

Biomimetic synthesis of silica/PDA hybrids with controllable morphology

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Supporting information

Materials and methods

Synthesis of silica/PDA hybrids

A total of 0.1 g of dopamine hydrochloride (Sigma-Aldrich, St. Louis, MO, USA) was dissolved in ultrapure water (18.2 MΩ/cm) from a Milli-Q system (Milli-pore, Bedford, MA, USA), and the solution pH was adjusted to 8.5, 9, 9.5, or 10 using 5 M NaOH solution. The mixture was stirred at 60 °C using a magnetic stirrer at 500 rpm. Different amounts (0, 5, 10, 20 mmole) of tetraethyl orthosilicate (TEOS; Sigma-Aldrich) was rapidly added to DA solution with final volume of 20 mL and stirred for 18 h. The silica/PDA hybrids were washed with deionized water and collected after centrifugation (Centrifuge 5415R, Eppendorf, Hamburg, Germany) at 12,800 rpm, then dried by lyophilization (FDU-1200, EYELA, Tokyo, Japan).

Characterization of silica/PDA hybrids

The morphology of silica/PDA synthesized at different condition was performed by field-emission scanning electron microscopy (FESEM; JSM-7401F, JEOL, Tokyo, Japan) associated with energy dispersive spectroscopy (EDS) and transmission electron microscope (TEM; JEM-1400, JEOL). To prepare the specimens for TEM observation, silica/PDA hybrids were resuspended in distilled water, and then dropped on carbon-coated copper grid and air-drying them overnight. The hydrodynamic size distributions of silica/PDA hybrids were determined by measuring the as-prepared hybrids resuspended in distilled water by dynamic light scattering (DLS) with a Zetasizer nano ZS (Malvern Instruments, Worcestershire, UK). The chemical structure of hybrids was examined by Fourier transform infrared spectroscopy (FTIR; Bomem DA8.3, Hartman & Braun, Canada) and solid-state ²⁹Si nuclear magnetic resonance (NMR; DSX400 WB, Bruker, Karlsruhe, Germany). The weight ratio of

silica and PDA in hybrids was determined with a thermalgravimetric analyzer (TGA; Q500, TA Instruments, New Castle, DE, USA) over a temperature range from room temperature to 1000 °C at a heating rate of 10 °C /min under atmosphere. To assess the silica distribution in silica/PDA hybrids, 50 mg of as-prepared powder of silica/PDA hybrids was immersed in 1 mL of 5 M HF for 1 h at room temperature. After that, the etched PDA was collected and washed with distilled water for 5 times, and then dried by lyophilization. The morphology and chemical structure was performed by TEM and FTIR, respectively.

Formation kinetic of silica/PDA hybrids

To investigate the formation of silica/PDA hybrids a Sunrise microtiter plate reader (Tecan, Austria Gesellschaft, Salzburg, Austria) was used to monitor the changes in absorbance in the reaction solution at different time periods, respectively. At each reaction end-point, a 10 µL aliquot of reaction solution was added to 490 µL of distilled water to avoid the absorbance was over the detection limit of the instrument. 200 µL of the solution in each sample was transferred to a 96-well plate and the absorbance was read at 400 nm. For determining the content of silicic acid formed after hydrolysis of TEOS, 20 µL of reaction solution was taken and added to 0.5 mL of distilled water at each reaction end-point. Immediately, 25 µL of 2 M H₂SO₄ and 25 µL of 0.08 M ammonium heptamolybdate tetrahydrate (Alfa Aesar, Ward Hill, MA, USA) were introduced to each sample and allowed to stand for 10 min. After incubation, 200 µL of each sample was transferred to a 96-well plate and read in a Sunrise microtiter plate reader at 400 nm. The molybdosilicate method is based on the formation of yellow silicomolybdic acid H₈Si(Mo₂O₇)₆ originating from the reaction between ammonium heptamolybdate and monomeric or oligomeric silicate species¹.

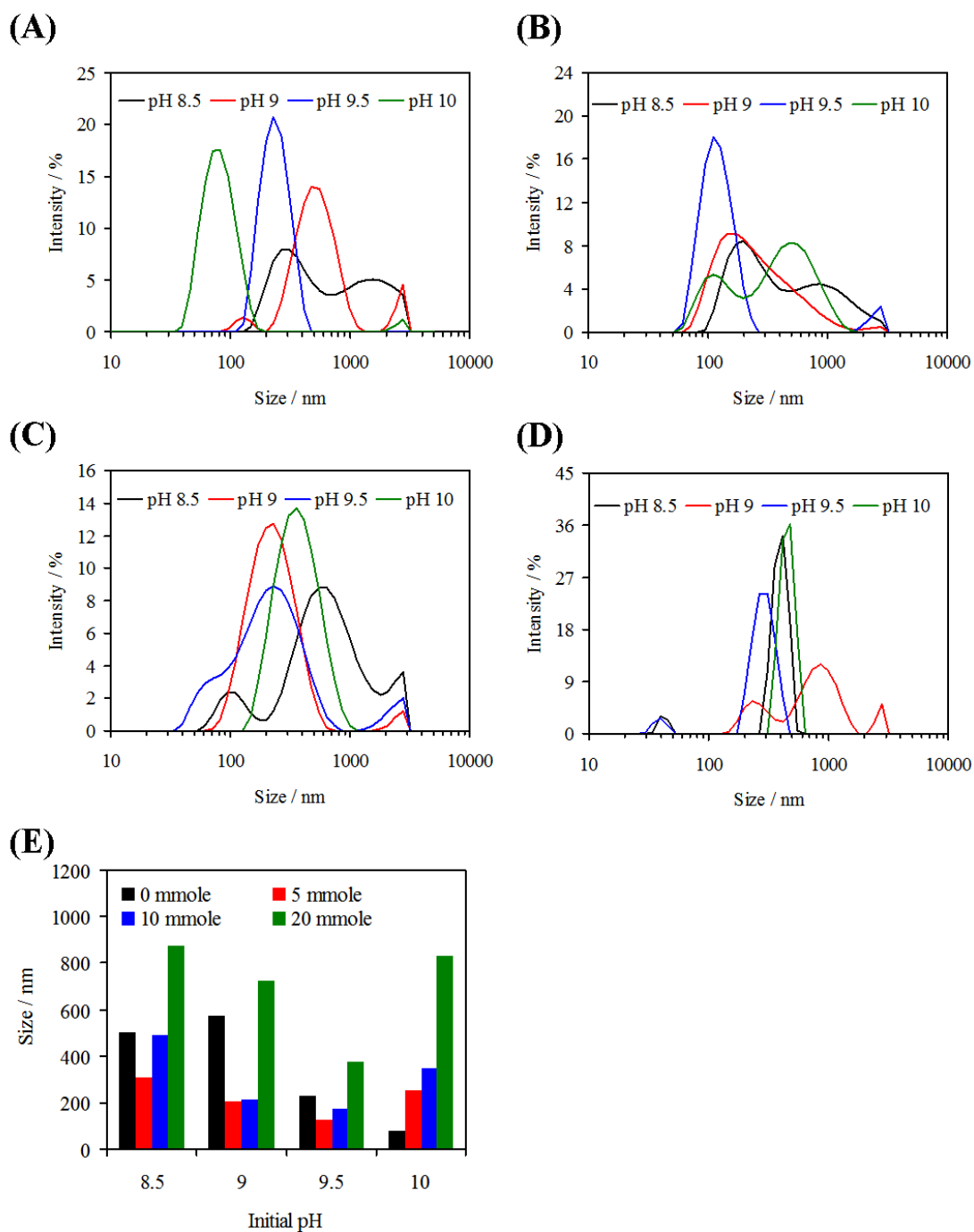


Fig. S1. Size distribution of silica/PDA hybrids synthesized at different initial pH in the presence of (A) 0, (B) 5, (C) 10, and (D) 20 mmole of TEOS. (E) The average size of silica/PDA hybrids synthesized at different condition.

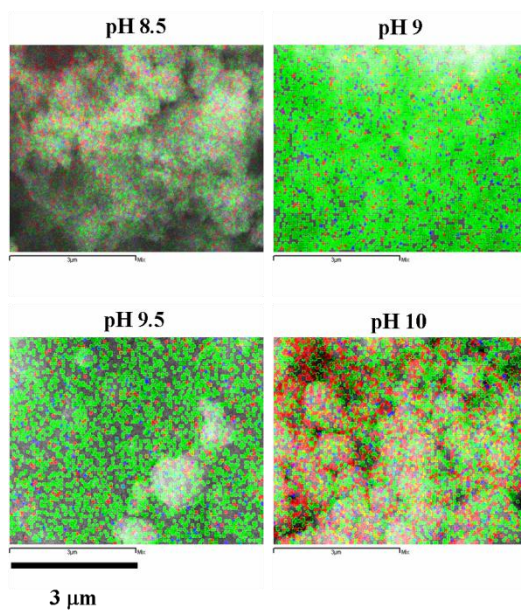


Fig. S2. EDS mapping of silica/PDA hybrids synthesized at different initial pH. Green, red, and blue dots indicate signals of Si, C, and N, respectively. Original magnification and scale bar are 20 kx and 3 μm, respectively.

Table S1. The content of Qⁿ of silica/PDA hybrids synthesized at different condition calculated from ²⁹Si NMR spectra.

TEOS (mmole)	Initial pH	Q2 (%)	Q3 (%)	Q4 (%)
10	8.5	14.3	64.6	21.1
10	9	10.5	62.1	27.4
10	9.5	9.4	60.7	29.9
10	10	9.5	61.2	29.3
5	9.5	9.9	62.1	28.0
20	9.5	10.8	61.5	27.7

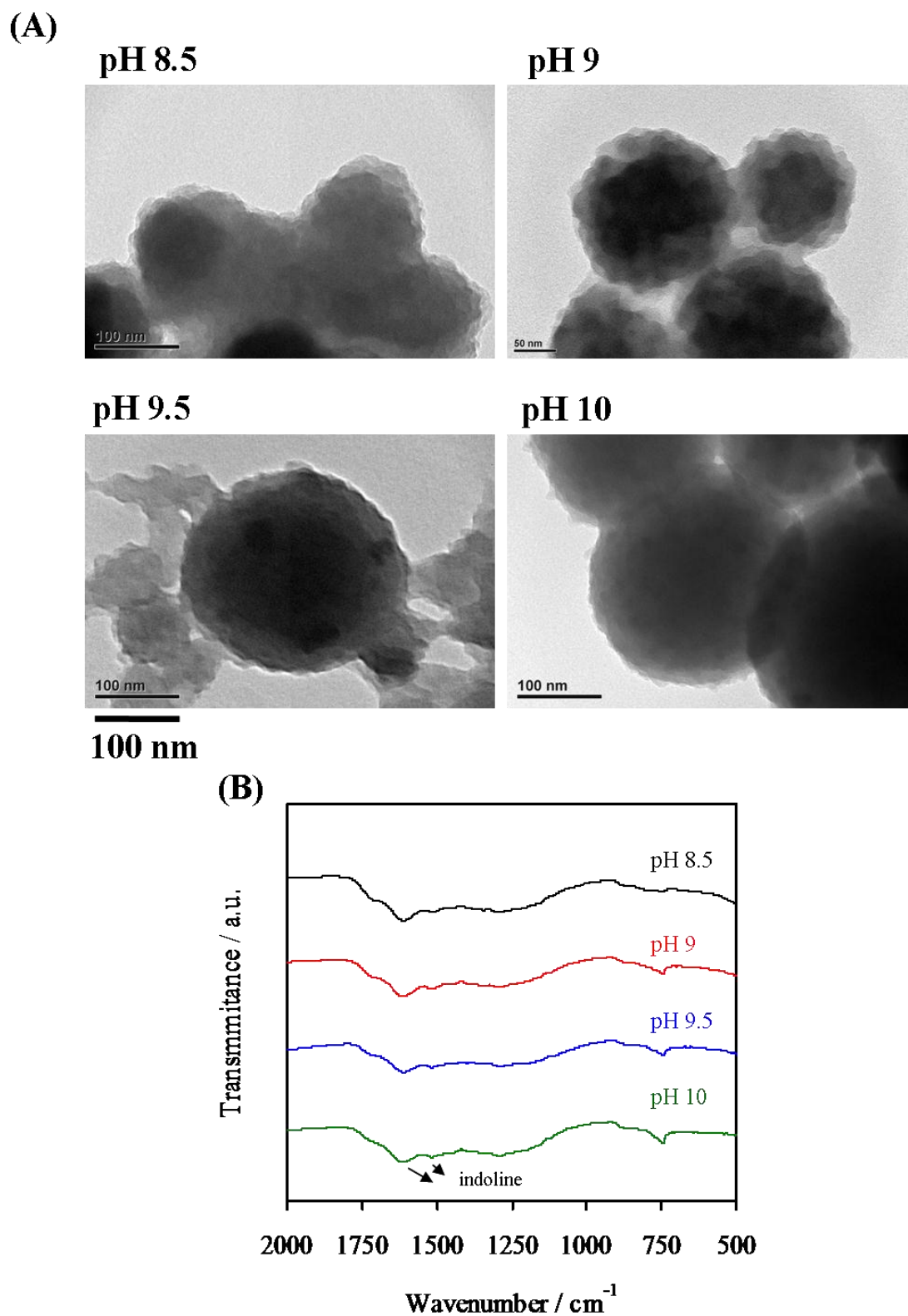


Fig. S3. (A) TEM images and (B) FTIR spectra of silica/PDA hybrids synthesized at different initial pH values in the presence of 10 mmole of TEOS, which the hybrids were etched by 5 M HF for 1 h at room temperature. Original magnification and scale bar are 400 kx and 100 nm, respectively.

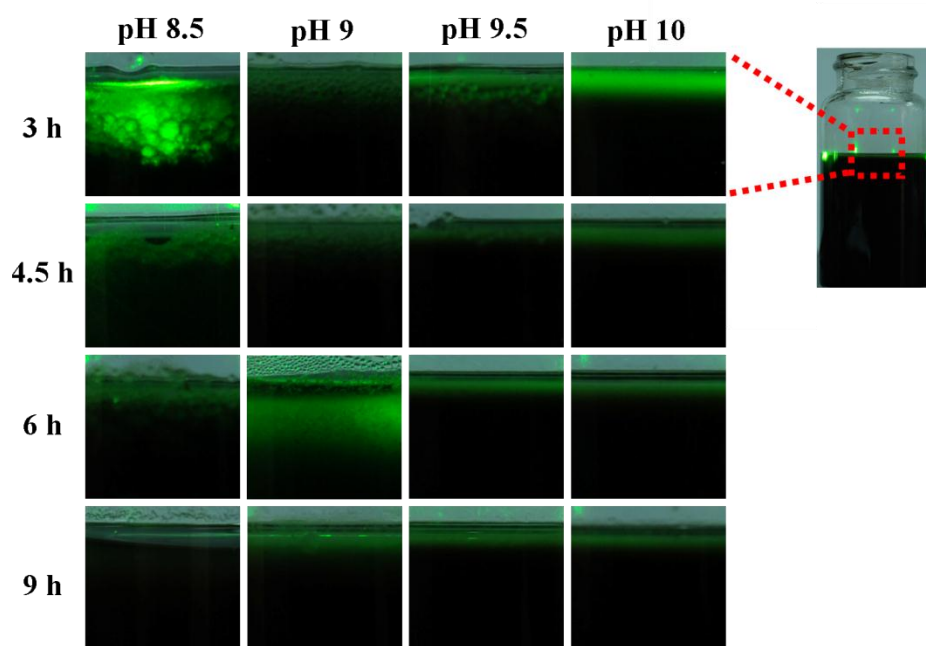


Fig. S4. Photographs of *in situ* observation of silica/PDA precursors synthesized at different initial pH and reaction time in the presence of 10 mmole TEOS.

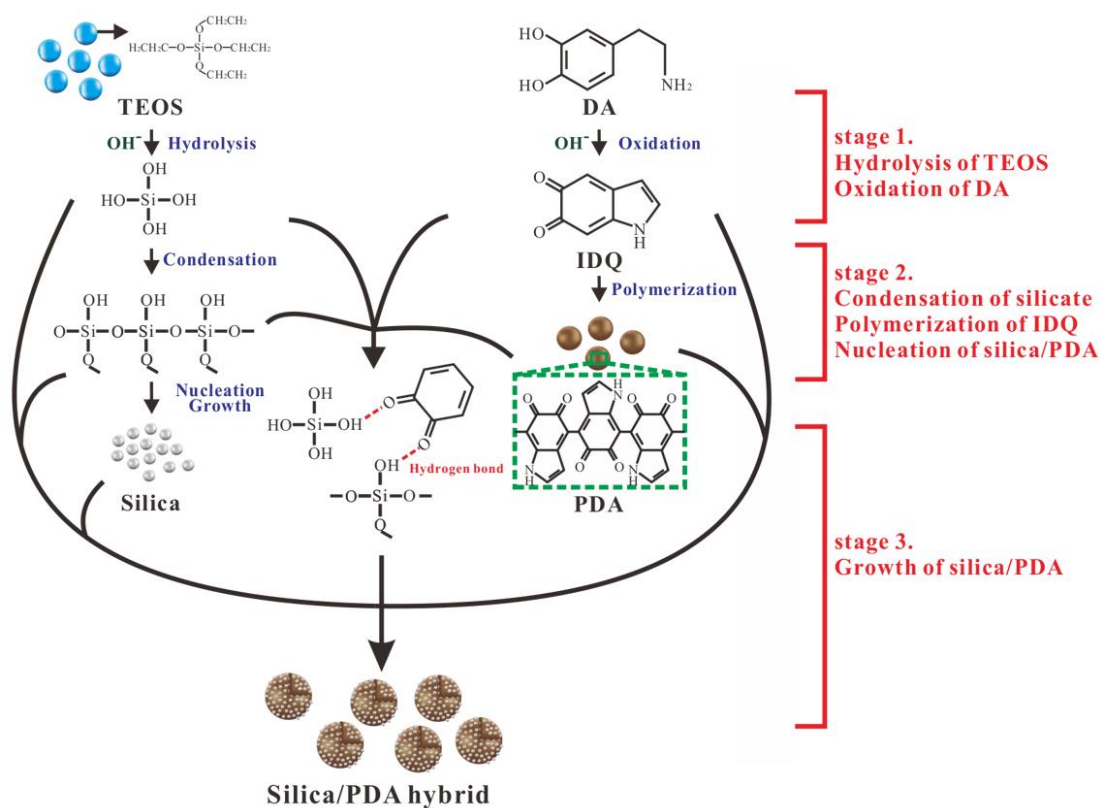


Fig. S5. Speculated formation pathway of silica/PDA hybrids synthesized in a water-DA-NaOH system with TEOS.

Reference for supporting information

- 1 T. Coradin and J. Livage, Colloids and Surfaces B: Biointerfaces, 2001, 21, 329.