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Surface modification of silicon plate by hydrothermal treatment with a copper–cerium metallamacrocyclic compound

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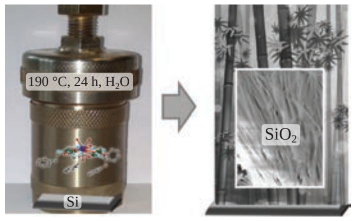
The hydrothermal treatment of a silicon plate with a copper–cerium metallamacrocyclic compound leads to the formation of bamboo-like silica nanowires with an average mean diameter of 30–50 nm and a length of 15–20 μm.



Among one-dimensional nanostructures such as nanowires, nanorods and nanotubes, the Si oxide-based nanomaterials are of interest due to their remarkable electronic, magnetic and optical properties.[1,2] Since the discovery of silica nanowires, many efforts have been made to explore strategies to control size, length and orientation for applications and device development. Recently, liquid synthesis methods became current leaders instead of well-established high temperature gaseous methods.[3–6] Diverse methods have been used to synthesize silica nanowires with a large diameter (about 1 μm), whereas a detailed study on the formation of silica nanowires with diameters of about 30 nm is still challenging.[7] Here, we demonstrate that the hydrothermal treatment of a silicon plate with a copper–cerium metallamacrocyclic compound at 190 °C for 24 h leads to the formation of bamboo-like silica nanowires with an average mean diameter of 30–50 nm and a length of 15–20 μm.

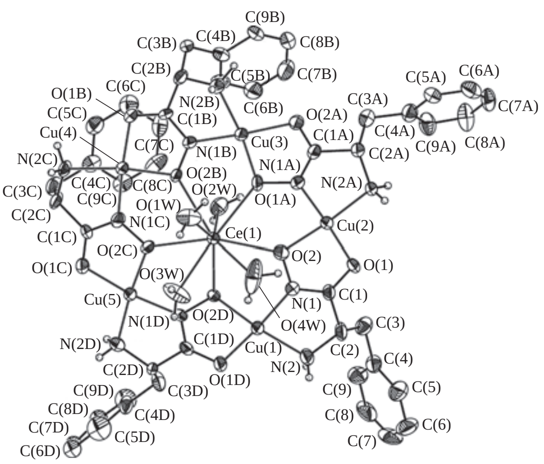


Figure 1 General view of an independent $Ce(H_2O)_4[15\text{-}MC_{CuPhalaha}\text{-}5]$ fragment in the representation of atoms by thermal ellipsoids (p = 50%). The water molecules and chloride ions in the apical positions of copper polyhedrons are omitted for clarity.

Earlier, we developed a one-pot synthesis of water-soluble polynuclear metallamacrocyclic Ln^{III}–Cu^{II} complexes based on glycinehydroxamic acid.[8–10] These complexes belong to a family of 15-MC-5 metallacrowns (MCs) as an exceptional class of supramolecular compounds with a metallamacrocyclic motif that structurally resembles crown ethers.[11–13] In these complexes, the neutral ring consists of five [Cu^{II}–N–O] repeat units, and the five hydroximate oxygen atoms encapsulate a Ln^{3+} ion within the central cavity. Here, water-soluble complex $Ce(H_2O)_4$-[15-$MC_{CuPhalaha}$-5]Cl_3 **1** based on α-phenylalaninehydroxamic acid was prepared similarly to glycinehydroximate derivatives.[†]

According to XRD data,[‡] there are two independent chiral $Ce(H_2O)_4[15\text{-}MC_{CuPhalaha}\text{-}5]$ fragments with similar geometrical parameters in a crystal of **1** (Figures 1, 2). Both cerium ions are

[†] Commercial reagents and solvents were used as received. The C, H, N elemental analyses were performed in the Microanalytical Laboratory of IOMC on an Euro EA 3000 elemental analyzer. The IR spectra were measured on a Perkin Elmer 577 spectrometer from 4000 to 450 cm^{-1} in a Nujol mull on KBr plates. The morphology and elemental composition were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) using a Zeiss Supra 50 scanning electron microscope (accelerating voltage, 10 kV).

Synthesis of $Ce_2(H_2O)_8[15\text{-}MC_{CuPhalaha}\text{-}5]_2Cl_6\cdot 23.5H_2O$ **1**. L-α-Phenylalaninehydroxamic acid (0.18 g, 1 mmol) was mixed with $Cu(OAc)_2\cdot H_2O$ (0.197 g, 1 mmol) and $CeCl_3\cdot 6H_2O$ (0.08 g, 0.2 mmol) in 25 ml of water. After stirring for 1.5 h, a clear dark blue solution was formed. After stirring overnight and filtering, the solution was left to evaporate slowly. Dark blue needle crystals were formed. The crystals were dissolved in water and recrystallized. Yield: 81%. IR (ν/cm^{-1}): 3376 (br.), 1583 (s), 1495 (m), 1403 (m), 1285 (m), 1179 (w), 1154 (m), 1135 (w), 1074 (m), 1025 (s), 971 (w), 935 (m), 886 (w), 847 (w), 832 (w), 765 (sh.), 740 (s), 702 (s), 566 (br.). Found (%): C, 31.01; H, 4.79; N, 8.01; Ce, 8.15. Calc. for $C_{90}H_{163}Ce_2Cl_6Cu_{10}N_{20}O_{51.5}$ (%): C, 31.08; H, 4.72; N, 8.05; Ce, 8.06.

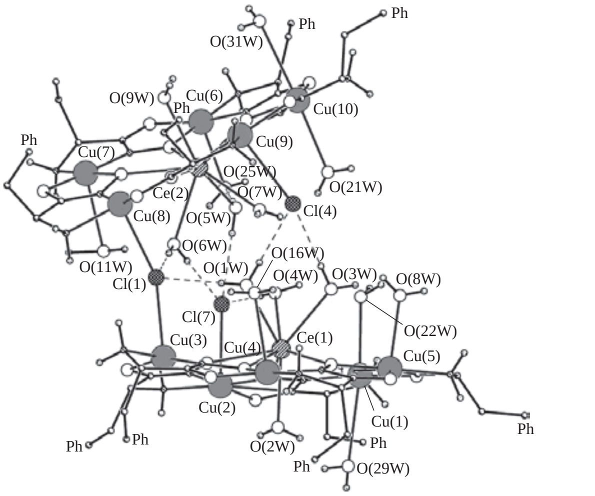


Figure 2 General view of the jaw-type sandwich structure of the $[Ce_2(H_2O)_8[15\text{-}MC_{CuPhalaha}\text{-}5]_2(\mu\text{-}Cl)Cl_2]^{3+}$ cation. The non-coordinated chloride ions, water molecules and phenyl groups are omitted for clarity. The positions corresponding to the Cl(4) and Cl(7) ions are partially occupied by chloride ions (0.77 and 0.70) and water molecules (0.23 and 0.30).

nine coordinated by five oxygen atoms of N–O groups and four water molecules [three of which are located on one side in respect to Cu(5) plane while the fourth one in the other]. The polyhedron of Ce ions is a three-capped trigonal prism. In contrast to cerium, the copper atoms in two independent metallamacrocyclic units are characterized by different coordination numbers. The Cu(1) and Cu(10) atoms are characterized by a 4 + 2 coordination environment, while all others, by 4 + 1 (Figure 2).

Furthermore, the ligands located in the apical positions of copper polyhedrons are also different [Cl^- in the case of Cu(2), Cu(3), Cu(7), Cu(8) and Cu(9) atoms and water molecules for the rest ones]. An unusual feature of **1** is the presence of a bridged chloride ion bonded with both Cu(3) and Cu(8) atoms [Cu–Cl bond lengths are 2.671(8) and 2.661(7) Å] interlinking two fragments in a jaw-like sandwich structure with chloride anion–water filling. In addition, this jaw is stabilized by hydrogen bonds of the $Cl^-\cdots H_2O$ and $HOH\cdots OH_2$ types, whose strengths can be comparable with that of the Ce–O(water) and Cu–O(water) bonds.[14] Note that the hydrogen bonding pattern is responsible for the non-equivalence of Ce–O(water) bonds [2.54(1)–2.64(1) Å] with maximum ones observed for water molecules participating in the $Cl^-\cdots H_2O$ interactions.[15] The rest chloride ions and 16 water molecules surround the sandwich in its equatorial plane assembling sandwiches into layers (parallel to the *bc* plane) with a predominantly benzyl coating. That is concerned the interlayer interaction, in addition to weak van der Waals ones (between aromatic rings) there are some weak hydrogen bonds between the coordinated water

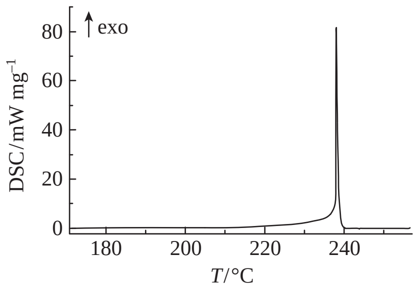


Figure 3 DSC thermogram of **1** at a heating rate of 5 K min^{-1} under nitrogen atmosphere.

situated in apical positions assembling **1** into an infinite 3D framework. Therefore, according to the X-ray data, a crystal formally contains three types of cluster ions, $Ce_2(H_2O)_8[15\text{-}MC_{CuPhalaha}\text{-}5]_2(\mu\text{-}Cl)Cl_2]^{3+}$, $[Ce_2(H_2O)_8[15\text{-}MC_{CuPhalaha}\text{-}5]_2(\mu\text{-}Cl)Cl(H_2O)]^{4+}$ and $[Ce_2(H_2O)_8[15\text{-}MC_{CuPhalaha}\text{-}5]_2(\mu\text{-}Cl)(H_2O)_2]^{5+}$, in a ratio of 0.7 : 0.07 : 0.23.

Previously, we described the advantage of analogous complexes based on glycinehydroxamic acid in hydrothermal processes for preparing nanostructured cerium–copper oxide materials on multiwalled carbon nanotubes.[16] It was established[17] that the decomposition of $Ln^{III}[15\text{-}MC_{CuRha}\text{-}5]$ complexes was accompanied by a sharp exothermal peak at 190–250 °C, which involved the oxidation of aminohydroxamic ligand by Cu^{2+}. The DSC curve of **1** (Figure 3) also shows a typical sharp exothermal peak corresponding to the oxidation of a phenylalaninehydroximate ligand by Cu^{2+}.

The hydrothermal treatment of **1** with silicon plate leads to the formation of silica nanowires. Apparently, reduction and oxidation reactions result in the formation of Si oxides and the growth of a 1D nanostructure under hydrothermal conditions at about 190 °C. Figure 4 shows the morphology of the nanowires.§ It clearly displays a high density of silica nanowires on

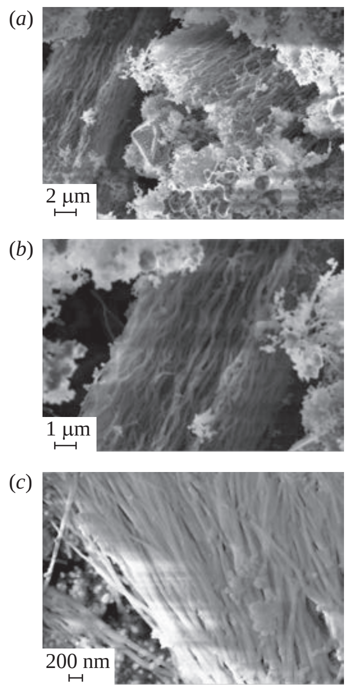


Figure 4 SEM images of the as-grown silica nanowires.

‡ *Crystal data for* **1**. At 100 K, crystals are triclinic, space group *P*1, a = 14.657(3), b = 15.627(3) and c = 17.300(3) Å, α = 82.975(4)°, β = = 90.056(4)°, γ = 62.004(3)°, V = 3464.9(11) Å^3, Z = 1, $F(000)$ = 1763, d_{calc} = 1.667 g cm^{-3}, μ = 23.46 cm^{-1}, a total of 59812 reflections ($2\theta_{max}$ > 56°) were collected, of which 32404 unique ones were used in a further refinement. The analysis of Fourier density synthesis and anisotropic displacement parameters have revealed that three of chloride ions are disordered by the four positions Cl(4), Cl(5), Cl(6) and Cl(7) due to superposition with water molecules [OC(4), OC(5), OC(6) and OC(7)]. Their occupancies were refined using EXYZ and EADP constraints. For disordered water molecules, the hydrogen atoms were not located. The refinement converged to wR_2 = 0.1885 and GOF = 1.018 for all independent reflections [R_1 = 0.0713 for 22664 observed reflections with $I > 2\sigma(I)$]. The Flack parameter is 0.03(2).

CCDC 1515195 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

§ A Supra 50VP scanning electron microscope (Carl Zeiss, Germany) equipped with an INCA EDX spectrometer (Oxford Instruments, UK) was used for the characterization of the samples. The SEM images of nanowires were obtained with an Everhardt Thornley secondary electron detector.

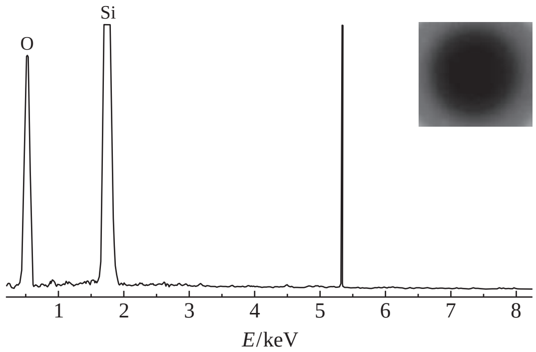


Figure 5 EDX spectrum of the nanowires. Inset: SAED pattern, which is characteristic of amorphous nanostructures.

the substrate with an average diameter of 30–50 nm and a length of 15–20 μm. The general morphology of the nanowires is very close to a bamboo-like one described previously.[18]

The crystal structure of the nanowires was examined using selective area electron diffraction (SAED). The inset of Figure 5 exhibits a SAED pattern taken in the core of the nanowires. A highly diffusive ring pattern was observed, indicating that the nanowires are completely amorphous. The elemental composition of the nanowires was evaluated using EDX spectroscopy. Figure 5 displays the EDX spectrum of the nanowires, which reveals that they are mainly composed of silicon and oxygen. In the EDX spectrum, the two dominant peak positions at 1.74 and 0.525 keV correspond to the energy pattern of the respective materials (Si, O). The Si/O atomic ratio was approximately 1/2, which is in agreement with the formation of amorphous SiO_2 nanowires.

Note that the low-temperature growth at about 190 °C allows one to perform a suitable control of the shape and length of silica nanowires. A similar alignment was already observed for SiO_2 nanowires grown using a vapor-liquid-solid mechanism at 190 °C;[19] this technique required a Ni catalyst. We used cheaper metals such as copper and cerium, and this allowed us to grow bamboo-like silica nanowires also at a low temperature of 190 °C.

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