

Synthesis of hyperbranched poly(amidoamine) conjugated silica (HBPCs) particles and their application to colorimetric detection of cadmium ion

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Abstract Hyperbranched poly(amidoamine) conjugated silica (HBPCs) particles were synthesized by grafting poly(amidoamine) dendrimers on multiple-functional hybrid silica (MHS) particles containing three different organosilane functional groups. Due to advantageous combination of dendrimers, with ample and controlled amount of amine groups, and monodisperse and stable MHS particles from simple one-pot synthesis, the HBPCs particles can serve as multifunctional platforms for various applications. The growth of the amine functional groups of the HBPCs particles with the generation number was confirmed by monitoring the amide peaks in IR spectra as well as indirectly by monitoring the amount of the molecules that are bound to the functional groups. As a proof of principle, colorimetric sensors for Cd ions were prepared by employing the HBPCs particles and organic Cd ion sensing molecules. Notably, the sensor particles from HBPCs particles of different generations showed different detection ranges due to the increase in the amount of amine functionalities by grafting processes.

Keywords Hyperbranched · Poly(amidoamine) · Multifunctional hybrid silica particles · Dendrimer · Colorimetric detection

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Introduction

Dendrimers—highly branched three-dimensional synthetic macromolecules—are one of the most interesting classes of polymers. These polymers have a highly defined and organized structure that is composed of a central core, branched repeating units, and end groups [1]. They are synthesized by a step-by-step procedure in which every repeated sequence of reactions produces a higher generation (G) molecule that would have a doubled molecular weight and a doubled number of functional end groups. Due to their unique structure, dendrimers have interesting characteristics such as narrow polydispersity, defined nanoscale size, and internal cavities and channels [2–4]. Importantly, dendrimers can have an ample amount of various functional groups in a limited volume, due to exponential growth in the number of their functional end groups with generation number. Because of these advantages, dendrimers have received considerable attention as novel supramolecules during the past few decades in wide ranges of fields [5–11]. Unfortunately, practical applications of the dendrimers suffer from their costly and time-consuming synthetic procedure. Moreover, their small size, typically less than 10 nm, makes them difficult to be recycled after use, limiting some of potential applications such as catalysts and metal chelates. To circumvent these problems, dendrimers have been grafted onto larger support materials, mostly silica-based ones. Surface modification of silica particles has been traditionally used to adjust adhesion characteristics or to improve dispersion properties as well as to introduce new types of chemical functionalities. In order to amplify the effect of surface functionalization, the structural ordering and the increase in the number of surface functional groups have been

recently emerged as the most important strategy. As a route to generate these hybrid materials with above characteristics, silica-dendrimer composites have been prepared by growing the dendrimers directly onto the surface of silica particles. Such dendrimer-grafted silica materials can exhibit the combined advantages of both the dendrimers (high density of active sites) and those of silica (inert and stable).

Herein, we developed hyperbranched poly(amidoamine) conjugated silica (HBPCs) particles by grafting multifunctional hybrid silica (MHS) nanoparticles—silica particles containing two or three different organic functional groups—with polyamidoamine (PAMAM) dendrimers [12, 13]. The MHS particles were prepared using our recently developed simple, one-pot synthetic method [14]. Notably, the PAMAM-MHS (HBPCs) particles were prepared without additional surface modification of the MHS particles, to introduce organic functional groups that serve as focal points to anchor dendrimers. The growth of the functional groups of the HBPCs particles with the generation number was demonstrated through IR analysis and analysis on the amount of dye molecules bound to the functional groups. The HBPCs particles have the advantageous features of both of the two materials: PAMAM has numerous branches of amine groups in end sites, exhibiting nontoxicity and good compatibility to biological systems, and MHS particles have stability from their solidity, easy modification of their functionality, and monodispersity. Furthermore, the HBPCs particles can serve as multifunctional platforms as they have additional MHS-borne organic functional groups, other than amine groups from PAMAM, which can be utilized for other reactions such as polymerization and binding with metal ions or other organic materials. As the MHS particles can be prepared in the average size ranging from submicron to micron with a very narrow size distribution [14], the potential application fields of the PAMAM-MHS (HBPCs) particles may include not only industrial applications but also intracellular or medical applications.

As a proof of principle, colorimetric sensors of cadmium ions were prepared by loading $\alpha, \beta, \gamma, \delta$ -tetrakis(1-methylpyridinium-4-yl)porphine-*p*-toluenesulfonate (TMPyP) molecules into the HBPCs particles of different generations. Note that the HBPCs particles are an excellent sensor matrix for optical and colorimetric measurements because of the high optical transparency and photo- and thermal stability of both PAMAM and silica [10]. TMPyP is an organic molecule which has been known as a highly sensitive chromogenic molecule for the detection of metal ions including cadmium ions due to the formation of stable coordination complexes that produces distinctive visible color changes [15, 16]. Recent studies showed that compared to free TMPyP

molecules, the immobilized TMPyP molecules in the solid supports, such as silica and graphene, have faster metal-chelate formation, by flattening the structures of TMPyP molecules and increasing their basicity, as well as enhanced sensitivity due to a high number density of the sensing TMPyP molecules adsorbed on inorganic support materials [17]. We expected that we could prepare the sensors with further enhanced and controlled sensitivity by controlled increase in the immobilized amount of TMPyP molecules in the support matrix. In this study, TMPyP molecules were immobilized to the HBPCs particles through the ion-pair interaction between TMPyP molecules and sulfonic acid groups modified from amine and mercapto groups of the particles, and therefore, the number density of the immobilized TMPyP molecules was supposed to depend on the amount of amine functional groups [14]. Consequently, the sensitivity and the detection range of the sensors would be controlled by the dendrimer generation number of the HBPCs particles. Visible color changes of the HBPCs particle sensors in the presence of cadmium ions were fast and notable by naked eyes, and the sensitivity and the detection range of the sensors varied with the dendrimer generation number.

Experimental section

Materials

All materials were analytical grade and used as purchased without further purification. Vinyltrimethoxysilane (VTMS, 98 %), 3-aminopropyltrimethoxysilane (APTMS, 99 %), methyl acrylate (MA, 99 %), ethylenediamine (EDA, 99 %), methylthioglycolate (95 %), $\alpha, \beta, \gamma, \delta$ -tetrakis(1-methylpyridinium-4-yl)porphine *p*-toluenesulfonate (TMPyP), and $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (98 %) were obtained from Sigma-Aldrich Company Ltd., USA. 3-Mercaptopropyltrimethoxysilane (MPTMS, 97 %) was purchased from Fluka. Ammonium hydroxide solution (30 %, *w/w*), nitric acid (60 %), hydrogen peroxide (34.5 %, *w/w*), and buffer solutions (pH 9, 10, and 11) were obtained from Sam-Chun Chemicals.

Physicochemical characterization

The size and morphology of the prepared particles were analyzed with field emission-scanning electron microscopy (FE-SEM, JEOL JEM-6340F). The chemical characterization of the particles was performed with the Fourier transform-infrared spectrometer (FT-IR, AAB FTLA2000), and nuclear magnetic resonance spectrometry (Mercury Plus 300 MHz). Spectroscopic

characterization of TMPyP sensor molecules and cadmium HBPCs sensor particles, before and after binding with Cd ions, was also carried out using ultraviolet and visible spectrometry (UV–Vis, Scinco S-4100).

Synthesis

Preparation of multifunctional hybrid silica (MHS) particles

MHS particles that consisted of vinyl, mercaptopropyl, and aminopropyl siloxanes were prepared by a two-step acid-base/hydrolysis-condensation process as previously described [14]. First, 0.2 mL of nitric acid (60 wt.%, 2.76 mmole) was added into a 500-mL three-neck round-bottom flask containing 150 mL of deionized water at 50 °C. A total of 2.5 mL of VTMS (16.03 mmole), 2.5 mL of MPTMS (12.85 mmole), and 0.5 mL of APTMS (2.75 mmole) were then injected to the acidic aqueous solution that was stirred at 300 rpm. The resultant solution was stirred for additional 90 s to initiate the hydrolysis reaction. Next, 20 mL of ammonium hydroxide (30 wt.%, 153 mmole) was poured into the mixture to induce the condensation reaction. The transparent solution became turbid, indicating that the colloidal particles were formed. After being stirred for 8 h, the suspension was filtered through a membrane filter and washed with 100 mL of deionized water twice. Thus formed, trifunctional silica particles, containing vinyl, amine, and mercapto groups, were obtained after drying under vacuum at 50 °C for 12 h.

Preparation of hyperbranched PAMAM-conjugated silica (HBPCs) particles

HBPCs particles were prepared by grafting poly(amidoamine) dendrimers onto the surface of MHS particles (0th generation particles, G(0) or G(n-1)), by repeating two successive reactions described as follows [12, 13, 18, 19]: (1) Michael addition of methyl acrylate (MA) to amino groups on the surface of MHS particles to construct methyl ester-terminated PAMAM dendron-modified MHS particles, which are (n-0.5)th generation particles, G(n-0.5); (2) amidation reaction of the ester moieties of G(n-0.5) particles with ethylenediamine (EDA) to produce nth generation of PAMAM-MHS particles, G(n). Here, n is the positive integer (1, 2 ...). The preparation procedure of hyperbranched poly(amidoamine) conjugated silica (HBPCs) particles, along with chemical structures of the grafted dendrimers, is shown in Scheme 1.

(1) Michael addition

A total of 0.5 g of MHS particles (0th particles) or G(n-1) PAMAM-MHS particles were dispersed into 20 mL of methanol in a 100-mL three-neck round-

bottom flask at 50 °C, and then, 0.2 mL of MA was added to the mixture. After stirring for 24 h, the mixture was filtered through a membrane and washed with 100 mL of methanol. G(n-0.5) particles, methyl ester terminated MHS particles or PAMAM-MHS particles, were obtained after drying under vacuum at 50 °C for 12 h.

(2) Amidation reaction

A total of 0.5 g of the G(n-0.5) particles were placed in a 100-mL round flask, and 5 mL of EDA (excess amount compared to the amount of terminal ester groups) was added both as a reactant and as a solvent. After stirring for 20 h at 70 °C, the mixture was filtered through a membrane filter and washed with 100 mL of methanol. The product was dried under vacuum at 50 °C for 12 h to obtain G(1) or G(n) particles.

Preparation of cadmium sensor particles: TMPyP loaded HBPCs particles

(1) Thiolation of MHS (or hyperbranched G(n) PAMAM-MHS) particles

MHS or hyperbranched G(n) PAMAM-MHS particles were thiolated using the substitution reaction reported previously [20, 21]. A total of 1.0 g of MHS or G(n) PAMAM-MHS particles were dispersed in 10 mL of deionized (DI) water. A total of 10 mL of methyl mercaptoacetate was then added to the flask and stirred at 50 °C for 9 h. The product suspension was filtered through a membrane filter and washed with DI water. Mercapto-terminated particles were obtained after drying under vacuum at 70 °C for 12 h.

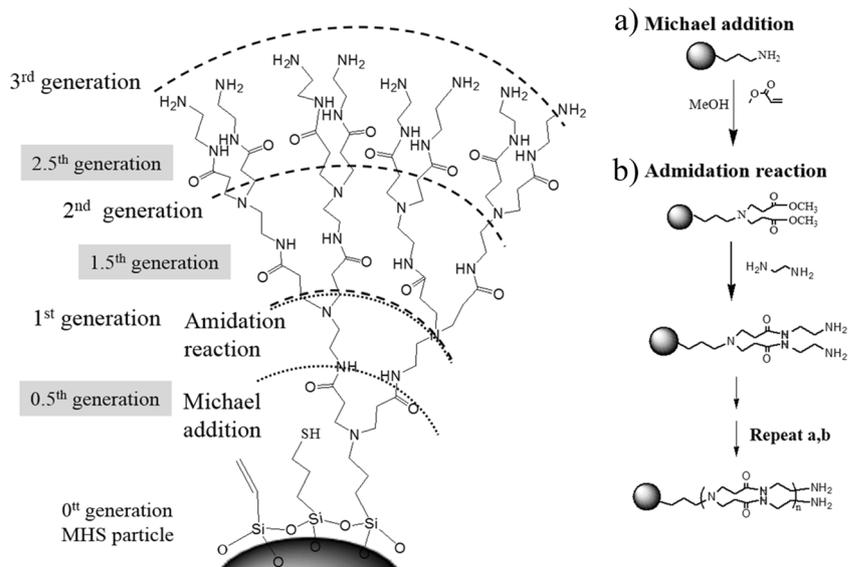
(2) Oxidation of mercapto functional groups in MHS or G(n) PAMAM-MHS particles to sulfonic groups

A total of 0.5 g of mercapto-terminated, MHS or hyperbranched G(n) PAMAM-MHS particles was dispersed in 150 mL of aqueous hydrogen peroxide solution (30 wt.%). After being stirred for 18 h, the mixture was filtered through a membrane filter and washed with DI water. Sulfonated MHS or G(n) PAMAM-MHS particles were obtained after drying under vacuum at 50 °C for 12 h.

(3) Immobilization of TMPyP molecules in the sulfonated MHS, or hyperbranched G(n) PAMAM-MHS particles

A total of 0.1 g of sulfonated, MHS or G(n) PAMAM-MHS particles was dispersed in a 250-mL Erlenmeyer flask charged with 100 mL of pH 10 buffer solution containing TMPyP sensor molecules at 40 °C. After being stirred for an hour, the mixture was filtered through a membrane filter and washed with pH 10 buffer solution several times. Cadmium sensor particles—TMPyP immobilized, MHS, or hyperbranched G(n) PAMAM-MHS particles—were obtained after drying.

Scheme 1 a Structure and b preparation method (Michael and amido addition reactions) of hyperbranched poly(amidoamine) conjugated silica (HBPCs) particles



Detection of cadmium ions using HBPCs sensor particles

The 20-mL aliquots of pH 10 buffer solutions containing 0, 1, 2, 3, 4, 5, and 13 ppm of cadmium ions were added to vials, each containing 0.02 g of the sensor particles (TMPyP immobilized, MHS, or hyperbranched G(n) PAMAM-MHS particles) and stirred at room temperature for 30 min. The color changes of the sensor particle dispersions were monitored by naked eyes and compared each other sequentially. For quantitative analysis, the mixture from each vial was filtered through membrane filter, dried at room temperature for 2 h, and then the products were analyzed by solid state UV-Vis spectroscopy.

Results and discussion

Synthesis and characterization of multifunctional hybrid silica (MHS) particles

MHS particles containing vinyl, mercapto, and amino groups were synthesized so as to be used as a base platform to prepare hyperbranched particles. A structural drawing of the MHS particles and their physicochemical characterization results are shown in Fig. 1. An SEM image of the MHS particles shows spherical particles having smooth surfaces with monodispersity in size and shape. The FT-IR spectrum exhibits characteristic stretching vibrational absorption bands for the corresponding organosilane functionalities such as C–H stretching vibrations from vinyl groups at 3100 cm^{-1} and C–H stretching vibrations from aliphatic mercapto-propyl groups at 2900 cm^{-1} . However, N–H stretching vibrations from aliphatic amino-propyl groups could not be found due to relatively small amount compared to other two

functional groups in MHS particles. Vibrational absorption peaks around $1000\text{--}1200\text{ cm}^{-1}$ corresponding to Si–O and Si–C functional groups were also observed. Solid-state ^{13}C NMR analysis reveals typical carbon resonance peaks for the three functional groups. For instance, strong peaks near 135 ppm are from unsaturated carbons, demonstrating the presence of vinyl functionality, while the peaks between 0 and 50 ppm correspond to aliphatic carbons from amino-propyl and mercapto-propyl functional groups.

Preparation and characterization of HBPCs particles

Hyperbranched PAMAM-conjugated MHS (HBPCs) particles of n th generation ($n=1$ to 5) were prepared by repeating two consecutive reactions for n times as shown in Scheme 1: (1) Michael addition of methyl acrylate (MA) to amine moieties on the surface of MHS or G($n-1$) particles and (2) the amidation reaction of the resultant ester moieties with alkylenediamine [12, 22, 23]. The morphology and size of HBPCs particles, G(n) PAMAM-MHS particles, were almost unchanged from those of original MHS particles (see SEM images in SI. 1). This may be due to relatively small size of PAMAM groups compared to size of MHS particles. IR characterization was employed for quantification of the PAMAM groups in HBPCs particles of each generation. Formation of G($n-0.5$) particles, by the Michael addition, and G(n) particles, by the amidation reaction, was confirmed by monitoring the ester and the amide absorption peaks, respectively, in IR spectra. As can be seen in Fig. 2a, an ester peak, appeared at 1735 cm^{-1} , was observed prominently for G($n-0.5$) PAMAM-MHS particles, while an amide peak at 1650 cm^{-1} was notable for both G($n-0.5$), except G(0.5), and G(n) PAMAM-MHS particles. The intensities of the two peaks for each generation of the particles were quantified as shown

Fig. 1 **a** Structural drawing, **b** SEM image, **c** FT-IR spectrum (ν =stretch, δ =bend), and **d** CP-MAS ^{13}C NMR spectrum

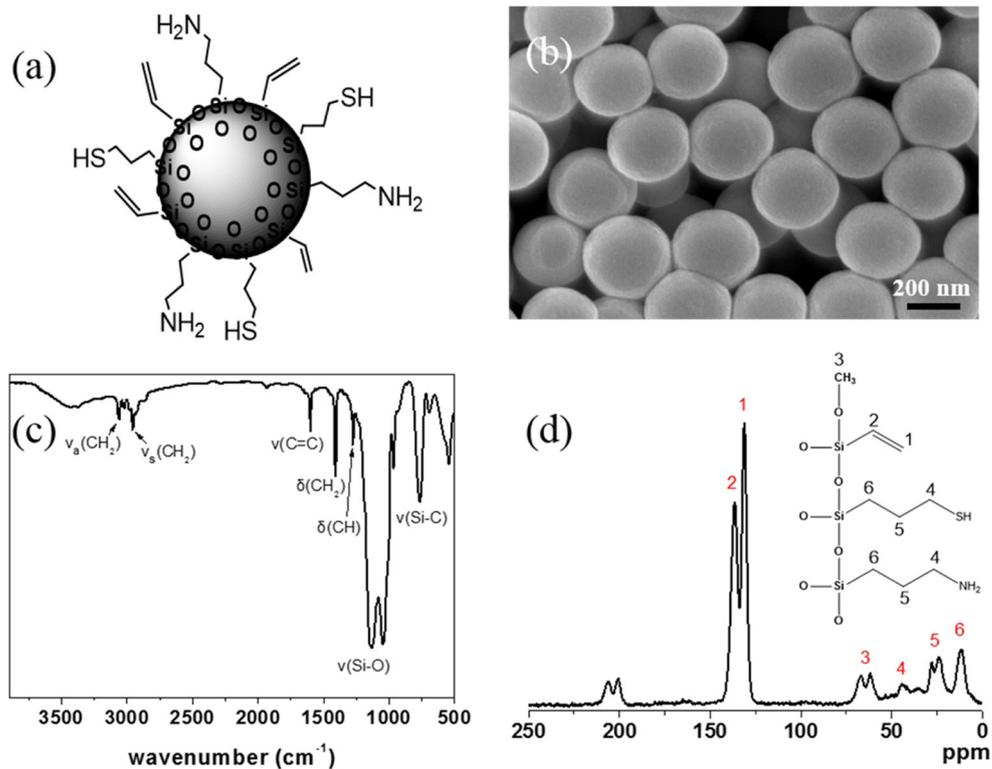
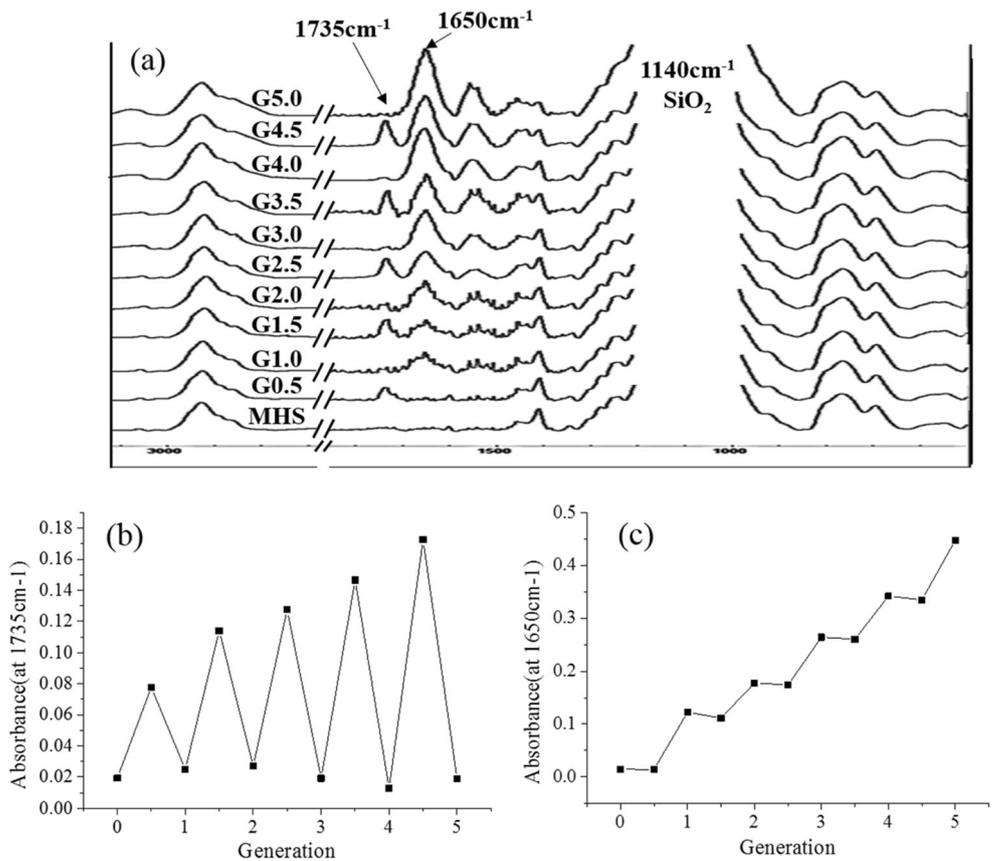


Fig. 2 IR spectra (a) and variation in the intensity of the ester peak (1735 cm^{-1}) (b), and variation in the intensity of the amide peak (1650 cm^{-1}) (c), of hyperbranched poly(amidoamine) conjugated silica (HBPCs) particles with respect to the generation growth



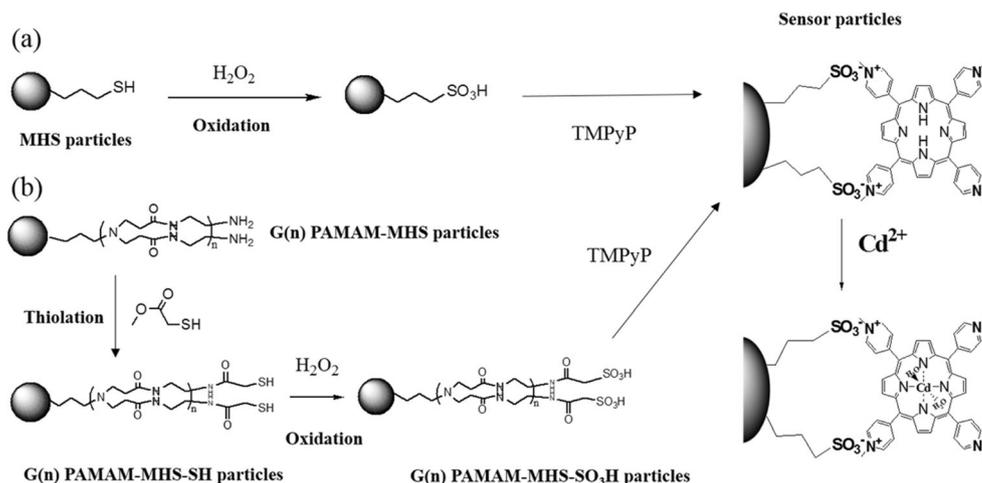
in Fig. 2b, c. It is noticeable that the intensity of the ester peaks for G(n-0.5) particles increased slowly with the dendrimer generation number while the ester peak intensity for G(n) particles with different nth generation approached to zero, indicating that most of the generated ester groups were converted into amides by the amidation reaction. In the meanwhile, the amide peak intensity for G(n) particles gradually increased as the generation number of the grafted dendrimers increased—highest for G(5) PAMAM-MHS particles (the highest generation HBPCs particles prepared in this study)—demonstrating the growth of the PAMAM branches. The normalized intensity ratio of the amide peak for G(n+1) particles to that of G(n) particles was calculated to be 1.45, 1.48, 1.30, and 1.31 for G(2), G(3), G(4), and G(5) particles, respectively (SI. 2). The absorbance intensity normalization of the amide peak for G(n) particles was carried out with respect to the Si–O peak as a reference which exhibited the highest absorption intensity in the IR spectrum. Theoretically, the absorbance ratio is supposed to be 2.0, 4.0, 8.0, and 16.0 for G(2), G(3), G(4), and G(5) particles, respectively, as the amount of amine functionalities should increase by 2 when the generation number of HBPCs particles increase by one. Finally, the conversion ratio of grafting for each G(n+1) particles—defined as ratio of the above experimental amide peak intensity for G(n+1)/G(n) to that of the theoretical ratio—was calculated. The conversion ratios of grafting decreased as the generation number increased, showing the values of 0.73, 0.37, 0.16, and 0.08 for G(2), G(3), G(4), and G(5) particles, respectively (SI. 2). The decreasing conversion ratio indicated that the higher the generation number was, the more incomplete propagation occurred. The incomplete propagation of hyperbranched PAMAM may be due to the fact that (1) the heterogeneous reaction prevents the complete Michael addition and the amidation with surface functional groups and/or (2) the grafted chains interfere with the propagation of dendrimer because of steric hindrance. Such decreasing trend in the conversion ratio of grafting with the generation number of PAMAM dendrimers is in accordance with the previous studies on hyperbranched PAMAM-grafted ultrafine silica by Murota et al. [24]. The growth of the amine groups of the HBPCs particles with the generation number of PAMAM dendrimers was also confirmed indirectly by monitoring the immobilization of sensor molecules in the HBPCs particles of each generation as detailed below in the section about colorimetric cadmium sensing by the TMPyP-bound HBPCs particles. Due to controlled expansion of functional groups and stable multifunctional silica-based cores, the HBPCs particles can be useful for many potential applications such as catalyst supports, biological matrices, building blocks for 3D structures, sensors, and polymeric resins. The expansion of dendrimer functional groups and the thermal stability of HBPCs particles were also studied by thermogravimetric analysis. From TGA curves of HBPCs particles of different generations, G(0), G(1), G(3), and G(5),

their percent weight losses from decomposition of organic groups and their decomposition temperatures were obtained (SI. 3). The decomposition temperatures of all the HBPCs particles were higher than 300 °C, indicating their excellent thermal stability. The percent weight losses of the HBPCs particles were increased from 42.5 % to 48.5, 52.5, and 58.5 %, with the increase in the generation number of HBPCs particles from 0 to 1, 3, and 5. This increase in % weight loss indicates the increase in the amount of combustible organic components, i.e., dendrimer amount, with the generation number. The wt% of dendrimer in HBPCs, calculated based on the % weight loss, were 6, 10, and 16 % for G(1), G(3), and G(5), respectively (SI. 4). Zeta potentials of HBPCs particles of different generations were measured at different pHs of particle dispersion using Zeta-potential and Particle size Analyzer ELSZ-1000 (Otsuka Electronics). The isoelectric points of HBPCs particles were obtained at pH of 6.8, 9.2, and 11.6 for G(0), G(3), and G(5) particles. The increase in the IEPs with the increase in the generation number also indicated that the amount of amine functional groups in HBPCs particles was increased along with the expansion of dendrimers as the generation number increased.

Preparation of cadmium ion sensors through immobilization of TMPyP molecules onto HBPCs particles

As a proof of principle, the HBPCs particles were utilized as a platform to construct a colorimetric cadmium sensor. As a sensing component, $\alpha,\beta,\gamma,\delta$ -tetrakis(1-methylpyridinium-4-yl)porphine-p-toluenesulfonate (TMPyP) molecule was employed. TMPyP molecules and their metal chelate complexes exhibit characteristic sharp and intensive absorption bands, known as Soret band, in the visible region. This Soret band is widely used for colorimetric as well as spectroscopic determination of metal-TMPyP complexes. Note that recently, the development of optical sensors that allow on-site, real-time detection without using time-consuming, complicated sample treatments and instrumentation have received considerable attention. The TMPyP-loaded HBPCs particles may serve as colorimetric sensors to meet such demand. Importantly, variation in the number density of TMPyP molecules in HBPCs particles, by using the particles of different generations, will allow the control of the sensitivity and detection range toward the Cd ions. TMPyP loading into the HBPCs particles was performed by immobilization of TMPyP molecules based on the ion-pair interaction between pyridinium groups in TMPyP molecules and sulfonic functionalities in the particles [15, 17]. The sulfonic functional groups in the HBPCs and MHS particles were introduced by modification of their amine and thiol groups as shown in Fig. 3. For mercapto functional groups, oxidation reaction of SH to SO₃H was performed using hydrogen peroxide (Fig. 3a).

Fig. 3 Immobilization of TMPyP sensor molecules onto hyperbranched poly(amidoamine) conjugated silica (HBPCs) particles and the detection of cadmium ion



For amine groups, thiolation reaction using a methyl mercaptoacetate reagent, converting amine groups to mercapto groups, was performed first, and then, the oxidation of converted mercapto groups with H_2O_2 was followed (Fig. 3b). The modification of amine groups to sulfonic groups was confirmed by the appearance of stretching vibrational peaks from S–O functionalities in sulfonic groups (SI. 5). After the conversion of the mercapto groups to sulfonic groups was completed, the immobilization of TMPyP molecules onto HBPCs particles was performed to construct cadmium sensors as shown in Fig. 3. It should be noted that the amount of immobilized TMPyP molecules in each generation of HBPCs particles can be used as a measure of generation evolution in HBPCs particles. The amount of TMPyP molecules immobilized through amine functional groups will increase with the generation number of HBPCs particles if the grafting and growth of the dendrimers on the core MHS particles are successful. The color of the TMPyP-loaded HBPCs particles got darker as the generation number of the particles increased—from light brown to dark brown (SI. 6), demonstrating that the immobilized TMPyP amount increased with the increase in particle generation number. The immobilized TMPyP amount was also quantified indirectly by evaluating the amount of unreacted TMPyP molecules as following: First, excess amount of TMPyP molecules are reacted with MHS particles or $G(n-1)$ HBPCs particles to form $G(n)$ HBPCs particles and the amount of unreacted TMPyP molecules was then determined by UV-Vis spectrometry using a calibration curve in the concentration range following the Beer-Lambert law. The measured amount of unreacted TMPyP molecules was subtracted from the initial input amount of TMPyP molecules to obtain the amount of immobilized TMPyP molecules. In order to maximize the amount of immobilized TMPyP in the HBPCs particles, reaction temperature, reaction time, and the pH of the reaction medium were varied. The optimum reaction condition for

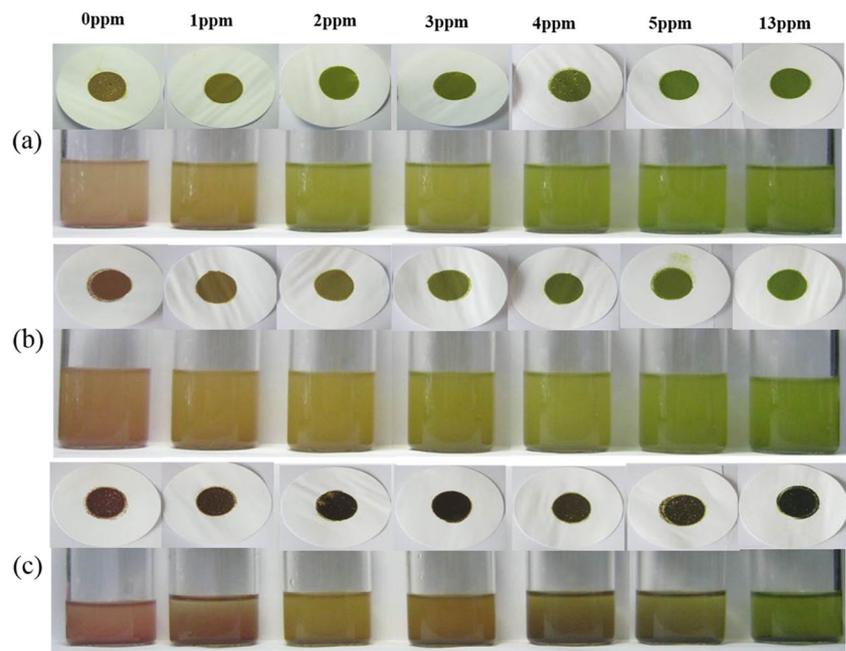
the immobilization of TMPyP molecules on MHS or HBPCs particles was found to be $40^\circ C$, pH 10, and 1 h (SI. 7).

The measured amounts of TMPyP molecules immobilized on $G(0)$ (MHS), $G(1)$, $G(2)$, $G(3)$, $G(4)$, and $G(5)$ HBPCs particles were 6.95, 5.21, 7.50, 9.45, 10.10, and 11.95 mg. These results, in general, show an expected trend in that the amount of immobilized TMPyP molecule increases with the generation number of HBPCs particles. For comparison with IR analysis results, the ratios of immobilized amount of TMPyP molecules in $G(n+1)$ particles to that in $G(n)$ particles were calculated, which were 1.44, 1.26, 1.07, 1.09 for $G(2)$, $G(3)$, $G(4)$, and $G(5)$ particles, respectively. These results are slightly lower than those from IR analysis, which may be due to following reasons: (1) access of TMPyP molecules to sulfonic groups, which were generated from hyperbranched amine groups by thiolation and oxidation reaction, in the core particles or in the low generation branches are often blocked due to steric hindrance; (2) TMPyP molecules are known to bind with sulfonic functional groups through bi-dentate type ligation as shown in Fig. 3 [15, 17]. With low level of sulfonic groups per particle, the chance for two sulfonic functional groups being in close proximity to each other for bi-dentate type ligation may be significantly reduced, resulting in significantly low amount of immobilized TMPyP molecules.

Colorimetric and spectroscopic detection of cadmium ions using HBPCs sensor particles

The HBPCs sensor particles with immobilized TMPyP molecules were exposed to various concentrations of Cd ions, and color changes were observed as shown in Fig. 4. The aqueous suspensions, as well as the filtered particles, of HBPCs sensor particles show progressive color changes from red-brown to green, distinguishable by naked eyes, as the Cd ion concentration increased from 0 to 13 ppm. It could also be observed that the hue of developed color after binding with Cd ions was

Fig. 4 The color changes of **a** MHS, G(0), **b** G(3), and **c** G(5) sensor particles in the presence of Cd(II) ions of various concentrations



getting intensified as the generation number of HBPCs sensor particles increased. Moreover, the sensor particles from the HBPCs particles of different generations show different detection ranges toward Cd ions. For MHS, G(0), sensor particles, distinct color changes were observed by naked eyes between 0, 1, 2–3, 4 ppm in Cd ion concentration, and the development in green color was saturated at concentration higher than 4 ppm. In a meanwhile, apparent color changes in G(3) sensor particles appeared between 0, 1–2, 3–4, and 5 ppm, showing the saturation in green color at concentration higher than 5 ppm. For G(5) sensor particles, noticeable color changes were detected between 0–1, 2, 3, 4–5, and 13 ppm.

Spectroscopic observation of the sensors upon binding with different concentrations of Cd ions was also performed. The sensor particles with or without bound Cd ions, obtained by filtering aqueous solutions of the sensors with or without Cd ions, were used for solid-state UV/Vis spectroscopic analysis. As presented in Fig. 5, an absorption peak at 425 nm, a

Soret band from TMPyP molecules, was red-shifted to 460 nm upon binding with Cd ions. For MHS sensor particles, the intensity of a Soret band at 425 nm was distinctively reduced with increase in the concentration of Cd ions from 0, 1, and 2 to 5 ppm while the absorption band at 460 nm that started to show up at Cd ion concentration of 5 ppm and over. For G(3) sensor particles, a similar decreasing pattern of the Soret band intensity with increase of Cd ion concentration was also observed. However, the absorption band at 460 nm appeared at the Cd ion concentration of 2 ppm for G(3) sensor particles. In the case of G(5) sensor particles, shapes of the Soret band from TMPyP sensor molecules and the red-shift of the band upon binding with Cd ions were not sharply defined, but the decrease in intensities due to the increase in bound Cd ion concentration was clearly observed in the Cd ion concentration between 5 and 400 ppm. For further applications, spectral changes in UV/Vis absorption spectra of the HBPCs particle sensors in the presence of other heavy metal ions such as

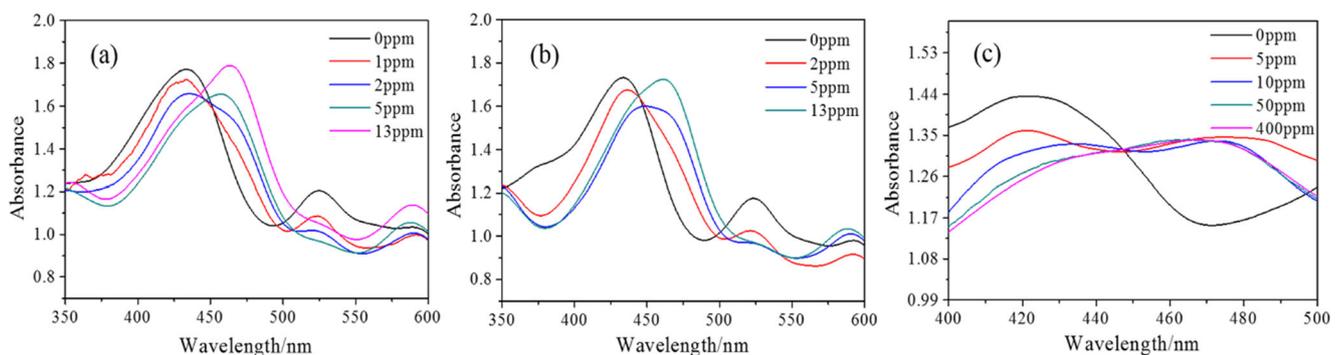


Fig. 5 The changes in UV-Vis spectra of **a** MHS, G(0), **b** G(3), and **c** G(5) sensor particles before and after binding with Cd(II) ions of different concentrations

zinc and mercury were also investigated. A Soret band from TMPyP molecules was red shifted from 422 to 448 nm for Zn ion bound TMPyP molecules and 464 nm for Hg ion bound TMPyP molecules, suggesting the possibility of selective spectroscopic detection of heavy metal ions from their mixture (SI. 8). In summary, HBPCs particles in combination with TMPyP molecules can be utilized as colorimetric and spectroscopic sensors for Cd ion detection with the detection ranges controlled by the generation number, enabling quantitative and qualitative analyses of toxic heavy metal ions to be accomplished on-site and in the laboratory.

Conclusion

Hyperbranched silica particles grafted with poly(amidoamine) of *n*th generation were synthesized from MHS particles, composed of vinyl, mercapto-propyl, and amino-propyl siloxanes, by repeating two consecutive reactions *n* times: (1) Michael addition of methyl acrylate (MA) to amine moieties on the surface of MHS particles and (2) the amidation reaction of resulting ester moieties with alkylendiamine. The increase in the amount of amine functional groups with increase in generation number of the hyperbranched poly(amidoamine) conjugated silica (HBPCs) particles was observed directly by IR analysis as well as indirectly by monitoring the amount of the molecule—TMPyP molecule, a sensor molecule for metal ions—bound to the functional groups—indicating that the HBPCs particles can serve as multifunctional platforms for various applications. As a proof of concept, the TMPyP-immobilized HBPCs particles were demonstrated for their ability as colorimetric sensors for Cd ions. Notably, the detection ranges of the sensor particles were controlled by the generation number of the HBPCs particles.

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