Synthesis of antimicrobial silsesquioxane-silica hybrids by hydrolytic co-condensation of alkoxysilanes

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S1 Co-condensation reaction scheme

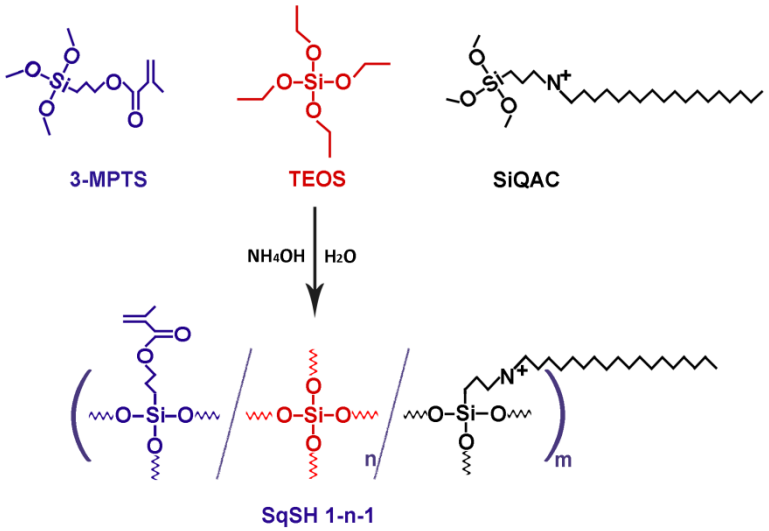

Figure S1. One-pot synthesis of silsesquioxane-silica hybrid particles

S2 FTIR spectra of SqSHs and sol-gel silica

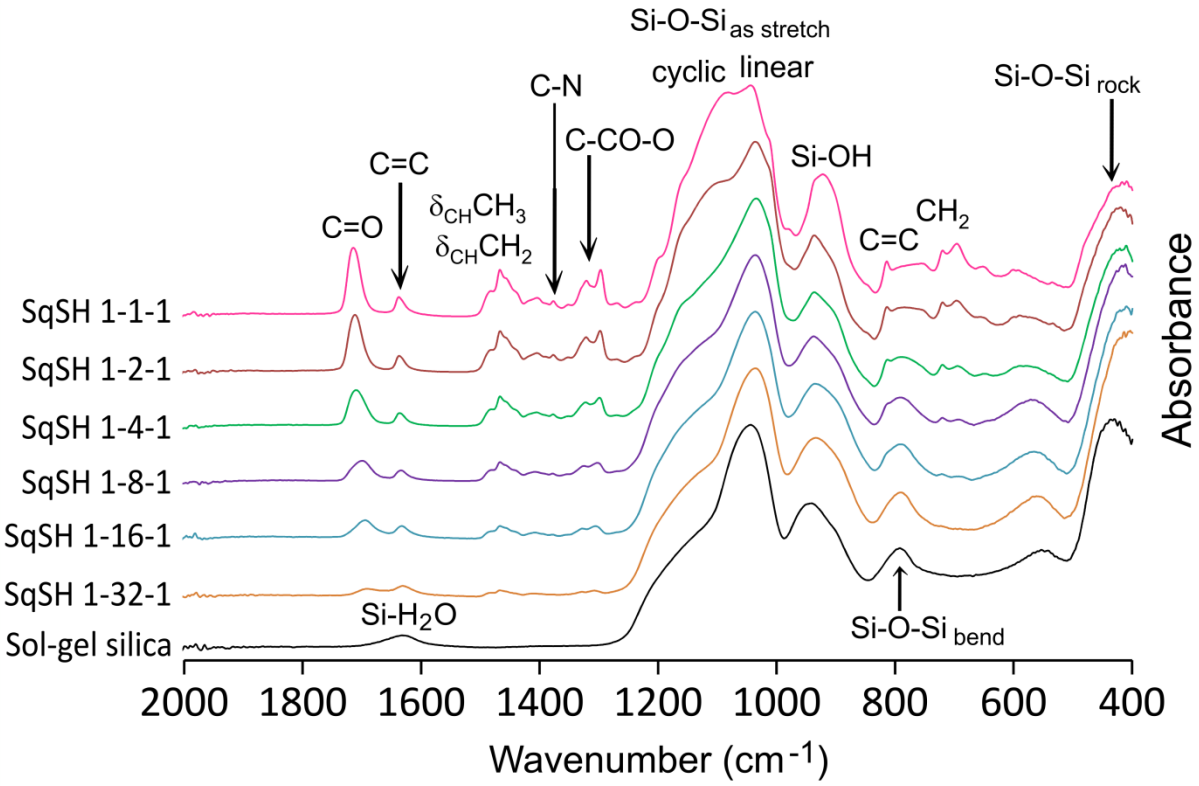

Figure S2. Infrared spectra of SqSHs and sol-gel silica. The broad absorbance band from ~1000-1100 cm^{-1} is assigned to asymmetric stretching vibration of Si-O-Si groups. With higher organic content in the hybrid (SqSH 1-1-1 and SqSH 1-2-1), two separate peaks are present, indicating two components from Si-O-Si groups in cyclic (~1080 cm^{-1}) and linear (~1040 cm^{-1}) structures. Cyclic structure of Si-O-Si is considered to be more condensed than linear Si-O-Si. This is consistent to ^{29}Si NMR results showing that SqSH 1-1-1 and SqSH 1-2-1 have higher degrees of condensation (Fig. 1d). The peaks at ~792 cm^{-1} and ~430 cm^{-1} are assigned to Si-O-Si bending and rock vibration, respectively. The peak at ~935 cm^{-1} is derived from silanol group (SiOH). The absorbance band peaking at 1633cm^{-1} is assigned to deformational vibration of absorbed water molecules (Si-H_2O). The presence of methacrylate from 3-MPTS are confirmed by peaks at 1690-1714 cm^{-1} (C=O), 1637 cm^{-1} (C=C), 1305 cm^{-1} (C-CO-O), 1295 cm^{-1} (C-CO-O), and 815 cm^{-1} (C=C). The C-N stretch vibration peaking at 1373 cm^{-1} validates the presence of SiQAC.

S3 Thermogravimetric Analysis (TGA) of SqSHs and sol-gel silica

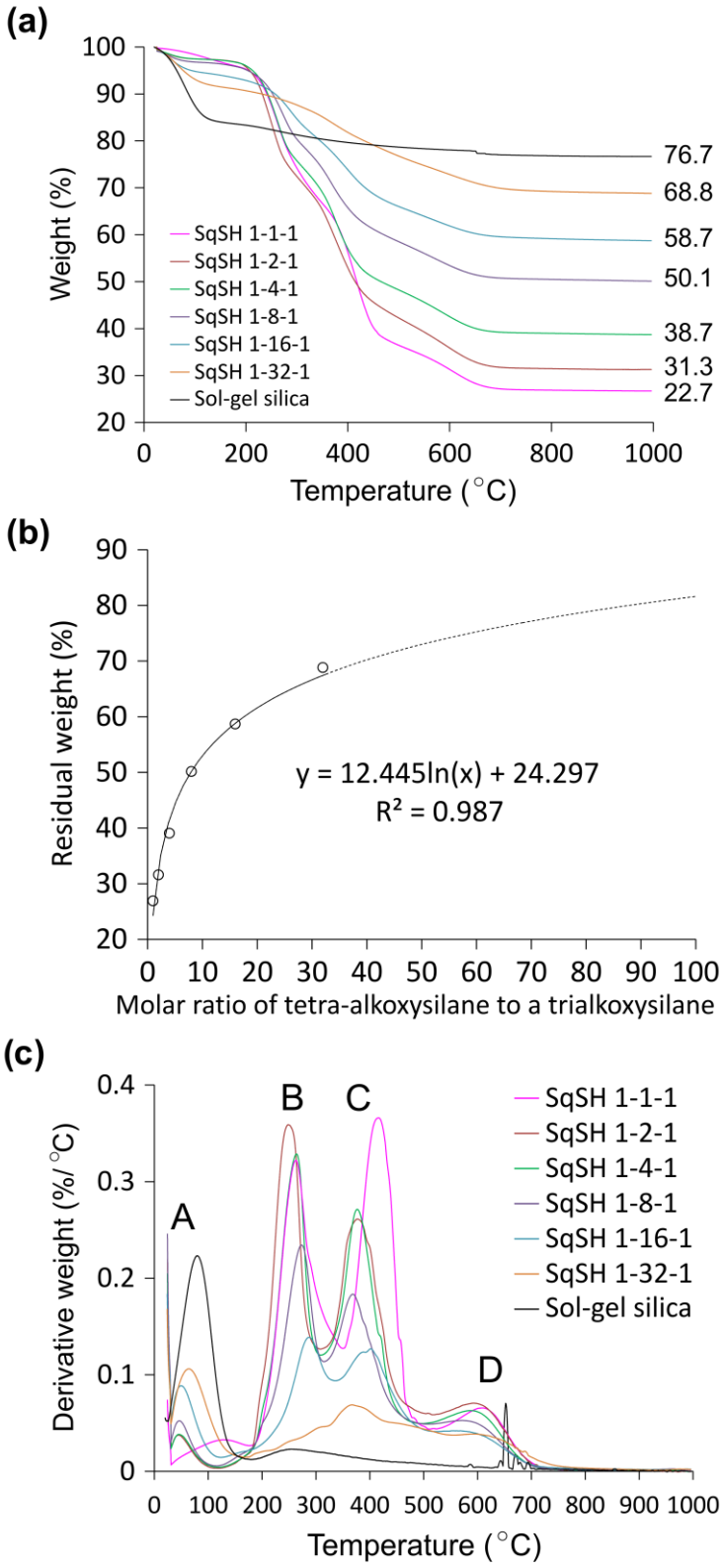

Figure S3. Thermogravimetric analysis (TGA) of SqSHs and sol-gel silica at a rate of 10°C/min from ambient temperature to 1000°C in atmospheric air. (a) Thermograms for SqSHs and sol-gel silica. The residual mass that remains after reaching at 700 °C is due to residual inorganic silica content. The weight percentage of remaining silica in SqSHs 1-1-1, 1-2-1, 1-4-1, 1-8-1, 1-16-1, 1-32-1 and sol-gel silica are 22.7, 31.3, 38.7, 50.1, 58.7, 68.8, and

76.7 wt%, respectively. (b) Logarithmic regression model provides an excellent fit (R^2 = 0.987; $P < 0.01$) for the relation between the residual weight percentage and the molar ratio of tetraethoxysilane to a trialkoxysilane. (c) Derivative weight loss curves for SqSHs and sol-gel silica. For the peak below 100 °C (A), the highest was seen with sol-gel silica while the lowest peak was seen with SqSH 1-1-1. This indicates that there is more water molecules inside the sol-gel silica network. The overall peak intensity of the derivative weight plots increases with the increased composition of organosilane in SqSHs. The two peaks (B and C) from 200 to 420 °C indicate the decomposition of organic constituents,[1] representing two-stage decomposition of organic substances from SqSHs.[2] The peaks (D) above 600 °C are attributed to further condensation of the silanol groups in the bulk silicate network.

S4 Partial coalescence of SqSHs to form peanut-like structures

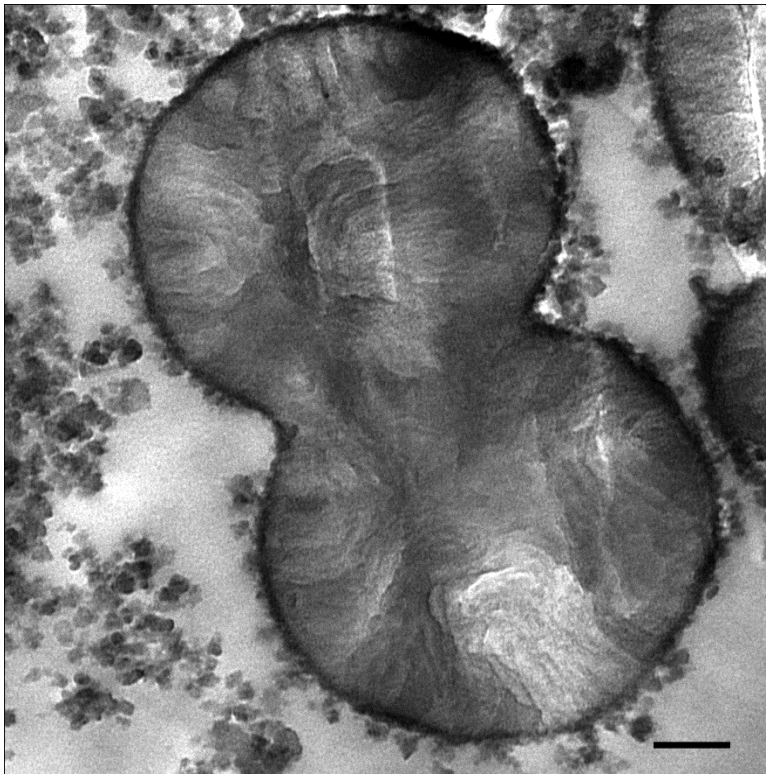

Figure S4. Unstained transmission electron microscopy image of the formation of partially coalesced, peanut-like particles derived from SqSH 1-4-1. This clumping phenomenon is observed in all SqSH versions with different feed ratios, but not for the sol-gel silica control. The process should have occurred while the SIQAC- and ethanol-stabilized droplets are in their liquid phase prior to solidification. It is possible that the quaternary ammonium trialkoxysilane (SiQAC) located on the surface of droplets with long hydrophobic alkyl chain protrudes from a lipophilic droplet into the continuous aqueous phase. Upon collision with another globule, these alkyl chains may pierce the other globule, making the droplets more prone to partial coalescence.[3] Scale bar = 100 nm.

S5 STEM-EDX mappings of elemental distribution within SqSH 1-32-1

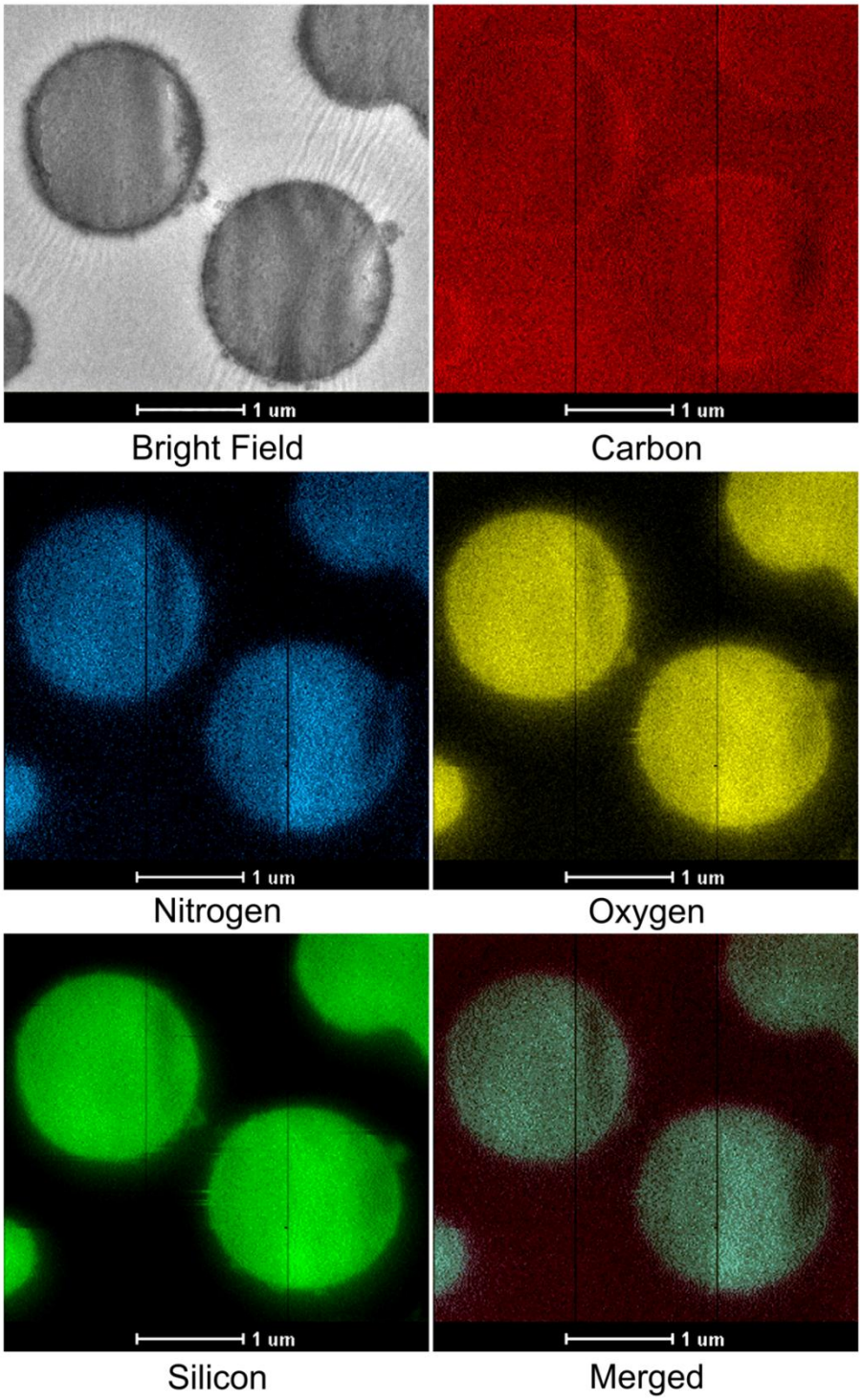

Figure S5. STEM-EDX mappings of distribution of carbon, nitrogen, oxygen, and silicon within SqSH 1-32-1.

S6 Cytotoxicity of SqSHs and sol-gel silica

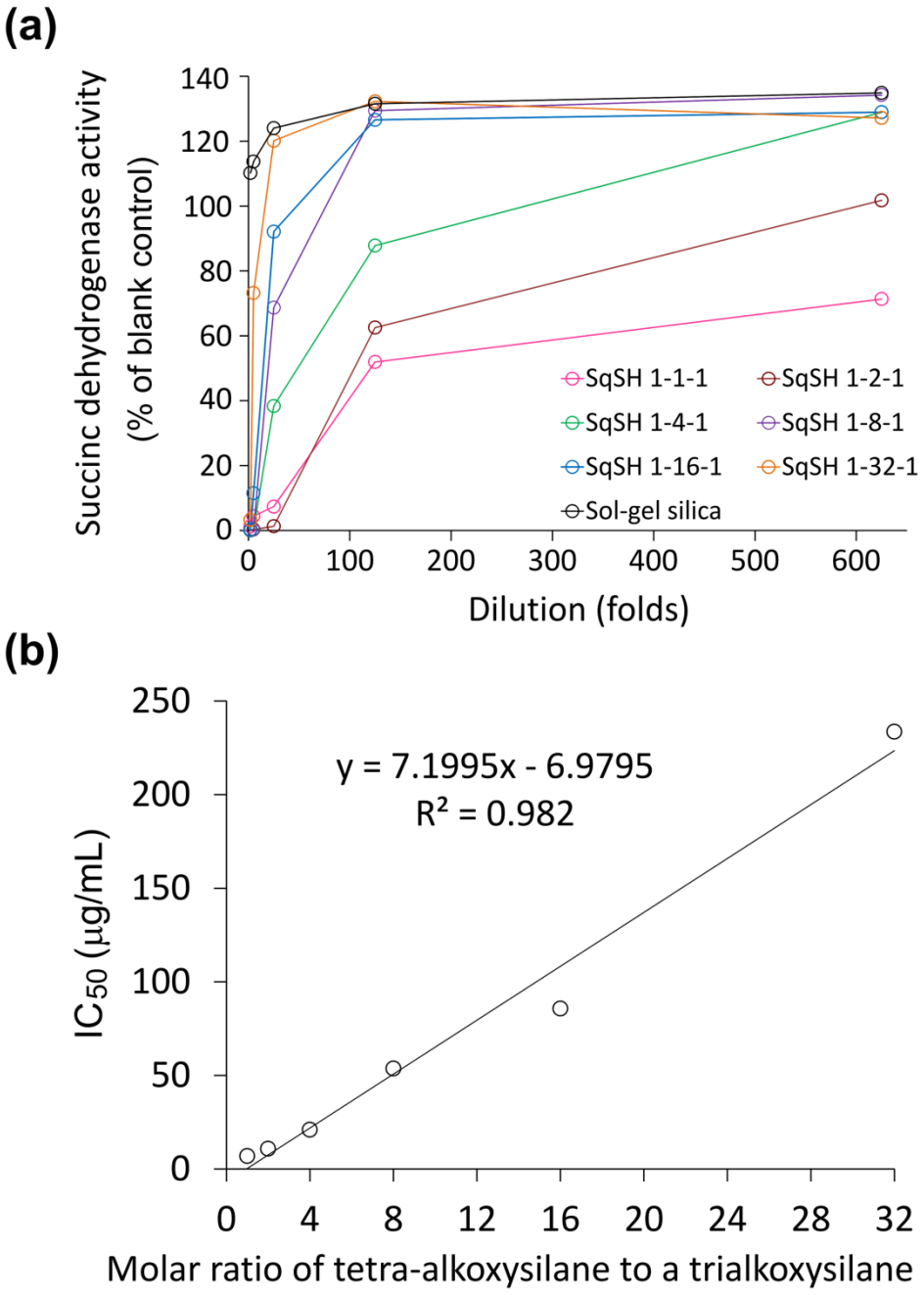

Figure S6. Cytotoxicity of SqSHs and sol-gel silica. (a) Mitochondrial succinic dehydrogenase activities of L-929 cells after incubating for 72 hours in DMEM containing SqSH or silica particles at different concentrations. Cytotoxicity of the SqSH particles on mammalian cells increased in a dose-dependent manner. (b) The concentration of different SqSH versions leading to 50% reduction in cell viability (IC_{50}) of the L-929 cells is illustrated here. IC_{50} was determined by plotting the logarithm of particle concentration *vs* reduction in cell viability. Note that sol-gel silica particles (predominantly inorganic in nature) are highly biocompatible and did not result in loss of cell viability reduction. A linear regression model was used to describe the relationship ($R^2 = 0.982$; $P < 0.05$) between the IC_{50} and the molar ratio of tetraethoxysilane to a trialkoxysilane.

S7 Additional references

[1] D. S. Bag, K. U. Rao, *J. Appl. Poly. Sci.* **2010**, *115*, 2352.

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[3] E. Fredrick, P. Walstra, K. Dewettinck, *Adv. Colloid Interface Sci.* **2010**, *153*, 30.