Cooperative assembly of redistributed aryl-germanium bearing alkoxy silane in mesostructured siloxane network

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S1: Experimental section:

S1a: Synthesis and characterization of Ph₃GeSi, Ph₂GeSi₂ and PhGeSi₃

Synthesis and characterization of Ph₃GeSi

A solution of triethoxyvinylsilane (0.46 g, 2.42 mmol) and triphenylgermane (0.75 g, 2.45 mmol) in toluene (2 ml) was heated in the presence of AIBN at 90°C for 2h. After evaporation of solvent, Ph₃GeSi₁ (1.10 g, 91%) was obtained as a white powder. M.p. 57 °C; δH(300.13 MHz; CDCl₃; Me₂Si) 0.69-0.75 (2 H, m, CH₂-Si), 1.12 (9 H, t, J 7.0 , OCH₂-CH₃), 1.48-1.54 (2 H, m, (CH₂-Ge), 3.71 (6 H, q, J 7.0, OCH₂-CH₃), 7.25-7.41 (15 H, m, C₆H₅); δC(75.48 MHz; CDCl₃) 11.84 (OCH₂), 18.51 (OCH₂CH₃), 58.62 (OCH₂CH₃), 128.36 (Cm), 129.04 (Cp), 135.19 (C₆), 137.11 (Cipso); δSi(59.62 MHz; CDCl₃; Me₄Si) -45.88; MS (El): m/z = 496 (1) [M⁺].

Synthesis and characterization of Ph₂GeSi₂

A solution of triethoxyvinylsilane (1.86 g, 9.78 mmol) and diphenylgermane (1.13 g, 4.91 mmol) in toluene (5 mL) was heated in the presence of AIBN at 90°C for 2h. After evaporation of solvent and distillation under reduced pressure, Ph₂GeSi₂ (2.70 g, 90%) was obtained as a colorless liquid. Bp: 140°C / 0.3 mmHg; δH(300.13 MHz; CDCl₃; Me₂Si) 0.59-0.64 (4 H, m, CH₂-Si), 1.13 (18 H, t, J 7.0 , OCH₂-CH₃), 1.20-1.27 (4 H, m, (CH₂-Ge), 3.72 (12 H, q, J 7.0, OCH₂-CH₃), 7.24-7.27 (6 H, m, C₆H₅), 7.36-7.38 (4 H, m, C₆H₅); δC(75.48 MHz; CDCl₃; Me₄Si) 4.28 (Si-CH₂-CH₂-Ge), 18.40 (OCH₂CH₃), 58.51 (OCH₂CH₃), 128.11 (Cm), 128.66 (Cp), 134.71 (C₆), 137.93 (Cipso); δSi(59.62 MHz; CDCl₃; Me₄Si) -45.77; MS (El): m/z = 533 (3) [M-Ph]⁺.

Synthesis and characterization of PhGeSi₃

A solution of triethoxyvinylsilane (2.36 g, 12.42 mmol) and phenylgermane (0.63 g, 4.12 mmol) in toluene (5 ml) was heated in the presence of AIBN at 90°C for 3h. After evaporation of solvent and distillation under reduced pressure, PhGeSi₃ (2.62 g, 88 %) was obtained as a colorless liquid. Bp: 140°C/0.04 mmHg; δH(300.13 MHz; CDCl₃; Me₂Si) 0.55-0.61 (6 H, m, CH₂-Si), 0.96-1.02 (6 H, m, CH₂-Ge), 1.15 (27 H, t, J 7.0 , OCH₂-CH₃), 3.71 (18 H, q, J 7.0, OCH₂-CH₃), 7.22-7.26 (3 H, m, C₆H₅), 7.33-7.35 (2 H, m, C₆H₅); δC(75.48 MHz; CDCl₃; Me₄Si) 2.14, 3.16 (Si-CH₂-CH₂-Ge), 17.27 (OCH₂CH₃), 57.35
(OCH₂CH₃), 126.81 (Cᵣ), 127.18 (Cᵣ), 133.07 (C₀), 137.98 (Cᵦ); δSi(59.62 MHz; CDCl₃; Me₄Si) -45.72; MS (El): m/z = 724 (1) [M]+.

**S1b: Synthesis of Ph₃GeSi@SiO₂, Ph₂GeSi₂@SiO₂ and PhGeSi₃@SiO₂**

**Synthesis of Ph₃GeSi@SiO₂**
The Pluronic P123 (0.9 g) was dissolved in an aqueous HCl solution (5.1 g of HCl 37%, in 25 g H₂O) with stirring at room temperature for 4 h. TEOS (1.89 g, 9.09 mmol) was added dropwise to this homogeneous solution. After 15 min, the Ph₃GeSi precursor (0.5 g, 1.01 mmol of Si) was added to the reaction mixture. The resulting mixture was kept stirring at 40 °C for 20 h and heated at 100°C under static conditions for an additional 24 h. After cooling, the solid product was recovered by filtration, successively washed with deionized water and ethanol to neutrality, and drying in air at 60 °C for 12 h giving 1.6 g of material as a white powder. The surfactant was removed by extraction in a Soxhlet with 250 mL of ethanol containing 2 mL of 37 % HCl aqueous solution at reflux temperature for 72 h. The recovered solid was washed with ethanol and air-dried at 60 °C.

**Synthesis of Ph₂GeSi₂@SiO₂**
The Pluronic P123 (1.46 g) was dissolved in an aqueous HCl solution (8.18 g of HCl 37%, in 36 g H₂O) with stirring at room temperature for 4 h. TEOS (3.07 g, 14.76 mmol) was added dropwise to this homogeneous solution. After 15 min, the Ph₂GeSi₂ precursor (0.5 g, 0.82 mmol of Si) was added to the reaction mixture. The resulting mixture was kept stirring at 40 °C for 20 h and heated at 100°C under static conditions for an additional 24 h. After cooling, the solid product was recovered by filtration, successively washed with deionized water and ethanol to neutrality, and drying in air at 60 °C for 12 h giving 2.2 g of material as a white powder. The surfactant was removed by extraction in a Soxhlet with 250 mL of ethanol containing 2 mL of 37 % HCl aqueous solution at reflux temperature for 72 h. The recovered solid was washed with ethanol and air-dried at 60 °C.

**Synthesis of PhGeSi₃@SiO₂**
The Pluronic P123 (1.84 g) was dissolved in an aqueous HCl solution (10.28 g of HCl 37%, in 46 g H₂O) with stirring at room temperature for 4 h. TEOS (3.88 g, 18.65 mmol) was added dropwise to this homogeneous solution. After 15 min, the PhGeSi₃ precursor (0.5 g, 0.69 mmol of Si) was added to the reaction mixture. The resulting mixture was kept stirring at 40 °C for 20 h and heated at 100°C under static conditions for an additional 24 h. After cooling, the solid product was recovered by filtration, successively washed with deionized water and ethanol to neutrality, and drying in air at 60 °C for 12 h giving 2.33 g of material as a white powder. The surfactant was removed by extraction in a Soxhlet with 250 mL of ethanol containing 2 mL of 37 % HCl aqueous solution at reflux temperature for 72 h. The recovered solid was washed with ethanol and air-dried at 60 °C.
S1c: Preparation of Chitosan–Ph₃GeSi₃-n@SiO₂ Films.

**Preparation of CS–Ph₃GeSi@SiO₂-f**

50 mg of chitosan was completely dissolved in 4 mL of 1% (v/v) acetic acid solution, and the mixture was kept under vigorous stirring for 120 min. tetraethylorthosilicate (7 mg) and Ph₃GeSi (7 mg) were added to the chitosan solution, and the resulting mixture was stirred for an additional 90 min. The resulting solution was cast into plastic Petri dishes allowing solvent removal and film formation after complete drying.

**Preparation of CS–Ph₂GeSi₂@SiO₂-f**

50 mg of chitosan was completely dissolved in 4 mL of 1% (v/v) acetic acid solution, and the mixture was kept under vigorous stirring for 120 min. tetraethylorthosilicate (8.8 mg) and Ph₂GeSi₂ (8.8 mg) were added to the chitosan solution, and the resulting mixture was stirred for an additional 90 min. The resulting solution was cast into plastic Petri dishes allowing solvent removal and film formation after complete drying.

**Preparation of CS–PhGeSi₃@SiO₂-f**

50 mg of chitosan was completely dissolved in 4 mL of 1% (v/v) acetic acid solution, and the mixture was kept under vigorous stirring for 120 min. tetraethylorthosilicate (10.5 mg) and PhGeSi₃ (10.5 mg) were added to the chitosan solution, and the resulting mixture was stirred for an additional 90 min. The resulting solution was cast into plastic Petri dishes allowing solvent removal and film formation after complete drying.
S2. Infrared spectra of bimetallic silyl-germyl precursors $\text{Ph}_3\text{GeSi}$, $\text{Ph}_2\text{GeSi}_2$ and $\text{PhGeSi}_3$.
S3. $^1$H, $^{13}$C and $^{29}$Si NMR spectra of bimetallic silyl-germyl precursors Ph$_3$GeSi, Ph$_2$GeSi$_2$ and PhGeSi$_3$
Ph₃GeSi

\[\text{(EtO)}_3\text{Si-Ge-Ph} \quad \text{δ = 45.88 ppm}\]

Ph₂GeSi₂

\[\text{(EtO)}_3\text{Si-Ge-Si(OEt)}_3 \quad \text{δ = 46.77 ppm}\]
S4. CP MAS $^{13}$C and $^{29}$Si NMR spectra of Ph$_3$GeSi@SiO$_2$, Ph$_2$GeSi$_2$@SiO$_2$ and PhGeSi$_3$@SiO$_2$
S5. TGA curves of Ph$_3$GeSi@SiO$_2$, Ph$_2$GeSi$_2$@SiO$_2$ and PhGeSi$_3$@SiO$_2$
S6. Scanning electronic microscopy analyses of $Ph_3GeSi@PhSiO_2$
S7. Digital photos of, CS-Ph$_3$GeSi@SiO$_2$, CS-Ph$_2$GeSi$_2$@SiO$_2$ and CS-PhGeSi$_3$@SiO$_2$ solutions
S8. Infrared spectra of CS-Ph$_3$GeSi@SiO$_2$-f, CS-Ph$_2$GeSi$_2$@SiO$_2$-f and CS-PhGeSi$_3$@SiO$_2$-f
S9. EDX of CS-Ph₃GeSi@SiO₂-f, CS-Ph₂GeSi₂@SiO₂-f and CS-PhGeSi₃@SiO₂-f
S10. Digital photos and Infrared spectra of CS-Ph\_3GeSi@SiO\_2-f-150°C, CS-Ph\_2GeSi\_2@SiO\_2-f-150°C and CS-PhGeSi\_3@SiO\_2-f-150°C
Transmission %

Wavenumber (cm\(^{-1}\))

CS-PhGeSi\(_3@\)SiO\(_2-f\)
CS-PhGeSi\(_3@\)SiO\(_2-f-150^\circ\)C

4000 3500 3000 2500 2000 1500 1000 500
40 50 60 70 80 90 100 110

4000 3500 3000 2500 2000 1500 1000 500