Supporting Information

Biomimetic synthesis of silica nanostructures with controllable morphologies and sizes through tuning interfacial interactions

*Shengjie Wang, Junyi Xue, Xin Ge, Haiming Fan, Hai Xu**, *Jian R. Lu**

Experimental Methods

Materials

Fmoc (9-fluorenylmethyloxycarbonyl) protected amino acids (Fmoc-L-isoleucine-OH, Fmoc-L-lysine(Boc)-OH), Rink amide-MBHA resin, *O*-(1H-benzotriazole-1-yl)-*N*,*N*,*N'*,*N'*-tetramethyluronium hexafluorophosphate (HBTU), *N*-hydroxybenzotriazole anhydrous (HOBt), *N*,*N'*-diisopropyl ethylamine (DIEA), trifluoroacetic acid (TFA), piperidine and triisopropylsilane (TIS) were purchased from GL Biochem. (Shanghai) Ltd and used as received. Dichloromethane (DCM) and dimethylformamide (DMF) were obtained from Sinopharm Chemical Reagent Co. Ltd., and redistilled and dried with molecular sieves prior to use. Tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTES), anhydrous ethanol, diethyl ether and other reagents were purchased from Sigma-Aldrich and used without further purification. All water used was from a Millipore water purification system with a minimum resistivity of 18.0 MΩ·cm.

Synthesis of I_3K Peptide

I_3K was synthesized by following the standard Fmoc solid phase synthesis on a CEM Liberty microwave peptide synthesizer. [1-2] Its C- and N-termini were amidated and acetylated, respectively, to limit the peptide charge purely arising from the lysine residue side chain. The crude product was deposited with copious cold ether and then purified by reverse-phase high performance liquid chromatography (RP-HPLC) to achieve a high purity (⩾95%), as indicated by HPLC and MALDI -TOF MS characterizations.

Self-Assembly of I_3K Peptide

The purified I_3K was dissolved in ultra-pure water at a concentration of 4 mMol L^{-1} giving a pH of 6, and the solution pH was then slightly adjusted to 7 using dilute NaOH solution. The peptide solution was kept at ambient temperature for at least one week to assure the complete self-assembly of I_3K molecules.

Preparation of Silica Hybrids

In all cases, the mineralization was carried out at 20 ± 1 ^{o}C under static conditions. The concentrations of siloxanes and peptide in the reacting mixtures were fixed at 0.045 Mol L^{-1} and 1 mMol L^{-1}, respectively. To regulate the silica nanostructures, the relative concentrations of TEOS and APTES and their addition sequences were varied, with the detailed procedures given in the following:

Method A: The relative molar ratios of APTES and TEOS were varied between pure TEOS, 1 (APTES)/39 (TEOS), 1/15, 1/4, and pure APTES. In a typical synthesis, APTES and TEOS were dissolved in 2 mL of ethanol, and immediately mixed with 1 mL of the preassembled I_3K solution and 1 mL of Tris buffer (0.05 M, pH 9.0). After reaction for 4 days, the precipitate was collected by centrifugation (10000 rpm × 30 minutes), followed by rinsing with copious water and ethanol. The final product was lyophilized. Similarly, control experiments were carried out where the I_3K solution was replaced by equal volume of water.

Method B: TEOS, APTES, 2mL of ethanol, and 1 mL of Tris buffer were firstly mixed and reacted for 5 minutes, and then 1 mL of the pre-assembled I_3K solution was introduced and the mixture kept for 24 hours. The precipitate was also collected via the same procedure as described in Method A. Note that in this case, the molar ratio of APTES and TEOS was fixed at 1/15 and the other compositions were the same as used in Method A.

Method C: TEOS, I_3K solution, ethanol and Tris buffer were mixed first and then reacted for 24 hours. APTES was added and the reaction continued for 3 days. The sample was collected via the same procedure as used in Method A. In this case, the molar ratio of APTES and TEOS was fixed at 1/15, with other compositions being kept the same as in Method A.

Characterizations

The structural and morphological information of hybrid silica samples was followed by transmission electron microscopy (TEM) using a JEOL-2100UHR electron microscope operated at 200 kV. The precipitates were dispersed in ethanol and then coated on TEM grid. For monitoring the formation process of silica hybrids, the samples were directly taken from the reaction solution and pipetted on to the TEM grid for subsequent characterization (e.g. Figure 2 (a), (b), and (c) and Figure 3 (a)).

The hybrid silica samples were characterized with ^{29}Si cross-polarization magic angle spinning nuclear magnetic resonance (^{29}Si CP-MAS NMR) on a Bruker Avance III 400 MHz NMR spectrometer. The relaxation delay for these measurements was 5 seconds, and the resonance frequency was 79.5 MHz. Date were processed using Origin 8.0 software and least squares fitted to Lorentz line shapes.

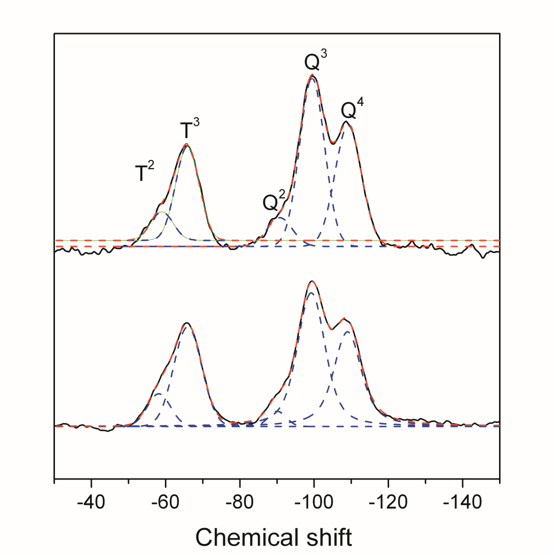

Figure S1. ^{29}Si CP MAS NMR spectra for the synthesized silica nanostructures obtained via Method A from the mixture of APTES, TEOS and I_3K (upper) and the mixture of APTES and TEOS (bottom).The molar ratio of APTES and TEOS was 1/15 in both cases.

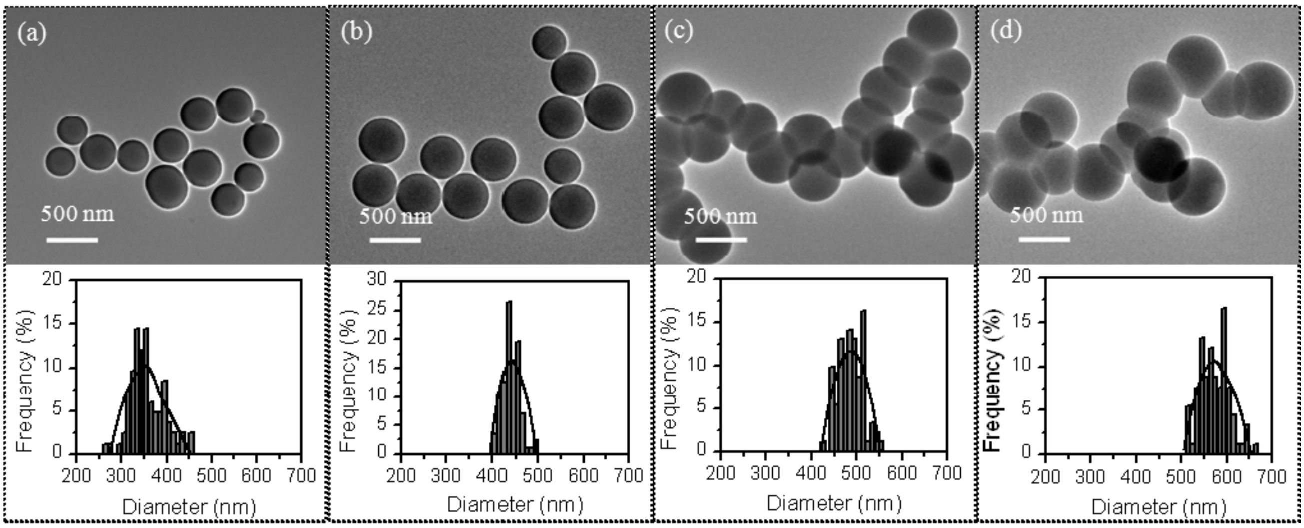

Figure S2. TEM images and statistical sizes of silica hybrids obtained from the mixtures of APTES and TEOS at the molar ratios of 1/39 (a), 1/15 (b), 1/9 (c) and 1/4 (d). The reactions were performed according to Method A in the absence of I_3K assemblies.

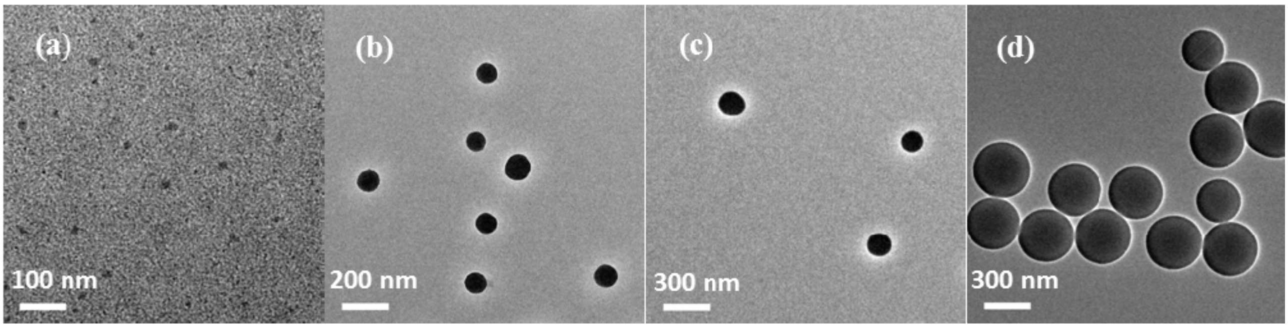

Figure S3. TEM images of the silica hybrids from a mixture of APTES and TEOS at the reaction period of 5 minutes (a), 15 minutes (b), 65 minutes (c) and 24 hours (d). In this case, I_3K solution was replaced by equal volume of water and others conditions were kept the same as in Method B.

References:

[1]. H. Xu, J. Wang, S. Y. Han, J. Q. D. Y. Yu, H. Y. Zhang, D. H. Xia, X. B. Zhao, T. A. Waigh, J. T. Lu, *Langmuir* **2009**, *25*, 4115–4123.

[2]. S. Y. Han, S. S. Cao, Y. M. Wang, J. Q. Wang, D. H. Xia, H. Xu, X. B. Zhao, J. T. Lu, *Chem. Eur. J.* **2011**, *17*, 13095-13102.