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ORIGINAL ARTICLE

Design of molecule-responsive organic–inorganic hybrid nanoparticles bearing cyclodextrin as ligands

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Novel organic–inorganic hybrid nanoparticles with a bisphenol A (BPA)-responsive hydrogel layer on the surface of SiO_2 nanoparticles were prepared via surface-initiated atom transfer radical polymerization of acrylamide (AAm), acryloyl-modified β-cyclodextrin (CD) and *N, N′*-methylenebisacrylamide. The resulting CD-PAAm/SiO_2 nanoparticles underwent a change in size in response to BPA. The BPA-responsive shrinkage of the CD-PAAm/SiO_2 nanoparticles was caused by an increase in the crosslinking density of the CD-PAAm hydrogel layer, which resulted from the formation of CD-BPA-CD complexes acting as dynamic crosslinks. The smart functions of BPA-responsive organic–inorganic hybrid nanoparticles can provide useful tools for constructing molecular sensors and adsorption materials.
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INTRODUCTION

Organic–inorganic hybrid nanoparticles have attracted considerable attention because of their fascinating optical, electronic and catalytic properties. In recent years, several works have focused on the preparation of organic–inorganic hybrid nanoparticles with stimuli-responsive polymer layers as hybrid nanomaterials. Silica (SiO_2) nanoparticles are the most extensively studied materials for the fabrication of organic–inorganic hybrid materials.[1] Spherical SiO_2 nanoparticles with narrow size distributions are easily synthesized using the Stöber process, in which the size of SiO_2 nanoparticles is controlled by the reaction conditions.[2] SiO_2 nanoparticles are used not only as inorganic filler for the reinforcing agent but also as optical materials based on the formation of colloidal crystals that exhibit structural colors. Furthermore, mesoporous silica, a type of SiO_2 nanoparticle with high specific surface area resulting from its porous structure, is also widely used because of its potential applications as a base material for adsorption, separation, catalysis, drug delivery systems and other functions. SiO_2 nanoparticles are easily dispersed in a solution without stabilizing agents such as polymers and surfactants. SiO_2 nanoparticles have clean surfaces and display silanol groups on their surface, which are converted to various functional groups by treating with silane coupling agents with functional amino and carboxy groups. Such surface modifications by treating with silane coupling agents enhance the compatibility between polymers and SiO_2 nanoparticles for the fabrication of organic–inorganic hybrid materials.

Recently, the development of controlled/living radical polymerization (CRP) enables the easy preparation of well-defined polymer brushes on the surface of glass plates, silicon wafers and SiO_2 nanoparticles by graft polymerization from their surfaces modified with a CRP initiator.[3] In particular, surface-initiated atom transfer radical polymerization (SI-ATRP) is widely used for the preparation of polymer brushes on the surface of SiO_2 nanoparticles because ATRP initiators can be easily introduced onto the surface of SiO_2 nanoparticles by using silane coupling agents. A variety of monomers such as styrene,[4] methacrylic acid,[5] oligo(ethylene glycol) methacrylate[6] and *N*-isopropylacrylamide[7] have been polymerized from ATRP initiators on the surface of SiO_2 nanoparticles to obtain organic–inorganic hybrid nanoparticles composed of a SiO_2 core and a polymer brush layer. However, few studies on the preparation of organic–inorganic hybrid nanoparticles with a stimuli-responsive hydrogel layer by SI-ATRP have been reported: to the best of our knowledge, only gold nanoparticles with a temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel layer have been prepared by SI-ATRP.[8]

We have proposed a novel strategy for the preparation of molecule-responsive hydrogel[9–17] and gel particles.[18] The stimuli-responsive behavior of most hydrogels reported previously was mainly based on changes in the hydrophilicity of polymer chains or in charged groups induced by pH and temperature changes. In contrast to the standard strategies for the preparation of stimuli-responsive hydrogels, our strategy utilizes molecular complexes as dynamic crosslinks that dissociate and associate in the presence and absence of a target molecule, respectively. The molecule-responsive hydrogels designed on the basis of this strategy exhibit volume changes in response to a target molecule because their crosslinking density changes with the association and dissociation of molecular complexes acting as dynamic crosslinks. For example, we prepared bisphenol A (BPA)-imprinted hydrogels with β-cyclodextrin (CD) via molecular imprinting with a minute amount of crosslinker.[17] The BPA-imprinted hydrogels shrank

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gradually in the presence of BPA because CDs as ligands formed sandwich-like CD-BPA-CD complexes with BPA, and their crosslinking density increased. In addition, the BPA-imprinted hydrogels showed greater shrinkage than non-imprinted hydrogels in response to BPA. This result implied that molecular imprinting enabled the CD ligands to be arranged at suitable positions for forming the CD-BPA-CD complexes that acted as crosslinks. Although the BPA-imprinted hydrogels exhibited BPA-responsive behavior, it took a long time for their hydrogels to reach equilibrium swelling after immersion in an aqueous BPA solution.

In this paper, a method for the preparation of novel BPA-responsive organic–inorganic hybrid nanoparticles with BPA-responsive hydrogel layers on the surface of SiO_2 nanoparticles is reported. The BPA-responsive hydrogel layers with CD ligands for target BPA were prepared on SiO_2 nanoparticles via SI-ATRP of acrylamide (AAm), acryloyl-CD and *N,N′*-methylenebisacrylamide (MBAA). The paper describes the BPA-responsive behavior of the resultant CD-containing poly(acrylamide) layer (CD-PAAm)/SiO_2 hybrid nanoparticles. The fundamental research on the preparation of molecule-responsive organic–inorganic hybrid nanoparticles will contribute significantly to creating smart hybrid nanomaterials for fabricating sensors, separation columns and drug delivery vehicles.

EXPERIMENTAL PROCEDURE

Materials

3-(Aminopropyl)triethoxysilane (APTES) and 2-bromoisobutyryl bromide were purchased from Tokyo Chemical Industry, Ltd. (Tokyo, Japan) and used as received. SiO_2 nanoparticles, Seahoster KE-W10, were purchased from Nippon Shokubai, Ltd. (Tokyo, Japan) and used after drying under vacuum. Acrylamide (AAm), *N, N′*-methylenebisacrylamide (MBAA), 2, 2′-bipyridyl (BPy), copper chloride (I) and dehydrated toluene were purchased from WAKO Pure Chemical Industries (Osaka, Japan). Acrylamide was used after purification by recrystallization from benzene, and the other chemicals were used as received. β-Cyclodextrin with a polymerizable acryloyl group was synthesized as previously described.[17] All other solvents and reagents were of analytical grade and were obtained from commercial sources and used without further purification.

Introduction of an ATPR-initiator onto the surface of SiO_2 nanoparticles

The ATRP initiator was introduced onto the surface of SiO_2 nanoparticles, as shown in Scheme 1a. SiO_2 nanoparticles (5.0 g) were dispersed in dehydrated toluene (25 ml) by sonication. APTES (2.7 ml, 11.56 mmol) was added to the dispersion of SiO_2 nanoparticles, and the reaction mixture was refluxed for 24 h. The solids were separated by centrifugation and washed with toluene and acetone. The final product was dried under vacuum to obtain amino-modified SiO_2 nanoparticles.

The amino-modified SiO_2 nanoparticles (1.27 g) were dispersed in chloroform (19 ml) by sonication, followed by the addition of triethylamine (2.54 ml, 18.22 mmol). The mixture was cooled in an ice water bath. A solution of 0.63 ml 2-bromoisobutyryl bromide (5.10 mmol) and 1.27 ml chloroform was added dropwise to cooled mixture, and then the mixture was stirred at room temperature for 24 h. The solids were separated by centrifugation and washed with chloroform and ethanol. The final product was dried under vacuum to obtain Br-modified SiO_2 nanoparticles on which alkyl bromide was introduced as a SI-ATRP initiator.

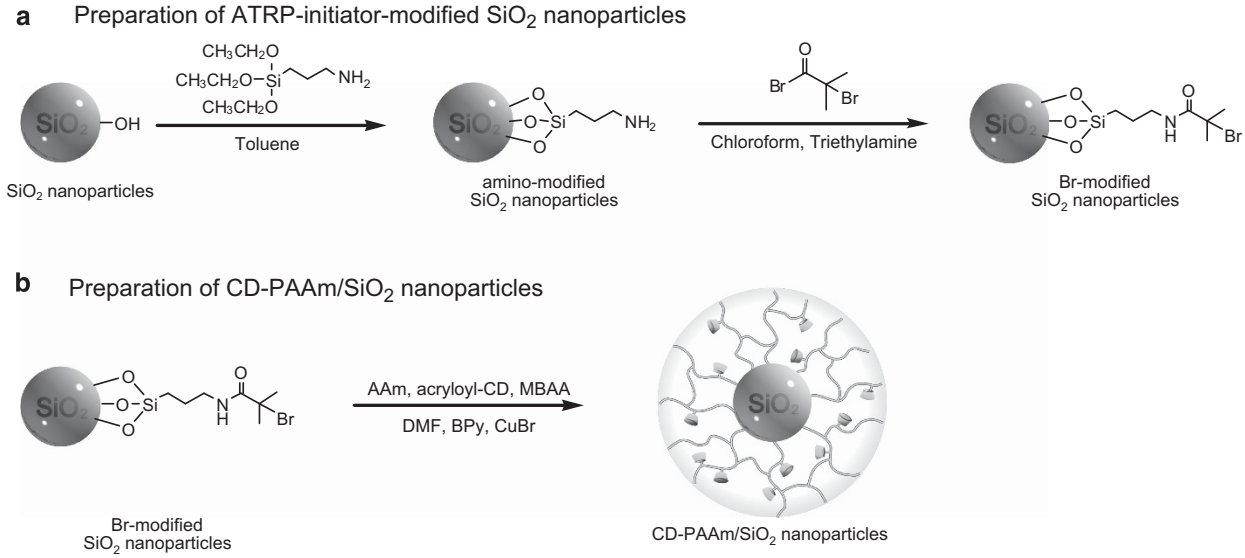
Synthesis of PAAm hydrogel with CD on the surface of SiO_2 nanoparticles via SI-ATRP

SiO_2 nanoparticles with a PAAm hydrogel layer with CD ligands (CD-PAAm/SiO_2 nanoparticles) were prepared via SI-ATRP, as shown in Scheme 1b. The feed compositions for the preparation of CD-PAAm/SiO_2 nanoparticles with various CD contents via SI-ATRP are summarized in Table 1. Br-modified SiO_2

Table 1 Preparative condition and diameters of CD-PAAm/SiO_2 nanoparticles via SI-ATRP

CD content (mol%)	*Br-SiO_2 nanoparticles* (mg)	*AAm* (mg)	*MBAA* (mg)	*Acryloyl-CD* (mg)	*Diameter*[a] (nm)
0.0	20	20	2	0.0	178
1.1				3.9	219
2.1				7.5	241
3.3				11.9	199
4.6				16.8	215
5.8				21.5	167
8.2				31.2	178

[a]Determined by DLS measurements.



Scheme 1 Preparation of (**a**) ATRP-initiator-modified SiO_2 and (**b**) CD-PAAm/SiO_2 nanoparticles. A full color version of this figure is available at *Polymer Journal* online.

nanoparticles (2.0 g) were dispersed in *N,N*-dimethylformamide (DMF) (2.0 ml) by sonication, followed by the addition of AAm, MBAA and acryloyl-CD. A DMF solution (10 μl) containing CuCl (0.1 mg, 1.01 μmol) and BPy (0.1 mg, 0.64 μmol) was added to the dispersion of monomers and SiO_2 nanoparticles, and the mixture was stirred for 8 h at 130 °C at 200 r.p.m. under a nitrogen atmosphere. The reaction mixture was poured into seamless cellulose tubing (molecular weight cut off = 12 000–14 000) and dialyzed against deionized water to purify the resultant CD-PAAm/SiO_2 nanoparticles. PAAm/SiO_2 nanoparticles without CD ligands were also prepared via SI-ATRP of AAm and MBAA from the Br-modified SiO_2 nanoparticles without acryloyl-CD.

Characterizations of CD-PAAm/SiO_2 nanoparticles

X-ray photoelectron spectroscopy (XPS) spectra of bare, amino-modified and Br-modified SiO_2 nanoparticles were recorded using an ESCA-3400 (Shimadzu, Kyoto, Japan). An Mg Kα X-ray source was used at a power of 200 W (20 mA × 10 kV), and the pass energy was set at 75 eV. The pressure in the analysis chamber was $\sim 4.0 \times 10^{-7}$ Pa. The charge correction in the binding energy scale was performed by setting the $-CH_2-$ peak in the carbon spectrum to 285.0 eV. SiO_2 nanoparticles were placed on a silicon wafer and dried under vacuum before XPS measurements.

The morphology of the amino-modified and Br-modified SiO_2 nanoparticles was observed by transmission electron microscopy (TEM) using JEM-1400 (JEOL, Tokyo, Japan) at an accelerating voltage of 100 kV. To prepare samples for TEM observations, diluted solutions of bare and modified SiO_2 nanoparticles were placed on poly(vinyl butyral)-coated grids and dried under vacuum.

The diameter of CD-PAAm/SiO_2 nanoparticles was measured by dynamic light scattering (DLS), using DLS7000 (Otsuka Electronics, Osaka, Japan). Vertically polarized light at 633 nm from the He–Ne ion laser was used as the incident beam, and all measurements were performed at 25 ± 0.3 °C.

The morphology of CD-PAAm/SiO_2 nanoparticles was observed by atomic force microscopy (AFM) in the tapping mode using SPI3800/SPA400 (SII nanotechnology, Tokyo, Japan), taking 256 points in a $1 \times 1\ \mu m^2$ area with a 0.5 Hz scan rate at room temperature.

Swelling ratio measurements

CD-PAAm/SiO_2 nanoparticles were dispersed in an aqueous solution with and without BPA (0.12 mg ml^{-1}). The diameter of the CD-PAAm/SiO_2 nanoparticles was measured by DLS. The swelling ratio (V/V_0) of the CD-PAAm/SiO_2 nanoparticles was determined from the particle diameter in aqueous solution with and without BPA by equation (1):

$$\text{Swelling ratio} = \frac{V}{V_0} = \left(\frac{d}{d_0}\right)^3 \quad (1)$$

where d and d_0 are the diameters of the CD-PAAm/SiO_2 nanoparticles in an aqueous solution with and without BPA, respectively.

RESULTS AND DISCUSSION

Preparation of CD-PAAm/SiO_2 particles via SI-ATRP

SiO_2 nanoparticles are the most commonly used inorganic nanoparticles for the fabrication of organic–inorganic hybrid materials because their surface is easily modified with various functional groups. The surface functionalization of SiO_2 nanoparticles enables the preparation of a stimuli-responsive hydrogel layer on their surface. One approach is the emulsion copolymerization of functional monomers and SiO_2 nanoparticles modified with polymerizable groups. Hellweg and colleagues[19] prepared temperature-responsive PNIPAAm hydrogel nanoparticles with SiO_2 cores by emulsion copolymerization of NIPAAm, MBAA and methacryloyl-modified SiO_2 nanoparticles.[20] Although PNIPAAm hydrogel/SiO_2 nanoparticles with narrow size distributions were formed by emulsion copolymerization, they included nanoparticles with no SiO_2 core or more than one. In contrast, organic–inorganic hybrid nanoparticles with a stimuli-responsive hydrogel layer can also be prepared by a 'grafting from' method using SI-ATRP. However, few studies on the preparation of organic–inorganic hybrid nanoparticles with a stimuli-responsive hydrogel layer by SI-ATRP were previously reported. To the best of our knowledge, only gold nanoparticles with a PNIPAAm hydrogel layer were prepared by SI-ATRP.[8]

We have succeeded in the preparation of thin hydrogel layers with biomolecular recognition sites on surface plasmon resonance (SPR) sensor chips by SI-ATRP.[21,22] The thickness of the hydrogel layers on the SPR chips was controlled by the polymerization time of ATRP. These results indicate that SI-ATRP is applicable for the preparation not only of polymer brushes but also of thin hydrogel layers on the surface of solid substrates. Therefore, we utilized SI-ATRP to prepare molecule-responsive hydrogel layers bearing CD ligands for the recognition of BPA on the surface of SiO_2 nanoparticles.

To introduce an ATRP initiator onto the surface of SiO_2 nanoparticles, we used a versatile method for the surface modification of SiO_2 nanoparticles (Scheme 1a): after functional groups such as carboxy and amino groups are introduced to the surface of SiO_2 nanoparticles through surface modification with organosilanes bearing a functional group, ATRP initiators are covalently attached to the functional groups on the modified surfaces. In this study, the surface of SiO_2 nanoparticles was modified with 3-aminopropyl triethoxysilane to introduce amino groups. The resulting amino-modified SiO_2 nanoparticles were then treated with 2-bromoisobutyryl bromide to obtain 2-bromoisobutylate-modified SiO_2 nanoparticles (Br-modified SiO_2). The introduction of alkyl bromide as an ATRP initiator onto the surface of SiO_2 nanoparticles was confirmed by the XPS measurements. The XPS measurements enable us to directly analyse the surface composition not only of polymeric materials but also of inorganic materials. The XPS analysis provides information about the surface composition of samples from the top to a depth of ~10 nm. Figure 1 shows the XPS spectra of the N_{1s} and Br_{3d} region of bare, amino-modified and Br-modified SiO_2 nanoparticles. In the N_{1s} spectrum of amino-modified SiO_2 nanoparticles, a distinct peak was observed, whereas no peaks were observed in the N_{1s} spectrum of bare SiO_2 nanoparticles (Figure 1a). This result indicates that the surface of SiO_2 nanoparticles was covered with amino groups by the condensation of APTES with the surface silanol groups of bare SiO_2 nanoparticles. Furthermore, a distinct peak was observed in the Br_{3d} spectrum of Br-modified SiO_2 nanoparticles (Figure 1b). Therefore, 2-bromoisobutylate was successfully introduced onto the surface of SiO_2 nanoparticles as an ATRP initiator by treating amino-modified SiO_2 nanoparticles with 2-bromoisobutyryl bromide. Figure 2 shows TEM images of the bare and Br-modified SiO_2 nanoparticles. Similarly to the bare SiO_2 nanoparticles, the Br-modified SiO_2 nanoparticles had spherical shape and uniform size with diameters of ~100 nm. During the introduction of amino groups onto the SiO_2 nanoparticles, a minute amount of water in toluene as a solvent results in the predominant condensation of APTES, followed by the formation of its aggregates.[23] However, no aggregates were observed in the TEM image of Br-modified SiO_2 nanoparticles. Therefore, the spherical shape and uniform size of Br-modified SiO_2 nanoparticles without any aggregation suggest that the predominant condensation of APTES was suppressed, and the ATRP initiators were introduced only onto the surface of the SiO_2 nanoparticles. Thus, the ATRP initiators were successfully introduced onto the surface of SiO_2 nanoparticles according to Scheme 1a.

ATRP of PAAm, acryloyl-CD and MBAA on the surface of Br-modified SiO_2 nanoparticles was conducted in DMF at 130 °C, using CuCl and BPy as the catalytic system. In this study, MBAA was used as a crosslinker for the preparation of a hydrogel layer on the surface of SiO_2 nanoparticles. The utilization of MBAA might induce the

formation of bulk hydrogel through an interparticle crosslinking reaction. However, the reaction mixture had high fluidity throughout the polymerization, and no bulk hydrogels formed after the reaction, which indicates that the crosslinking reaction occurred in the thin gel layers on the surface of the SiO_2 nanoparticles. The DLS measurements indicated that resultant CD-PAAm/SiO_2 nanoparticles with various CD contents were larger in diameter than the bare-SiO_2 nanoparticles, that is, 100 nm (Table 1). Figure 3 shows the AFM images of Br-modified SiO_2, PAAm/SiO_2 and CD-PAAm/SiO_2 nanoparticles. The AFM images also demonstrate that the PAAm/SiO_2 and CD-PAAm/SiO_2 nanoparticles were larger than the Br-modified SiO_2 nanoparticles. Although aggregation resulting from drying was

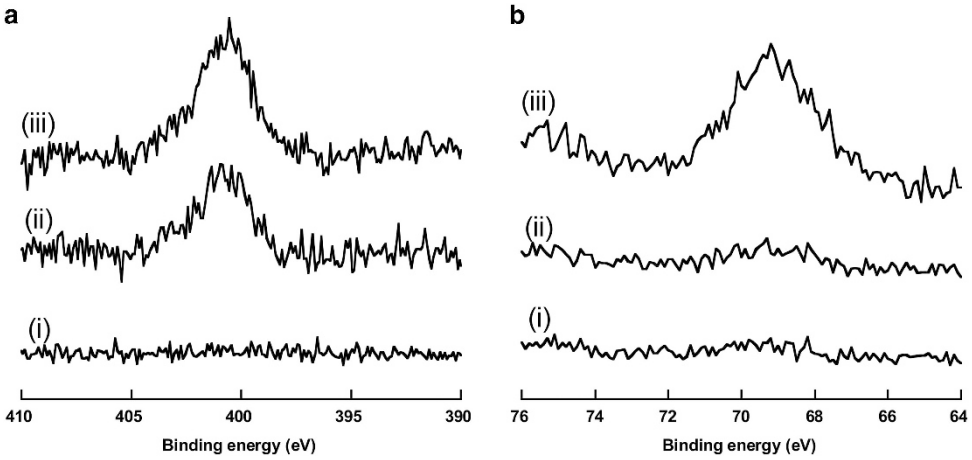


Figure 1 XPS spectra of (**a**) N_{1s} and (**b**) Br_{3d} region of (i) bare SiO_2, (ii) amino-modified SiO_2 and (iii) Br-modified SiO_2 nanoparticles.

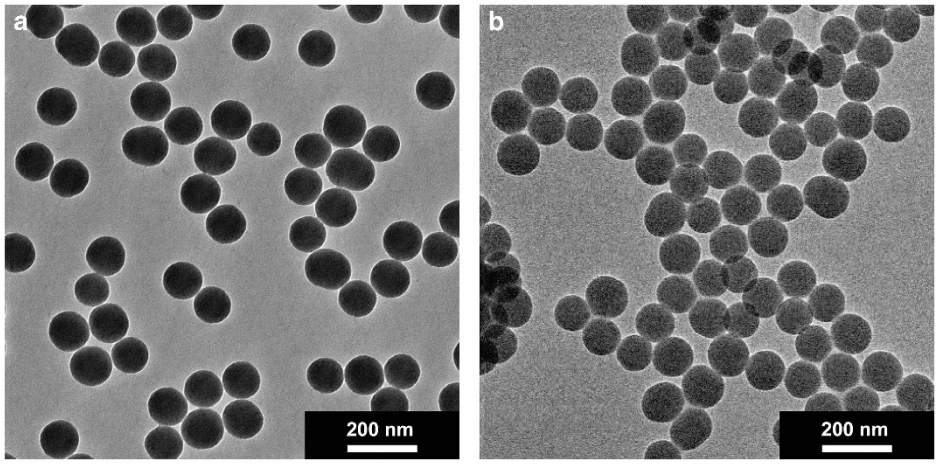


Figure 2 TEM images of (**a**) bare and (**b**) Br-modified SiO_2 nanoparticles.

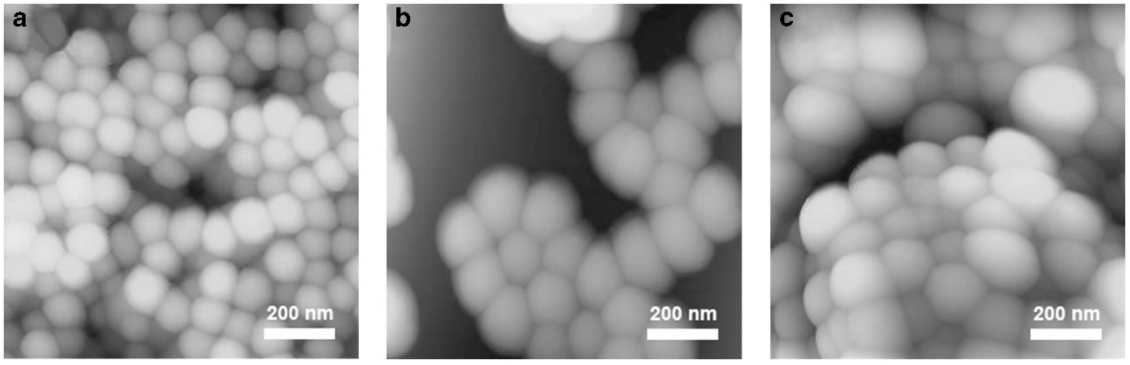


Figure 3 AFM images of (**a**) Br-modified SiO_2, (**b**) PAAm/SiO_2 and (**c**) CD-PAAm/SiO_2 nanoparticles (CD content: 3.3 mol%). A full color version of this figure is available at *Polymer Journal* online.

observed in the AFM images, the PAAm/SiO_2 and CD-PAAm/SiO_2 nanoparticles had individual spherical shapes. The monomodal size distributions of PAAm/SiO_2 and CD-PAAm/SiO_2 nanoparticles determined by DLS measurements also indicated that PAAm/SiO_2 and CD-PAAm/SiO_2 nanoparticles were dispersed in aqueous solution without interparticle aggregation (Supplementary Figure S1). These results indicate that the PAAm and CD-PAAm hydrogel layer formed on the surface of SiO_2 nanoparticles without interparticle crosslinking. Figure 4 shows the FTIR spectra of bare SiO_2, PAAm/SiO_2 and CD-PAAm/SiO_2 nanoparticles. The strong absorption peak assigned to the Si–O stretching vibration bands was observed at 1,100 cm^{-1} in the spectra of each type of nanoparticle. It should be noted that the absorption peak assigned to the distinctive C = O stretching vibration of amide groups (amide I) appeared at 1,669 cm^{-1}, and the N–H bending vibration band of amide groups (amide II) appeared at 1,636 cm^{-1} in the spectra of the PAAm/SiO_2 and CD-PAAm/SiO_2 nanoparticles. The representative amide I and amide II peaks, which were not observed in the FTIR spectrum of Br-SiO_2 nanoparticles, indicated the formation of PAAm and PAAm-CD hydrogel layers on the surface of SiO_2 nanoparticles via SI-ATRP. These results suggest that the PAAm/SiO_2 and CD-PAAm/SiO_2 nanoparticles had a core-shell structure composed of an inorganic SiO_2 core and a PAAm hydrogel shell because polymerization was initiated and preceded on the surface of SiO_2 nanoparticles without interparticle crosslinking.

BPA-responsive behavior of CD-PAAm/SiO_2 particles

BPA is an important industrial compound that is used as a monomer in the manufacture of polycarbonate plastics and epoxy resins. However, BPA may be able to mimic the effect of estrogens, thereby disrupting endocrine systems.[24] Therefore, methods to detect and remove BPA are in considerable demand. To develop smart materials for detecting and removing BPA, we have prepared BPA-responsive hydrogels that shrink in response to BPA. However, it took several hours for a BPA-responsive hydrogel to attain equilibrium swelling when immersed in an aqueous BPA solution. In general, the kinetics of the swelling and shrinking of hydrogels are governed by the diffusion-limited transport of the polymer chains in water. Therefore, rapidly responsive swelling/shrinking behavior can be achieved by reducing the size of stimuli-responsive hydrogels because of the increase in their surface area. For example, we reported that it took comparable time for glucose-responsive bulk hydrogels to reach equilibrium in a swollen state in response to the target glucose, while glucose-responsive gel particles with a diameter of 750 nm swelled rapidly to attain an equilibrium swelling ratio in a buffer solution with glucose.[18] As described in the previous section, we succeeded in preparing CD-PAAm/SiO_2 nanoparticles with a CD-containing hydrogel layer on the surface of SiO_2 nanoparticles. Thus, we investigated the BPA-responsive behavior of CD-PAAm/SiO_2 nanoparticles in the presence of BPA. Changes in the swelling ratio of CD-PAAm/SiO_2 particles in response to BPA were measured using DLS. Figure 5 shows the relationship between CD content and the swelling ratio of CD-PAAm/SiO_2 nanoparticles in the presence of BPA. Here, a swelling ratio of less than one means that the nanoparticles shrink in response to BPA because the swelling ratio was determined from the ratio of the particle size in an aqueous BPA solution to the particle size in water. The swelling ratio of PAAm/SiO_2 nanoparticles without CD ligands remained unchanged in the presence of BPA. By contrast, the CD-PAAm/SiO_2 nanoparticles immediately shrank and attained equilibrium during the DLS measurements (that is, within 10 min) without any aggregation when they were dispersed in aqueous BPA solution. The swelling ratio of CD-PAAm/SiO_2 nanoparticles in aqueous BPA solution decreased with increasing CD content and remained constant above the CD content of 4.6 mol%. Our previous paper reported that BPA-imprinted and non-imprinted hydrogels with CDs as ligands shrink gradually in response to target BPA. The compressive modulus measurements of their hydrogels revealed that the BPA-responsive shrinkage was induced by an increase in crosslinking density based on the sandwich-like CD-BPA-CD complex formation. Therefore, the shrinkage behavior of CD-PAAm/SiO_2 nanoparticles prepared in this study can be explained by a tentative model schematically illustrated in Figure 6. The CD-PAAm/SiO_2 nanoparticles have CDs as ligands for BPA in the networks of the CD-PAAm hydrogel layer. When the CD-PAAm/SiO_2 nanoparticles are dispersed in aqueous BPA solution, BPA

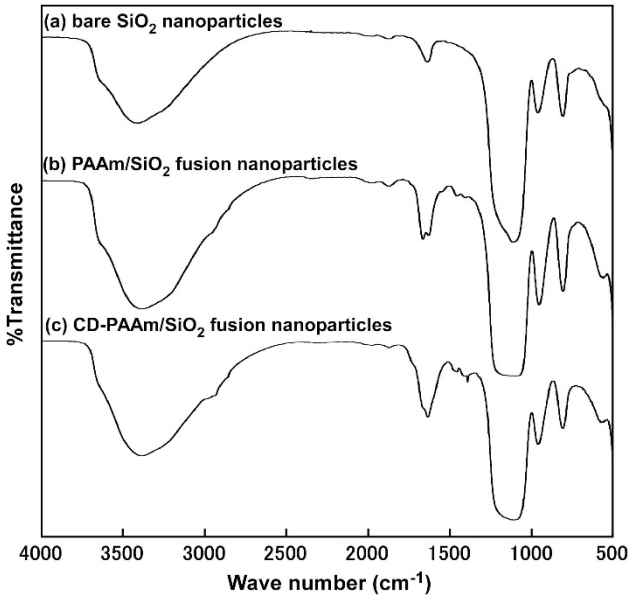


Figure 4 FTIR spectra of (a) bare SiO_2, (b) PAAm/SiO_2 and (c) CD-PAAm/SiO_2 nanoparticles (CD content: 3.3 mol%).

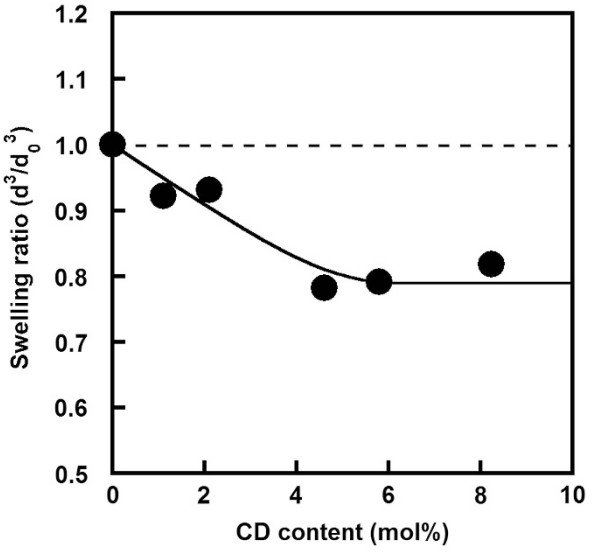


Figure 5 Relationship between CD content and swelling ratio of CD-PAAm/SiO_2 nanoparticles in the presence of BPA (0.12 mg ml^{-1}).

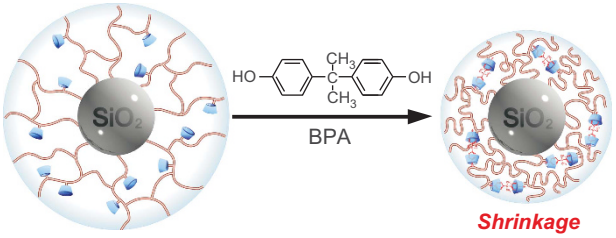


Figure 6 Schematic of BPA-responsive behavior of CD-PAAm/SiO_2 nanoparticles.

easily diffuses into the CD-PAAm hydrogel layer. Then, the CD ligands within the hydrogel layer form sandwich-like CD-BPA-CD complexes with the target BPA. The formation of the CD-BPA-CD complexes that act as dynamic crosslinks leads to an increase in the crosslinking density of the CD-PAAm hydrogel layer, followed by BPA-responsive shrinkage. Moreover, the increase in the CD content of the CD-PAAm hydrogel layer results in an increase in crosslinking density based on the complex formation between CD and BPA. Therefore, the CD-PAAm/SiO_2 nanoparticles with higher CD content showed greater shrinkage in response to BPA. However, the shrinkage of the CD-PAAm/SiO_2 nanoparticles with a CD content of more than 4.6 mol% became constant because the quantity of CD-BPA-CD complex crosslinks was unchanged above the CD content of 4.6 mol% due to an excess of CD ligands over BPA molecules in water. More rapidly, BPA-responsive shrinkage of the CD-PAAm/SiO_2 nanoparticles compared with the bulk BPA-imprinted hydrogels reported previously was attributed to the large surface area of the nanoparticles. Such BPA-responsive CD-PAAm/SiO_2 nanoparticles can provide a useful platform for designing rapidly responsive nanomaterials for use in molecular sensors and separation technology.

CONCLUSION

This paper describes the preparation of smart organic-inorganic hybrid nanoparticles with inorganic SiO_2 cores and BPA-responsive hydrogel layers. The ATRP initiator was successfully introduced onto the surface of SiO_2 nanoparticles by a versatile method for amino functionalization onto an SiO_2 surface, followed by transformation to alkyl bromide through a condensation reaction. ATRP of AAm, acryloyl-CD and MBAA from the ATRP initiator on the surface of SiO_2 nanoparticles was performed to form a CD-PAAm hydrogel layer on their surface. The resultant CD-PAAm/SiO_2 nanoparticle had an inorganic SiO_2 core and CD-PAAm hydrogel layer with the CD ligand for BPA. Similarly to the BPA-responsive bulk hydrogels we reported previously, the CD-PAAm/SiO_2 nanoparticles exhibited shrinkage in response to the target BPA. As the CD ligands in the CD-PAAm hydrogel layer formed sandwich-like CD-BPA-CD complexes with BPA, the CD-PAAm/SiO_2 nanoparticles shrank immediately owing to an increase in crosslinking density of the CD-PAAm hydrogel layer. Although CD-PAAm/SiO_2 nanoparticles require further research, they will likely become an important organic–inorganic hybrid nanomaterial for constructing molecular sensors and drug delivery systems.

ACKNOWLEDGEMENTS

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