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To cite this article: Yoshiyuki Kuroda and Kazuyuki Kuroda 2008 Sci. Technol. Adv. Mater. 9 025018

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Layer-by-layer assembly of imogolite nanotubes and polyelectrolytes into core-shell particles and their conversion to hierarchically porous spheres

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Received 31 January 2008
Accepted for publication 2 March 2008
Published 24 July 2008
Online at stacks.iop.org/STAM/9/025018

Abstract
Core-shell particles were prepared by the layer-by-layer (LbL) assembly of imogolite (IMO) nanotubes and poly(sodium 4-styrenesulfonate) (PSS) on polystyrene particles (diameter: 800 nm) coated preliminarily with poly(diallyldimethylammonium chloride) (PDDA). PSS and imogolite were alternately adsorbed on the particles to form core-shell particles with one to three bilayers of PSS/IMO. Macroporous hollow spheres were formed by removing polystyrene cores via heat treatment or extraction when the number of bilayers was 2 or 3. The sample formed by extraction (the number of bilayer was 3) showed only macroporosity and PSS remained in the shell, whereas the heat-treated sample showed hierarchical micro- and macroporosities. When the diameter of polystyrene particles decreased from 800 nm to 300 or 100 nm, hollow spheres were deformed because of the increase in the relative length of imogolite nanotubes against the size of polystyrene particles. Imogolite is a promising building block of hierarchically porous materials with core-shell morphologies using LbL assembly.

Keywords: hierarchically porous materials, layer-by-layer, colloidal templating, core-shell particles, hollow spheres, imogolite, nanotubes

1. Introduction

Many porous materials have been investigated for their diverse applications including adsorption, catalysis, and separation [1–3]. The preparation of materials with hierarchically organized pores is an important issue for the development of porous solids for much higher diffusion, and easier accessibility of guest species onto reactive sites within pores, among other [4]. There are many reports on the preparation of hierarchically porous materials via various templating methods, such as colloidal templating [5–11], the combination of surfactant templating and substrate patterning [12, 13], and the use of biomimeralization processes [14, 15]. To design hierarchical architectures, the use of monodispersed colloidal particles of polymers and silica as sacrificial templates (colloidal templating) is quite useful because highly ordered and well-defined macropores are formed by this method and the morphology of products can be varied as monoliths, films, and particles [16–21]. Although the method using both colloidal particles and surfactants as templates is applicable to the formation of hierarchically porous materials with various compositions,
the structural control of the formed materials is limited because of complex interactions among templates [6, 22]. The use of building blocks with inherent nanopores within their structures is another useful approach to forming multimodal architectures [9–11, 23, 24]. For example, zeolites are widely used building blocks with microporosity [10, 23]. A unique structural control has also been achieved using nanosheets, prepared by exfoliating layered materials, as an anisotropic building block [25].

Layer-by-layer (LbL) assembly is useful for fabricating hierarchically porous materials with highly organized architectures [26–28]. Various positively or negatively charged polyelectrolytes and/or colloids are adsorbed alternately on flat or curved surfaces depending on the type of electrostatic interaction [29–31]. By combining colloidal templating and LbL assembly, macropore walls have been precisely designed. The wall thickness, structure, and composition of macropore walls can be tailored by tuning LbL processes. For example, the combination of nanosheets and nanoparticles provides micro- and mesoporosities in macropore walls by the LbL process [11]. In this case, however, the micro- and mesopores come from nanospaces among nanosheets and nanoparticles. Therefore, the porosities are not well defined. In order to design multimodal porous materials, the use of a building block with well-defined porosities within its structure is important.

Nanotubes are one of the most promising building blocks for LbL assembly because they have a well-defined 1D-microchannel within their structure, and random pores among their bundles [32, 33]. There are several reports on LbL assembly using nanotubes, such as hydrated halloysite [34], titanate nanotubes [35], and carbon nanotubes [36]. However, the porosities of the final products have not been discussed.

In this study, we focused on imogolite as a nanotubular building block. Imogolite (IMO) is an aluminosilicate nanotube with a composition of Al₂SiO₅(OH)₄ with 1 and 2 nm in inner and outer diameters, respectively, and several hundreds of nanometer in length [37, 38]. There are micropores within nanotubes and mesopores among nanotubes [33], so that imogolite is a promising adsorbent [33, 39], catalyst [40] and catalyst support [41]. Surface modifications of imogolite [42, 43] have also been investigated, and modified and unmodified imogolites have been used as intercalating species into clays [44, 45] and as nanofillers for nanocomposites with polymers [46]. We previously reported the fabrication of hierarchically porous materials composed of imogolite by replicating close-packed polystyrene particles via direct infiltration, confirming the formation of materials with micro-, meso- and macroporosities [9].

By using LbL assembly, the amounts of cationic and anionic species of products are controlled, resulting in the control of the thickness of the formed shells. Imogolite can be used as polycationic species because of the protonation of the outer surface aluminol groups under acidic conditions [47]. Here, we report the fabrication of core-shell particles via the LbL assembly of poly(sodium 4-styrenesulfonate) (PSS) and imogolite on polystyrene particles coated preliminarily with poly(diallyldimethylammonium chloride) (PDDA). Macroporous hollow spheres were formed through the removal of polystyrene cores. To the best of our knowledge, this is the first report on the use of imogolite for LbL assembly, although imogolite/pepsin conjugate [48] and microtubes composed of imogolite and polyelectrolytes fabricated using ionic interactions of imogolite [49] have been reported recently.

2. Experimental

2.1. Starting materials

Sodium orthosilicate was purchased from Junsei Chemical Co., Ltd. AlCl₃, nitric acid, and sodium chloride were purchased from Kanto Chemical Co., Inc. Sodium hydroxide, 0.1 M hydrochloric acid, concentrated sulfuric acid, and toluene were purchased from Wako Pure Chemical Ind. Ltd. Polystyrene particles (Uniform Latex Particle 10 wt.% aqueous dispersion with diameters of 0.835, 0.298, and 0.115 µm) were purchased from Seradyn Inc. The size of the particles has a certain distribution; here, the diameters are rounded off to 800, 300, 100 nm, respectively. Polystyrene particles were dispersed in deionized water and stirred for 10 min, followed by centrifugation (at 20 000 rpm for 10 min). Poly(sodium 4-styrenesulfonate) (Mw: 70 000) and a 20 wt.% aqueous solution of poly(diallyldimethylammonium chloride) (Mw: 100 000–200 000) were purchased from Sigma-Aldrich Co. An aqueous solution containing 1 mg ml⁻¹ PDDA and 0.5 M NaCl, whose pHe was adjusted to 3.5 by adding 1 M HCl, was used for PDDA adsorption. NaCl was added to the PDDA solution for PDDA to form a random coil, which leads to the formation of a thick PDDA layer [50]. A solution (pH 3.5) containing PSS plus 0.5 M NaCl and a sol (pH 3.5) containing 0.7 mg ml⁻¹ imogolite were used for the adsorptions of PSS and imogolite, respectively. A 0.1 M NaCl solution (pH 3.5 adjusted by adding 1 M HCl) was used to wash the core-shell particles. Si (100) wafers were purchased from Shin-Etsu Chemical Co., Ltd. They were cut into 1 cm × 1 cm pieces and immersed in concentrated H₃SO₄ overnight and washed with copious deionized water before use.

2.2. Synthesis of imogolite

The imogolite used in this study was synthesized according to the literature [9, 38, 51, 52]. 20 mM Na₂SiO₄ (250 ml) was added to 30 mM AlCl₃ (250 ml), and the resulting solution was stirred for 30 min. The pH of the precursor solution was adjusted to 6.7 by adding to 1 M NaOH dropwise (1.0 ml min⁻¹), and then precipitates formed. NaCl in the precipitates was removed by repeated centrifugation and washing with deionized water three times. The centrifuged precipitates were dispersed in deionized water (500 ml) and 1 M HNO₃ (2 ml) was added. Imogolite sol was obtained after refluxing the suspension at 95°C for 5 d. Imogolite was flocculated at pH 9.5 by adding 1 M NaOH to the sol. NaNO₃ in the imogolite gel was removed by three cycles of centrifugation and washing with deionized water. The imogolite gel was dispersed again in water, the concentration
being adjusted to 0.7 mg ml\(^{-1}\), and the pH was adjusted to 3.5 by adding 0.1 M HCl. The formation of imogolite (dried powder) was confirmed by XRD analysis, FT-IR, SEM, and TEM. The width of the synthetic imogolite nanotubes was estimated to be ca. 2 nm and they formed bundles 10–20 nm in width.

2.3. Layer-by-layer adsorption of polyelectrolytes and imogolite on polystyrene particles

Polystyrene particles (ca. 100 mg) were dispersed in a PDDA solution (15 ml) and stirred for 30 min to coat the surface with PDDA. A general procedure for the adsorption of polyelectrolytes was employed according to the literature [10, 11, 29], and it was also applied to imogolite adsorption. PSS and imogolite were adsorbed alternately onto polystyrene particles coated with PDDA. The adsorption was repeated three times to fabricate core-shell particles with one to three bilayers of PSS/IMO. The samples with 1, 2, and 3 bilayers are denoted C\(_1\), C\(_2\), and C\(_3\), respectively. Core-shell particles were collected as ca. 1 wt.% aqueous dispersions and the samples (C\(_1\), C\(_2\), and C\(_3\)) were cast on Si and glass substrates, and air-dried. Core-shell particles with 3 bilayers, using 300 and 100 nm polystyrenes as cores, were also prepared in the same procedure (denoted C\(_3\)_300 and C\(_3\)_100, respectively).

2.4. Removal of polystyrene cores

Polystyrene cores in C\(_1\), C\(_2\), and C\(_3\) were removed by heat treatment at 500 °C for 2 h in air atmosphere (denoted H\(_1\), H\(_2\), and H\(_3\), respectively) or by extraction with toluene for 1 d (denoted E\(_1\), E\(_2\), and E\(_3\), respectively). Polystyrene cores in C\(_3\)_300 and C\(_3\)_100 were also removed by the same procedures of heat treatment and extraction (denoted H\(_3\)_300 and H\(_3\)_100, and E\(_3\)_300 and, E\(_3\)_100, respectively).

2.5. Characterization

Powder XRD patterns were obtained using a Bruker AXS MXP3 diffractometer with monochromated CuK\(\alpha\) radiation (40 kV, 30 mA). FT-IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer using a KBr disk technique. The transmittance of the spectra was normalized by the band at 698 cm\(^{-1}\) corresponding to the out-of-plane ring deformation of polystyrene [53, 54]. The morphologies of imogolite, core-shell particles, and hollow spheres were observed by FE-SEM (JEOL JSM-6500F) (the samples were coated with Pt before the observation) and TEM (JEOL JEM-2010 with an acceleration voltage at 200 kV). TG data were recorded using a Rigaku TG8120 instrument at a heating rate of 10 °C min\(^{-1}\) in a dry air flow. Residual weight heated up to 900 °C was used for the evaluation of the amount of imogolite adsorbed. CHN analysis was performed using a Perkin-Elmer PE-2400II apparatus. N\(_2\) adsorption-desorption isotherms were measured using a Quantachrome Autosorb-1 apparatus. Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method using the volume of N\(_2\) adsorbed in the relative pressure range from 0.05 to 0.10. Pore size distribution was calculated by the Saito-Foley method [55]. Microporous surface area and micropore volume were calculated by the t-plot method.

3. Results and discussion

3.1. Core-shell particles

The FT-IR spectra of the core-shell particles (C\(_1\), C\(_2\), and C\(_3\)) are shown in figure 1. Absorption bands assigned to polystyrene were observed [53, 54]. Although most of the bands corresponding to PSS are similar to those of polystyrene, PSS is distinguished from polystyrene by the characteristic bands at 1129 and 1155 cm\(^{-1}\) (SO\(_3^−\) asymmetric stretching vibrations). The spectrum of pure imogolite (figure 1(d)) shows the lattice vibrations containing Si-O stretching vibrations at 935 and 995 cm\(^{-1}\) and various Al-O vibrations at 425, 500, 565, 595, and 685 cm\(^{-1}\) [56, 57]. The band at 980 cm\(^{-1}\) observed in the spectra of C\(_1\), C\(_2\), and C\(_3\) are attributed to the Si-O stretching vibration and the bands at 425 and 500 cm\(^{-1}\) to the Al-O vibration. The band due to the Si-O vibration was not split because it overlaps with the bands due to polystyrene and PSS. The results show the presence of polystyrene, PSS, and imogolite in the core-shell particles.

The stepwise adsorption of imogolite and PSS is supported by the increase in the absorbance of the bands corresponding to the Si-O stretching vibration of imogolite and the SO\(_3^−\) asymmetric stretching vibrations of PSS with a number of bilayers. The increase in the amount of imogolite with the number of bilayers (table 1), as determined by TG, also strongly supports LbL assembly. The adsorbed amount of imogolite in the third bilayer was relatively lower than those of the first and second bilayers. Although the reason for

Figure 1. FT-IR spectra of core-shell particles (a) C\(_1\), (b) C\(_2\), and (c) C\(_3\), and (d) imogolite.
shows the FT-IR spectra of the sample obtained by extraction (E3) and the heat-treated sample (H3). The bands corresponding to imogolite and remaining PSS were observed for the E3 spectrum (figure 4(b)), and no shift of the band corresponding to the Si-O stretching vibration was observed. Therefore, E3 is composed of imogolite and PSS, which is reasonable because polystyrene particles are the only soluble component in toluene. Although polystyrene particles were almost extracted, the sharp band at 698 cm$^{-1}$ is assignable to a small amount of residual polystyrene. Although the PDDA content could not be assessed by FT-IR, PDDA may remain in E3 because of its hydrophilicity.

On the other hand, the band due to the Si-O stretching vibration at about 980 cm$^{-1}$ shifted to 1060 cm$^{-1}$ after heat treatment, indicating the conversion from octahedral aluminum to tetrahedral aluminum through imogolite dehydroxylation [37] (figure 4(b)). No band corresponding to PSS or polystyrene was observed, and the carbon content was 0.5% (CHN analysis). Therefore, H3 is basically composed of dehydroxylated imogolite. The crystal structure of imogolite in E3 and H3 cannot be discussed, because no diffraction peaks corresponding to imogolite were observed even in the XRD profiles of the core-shell particles (data not shown), which may be due to the low imogolite content. However, our previous study [9] showed that extraction with toluene has no effect on the imogolite structure, suggesting that the crystal structure of imogolite is retained in E3, which is consistent with the FT-IR spectrum.

The FE-SEM images of E3 and H3 (figure 5) show a hollow spherical morphology of the samples. When the number of bilayers was 1, the spherical shells collapsed after both extraction (E1) and heat treatment (H1) (data not shown), which is consistent with the results of a study using silica nanoparticles as the inorganic component in the shells [28]. When the numbers of bilayers were 2 and 3, the spherical shells were retained after both extraction (E2 and E3) and heat treatment (H2 and H3). However, the structural difference caused by the number of bilayers is unclear, which is probably due to the incomplete coverage of the third bilayer. In the literature using silica nanoparticles [28], the shells were successfully formed up to 5 bilayers because the high charge density and small size (diameter: ca. 25 nm) of silica nanoparticles are suitable for LbL assembly, although the nanoparticles have no pores. On the other hand, the morphology of H3 becomes less spherical than that of E3,
Figure 3. TEM images of core-shell particles (a) C1, (b) C2, and (c) C3, and their corresponding magnified images (insets).

Figure 4. FT-IR spectra of samples formed by (a) extraction E3 and (b) heat treatment H3.

probably owing to the shrinkage induced by heat treatment. The TEM images of E3 and H3 (figure 6) also confirmed that the cores were removed by both extraction and heat treatment.

3.3. Hierarchical porosities in hollow spheres

Macropores inside the shells of E3 and H3 are distinct in the SEM and TEM images. E3 has neither micro- nor mesoporosities, as determined by nitrogen adsorption measurement. This is because the porosities of imogolite in E3 cannot be changed [9], being blocked by residual PSS. The nitrogen adsorption-desorption isotherm of H3 is shown in figure 7. The specific surface area of H3 was estimated to be 292 m² g⁻¹ and the value is similar to that of imogolite. The total pore volume of such macroporous materials, which shows no plateau in a high-relative-pressure region, cannot be determined [58]. The micropore volume of 0.073 cm³ g⁻¹ was estimated by the t-plot method. The pore size distribution (figure 7, inset) of H3, determined by the SF method, shows
Figure 6. TEM images of samples formed by (a) extraction E3 and (b) heat treatment H3.

a narrow distribution of micropore size centered at 0.51 nm. The average inner diameter of imogolite heat-treated at 650 °C for 3 h was reported to be 0.65 nm, as determined by TEM, [59] being similar to that estimated here. Therefore, the hierarchical porosity of H3 with micropores from imogolite and macropores inside the shells were confirmed. A hysteresis loop, similar to the H3 type (IUPAC classification), suggests the presence of slitlike pores [58], and the formation of such mesopores should be due to aggregates of imogolite bundles and PSS in this case.

3.4. Influence of polystyrene particle size

The FE-SEM images (figure 8) of the samples (E3_300, H3_300, E3_100, and H3_100) show a hollow spherical morphology for H3_300 and E3_300, whereas such a morphology was only partially observed for H3_100 and E3_100. Many fibrous components on the particles are observed in the images of the heat-treated samples (H3_300 and H3_100) (figures 8(b) and (d)). The length of imogolite bundles relative to the size of polystyrene particles increases with a decrease in the diameter of polystyrene particles, which is not appropriate for the formation of hollow spheres.

3.5. Uniqueness of materials prepared by LbL assembly of imogolite and polyelectrolytes

In our previous study [9], macroporous films with micro- and mesoporosities in macropore walls were fabricated by the infiltration of imogolite into the void space of a film composed of arranged polystyrene particles. In such a case, the amount of imogolite in macropore walls was not controlled and the morphology of the samples was limited to the film. On the other hand, the amount of imogolite in macropore walls can be tuned via LbL assembly in the present method. In fact, the retention of the shells after the removal of polystyrene cores can be controlled by adjusting the number of PSS/IMO bilayers. The products are obtained as particles in this study because imogolite adsorbed onto coated polystyrene particles in liquid phase. There are some examples of film formation of macroporous materials prepared via LbL assembly [23, 60]. Therefore, the present method can be extended to the fabrication of films. The polyelectrolytes used in this study block the micro- and mesopores of imogolite. Consequently, the previous infiltration method that does not use binding polymers has its own advantage. The LbL assembly utilized here is a promising technique for fabricating hierarchically porous materials with core-shell morphology using imogolite in macropore walls. Compared with other building blocks, such as zeolite nanocrystals [10, 23] and nanosheets [11], imogolite can provide unique well-defined micropores and possibly mesopores among bundles.

The materials formed via the LbL assembly of imogolite and polyelectrolytes are promising matrices for biomaterials
such as proteins. A hybrid hydrogel composed of imogolite and pepsin is formed by the interaction between the Al-OH group of imogolite and the phosphoric group of pepsin \[48\]. Accordingly, LbL assembly in the present method can be applied to the formation of a heterogeneous catalytic system with a macroporous architecture. Inner straight channels of nanotubes can be regarded as separate and independent single straight nanopores. Because various nanotube assemblies may produce unique porous architectures, LbL assembly using nanotubes is crucial for porous materials design.

4. Conclusions

The LbL assembly of imogolite is a promising technique for fabricating hierarchically porous materials with micro- and macroporosities. Core-shell particles and macroporous hollow spheres can be prepared by this method and the morphological variation is expected by tuning the LbL processes. Consequently, the electrostatic self-assembly of imogolite by ionic interactions with polyelectrolytes is very useful and important for materials design.

Acknowledgments

The authors thank Dr K Takahashi and Mr M Fuziwara (Kagami Memorial Laboratory for Materials Science and Technology, Waseda University) for the SEM and TEM observations, and Prof Y Honda and Prof T Asahi (Consolidated Research Institute for Advanced Science and Medical Care, Waseda University) for the zeta potential measurement. This work was conducted as part of the Global COE Program of MEXT ‘Center for Practical Chemical Wisdom’. This work is supported by the A3 Foresight Program ‘Synthesis and Structural Resolution of Novel Mesoporous Materials’ from Japan Society for the Promotion of Science (JSPS). This work is also supported by a Grant-in-Aid for
Scientific Research on Priority Areas (New Materials Science Using Regulated Nano Spaces -Strategy in Ubiquitous Elements) from MEXT, Japan.

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