Fabrication and Functionalization of Inorganic Materials Using Amphiphilic Molecules

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Abstract: In this review, the synthesis of inorganic materials with various properties using amphiphilic molecules is examined. Amphiphilic molecules are used for the formation of highly ordered mesostructures and the surface modification. Two examples of the mesostructures are crystalline mesoporous titania (TiO₂) and the novel visible light responsive mesostructured titania modified with dye in the pores, which can be fabricated using the molecular self-assemblies of amphiphiles as templates. Surface modification using amphiphilic molecules enables the construction of self-assembled arrays of silica particles and the preparation of a film that can control adsorption/desorption behavior of bovine serum albumin (BSA) by light irradiation.

Key words: mesoporous materials, surface modification, photocatalyst, amphiphilic molecules

1 Introduction

Amphiphilic molecules have a variety of properties such as the ability to form molecular self-assemblies in solution, specific adsorption on solid surfaces, and solubilization. Because of these properties, amphiphilic molecules have been used in the toiletry, cosmetics, and food industries. In addition, they enable to provide a reaction field, control the structures of materials, and change the surface properties of materials.

Controlling the structural properties of materials is an important technique in fabricating materials with innovative functions. Porous materials have garnered considerable attention because of the chemical and physical properties originating from the pore structure. Many reports describe traditional and novel pore materials such as zeolite, metal-organic framework (MOF) materials, porous carbon materials. Template materials for pore structure formation have also been investigated. These templates are roughly classified into "hard" and "soft" materials, which use inorganic and organic compounds, respectively. Self-assembled amphiphilic molecules have been one of the most widely used soft template materials. Mesoporous materials prepared using molecular self-assemblies of amphiphiles as templates are applicable as catalysts, separatory materials, and adsorbents owing to their high surface area, uniform pore size, and highly ordered pore structure. Recently, they have also been investigated as materials for biological applications, such as carriers for drug delivery systems and scaffolds for immobilizing biomolecules.

Surface modification using silane coupling agents, which can work as amphiphiles, is well known as a classical technique to create functionalized surfaces with specific characteristics due to silane coupling agents and the original properties of the materials. The investigations on surface modification for improved dispersive stability have been reported. In this case, silane coupling agent plays an important role in improving their compatibility with dispersion medium. This improvement results from the interaction between the dispersion medium and the terminal functional group of silane coupling agent. This also means that the surface design of materials using this technique can allow control of the adsorption/desorption properties by adjustment of the interaction between various molecules and the silane coupling agent.

This review describes the synthesis and functionalization of inorganic materials by applying a soft template system and a surface modification technique using amphiphilic molecules. The former describes the synthesis of functionally novel mesostructured materials using one of the typical materials, and the latter describes the surface modification.
cationic amphiphiles. The latter approach is the control of adsorption and desorption behavior at the surface of the inorganic materials modified with amphiphilic molecules.

2 Fabrication of nanostructured inorganic materials using amphiphilic molecules

2.1 Preparation of crystalline mesoporous materials using molecular self-assembles of amphiphilic molecules as templates

The walls of mesoporous materials are generally amorphous, and crystallization through heat treatment results in decreased surface area due to the collapse of the uniform mesopore structure. Thus, various methods have been investigated to produce mesoporous materials with a crystalline wall. Katou et al. reported on a crystalline mesoporous material that was prepared by calcination after coating the pores of an amorphous mesoporous material with carbon. Kapoor et al. showed that mesoporous organic-silica hybrid particles with a crystalline wall could be synthesized using organic-inorganic hybrid molecules as silica precursors. However, the methods mentioned so far require complicated processes when compared to the fabrication of amorphous mesoporous materials. Ozin et al. described that mesoporous titania thin films with an anatase wall could be fabricated by the calcination of thick-walled amorphous mesoporous materials synthesized using triblock copolymers as template materials. This process required calcination for the crystallization of titania (TiO₂).

On the basis of this background, direct synthesis of crystalline mesoporous materials has been investigated by applying a low-temperature crystallization technique. Titania, a well-known n-type semiconductor, was used for the wall of these mesoporous materials. Titania can be applied as a photocatalyst to remove hazardous organic compounds due to holes and electrons generated by UV light irradiation. Two of the most important factors affecting the photocatalytic activity of titania are crystallinity and surface area. Therefore, mesoporous titania with a crystalline wall would be a novel and useful material applicable to high-performance photocatalysts.

Titanium oxysulfate sulfuric acid hydrate (TiO₃SO₄·xH₂SO₄·xH₂O) and cetyltrimethylammonium bromide (CTAB) were used as a titania precursor and a template material for mesopore formation, respectively. Particles were obtained by stirring the CTAB and TiOSO₄ mixture for 24 h. When stirred at room temperature, the wall of the obtained mesostructured material was amorphous. Calcination led to the collapse of the uniform mesostructure by crystallization of the titania. Then, when the reaction temperature was changed from room temperature to 333 K, the particles were mesostructured titania with an anatase crystalline wall containing CTAB in the pores. Finally, calcination at 723 K for 2 h was performed to remove CTAB. Although the regularity of the mesostructure had declined, the titania particles maintained their uniform mesostructure even after the removal of CTAB by calcination (Fig. 1).

After the particles were synthesized, their photocatalytic activity was investigated. 2-propanol was used as a reaction substrate to investigate photocatalytic activity, since it is oxidized to acetone only by a photocatalytic reaction on the titania surface. In the dark, the concentration of 2-propanol initially decreased without producing acetone. This concentration change was due to adsorption onto large surface area of the mesoporous titania particles. UV light irradiation resulted in the production of acetone, in addition to the consumption of 2-propanol. The concentration changes of both 2-propanol and acetone under visible light irradiation followed the same trend as those under UV light irradiation. These results indicate that the obtained crystalline mesoporous titania had good adsorbability and photocatalytic activity under both UV and visible light irradiation.

Direct synthesis of a novel crystalline mesoporous titania was demonstrated using a low-temperature crystallization technique. This unique method was also effective for the direct synthesis of crystalline mesoporous zirconia (ZrO₂), which can act as a solid acid catalyst. This methodology could be important in the future synthesis of crystalline nanostructured inorganic materials.
2.2 Fabrication of mesostructured titania particles modified with dye in the pores using molecular self-assemblies with solubilized dye as a template

Titania is used as an important material in the electrodes of solar cells. In this case, the surface of titania is modified with a dye, which can work as a visible light absorber. Electric energy can be produced by the transfer of electrons from the dye to the titania electrode under visible light irradiation. Recent reports have described that when titania particles in aqueous media containing a dye are irradiated with visible light, the dye molecules are decomposed by the electrons transferred from the dyes to the titania particles. This suggests that novel visible light responsive photocatalysts can be synthesized using the principle of a dye-sensitized solar cell. The preparation and photocatalytic activity of titania modified with dyes have been investigated. In this system, photolysis of the dye that acts as a visible light absorber by the reduction reaction remains an important problem to be solved.

Mesostructured titania particles modified with dyes in the pores shown in Fig. 2 will be a novel photocatalysts with photocatalytic activity under visible light irradiation due to the photo-induced reduction reaction at the titania surface by the electrons transferred from the dyes to titania. This reaction scheme shows that photo-induced decomposition of the reaction substrates occurs only at the outer surfaces of the mesostructured titania particles, without decomposition of the dyes present in the pores, which acts as a visible light absorber. However, uniform introduction of the dyes into the pores after the framework formation was difficult due to their low dispersibility. Here, one of the most important properties of surfactants is solubilization. The use of molecular self-assemblies of surfactants solubilized dyes as a template enables uniform introduction of the dyes into the pores. Then, fabrication of mesostructured titania particles modified with dye in the pores using molecular self-assemblies of surfactants containing dye, and their photocatalytic activity under visible light irradiation were investigated.

In this fabrication, TiOSO₄ and CTAB were used as the titania precursor and the template material for mesostructure formation, respectively. Phthalocyanine (Pc) was used for modifying the pores. Fig. 3 shows the schematic illustration of this reaction process. Pc was added to an aqueous solution of CTAB, and stirred at room temperature for 24 h. This Pc/CTAB solution was uniformly blue, and Pc was solubilized by the CTAB molecules. Then, the CTAB aqueous solution containing Pc was mixed with a TiOSO₄ aqueous solution and stirred at room temperature for 24 h. At this point, the Pc/CTAB aqueous solution mixed with TiOSO₄ was colorless and transparent. After stirring, sky

Fig. 2 Schematic illustration of the mesostructured titania particles modified with dyes in the pores.

Fig. 3 Photographs and schematic illustrations of the process for the fabrication of the mesostructured titania particles modified with Pc.
blue particles having uniform mesostructures were formed. This indicated that Pc was absent in the aqueous media and located in the pores of the mesostructured titania particles. These results clearly showed that the mesostructured titania particles modified with Pc in the pores could be synthesized using molecular self-assemblies of surfactants solubilized Pc as a template.

Next, the photocatalytic activity of the mesostructured titania particles containing Pc was investigated under visible light irradiation. Methyl orange (MO) was chosen as the reaction substrate because its absorption band is different from that of Pc. Mesostructured titania particles modified with Pc were added to MO aqueous solution and stirred at room temperature for 15 min in the dark. Then, the particles were filtrated and dried at 373 K for 1 h. The sample was obtained by mixing the dried particles with KBr, and then irradiated with visible light (>610 nm) to investigate the photocatalytic activity. The absorption of MO decreased with increasing irradiation time, whereas the absorption of Pc remained unchanged. This means that the decrease in absorption of MO was due to the reduction reaction of electrons transferred from Pc to titania. These results clearly showed that mesostructured titania particles modified with Pc in the pores are a novel visible light responsive photocatalyst that allows for the selective photolysis of MO the electrons transferred from Pc.

Preparation of the novel dye-sensitized photocatalyst and its photosensitization and charge separation abilities were demonstrated. This photo-functional material can also be applied to the electrode of a dye-sensitized solar cell. This methodology and concepts for its design will be important in the synthesis of future photo-functional materials.

3 Creation of functionalized inorganic materials surfaces using modification with silane coupling agents

3.1 Self-assembled arrays of silica particles on functionalized templates fabricated from mixed Langmuir-Blodgett films

The Langmuir-Blodgett (LB) technique has been used to fabricate organic ultrathin films with well-defined structures. Phase separation at the nanometer scale often occurs in mixed LB films, resulting in various structures such as circles, wires, and spirals. These structures can be controlled by adjusting intermolecular interactions. In particular, the phase separated structures of the mixed LB films containing amphiphilic silane coupling agents can be immobilized on substrates having surface hydroxyl groups. This occurs through the formation of covalent bonds between the surface hydroxyl groups and the silane coupling agents. Then, the films can be used as templates for the accumulation of various compounds after the immobilization of the phase-separated structures. Previous reports clearly demonstrated methods for the synthesis of the functionalized templates. Fig. 4(a) shows an AFM image of a phase-separated functionalized template. This AFM image shows the presence of 1-5 μm sized disk domains. The circular domain and the surrounding regions were modified with silane coupling agents having amino and trifluoromethyl groups, respectively. A functionalized template with nanowire structures has also been fabricated (Fig. 4(b)).

Self-assembled arrays of silica particles were investigated using the functionalized templates shown in Fig. 4(a) and (b). Silica particles (size: 70 nm) whose surfaces were modified with bovine serum albumin (BSA) were used. Fig. 4(a’) shows an AFM image of the functionalized template after immersion into a silica particle dispersion. The silica particles selectively adsorbed on the circular domain. In the same way, a nanowire pattern was formed on the functionalized templates fabricated from mixed LB films. These films had phase-separated nanowire structures when immersed in a silica dispersion (Fig. 4(b’)). The stability of the self-assembled arrays of silica particles was also investigated by ultrasonication in ethanol for 1 min. The patterns of the silica particle arrays remained unchanged even after ultrasonication. These results clearly revealed that the stable self-assembled arrays of silica particles could be fabricated on functionalized templates with circular and nanowire patterns.

The formation of self-assembled arrays was explained by
mainly considering the local zeta potential of the functionalized templates. The pH of the silica dispersion was about 6. The BSA-modified silica particles surface was negatively charged in the dispersion because of the dissociation of carboxylic groups. Aminos groups in the domain region of the functionalized templates were positively charged at around pH = 6. The rest of the functionalized template surface was covered with trifluoromethyl groups and was negatively charged. Electrostatic attractive forces between the silica particles and the amino groups resulted in the formation of self-assembled arrays of silica particles only in the region covered with amino groups.

The construction of self-assembled arrays of silica particles on the patterns reflecting the structures of the functionalized templates fabricated from phase-separated mixed LB films was demonstrated. The patterned silica particles on the functionalized templates were strongly adsorbed by the electrostatic attractive force between the carboxylic groups of the silica particles and the amino groups on the functionalized templates. In addition, the pattern of silica particle arrays could be controlled through the phase-separated structures of the original mixed LB films. This method can be a powerful tool for the fabrication of patterned arrays of nanoparticles.

### 3.2 Fabrication and BSA adsorption/desorption properties of titania/silica composite films modified with amphiphilic molecules

The results mentioned so far clearly show that control of the electrostatic interaction between the carboxylic groups of BSA and the amino groups on the functionalized templates enables the formation of patterned self-assembled arrays of silica particles. This suggests that BSA can be adsorbed and immobilized on the surface of inorganic oxide materials modified with silane coupling agents having amino groups as terminal functional groups.

Titania is well known as a photocatalyst that can also allow for control of wettability due to the formation of superhydrophilic surfaces under UV light irradiation. Based on this, titania/silica composite films were modified with silane coupling agents containing amino groups. The BSA adsorption/desorption properties under light irradiation were also investigated.

Titania/silica composite films were synthesized by spin-coating a suspension of titania particles and tetramethoxysilane on glass substrates, followed by calcination for 6 h at 723 K. The obtained films were immersed in an N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA-Si) methanol solution for 24 h at room temperature and then dried for 12 h at 393 K.

The BSA adsorption/desorption properties were investigated by immersing the composite films in a BSA dispersion for 3 h at room temperature in the dark. The samples were characterized after the BSA adsorption treatment by FT-IR measurements using the attenuated total reflectance (ATR) technique along with contact angle measurements. After these measurements, the samples were immersed into a BSA dispersion for 3 h at room temperature either in the dark or under light irradiation from their bottom side. Then, ATR/FT-IR and contact angle measurements were carried out again.

Figure 5 shows a schematic illustration of the BSA adsorption/desorption property experiments, ATR/FT-IR spectra, and contact angles. The contact angle of the composite film first immersed in the BSA dispersion was higher than that of the film modified with EDA-Si. In the ATR/FT-IR spectrum of the composite film after BSA adsorption treatment, the peaks assigned to N-H stretching vibration, C = O stretching vibration and N-H deformation vibration of BSA appeared at around 3300, 1650, and 1540 cm\(^{-1}\) respectively. These results indicated that BSA adsorption occurred on the composite films.

After BSA adsorption treatment, the films were immersed in a BSA dispersion either in the dark or under light irradiation. The contact angles after immersion in the dark were almost the same as that of the film after the BSA adsorption treatment, and the contact angles of the light irradiated film were lower. Although the ATR/FT-IR spectrum of the film after immersion in the dark had three clear peaks assigned to BSA, the intensities of these peaks decreased after light irradiation. These results showed that BSA was adsorbed on the film in the dark and desorbed from the film under light irradiation. This means that the composite films modified with silane coupling agents having amino groups can control BSA adsorption/desorption behavior through light irradiation.

In this system, the adsorption of BSA occurred in the dark due to the electrostatic attractive force between the carboxylic groups of BSA and the amino groups of silane coupling agents on the composite film. Photoinduced superhydrophilicity resulted in the desorption of BSA from the composite film. Surface modification with silane coupling agents having various terminal functional groups has been used for the separation of amino acids. This methodology can aid the preparation of novel separation materials for biomolecules using photoinduced superhydrophilicity and the interactions between the biomolecules and terminal functional groups of the silane coupling agents. Our research group has also been investigating the fabrication of cell sheets using these composite films.

### 4 Conclusion

This review demonstrates techniques for the synthesis and functionalization of inorganic materials using amphiphilic molecules. The use of molecular self-assemblies of amphiphiles has allowed for the fabrication of crystalline forms.
mesoporous titania particles and the novel visible light responsive mesostructured titania particles modified with Pc in the pores. Surface modification using silane coupling agents allowed functionalization of inorganic material, which in turn can facilitate control of the adsorption/desorption behavior. These techniques using amphiphiles can be applied not only to titania but also to other inorganic materials. In addition, different combinations of amphiphiles and inorganic precursors show promise in the synthesis of inorganic materials with various structures and specific characteristics. These methods and concepts using amphiphilic molecules would be important in the fabrication of functionalized inorganic materials.

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