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Periodic Arrangement of Silica Nanospheres Assisted by Amino Acids

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In the past decade, bio-inspired chemistry using intricate and organized biomolecules, such as peptides, proteins, viruses, and enzymes, has demonstrated the marvelous power for assembling and structure-directing small species into unique materials due to their highly elaborate, self-assembling capability in nature, leading to the emergence of unique physiological properties.[1−3] Recently, anionic surfactants derived from diverse amino acids have been applied to the synthesis of mesoporous materials.[4] In particular, the use of a chiral anionic surfactant *N*-myristoyl-L-alanine sodium salt enabled us to obtain a chiral mesoporous silica with a twisted hexagonal rod-like morphology.[5] The usefulness of a polypeptide as a template for assembling inorganic materials with a unique structure has also been reported.[6] These accomplishments have inspired us to use amino acids in preparing materials unique in structure.

The realm of artificial silica spheres has been extended by the emergence of an innovative synthetic method, the Stöber method, which was reported in 1968.[7] The need for silica spheres with a size of below 100 nm and two- or three-dimensionally periodic arrangement is constantly increasing because high-tech industries spur a tremendous demand for such silica spheres.[8]

Here we report the formation of the silica nanospheres with a size of 12−23 nm and with a well-ordered arrangement. Our method for forming the silica nanospheres is analogous to the so-called "Stöber method",[7] but basic amino acid monomers have been used in place of NH_3; the hydrolysis and condensation reactions of tetraethyl orthosilicate (TEOS) as a silica source were carried out in the presence of L-lysine.

Various organic amines, such as biomolecules, polyamines, and polypeptides, can catalyze hydrolysis and polycondensation of TEOS in water, leading to the formation of controlled siloxane-based materials.[9] In this study, we successfully demonstrate that a simple amino acid monomer promotes the formation of silica, resulting in preparation of the well-ordered silica nanospheres.

In a typical synthesis, L-lysine (0.146 g, 1 mmol) was dissolved in the solution containing deionized water (139 g) and octane (7.3 g) with stirring at 333 K. The pH of the resulting solution was increased to 9.2. TEOS (10.41 g, 50 mmol) was added to the mixture with stirring at 333 K. The final molar composition in the solution was 1 TEOS:0.02 L-lysine:1.3 C_8H_{18}:154.4 H_2O. The resulting mixture was stirred for 20 h at 333 K followed by being kept statically at 373 K for 20 h. Finally, the solution was directly evaporated in an oven at 373 K. Thus obtained silica was calcined in an oven at 873 K to remove organic components, such as L-lysine and octane.

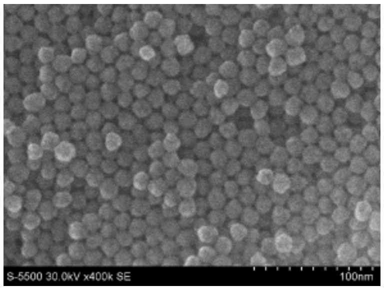

Figure 1. HRSEM image of the obtained silica spheres.

High-resolution scanning electron microscopic (HRSEM) images of the silica product revealed that each silica micro-sized block with a size of $1-3\ \mu$m consisted of uniform-sized nanospheres with a three-dimensional array (Figure S1). Interestingly, the silica nanospheres with a uniform size of around 12 nm were well ordered (Figure 1). The HRSEM image also revealed that there was a uniform nanospace between the nanoparticles, and that its size was estimated to be around 3 nm. Further structural characterizations were performed by high-resolution transmission electron microscopy (HRTEM) with the Fourier transform (FT) patterns (Figure 2a−c). From HRTEM analysis, it is concluded that the arrangement of the silica nanospheres exhibited the ccp structure, $Fm\bar{3}m$ space group. Although silica spheres with sizes of 100−200 nm have been easily obtained by the Stöber method, to the best of our knowledge, silica nanospheres with a size of 10 nm arranged in a highly regular order is unprecedented.

The X-ray diffraction (XRD) pattern of the silica nanospheres is shown in Figure 2d. This sample shows three X-ray diffraction peaks in the region of $2\theta = 0.5-2.0°$ (Cu Kα). Considering the HRTEM observations, these peaks can be indexed as the 111, 220, and 331 reflections based on the ccp structure. The nitrogen adsorption−desorption isotherms of the silica nanospheres after the removal of the organic moieties by calcination exhibit the type IV pattern (Figure S2). The BET (Brunauer−Emmett−Teller) surface area and the average pore size were found to be 228 $m^2\ g^{-1}$ and 3.2 nm, respectively. The uniform mesopores are attributed to the interstitial space between uniform-sized silica nanospheres. ^{29}Si MAS NMR measurements indicate that the product is highly condensed silica nanospheres (Figure S3).

Since the pK_a's of α-COOH, α-NH_3^+, and α-$(CH_2)_4NH_3^+$ in L-lysine are estimated to be 2.18, 8.90, and 10.28, respectively, and the isoelectric point of L-lysine is 9.74,[10] about 92% of α-$(CH_2)_4NH_2$ and 33% of α-NH_2 would be protonated under the synthesis conditions (pH 9.2). Herein, two kinds of interactions comprising the electrostatic one between anionic silicates ($\equiv SiO^-$) and protonated amino groups in L-lysine and hydrogen-bonding between L-lysine molecules could be operative. The L-lysine molecules can cover the nanosphere surface in the growth process through the interaction of their protonated amino groups with the

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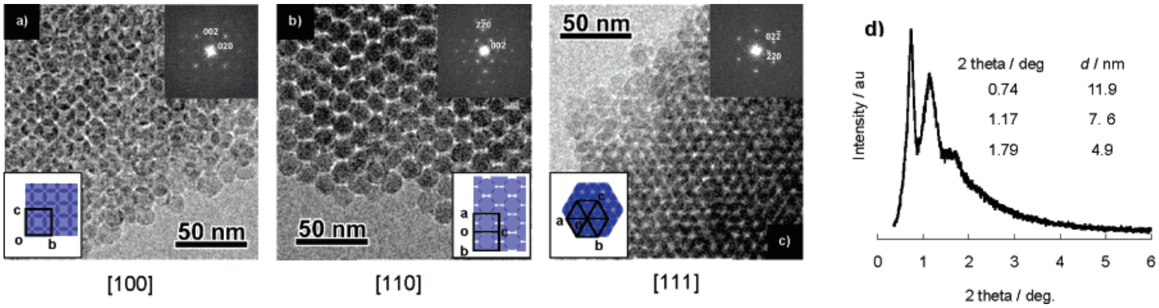

Figure 2. (a−c) HRTEM images with their corresponding FT patterns (inset) and the projection charts (inset) recorded along the [100], [110], and [111] zone axes based on a cubic closed pack (ccp) lattice, respectively. (d) XRD pattern of the obtained silica nanospheres.

silicates, leading to the control of the silica sphere size. Thus uniform-sized spheres would contribute to the well-packed structure with the assistance of the hydrogen-bonding interaction between L-lysine molecules.

TG-DTA measurements of the silica nanospheres before the calcination show the nearly same profile as that of L-lysine molecules (Figure S4). Combining the data from the CHN elemental analysis and the TG-DTA measurement of the obtained silica sample before the calcination, the contents of silica and L-lysine are estimated to be 15.02 and 0.33 mmol·g^{-1}, respectively; the molar ratio of L-lysine/SiO$_2$ is found to be 0.022, which is consistent with the starting molar gel composition.

The influence of stereoisomer of the amino acid on the formation of silica nanospheres and their arrangements was also investigated. When D-lysine was used in place of L-lysine, the obtained silica was almost similar in the structural properties to those assembled in the presence of L-lysine (Figure S5). When the mixtures of L-lysine and D-lysine with varying proportions were used, the size of the uniform nanospheres was increased with increasing proportion of the opposite optical isomer. Finally, the use of the mixture of L-lysine and D-lysine at 50/50 mol % gave well-ordered silica nanospheres with the largest size, and the size was found to be about 23 nm by HRSEM images (Figures S6). These results indicate that the size of the silica nanospheres can be finely controlled between 12 and 23 nm by varying the optical purity of the amino acid. The details of the formation mechanism of the nanospheres and their arrangements are currently being studied.

Among 20 types of essential amino acids in protein, L-lysine, L-histidine, and L-arginine are categorized as basic amino acids. We found that the use of L-arginine led to the formation of similar well-ordered silica nanospheres. On the other hand, the use of L-histidine was unsuccessful probably due to the relatively low basicity. Attempts to synthesize silica nanoparticles by using neutral amino acids, such as L-alanine and L-leucine, in combination with ammonia as a base catalyst were not successful either; XRD patterns and HRSEM images revealed that the obtained products from the control experiments were merely aggregates of silica particles without any regularity. It is concluded that the presence of amino acids with basicity, such as L-lysine and L-arginine, that have two amino groups in each molecule is indispensable for the three-dimensionally well-ordered arrangement of the silica nanospheres.

Thus obtained well-ordered silica nanospheres having three-dimensional mesopores can serve as a template for fabricating the porous carbon replica, which are materials of great interest because of their potential applications to templates, electrodes, electric double-layer capacitors, and fuel cells.[11,12] We successfully prepared a well-ordered mesoporous carbon by using the obtained well-ordered silica nanospheres as a template. HRSEM and HRTEM images of the obtained carbon replica indicate the carbon replica has well-defined mesopores with the ccp structure, $Fm\bar{3}m$ space group (Figure S7). The inverse contrast between the silica template and the carbon replica was observed, showing the exact replication of the template structure with the symmetry being kept. XRD pattern and nitrogen adsorption−desorption isotherms also support the exact replication (Figure S9).

Thus we have discovered an interesting talent of a basic amino acid monomer for assembling silica nanospheres with high regularity, leading to the formation of a novel mesoporous material. In this case, basic amino acids worked to induce the orderly three-dimensional arrangement as well as a catalyst for the formation of silica. Our approach to preparing mesostructured materials by means of assembling nanospheres with regularity is not a general liquid-crystal templating method and will stimulate the development of a new family of ordered mesoporous materials. In addition to the novel silica nanospheres, success in the preparation of the carbon replica would offer the prospects for a wide diversity of applications.

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Supporting Information Available: Details of experimental procedures and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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