Solid-Phase Synthesis of Amphiphilic Dendron-Surface-Modified Silica Particles and Their Application Toward Water Purification

Chih-Chien Chu,[†] Norio Ueno,[‡] and Toyoko Imae*[,†]

Graduate School of Science and Technology, Keio University, Hiyoshi, Kohuku-ku, Yokohama 223-8522, Japan, and Material Science Research Center, Shiseido Co. Ltd., Hayabuchi, Tsuzuki-Ku, Yokohama 224-8558, Japan

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Surface modification of silica particles by an amphiphilic poly(amido amine) (PAMAM) dendron and investigation of their advanced application toward water purification have been demonstrated. The amphiphilic dendron-surface-modified silica particles (C18GnS, $n = 1-3$) were prepared by solid-phase synthetic strategy including the propagation of PAMAM dendrons on silica surface through conventional divergent pathway and the end-group functionalization of dendrons by long aliphatic chains. Infrared absorption analyses confirmed the characteristic vibration modes of amide and methylene groups on the dendritic backbone and long alkyl peripherals, respectively. The gradual increasing amount of organic grafts determined by thermogravimetric and elemental analyses also supported the successful modification of amphiphilic dendron on the silica surface. C18GnS effectively adsorbed anionic targets such as organic dyes and surfactants in water, and the adsorption behavior obeyed a Langmuir adsorption isotherm. Moreover, the adsorption isothermal studies indicated that adsorption of surfactants on C18GnS was due to the assistance of hydrophobic interaction between the aliphatic peripherals on the dendron and the alkyl tail on the surfactant, while the electrostatic interaction with C18GnS mainly played a role for the adsorption of dyes. Anionic adsorbates were released from C18GnS in an alkaline environment because of the pH-dependent nature of PAMAM dendron, and thus the surface-modified silica particles were recovered and reused.

Introduction

Dendrimers, which are well-defined hyperbranched polymers, attract much attention as one of the key materials in nanoscale science because of their unique characteristics including a roughly spherical structure, loosely packed interior pockets, and functional end groups.[1] Thus numerous studies of dendrimers as DNA vector, drug carrier, reaction catalyst, metal chelator, and so on were intensively explored in recent years.[2] However, because the synthesis of dendrimers involves a series of repetitive steps, the construction of dendrimers will be a tedious and time-consuming work. Moreover, large excesses of monomers required to drive the complete reaction may render subsequent purification difficult. Therefore, adopting solid-phase techniques is an alternative to generating these dendrimers via a quick and simple process.[3] In 1997, Swali et al.[4] pioneered the solid-phase synthesis of poly(amido amine) (PAMAM) dendrons from polystyrene−poly(ethylene glycol) resin beads (TentaGel). Then Tsubokawa et al., Bourque et al., and Sakai et al.[5] described the grafting of PAMAM dendrons on the silica, which was prefunctionalized by 3-aminopropyltriethoxysilane, and they proposed potential applications of dendron-grafting silica to catalytic reaction and size exclusion chromatography. Later on, Bu et al.[6] suggested that an inevitable “cross-linking” reaction occurring in the amidation process could generate the structural defect in the propagation of PAMAM dendrons on silica. Thus, although the solid-phase strategy is slightly difficult for generating dendrimers or dendrons bearing perfect symmetrical branch structure, it provides a convenient approach to dendritic graft polymers onto various inorganic nanostructures such as silica, titanium dioxide, and magnetic nanoparticles through the solid−liquid reaction.[7]

One of the unique characteristics of dendrimers is an ability to act as host for trapping guest molecules, due to functionality of tailored core, interior, and terminals.[8] For example, the binding constant between pyrene and second generation

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* Corresponding author. TEL/FAX: +81-45-566-1799. E-mail: imae@educ.cc.keio.ac.jp.

[†] Keio University.

[‡] Shiseido Co. Ltd.

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PAMAM dendrimer in aqueous media has been found to be 1.6×10^5 M^{-1}, and the similar result has also been reported for diaminobutane poly(propyleneimine) (DAB-PPI) dendrimers.[9] In this connection, scientists synthesized "water-insoluble" amphiphilic dendrimers, bearing hydrophilic interior and lipophilic periphery, for the removal of organic pollutants from water.[10–12] Cooper et al.[10] demonstrated the effective extraction of a hydrophilic compound from water into supercritical CO_2 using fluorinated DAB-PPI dendrimers. Maurice et al.[11] showed effective liquid–liquid extraction of various water-soluble organic dyes into propadecyl-terminated DAB-PPI dendrimers. Arkas et al.[12] supported that DAB-PPI dendrimers with octyl and octadecyl periphery acted as "nanosponges" for the removal of polycyclic aromatic hydrocarbons from water down to ppb order. Therefore, on the basis of these observations, amphiphilic dendrimers should be a promising candidate for water purification. However, there is a disadvantage like tedious separation of amphiphilic dendrimers from entrapped pollutions or extraction media. Thus, the development of efficient pollutant extractors like a solid phase adsorbent is expected.

In the present study, porous silica particles were first modified by low generations (G1−G3) of PAMAM dendrons via divergent pathway[13] and then treated with an *n*-octadecyl isocyanate (ODI) reagent to yield "amphiphilic silica particles" bearing the hydrophilic dendron surface moieties and the hydrophobic long aliphatic peripheral moieties on the silica. Since porous silica modified by organic molecules acts as an effective adsorbent to remove organic or heavy metal pollutants from wastewater as a result of their high loading capacities,[14] we studied the solid phase extraction, instead of conventional liquid–liquid extraction, eliminating the typical water pollutants such as organic dyes and surfactants by using the amphiphilic silica particles as the adsorbents. The utilization of these novel amphiphilic dendron-surface-modified silica particles as a solid phase extractor for water purification provided processes of efficient adsorption, easy separation, and useful recovery.

Experimental Section

Materials. Methyl acrylate (MA) and ethylenediamine (EDA) were purchased from Tokyo Chemical Industry, Japan, and ODI was obtained as technical grade from Aldrich Chemical, U.S.A. Dehydrated methanol, toluene, and hexane were purchased from JUNSEI Chemical, Japan. For the adsorption tests, methyl orange (MO), ethidium bromide (EB), and sodium dodecylbenzenesulfonate (SDBS) were purchased from Wako Chemical, Japan. As cationic surfactants, benzyldimethyltetradecylammonium chloride and 1-dodecylpyridium chloride were obtained from Tokyo Chemical Industry and Aldrich Chemical, respectively. All reagents were used without further purification. Ultrapure water (Millipore Milli-Q) was used throughout all experiments.

Preparation of Dendron-Modified Silica Particles. Aminopropyl-surface modified silica particles (APS) were kindly given by Shiseido Powder Material & Formulation Research Laboratory, Yokohama, Japan. The average particle size, pore size, and specific surface area of APS were 5.0 μm, 8.5 nm, and 460 m^2/g, respectively (Figure SI1–3, Supporting Information). The spherical morphology of silica was observed by scanning electron microscopy (SEM) (Figure SI2, Supporting Information). The content of primary amino groups in APS determined by elemental analysis was 1.53 mmol/g silica. Propagation of PAMAM dendrons on APS was followed by a conventional divergent procedure.[15] For the construction of methyl ester-terminated PAMAM dendron-modified silica particles [$(n + 0.5)$th generation particles, G$(n + 0.5)$S], a large excess of MA was slowly added into a methanol solution of APS or amino-terminated PAMAM dendron-modified silica particles (*n*th generation particles, GnS), and then the mixture was reacted at 40 °C with mild stirring under N_2 inert atmosphere. After 72 h, the solvent was filtrated, and the remaining silica particles were repeatedly rinsed by methanol. The products were dried under vacuum to yield G$(n + 0.5)$S ($n = 1, 2$) as white fine powder. GnS ($n = 1-3$) was synthesized from G$(n + 0.5)$S by the same procedure, only a large excess of EDA was introduced as a monomer instead of MA.

Preparation of Amphiphilic Silica Particles. The following is the general procedure for the preparation of octadecyl-terminated *n*th generation PAMAM dendron-modified silica (C18GnS, $n = 1-3$). A toluene solution of 2-fold excess of ODI relative to the nitrogen contents on GnS, determined by elemental analysis, was added into a toluene solution of GnS particles through a syringe filter (pore size: 0.20 μm, Advantec), and then the mixture was reacted at 50 °C with mild stirring under N_2 inert atmosphere. After 4 h, the excess ODI was quenched by methanol with stirring for 1 h. The solvent was then filtrated, and the remaining silica particles were thoroughly rinsed by toluene and hexane. The products were dried under vacuum to yield amphiphilic silica particles (C18GnS, $n = 1-3$) as white fine powder.

Characterization of Surface Modified Silica Particles. The characteristic functional groups of silica samples were analyzed by a Nicolet 6700 FT-IR spectrometer. The organically grafted amounts on silica particles were measured by a Seiko EXSTAR 6000 TG/DTA thermogravimetric analyzer. Using 300 cm^3/min airflow, the silica samples were first heated at 110 °C for 10 min to remove residual solvents and water on the surface, and then the temperature was raised to 700 °C, which was sufficiently high to

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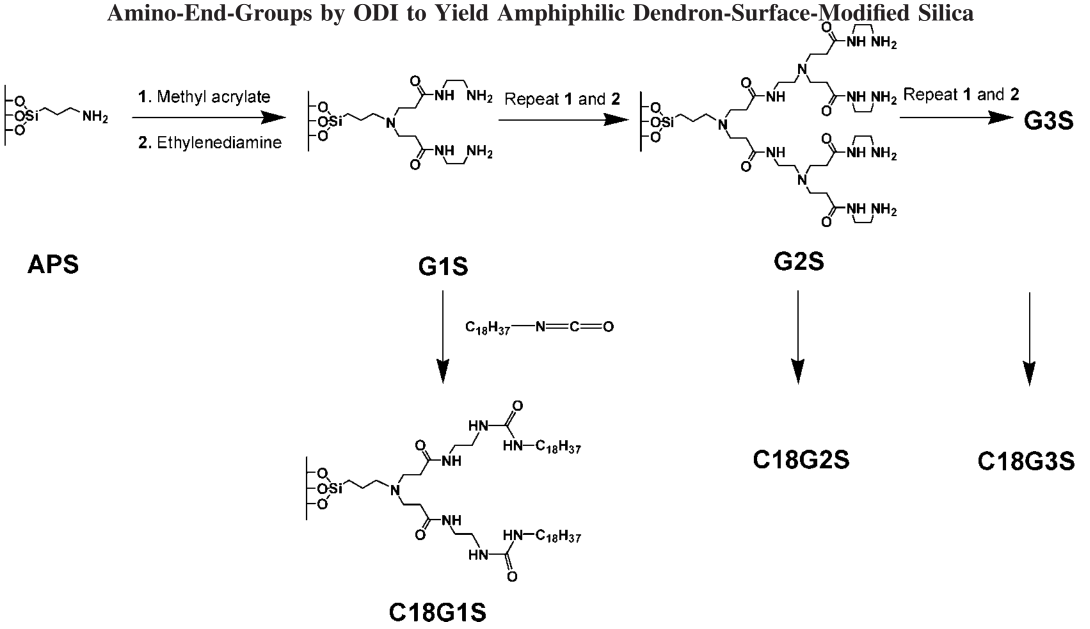
Scheme 1. Construction of PAMAM Dendrons on Silica Surface via Conventional Divergent Pathway and Modification of Amino-End-Groups by ODI to Yield Amphiphilic Dendron-Surface-Modified Silica



remove all organic moieties,[16] at a constant rate of 5 °C/min. The carbon and nitrogen contents on the modified silica particles were determined by a PerkinElmer 2400 series II CHNS/O elemental analyzer. *N*-Phēnylacetamide was used as the calibration standard, and the measurement for each silica sample was repeated three times.

Adsorption Experiments. For the isothermal adsorption studies, 1 mM of anionic adsorbates, that is, MO or SDBS, in water were prepared as stock solutions, and then 1 cm^3 of the adsorbate solutions ranging from 0.1 mM to 1 mM were mixed with 2.5 mg of C18GnS sample in the 1.5 cm^3 microtubes. After being shaken overnight, C18GnS was allowed to precipitate by centrifuge, and the supernatants were analyzed by a Shimadzu BioSpec-1600 Ultraviolet–visible (UV–vis) spectrometer to determine the concentration of nonadsorbed adsorbates from absorbance of an absorption band at 465 and 224 nm for MO and SDBS, respectively.

Results and Discussion

Synthesis and Characterization of Amphiphilic Dendron-Surface-Modified Silica Particles. Scheme 1 shows the reaction pathway for the preparation of amphiphilic dendron-surface-modified silica particles, bearing hydrophilic PAMAM dendron interiors and hydrophobic long aliphatic chain peripheries. The preparation of PAMAM dendron moieties from APS involves repetitive Michael addition and amidation reactions. After the construction of PAMAM dendrons on silica particles, ODI was introduced for the modification of end-groups of dendrons to long aliphatic chains through the formation of urea bonding. Fourier transform infrared (FT-IR) absorption spectrometry, thermogravimetric analysis (TGA), and elemental analysis were performed to verify the chemical structure of grafted PAMAM dendrons on silica surface.

FT-IR spectra of G1S, G2S, and G3S showed distinct absorption bands at 1650 and 1560 cm^{-1}, which were assigned to the characteristic vibration modes of amide groups in PAMAM dendrons (Figure 1). The increasing intensity of amide bands followed the propagation of dendrons from G1 to G3, in comparison with a siloxane (Si−O−Si) band at 1100 cm^{-1}. The result suggested the successful divergent reaction on the silica surface. After the surface amino terminals on G1S, G2S, and G3S were capped with long aliphatic chains, FT-IR absorption spectra of C18G1S, C18G2S, and C18G3S shown in Figure 1d−f, respectively, revealed absorption bands at 2930 and 2850 cm^{-1}, which were assigned to the methylene stretching vibration modes of long aliphatic chains.

The TGA profiles of G3S and C18G3S are shown in Figure 2. A remarkable degradation before 270 °C was assigned to the thermal decomposition of aliphatic peripheries, which were covalently linked to PAMAM dendron through urea bonding. The thermal degradation before 450 °C was attributable to the decomposition of the PAMAM dendritic backbone, involving the retro-Michael process and

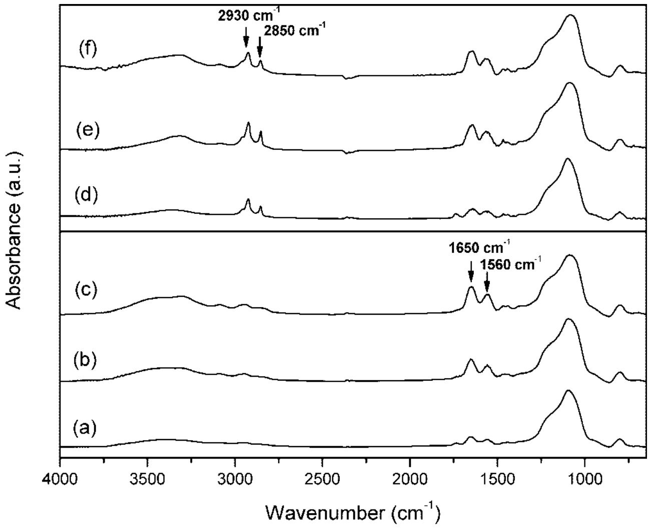


Figure 1. FT-IR absorption spectra of PAMAM dendron-modified silica: (a) G1S, (b) G2S, (c) G3S, (d) C18G1S, (e) C18G2S, and (f) C18G3S.

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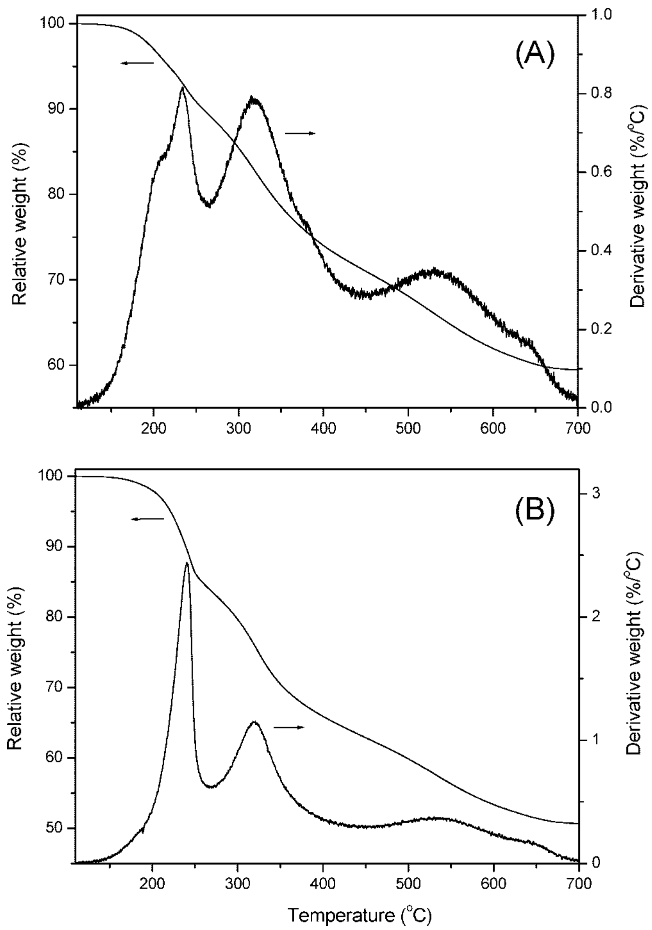


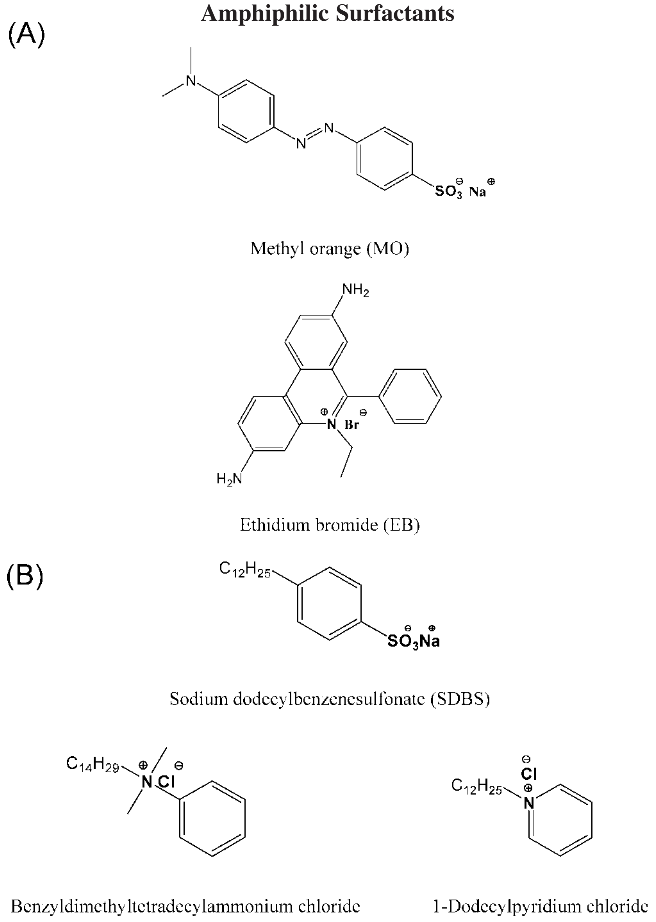
Figure 2. TGA of PAMAM dendron-surface-modified silica: (A) G3S, (B) C18G3S.

Table 1. Characteristics of APS and PAMAM Dendron-Modified Silica Particles

silica	grafted amounts[a] (wt %)	C^b (wt%)	N^b (wt %)	C/N[c]
APS	10.6	6.9	2.1	3.8 (3.0)
G1S	30.9	13.9	4.1	3.9 (2.6)
G2S	50.2	18.0	6.7	3.1 (2.5)
G3S	68.4	22.5	8.7	3.0 (2.3)
C18G1S	62.6	25.8	4.1	7.3 (7.3)
C18G2S	83.2	30.1	6.6	5.3 (6.4)
C18G3S	97.2	32.0	8.3	4.5 (5.6)

[a] Organically grafted amounts on silica particles were determined from thermogravimetric results, as the decomposed weight/residual (SiO_2) weight at 700 °C × 100, which corresponds to amount based on 1 g of SiO_2 [b] Carbon and nitrogen contents in organically modified silica particles were determined by elemental analyses. [c] The C/N values represent the molar ratio of carbon to nitrogen. The data in parentheses denote the calculated values of the perfect propagation of organic moieties on silica particles.

Chart 1. Chemical Structures of Various Ionic Adsorbates for Amphiphilic Silica Particles: (A) Organic Dyes, (B) Amphiphilic Surfactants



transamidation.[17] In addition, the decomposition of moieties oxidized by the airflow occurred at temperatures up to 700 °C. The thermal behaviors of G3S and C18G3S were similar to each other, although the grafted amounts of organic moieties calculated from the weight difference between 110 and 700 °C on TGA were different (Table 1, where the grafted amounts on APS, GnS, and C18GnS ($n = 1-3$) were listed). The grafted values increased from $n = 1$ to 3 and after octadecyl-termination, indicating the successful construction of amphiphilic PAMAM dendrons on silica surface.

As listed in Table 1, the carbon (C) and nitrogen (N) contents of GnS determined by elemental analysis increased with generation, and octadecyl- termination resulted in an increase in carbon content and a slight decrease in nitrogen content for C18GnS. These results confirmed the successive growth of the dendron generation and the successful modification of end groups with long aliphatic moieties. However, C/N ratios of GnS were higher than the calculated values. The result demonstrates the undesirable structural defect of PAMAM dendrons on silica particles. It can be suggested that the reduction of nitrogen contents resulted from a side reaction as well as the regular amidation process. According to the previous study,[6] the side reaction (cross-linking of neighboring methyl ester groups) occurring in amidation process from ($n + 0.5$)th to nth generation dendrons generated the structural defects, significantly inhibiting the construction of dendrons on silica. Meanwhile, as a result of the imperfect dendron construction on the silica surface, the content of the long alkyl terminals on C18GnS decreases, inducing the lower intensity of the methylene stretching vibration bands of C18GnS in FT-IR analyses (Figure 1).

Adsorption of Water-Soluble Organic Adsorbates. On the basis of the FT-IR absorption bands, TGA analysis, and elemental analysis, it is evident that the surface of silica particles was successfully modified by the "amphiphilic dendrons", composed of the lipophilic aliphatic terminals and

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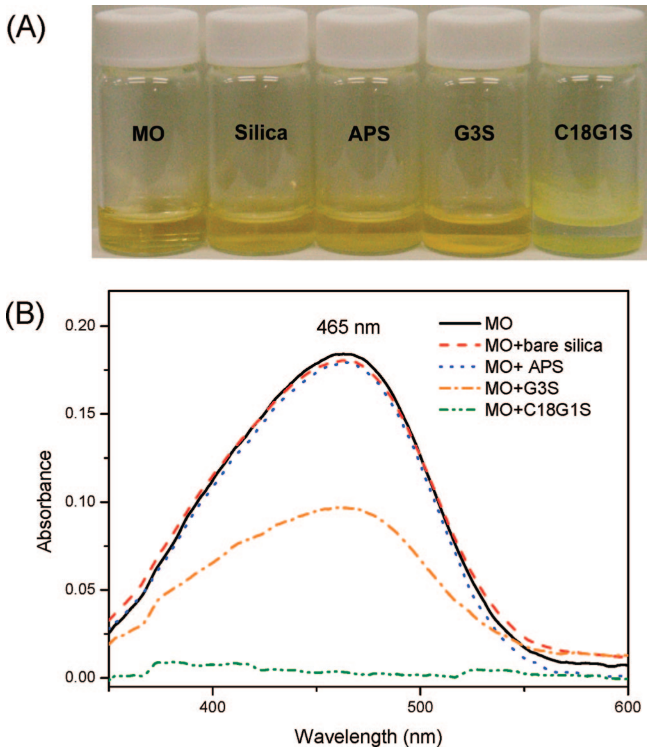

Figure 3. (A) Visual observation and (B) UV–vis absorption spectra of supernatants after adsorption examination from an aqueous solution (5 cm^3) of 10^{-2} mM MO on 10 mg of bare silica (dashed line), APS (dotted line), G3S (dashed-dotted line), and C18G1S (dashed-dotted-dotted line) in comparison with a solution of free MO (solid line).

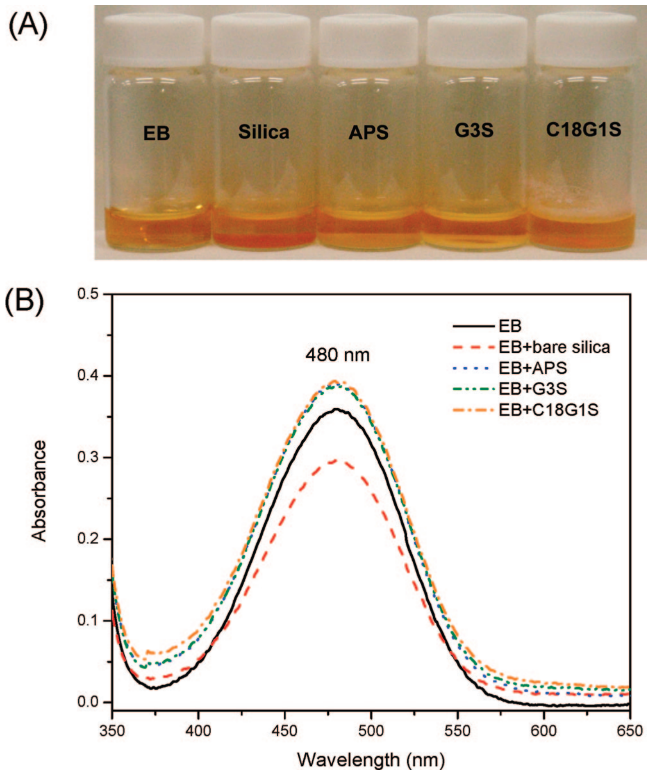

Figure 4. (A) Visual observation and (B) UV–vis absorption spectra of supernatants after adsorption examination from an aqueous solution (5 cm^3) of 10^{-2} mM EB on 10 mg of bare silica (dashed line), APS (dotted line), G3S (dashed-dotted-dotted line), and C18G1S (dashed-dotted line) in comparison with a solution of free EB (solid line).

hydrophilic PAMAM dendron interior. Since porous silica and amphiphilic dendrimers themselves possess high loading capacities and host–guest affinity, respectively, the amphiphilic dendron-modified silica particles potentially can be the efficient adsorbents to remove organic compounds in water and are regarded as the solid phase extractor for water purification. Besides, after adsorbing organic compounds, amphiphilic silica particles can be easily separated from an aqueous medium by filtration or centrifugation. To examine the adsorption ability, cationic C18G1S was immersed into aqueous solutions of two organic dyes, which were anionic MO and cationic EB (Chart 1). Additionally, bare silica, APS, and G3S were also mixed with both dyes in water as the control experiments. After equilibrating for overnight, as shown in Figure 3A, the medium in the mixture of MO with C18G1S turned colorless, different from that in the mixture with bare silica, APS, or G3S. It was clarified from UV–vis absorption spectroscopic analyses (Figure 3B) that MO was completely adsorbed by C18G1S and partially adsorbed by G3S, while MO was adsorbed by neither silica nor APS. On the contrary, as seen in Figure 4, EB was unable to be adsorbed by any modified silica particles and was only partially adsorbed by bare silica particles.

On the basis of the fact that silica itself and any organically modified silica particles carry high densities of negative and positive charges, respectively, in neutral water, it is first suggested that silica particles examined do not adsorb water-soluble coionic dyes due to the electrostatic repulsion. Second, bare silica and APS were unable to trap effectively even water-soluble counter-ionic dyes, suggesting that the electrostatic interaction is not necessarily enough. Because the dye molecules have high mobility unlike surface-bonded silanol and amino groups, they favor to be solved in water rather than to be adsolved on the silica particles. However, once the silica particles were modified by dendritic polymers, they are indeed very efficient for the adsorption of anionic dyes in neutral water. It is mentioned that anionic dyes are energetically favorable to be trapped and then stabilized in the interior nanocavities of dendritic polymers through host–guest affinity besides electrostatic attraction. Moreover, the hydrophobic long alkyl terminals of dendron also dominate the adsorption behavior of organic dyes on dendron-modified silica particles. Amphiphilic C18G1S exhibits better adsorption ability toward anionic dye than cationic G3S does, although G3S has abundant amino groups, which are charged positively in neutral water, in contrast to C18G1S. This fact supports that the formation of the hydrophobic shell layer on nanocavities as a host assists the retention of organic guests more predominantly than the electrostatic interaction does.

Ionic surfactants shown in Chart 1 were also selected as the adsorbates for amphiphilic silica particles. UV–vis absorption spectra (Figure 5) indicated that anionic alkylbenzenesulfonate (SDBS) was efficiently adsorbed on amphiphilic silica particles differently from bare silica and APS. Figure 6 shows the variation of adsorption yields of SDBS versus quantities of C18GnS. The adsorption yields were calculated from absorbance at a 224 nm absorption band. The adsorption efficiency toward SDBS was best for C18G1S and decreased with increasing dendron generation, although

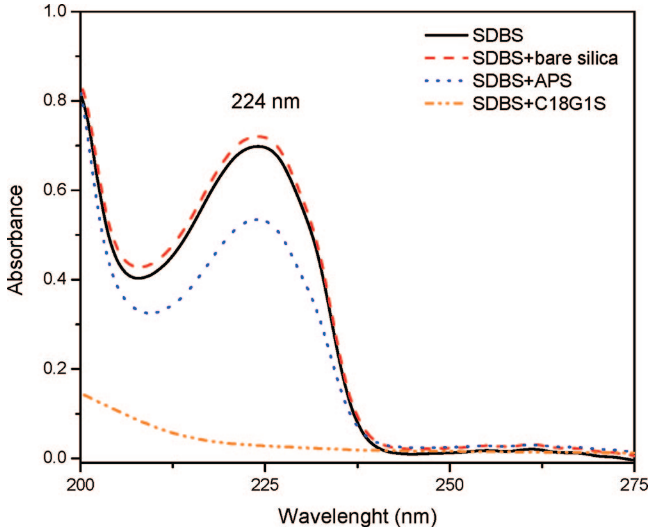

Figure 5. UV–vis absorption spectra of supernatants after adsorption examination from an aqueous solution (5 cm^3) of 10^{-2} mM SDBS on 10 mg of bare silica (dashed line), APS (dotted line), and C18G1S (dashed-dotted-dotted line) in comparison with a solution of free SDBS (solid line).

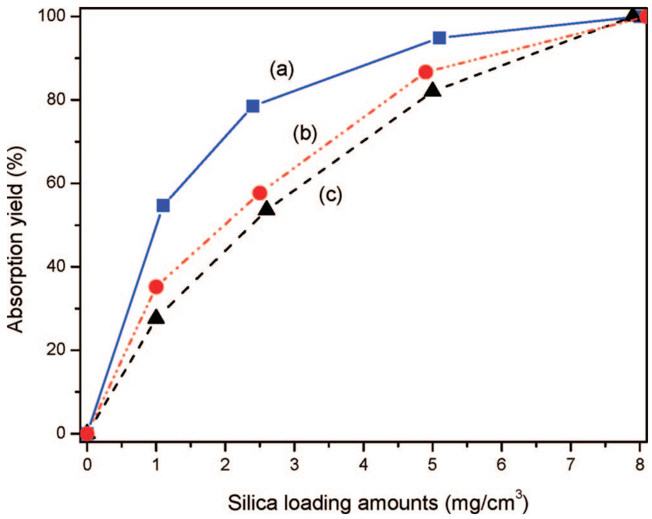

Figure 6. Plot of adsorption yield of SDBS versus quantity of amphiphilic silica particles: (a) C18G1S, (b) C18G2S, and (c) C18G3S.

the adsorption of SDBS (0.17 mg/cm^3) increased with loading amount of silica particles, as expected, and saturated at 8 mg/cm^3 of particles. On this adsorption, although SDBS molecules interact with silica particles by hydrophobic as well as electrostatic attraction, the former attraction must be stronger than the latter.

As seen in Figure 7, the adsorption efficiency of two cationic surfactants (benzyldimethyltetradecylammonium chloride and 1-dodecylpyridium chloride) on amphiphilic silica particles decreased, as the generation of dendron increased. In other words, C18G1S adsorbed a certain amount of cationic surfactants, but C18G3S did scarcely. Moreover, the effect of generation on the adsorption of cationic surfactants was more drastic than a case of anionic surfactant (Figure 6). It is supposed that the electrostatic repulsion between C18G1S and cationic surfactants is unable to suppress perfectly the adsorption resulting from the strong hydrophobic interaction between the long alkyl tails on the surfactants and the *n*-octadecyl peripheries on amphiphilic silica particles; nevertheless, a large number of positive charges on C18G3S give rise to the strong electrostatic repulsion toward cationic surfactants and then restrain the adsorption resulting from the hydrophobic interaction. The hydrophobic attraction competitive with the electrostatic repulsion is stronger for a longer alkyl chain surfactant.

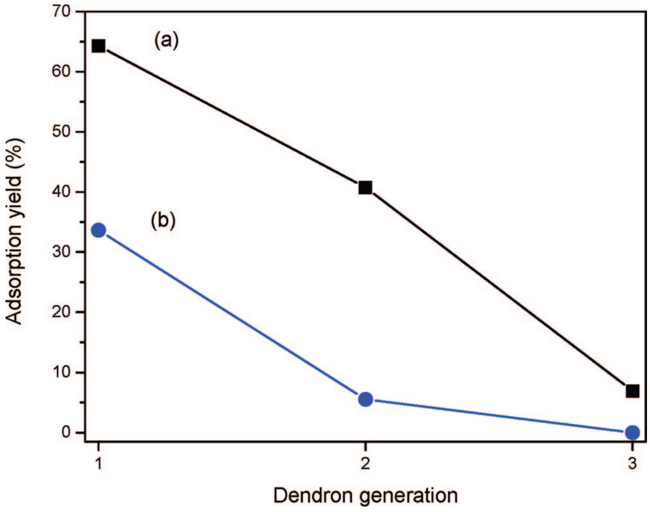

Figure 7. Plot of adsorption yield of cationic surfactants versus dendron generation of C18GnS ($n = 1-3$): (a) benzyldimethyltetradecylammonium chloride, (b) 1-dodecylpyridium chloride.

The pore size distributions of APS, G3S, and C18G3S were determined by the nitrogen adsorption/desorption method (see Figure SI3, Supporting Information). The fitting data shows that APS has an average pore size of 8.5 nm. However, after the fabrication of G3 and C18G3 dendrons, the pore apparently shrinks to be 5.5 and 3.8 nm, respectively, as a result of the successful surface modification. The result suggests that the layer of G3 or C18G3 dendron covers the silica surface and that the fabrication of large molecules shrinks pore size. Nevertheless, the adsorption efficiency toward target molecules is not necessarily on the order of the pore size. Therefore, it is demonstrated that the adsorption of the target molecules is mainly controlled by the specific adsorbability of the organic adsorbent (surface-modified amphiphilic dendrons) but not the porosity of the silica.

Adsorption Isotherm of Water-Soluble Anionic Adsorbates. Figure 8A reveals the variation of quantity (q) of adsorbed MO per gram of C18G1S and C18G3S versus concentration (C) of MO remaining in solution after the overnight adsorption process. On these adsorption isotherms, the quantity of adsorbed MO for both particles increased and reached a constant with increasing the concentration of MO. The inset of Figure 8A shows plots of the ratio C/q versus C. The good linear relationship between the two parameters indicates that the adsorption behavior obeys the Langmuir adsorption isotherm.[18] Then the binding constant K_L is obtained from eq 1:

$$C/q = 1/(NK_L) + C/N \tag{1}$$

where N is the total number of adsorption sites per unit weight of adsorbent. For C18G1S and C18G3S toward MO, the K_L was 6.56 and 9.54 cm^3/mg, respectively. Similar

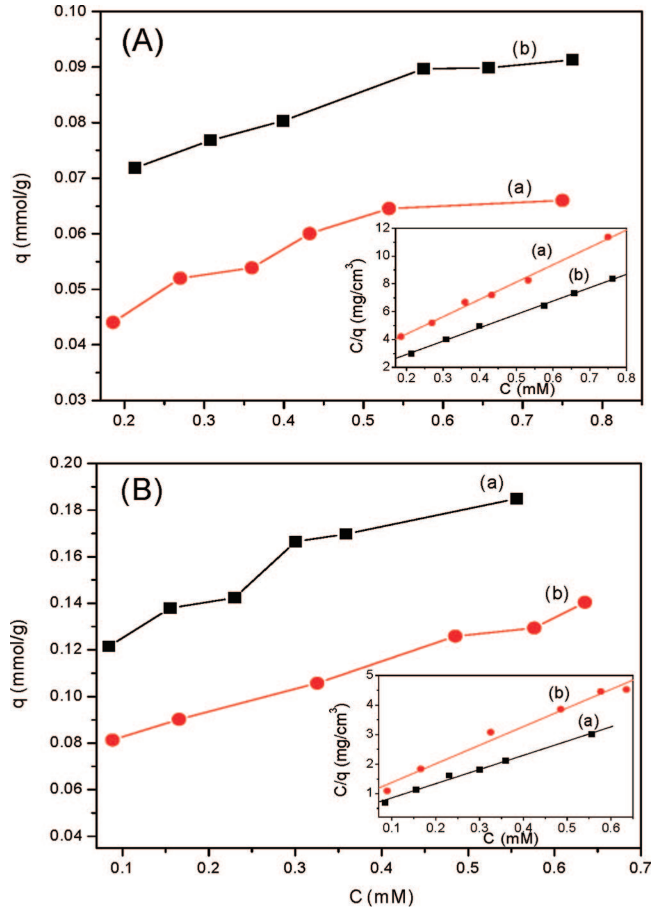

Figure 8. Adsorption isotherms for quantity (q) of adsorbed adsorbates per gram of (a) C18G1S and (b) C18G3S versus concentration (C) of adsorbates remaining in water. The inset shows the plots following a Langmuir equation: (A) MO, (B) SDBS.

adsorption isothermal behavior was also observed on C18G1S and C18G3S toward SDBS (Figure 8B). In this regard, the binding constants K_L were obtained from the fitting plot shown in the Figure 8B inset, and the values were on the same order as those toward MO. These values were quite comparable to those of organically modified mesoporous silica and of ureasil gels toward organic pollutants in water.[19] The result suggests that the amphiphilic dendron-surface-modified silica can be a promising solid phase extractor for water purification. It should be noticed that the surface areas of the porous silica particles utilized in this study are much smaller than that of fine mesoporous silica such as MCM-41[20] and that the mesopores of these silica particles are irregularly distributed on the surface. Therefore, it is unsurprised that bare and aminopropyl-surface-modified porous silica particles are unable to trap effectively any target molecules in water. After facile amphiphilic dendron-surface modification, the porous silica particles show remarkable adsorption ability, which is usually found in organically modified mesoporous materials.[14]

The constants K_L and N obtained from an optimum fitting to the Langmuir equation are presented in Table 2. It must be noticed that the number N of adsorption site on amphiphilic silica is smaller for MO dye than for SDBS surfactant. On the other hand, the amphiphilic silica bearing C18Gn dendron moieties exhibits opposite generation dependency toward MO and SDBS on the binding constant K_L as well as the site number N of adsorption. These results suggest that (1) the adsorption sites must be different between anionic dye and surfactant and that (2) the adsorption affinity for such sites depends on the generation of C18GnS. First, the fact that C18GnS has different adsorption sites toward MO and SDBS can be ascribed to the distinct structural domains of the adsorbates. This refers the lacking of hydrophobic domains on MO in comparison with SDBS. On the other hand, the number of adsorption sites toward SDBS enlarges because of the hydrophobic interaction between the aliphatic periphery of C18GnS and the long alkyl tail of SDBS.

Among all the K_L values in Table 2, C18G1S shows the highest and lowest binding affinities toward SDBS and MO, respectively, and C18G3S exhibits medium binding affinities toward two anionic adsorbates. It is reasonable that the binding affinity of C18G3S is promoted by dimensional similarity of the interior pockets of G3 dendron to target molecules. MO is regarded as an anionic adsorbate preferring less hydrophobic domains, and thus the interior cavities of dendron predominate the adsorption of C18GnS toward MO. Therefore, C18G3S shows a higher binding affinity toward MO than C18G1S does. However, the SDBS adsorption shows a reverse result against the MO adsorption on generation dependency. It is obvious that only the interior cavities of C18Gn dendrons do not afford the firm complexation with the target molecule as a result of the amphiphilic chemical structure of SDBS with hydrophobic alkyl chains. Therefore, it is quite understandable that C18GnS adsorbs effectively SDBS molecules through the hydrophobic interaction between the long alkyl chains of amphiphilic silica and surfactant. The higher binding affinity of C18G1S results from the densely packed aliphatic chains of C18G1 dendron. Chart 2 schematically illustrates the dimensional relationship of C18G1S with SDBS together with the relationship with MO. After the propagation of C18G3, the aliphatic peripheries loosely locate outside of the dendron owing to branching structure, and thus the adsorption of SDBS on C18G3S through the promotion of hydrophobic interaction is incomparable to a case of C18G1S.

Recovery and Reuse of Amphiphilic Silica Particles. To examine the recovering and reusing abilities of amphiphilic silica particles through the adsorption/desorption process, 50 mg of C18G2S was mixed with an aqueous solution (1 cm^3) of 1 mM MO in the microtube. After being shaken overnight, the silica particles were allowed to precipitate by a centrifuge, and the supernatant was analyzed by a UV–vis absorption spectrometer to determine the concentration of nonadsorbed MO molecules. The measurement concluded that 1.96×10^{-2} mmol of MO molecules

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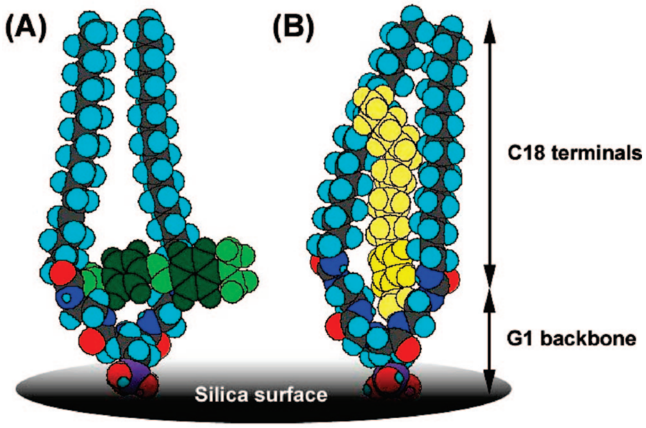
Table 2. K_L and N Values in a Langmuir Adsorption Isothermal Equation

	adsorbate			
	MO		SDBS	
adsorbent	K_L [cm^3/mg (10^3 M^{-1})]	N (mmol/g)	K_L [cm^3/mg (10^3 M^{-1})]	N (mmol/g)
C18G1S	6.56 (2.13)	0.0803	12.7 (4.43)	0.2082
C18G3S	9.54 (3.05)	0.1042	8.42 (2.94)	0.1587

Chart 2. Dimensional Relationships of C18G1S with (A) MO and (B) SDBS.



were adsorbed per gram of C18G2S. Then the C18G2S/MO precipitates were dispersed and shaken overnight in aqueous solutions bearing different pHs ranging from 2.0 to 13.0. The concentration of released MO molecules in the supernatants, which were determined by a UV–vis absorption spectrometry, is plotted as a function of pH in Figure 9.

MO molecules were released above pH 7, and desorption yield reached the maximum (ca. 90%) at pH 11. It must be noticed that the release of MO molecules occurred under basic environments as a result of the basic nature of amines in the dendrons. The result was consistent with the back-extraction of the palmitoyl-terminated poly(propyleneimine) dendrimers toward organic dyes in water and also indicated the pH-dependent desorption behavior of the amphiphilic silica.[11] Moreover, the extraction yield always keeps the same level (ca. 80%) during the adsorption/desorption cycles, which indicates the intact structure of amphiphilic dendrons on silica surface after the treatment by an alkaline solution and the reuse.

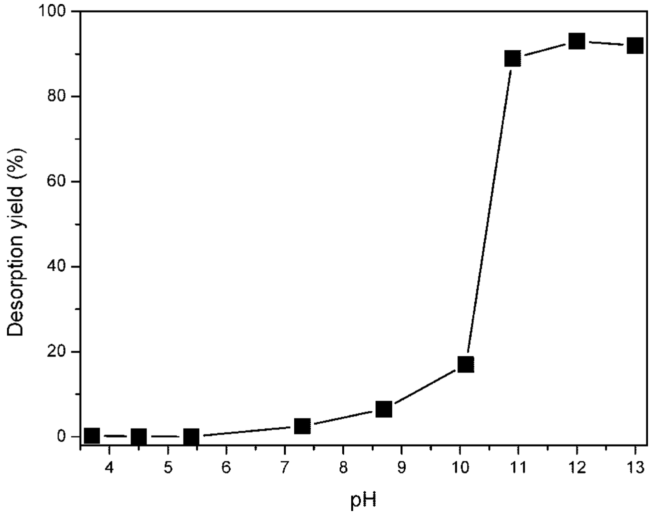


Figure 9. Desorption yield of MO from C18G2S as a function of pH.

Conclusion

This article reports the facile surface modification of porous silica particles with low generation (G1−G3) of amphiphilic PAMAM dendrons and their potential applications in water purification. FT-IR, TGA, and elemental analyses confirmed the successful propagation of PAMAM dendrons on silica surface and the following functionalization of dendrimer end-groups with ODI. The surface-modified silica particles can effectively adsorb anionic dyes and surfactants in water mainly as a result of the host–guest affinity and the hydrophobicity of amphiphilic dendron on the silica surface. The adsorption isotherms of C18GnS toward anionic adsorbates follow the Langmuir equation, and the results also indicate that the adsorption of surfactant on C18GnS is promoted by the hydrophobic interaction between the aliphatic peripherals of dendron and the long alkyl tails of surfactants, different from hydrophilic dye. Furthermore, the dimensional relationship of the densely packed aliphatic chains fairly supports the result that C18G1S particularly exhibits the highest binding affinity toward anionic surfactant. The anionic targets adsorbed on the surface modified silica particles can be released at alkaline condition because of the deprotonation of PAMAM dendron, which suggests the convenient recovery and reuse process. In conclusion, C18GnS can be a packing material for an ion-exchange column or an adsorbent for batch processing toward ionic target molecules in wastewater. On the batch processing, adsorption of those contaminents is achieved by simple shaking or stirring, and then filtration or centrifugation separates the clean water from adsorbed silica, which can be recovered and reused after treatment at alkaline condition. Moreover, counting in the cost efficiency and environmental low load, as-prepared amphiphilic dendron-modified silica is a promising solid phase adsorbent for water purification.

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Supporting Information Available: Additional characterization for APS and dendron-surface-modified silica, including particle size distribution, pore size distribution, and morphology (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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