

Template Synthesis of Precisely Monodisperse Silica Nanoparticles within Self-Assembled Coordination Spheres

Kosuke SUZUKI, Sota SATO, Makoto FUJITA*

Department of Applied Chemistry, The University of Tokyo, CREST, Japan Science and Technology Corporation (JST), Bunkyo-ku, Tokyo 113-8656, Japan

Introduction

The precise control of the shape and the size of inorganic nanoparticles is of great importance in materials science. The most efficient methods for preparing controlled nanoparticles exploit hollow structures as “endo-templates” to restrict the size and shape. Polymer capsules such as micelles are commonly employed but are imprecise templates as they are structurally ill-defined. Here, we report the preparation of highly monodisperse silica nanoparticles by utilizing self-assembled coordination spheres as endo-templates. The spheres assemble from 12 metals and 24 organic ligands and possess a rigid and well-defined framework that can be precisely expanded up to a diameter of 6.5 nm. When the sphere interior is lined with sugar residues, the spheres act as a precise endo-template for the sol-gel condensation of tetramethoxysilane (TMOS). Remarkably, the polydispersities of the formed silica nanoparticles approach unity ($M_w/M_n < 1.01$). The component ligands are easily modified by organic synthesis, enabling the accurate expansion of the templates and the subsequent control of the monodisperse silica nanoparticles spanning molecular weights of 5000–31000 Da, corresponding to 2–4 nm in diameter.

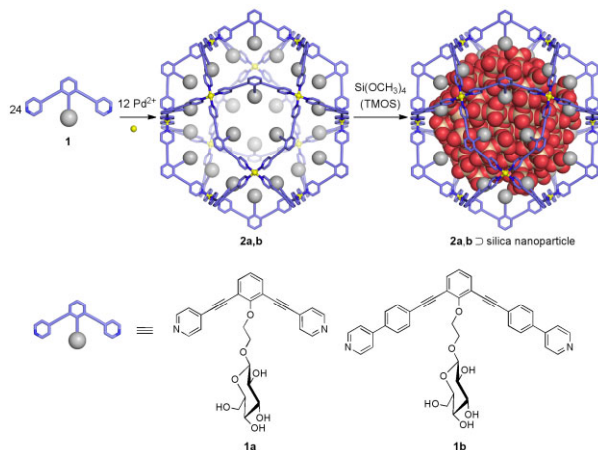


Figure 1. Synthesis of silica nanoparticles within sphere 2.

Results and Discussion

Ligand **1** was designed so that the 24 pendant glucose units would line the sphere interior. These glucose units act as an endo-template for the sol-gel condensation of alkoxy silanes and formation of silica nanoparticles based on the reversible condensation reaction between silanols and sugars. Treatment of ligand **1** with $\text{Pd}(\text{NO}_3)_2$ (0.5 equiv.) in dimethylsulfoxide (DMSO)- d_6 for 1 h at 50 °C

resulted in the quantitative formation of sugar-lined complex **2**. A DMSO- d_6 solution of **2a** was diluted with CDCl_3 (DMSO- d_6 : $\text{CDCl}_3 = 1:9$), and 170 equivalents of TMOS and 100 equivalents of H_2O was added. When mixture was stirred at room temperature for 4 d, ^1H NMR spectra showed the growth of silica nanoparticle within **2a**. The rigid shell framework of **2a** favours crystallization and single crystals of **2a**⊃silica, after the reaction with 170 equivalents of TMOS, were obtained by slow vapor diffusion of chloroform into a solution of **2a**⊃silica. Synchrotron X-ray analysis revealed the robust framework of sphere **2a**, with a diameter of 4.6 nm, remained intact even after the formation of silica nanoparticle (Figure 2a). Then, the silica nanoparticle consisting of 170 SiO_2 units, with a diameter of ca. 2.8 nm, was modeled within the structure of shell framework of **2a** elucidated by an X-ray diffraction study (Figure 2b).

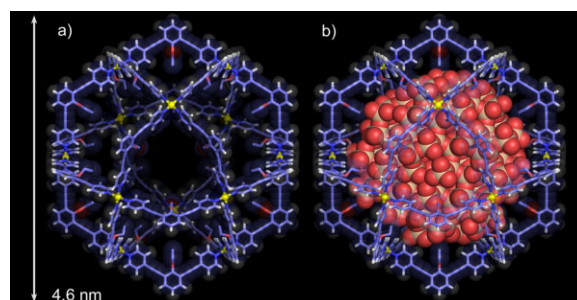


Figure 2. a) The X-ray crystal structure of **2** and b) combined structure of **2a**⊃silica.

The molecular weight of silica nanoparticle formed in **2a** ($M_w = 11,100$) was directly measured by laser desorption ionization mass spectrometry (LDI-MS). Sphere **2a** successfully templated almost perfectly monodisperse silica nanoparticles, and polydispersity (M_w/M_n) of the obtained nanoparticles was almost unity (1.007). The size of the silica nanoparticle is defined by the spherical shell and larger monodisperse silica nanoparticles can be prepared by expanding the diameter of the sphere. When condensation of TMOS was examined in the presence of sphere **2b**, LDI-MS measurement confirmed the formation of silica nanoparticles with a number average molecular weight of 31,570 Da and M_w/M_n of 1.004.

References

[1] K. Suzuki et al., *Nat. Chem.*, 2, 25–29 (2010).

* mfujita@appchem.t.u-tokyo.ac.jp