NI-nS; (c) NI-MPW; (d) NI-PMO.

## 10. LDI TOF mass spectra

The raw LDI TOF mass spectra of angiotensin I obtained using NI- $\mu$ S, NI-nS, and NI-PMO are shown in Fig. S11. Fig. S12 shows mass spectra of angiotensin II (Mw: 1046.2) and verapamil (Mw: 454.6) obtained using NI-MPW.



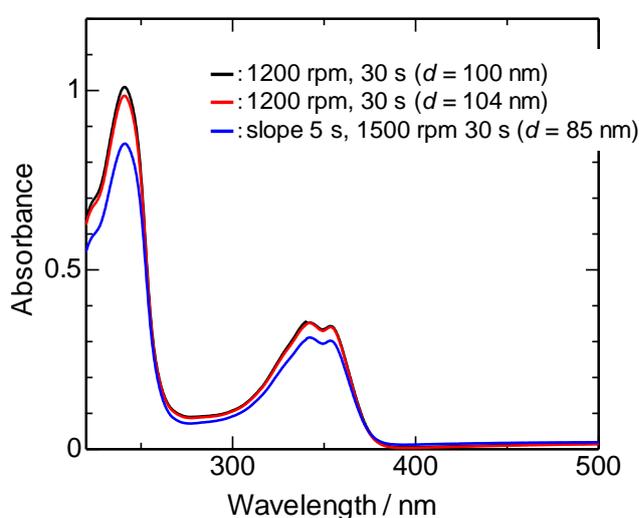
**Fig. S11** LDI TOF mass spectra of angiotensin I obtained using (a) NI- $\mu$ S, (b) NI-nS, and (c) NI-PMO.



**Fig. S12** LDI TOF mass spectra of (a) angiotensin II (5 pmol) and (b) verapamil (5 pmol) obtained using NI-MPW.

## 11. Determination of absorption coefficient

To determine the absorption coefficient ( $\alpha$ ) of NI-silica framework, NI-silica sol-gel films were prepared by spin-coating of an acidic sol solution of NI-d-Si(IP) (NI-d-Si(IP): 0.08 g, ME: 1.5 mL, 2 M HCl aq.: 15  $\mu$ L, stirred for 4 h at 25 °C). Fig. S13 shows UV-vis absorption spectra of the films prepared under different spin-coating conditions. From the absorbance ( $A$ ) of the films and the film thicknesses ( $d$ ), the  $\alpha$  of the NI-silica framework was determined using the equation  $\alpha = 2.303A/d$  to be  $7.8 (\pm 0.3) \times 10^4 \text{ cm}^{-1}$  at  $\lambda = 355 \text{ nm}$ .



**Fig. S13** UV-vis absorption spectra of NI-silica spin-coated films.

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