論 文 の 内 容 の 要 旨

論文題目 　　Synthesis of Monodisperse Colloidal Nanoparticles and Their
　　　　　　Controlled Self-Assembly
　　　　　　　　（単分散コロイドナノ粒子の合成および配列制御）

氏　　　名　　　王 軍政

Colloidal nanoparticles (NPs) have been significant research subjects for decades. The study of these subjects can range widely from relatively simple colloidal synthesis to extremely complex assembly. Recently, colloidal NPs as building blocks for fabricating various functional nanomaterials, just like atoms are the bricks of molecules, have attracted much attention. To precisely control the self-assembly of colloidal NPs, the features of both building blocks and assemblies should be studied systematically.

Brief introduction for synthesis and self-assembly of colloidal NPs, and the structure of doctoral thesis are presented in chapter 1. Four types of colloidal NPs, including silica nanospheres (SNSs), mesoporous silica nanospheres (MSNs), hollow silica nanospheres, and metal oxide NPs are reviewed in detail. Furthermore, one-, two-, and three-dimensional (1D, 2D, and 3D) self-assemblies of colloidal NPs are introduced in this chapter.

Yokoi et al. (JACS, 2006) developed a facile method based on hydrolysis and condensation of tetraethoxysilane (TEOS) with amino acid (e. g., lysine) under weakly basic condition (pH ~9.8) in liquid–liquid (TEOS–water) biphasic system for synthesis of uniform colloidal SNSs. It is effective for precisely controlling the SNSs size and polydispersity. Syntheses of various colloidal NPs containing SNSs, MSNs, and hollow silica nanospheres, as building blocks for the assembly are described in chapter 2. A modified approach, in which primary amine is used as a catalyst for the synthesis of uniform SNSs in liquid–liquid (TEOS–water) biphasic system at relatively high pH conditions (10.8–11.4), has been developed. The size of SNSs can be tuned from 12 to 36 nm by changing the initial pH values of the aqueous phase in reaction mixtures. This biphasic reaction method is applied to synthesize MSNs. Discrete MSNs with a narrow size distribution can be prepared by using biphasic reaction system containing TEOS, water, cationic surfactant, and primary amines under basic conditions (pH 11.3–11.5). The MSNs with diameter in the range of 15 to 30 nm have uniform mesopores about 3 nm in size. The size of the mesopores can be finely tuned by

changing the initial pH of the solution, or by the addition of pore expanding agent, *N, N*-dimethylhexadecylamine. Finally, a facile synthesis method for preparing hollow silica nanospheres with size of about 20 nm and cavity diameter of about 7 nm has been developed by using block copolymer F127 as a soft template in the presence of basic amino acids under neutral condition (pH ~7.5).

Monodisperse colloidal SNSs synthesized by primary amine have been chosen as the starting building blocks for investigating 3D self-assembly process. In chapter 3, the influences of chemical additives on the 3D self-assembly of SNSs are demonstrated. Yokoi et al. (JACS, 2006) reported that uniform SNSs synthesized by basic amino acid assembled into well-ordered nanostructure (face-centered-cubic). For example, SNSs with diameter about 20 nm assemble into close packed SNSs arrays possessing about 5.8 nm interparticle mesopores. In this chapter, SNSs arrays with large interparticle mesopores about 13 nm are observed upon solvent evaporation of as-synthesized sol in the presence of primary amine. This indicates that loosely packed nanostructure are formed. In contrast, SNSs arrays having smaller mesopores in the range of 4.7−6.8 nm are achieved with the aid of the organic buffer or a basic amino acid, lysine. It is suggested that the chemical additives with the ability to maintain relatively strong repulsive interaction until the final stage of evaporation play a vital role in the fabrication of well-ordered SNSs arrays.

In chapters 4 and 5, 1D self-assembly of SNSs with basic amino acids in liquid phase is described. The detailed study of amino acid−assisted 1D assembly of SNSs is discussed in chapter 4. A facile solution process for the preparation of anisotropic silica nanoparticles (ASNPs) is presented in chapter 5. ASNPs are prepared via controlled self-assembly of spherical silica seeds (22 nm) in alcohol−water solution, followed by *in situ* fixation and overgrowth with TEOS. Ethanol and arginine are used to modify the dielectric constant and ionic strength of the reaction media, by which seed assembly is controlled through the adjustment of electrostatic interaction. Ethanol and arginine also serve as a cosolvent and a catalyst for hydrolysis and condensation of TEOS, respectively, which enables us to produce ASNPs in a simple one-pot process. In addition to ASNPs with wormlike structures, different kinds of NPs (bimodal spherical NPs, monodisperse spherical NPs, and spherical aggregates) have also been obtained by changing the concentrations of ethanol and arginine. The length, thickness, or both of ASNPs are controlled systematically by varying the concentrations of arginine, seed NPs, and TEOS. Other alcoholic cosolvents, such as methanol, 1-propanol, 2-propanol, and *t*-butanol, are also effective to give ASNPs when the dielectric constant of the alcohol−water mixed media is properly adjusted, showing the versatility of the present method.

Previously, Fukao et al. (JACS, 2009) found that SNSs (ca. 15 nm) synthesized by basic amino acid (lysine) assembled into 1D chain-like nanostructure in the liquid phase with the aid of an amphiphilic block copolymer, F127. However, the formation mechanism of 1D chain-like nanostructure and the role of lysine playing in the 1D self-assembly have not been clarified yet. In an effort to confirm the role of lysine in the 1D assembly process, the experiments on 1D self-assembly of lysine-free SNSs are investigated in chapters 6 and 7. It is shown in chapter 6 that 1D chain-like nanostructure is formed at different pH conditions when changing the type of silica sols. The optimal pH of lysine-free system is not consistent with the pH in the case of lysine. It suggests that lysine is not indispensable for 1D self-assembly of SNSs. It seems that ionic strength of the suspension affects the interparticle interaction, leading to a minor shift in the optimal pH. Instead of the addition of HCl for pH adjustment, dialysis of suspension against distilled water is performed to adjust pH. The dialyzed silica sols without containing amino acid can also assemble into 1D chain-like nanostructure. These findings suggest that fine-tuning of the interparticle interaction by using dialysis method is also effective for preparing 1D chain-like nanostructure. This method can be applied to other types of silica NPs with different surface properties, such as MSNs, which is summarized in chapter 7.

The dialysis method is applied for assembly of other metal oxide colloids into 1D as presented in chapter 8, since basic amino acids are not indispensable for 1D self-assembly of NPs with block copolymer. Titanium oxide NPs are used as building blocks for 1D self-assembly, because titanium oxide NPs are widely studied owing to their broad applications and it is extremely difficult to assemble them into 1D nanostructure in aqueous system. Monodisperse titanium oxide sol is prepared by acid peptization. Dialysis method is used to adjust the pH for controlling the charge density of NPs' surface. After dialysis to the proper pH, F127 is introduced into the titanium oxide sol. 1D nanostructure can be formed after heat treatment of this sol for several days. The effects of pH, the amount of F127, and the heating time are investigated systematically. Finally, it is found that oriented attachment proceed between adjacent NPs in aqueous system.

The driving force for 1D self-assembly of SNSs with block copolymer may be related to depletion interaction in the system. The free micelles of block copolymer are formed in the suspension, and this micelle-mediated depletion interaction may be one of the driving forces for 1D self-assembly. To validate this hypothesis, other water soluble polymers (e. g. polyvinyl alcohol, polyvinylpyrrolidone) that can not form micelle in the solution are examined in chapter 9.

Finally, chapter 10 presents general conclusions and future perspectives of this doctoral thesis.