

## Preparation of ORMOSIL particles with controlled amounts of binary organic functional groups and their application to colorimetric sensors for cadmium ion

Jung Min Ha<sup>a</sup>, Sun Teak Kim<sup>b</sup>, Seong Je Jeon<sup>b</sup> and Sang Man Koo<sup>a,b,\*</sup>

<sup>a</sup>Department of Fuel Cells and Hydrogen Technology, Hanyang University, Seoul, 133-791, Korea

<sup>b</sup>Department of Chemical Engineering, Hanyang University, Seoul, 133-791, Korea

Binary functional ORMOSIL particles were prepared by the one pot process using organosilane mixtures of mercaptopropyltrimethoxysilanes and vinyltrimethoxysilanes. Colorimetric cadmium ion sensors were then prepared by immobilizing  $\alpha,\beta,\gamma,\delta$ -tetrakis(1-methylpyridinium-4-yl)porphine-p-toluenesulfonate molecules in ORMOSIL particles containing a controllable amount of mercaptopropylsilanes that served as binding sites. The relative amount of mercaptopropyl and vinyl functionalities in particles were controlled by adjusting molar ratios of organosilanes and thereby the amount of immobilized TMPyP molecules was easily controlled, which allowed a facile control of the detection range and sensitivity toward Cd ion detection. A particle sensor grid capable of colorimetric detection of Cd ions in a concentration range from 10 ppb to 5 ppm was constructed by combining three cadmium sensors with a different amount of mercaptopropylsilanes and showed distinctive visible color changes in a different concentration range of cadmium ions. Recycled sensor particles exhibited almost the same sensing performance as freshly prepared ones.

**Key words:** Binary ORMOSIL particles, Organic functional groups, Colorimetric sensor, Cadmium ion.

### Introduction

Organically-modified silica (ORMOSIL) particles are organic-inorganic hybrid materials in which organic components are chemically bound to a sturdy inert inorganic silica backbone [1-3]. The resulting ORMOSIL particles can achieve novel properties and high functionalities for a wide variety of multiplex applications through control of the types and concentrations of organic components in the particles. However, such control is not easy for most of the currently available methods used to prepare ORMOSIL that are based on a two-stage procedure in which core silica particles are first formed, and then desired organic functional groups are introduced by surface modification with organosilanes containing the functional groups [4, 5]. The surface modification process is a slow and time consuming process and a single type of an organic functional group is usually introduced per each process. Therefore, multiple modification processes have to be employed in order to prepare multitasking functional ORMOSIL particles. Moreover, these methods do not guarantee the production of ORMOSIL particles with a reproducible amount of organic functional groups.

Previously, we reported a “one-pot, single-stage” synthetic method that can produce ORMOSIL particles containing multiple, organic functional groups. Because

of their uniform size and morphology as well as the simple, but efficient procedure to introduce the organic functionalities, the ORMOSIL particles from the one-pot synthetic method are expected to be useful for a broad spectrum of applications in academic science and industrial fields. In this study, we applied this method to prepare a recyclable colorimetric cadmium ion sensor grid. Cadmium is a widely used element in many industrial fields such as electroplating, batteries, nuclear fission, and metallurgy. On the other hand, cadmium is a highly toxic heavy metal, with a fatal influence on human health even at very low doses (critical level of  $10\ \mu\text{g L}^{-1}$  in blood or urine samples) [6]. Chronic cadmium exposure leads to cadmium accumulation in humans, causing renal dysfunction, calcium metabolism disorder, as well as certain forms of cancer [7-10]. The most well-known case of cadmium poisoning is the itai-itai (ouch-ouch) disease in Japan [11-14]. Currently, cadmium ion detection is typically performed in the laboratory using analytical instruments such as Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Differential Pulse Anodic Stripping Voltammetry (DPASV), and Neutron Activation Analysis (NAA) [15, 16]. These methods provide high sensitivity, but they are costly and often require complex and laborious procedures, which makes them unsuitable for on-site measurements. Therefore, there is a significant need for alternative cadmium ion detection methods that are inexpensive, simple, rapid and portable. Chemical sensors may be good candidates to satisfy these demands due

\*Corresponding author:  
Tel : +82-2-2220-0527  
E-mail: sangman@hanyang.ac.kr

to the advantage of high sensitivity and selectivity as well as providing real-time analysis. In particular, low-cost, or recyclable, colorimetric chemical sensors may be ideal candidates for on-site measurements of industrial toxic elements, such as cadmium, where detection is simplified by monitoring color changes with the naked eye [17, 18].

Our cadmium sensor grid contains sensor particles with different levels of detection and sensitivities towards the cadmium ion so as to cover a wide range of cadmium ion concentrations. The sensor particles are constructed by using the ORMOSIL particles as a stable solid-state platform and  $\alpha,\beta,\gamma,\delta$ -tetrakis(1-methylpyridinium-4-yl)porphine p-toluenesulfonate (TMPyP) molecules as a sensing component. TMPyP is a phorphyrin compound which has been known as a highly sensitive chromogenic molecule for the detection of metal ions due to the formation of stable metal coordination complexes [19-26]. TMPyP exhibits a characteristic sharp and intensive absorption band in the visible region, known as a Soret band. Upon binding with metals, this Soret band undergoes a peak shift that causes visible changes in the dye color, which makes TMPyP widely used for colorimetric as well as spectroscopic determination of various metals. In recent studies, TMPyP sensor molecules were immobilized in the solid supports, which resulted in the enhancement of both the rate of metal-chelate formation and the sensitivity when compared to free TMPyP molecules [20-22, 27]. The solid supports are considered to hold TMPyP in a flattened structure and/or to increase the basicity of TMPyP [20, 23, 24]. Note that silica-based particles are regarded as an excellent sensor matrix for optical and colorimetric measurements because of their high optical transparency and photo- and thermal stability as well as their non-toxicity. Moreover, the sensor molecule loaded in the inert silica matrix is less toxic than the sensor molecules alone, allowing for easier handling in the industrial field [28-33]. In our case, ORMOSIL particles are employed as a solid support so as to provide this sensitivity enhancement. Our synthetic strategy to produce the sensor particles of different dynamic ranges involves: 1) preparation of the ORMOSIL particles with a controlled amount of desired organic functional groups, based on the "one-pot" method, by adjusting the mole fraction of organosilanes containing the desired functional groups in the reaction mixture.; 2) chemical attachment of TMPyP molecules to the organic functional groups so as to obtain the sensor particles of a controllable detection range and sensitivity through a controlled amount of the sensing molecules. The ORMOSIL particles containing mercaptopropyl groups were prepared from a mixture of 3-mercaptopropyltrimethoxysilane (MPTMS) and vinyltrimethoxysilane (VTMS). Here, the mercaptopropyl functional group is utilized as an organic functional group for chemical attachment of the TMPyP molecules. The mercaptopropyl groups in the ORMOSIL particle

were oxidized to negatively charged sulfonic acid groups so as to be bound to the positively charged pyridinium groups in TMPyP molecules. Chemical fixation of the sensing molecules may enable the control of the cadmium ion sensitivity and detection ranges of the sensor particles by controlling the amount of bound TMPyP molecules per particle through the amount of mercaptopropyl groups per particle (which is controlled by adjusting the relative ratio of the two organosilanes in the reaction mixture). A colorimetric Cd sensor grid was constructed by combining three ORMOSIL sensor particles with different amounts of mercaptopropyl functional groups-each showing distinctive color changes in different concentration ranges of Cd ions-for fast and facile on-site cadmium ion detection over a wide range of cadmium concentrations. The recyclability of the ORMOSIL sensor particles through EDTA treatment was also demonstrated. The present design of the sensors can be extended to other recyclable types of sensors by switching the sensing molecules and/or organic functional groups of the ORMOSIL particles.

## Experimental

### Materials

All materials were of analytical grade and used as purchased without further purification. Vinyltrimethoxysilane (VTMS, 98%),  $\alpha,\beta,\gamma,\delta$ -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. Ethylenediaminetetraacetic acid (EDTA) was obtained from Junsei Chemical Co., Ltd. Ammonium hydroxide solution (30 wt%), nitric acid (60%), hydrogen peroxide (34.5%), and buffer solutions with pH values of 9.0, 10.0, 11.0 were purchased from Sam-Chun Chemical.

### Synthesis and sensor applications

#### *Synthesis of ORMOSIL sensor particles: TMPyP-loaded ORMOSIL particles*

The Cd ion sensing particles were prepared by three steps: 1) Preparation of ORMOSIL particles containing SH groups as base particles; 2) Oxidization of mercaptopropyl groups in ORMOSIL particles to sulfonic acid groups (ORMOSIL-SO<sub>3</sub>H); 3) Preparation of Cd ion sensing particles by immobilizing TMPyP dye molecules onto ORMOSIL-SO<sub>3</sub>H particles.

1) Preparation of ORMOSIL particles containing mercaptopropyl and vinyl silanes

ORMOSIL particles containing various amounts of mercaptopropylsilane groups were prepared by a procedure modified from a previously reported one-pot synthetic method [34]. One hundred fifty milliliters of de-ionized water was placed in a 500 ml three-neck round bottom flask at 50 °C, and 0.2 ml of nitric acid (60 wt%, 2.76 mmol) was added with stirring at

300 rpm using a mechanical stirrer. Mixtures of VTMS and MPTMS at a molar ratio of 1 : 1, 1 : 0.75 or 1 : 0.5, with a total concentration of 32.1 mmol, were injected into the acidic aqueous solution. After stirring for 90 seconds to initiate a hydrolysis reaction, 20 ml of ammonium hydroxide (30 wt%, 153 mmol) was added into the reaction mixture to induce a condensation reaction. The transparent solution became opalescent in a few minutes, indicating that colloidal particles were formed. The suspension was filtered through a membrane filter and washed with 100 ml of de-ionized water three times. ORMOSIL particles containing vinyl and mercaptopropyl groups were obtained after drying under vacuum at 50 °C for 12 hours.

2) Preparation of ORMOSIL particles containing sulfonic acid groups (ORMOSIL-SO<sub>3</sub>H)

0.5 g of the ORMOSIL particles as prepared above was placed in a 250 ml three-neck round bottom flask and 150 ml (excess) of aqueous hydrogen peroxide solution was added. The mixture was stirred at room temperature for 18 hours, filtered through a membrane filter, and washed with 100 ml of de-ionized water three times. The filtered product was dried under vacuum at 50 °C for 12 hours.

3) Preparation of ORMOSIL sensor particles: Immobilization of TMPyP molecules onto ORMOSIL-SO<sub>3</sub>H particles

0.1 g of ORMOSIL-SO<sub>3</sub>H particles was dispersed in a buffer solution of pH 10 containing TMPyP molecules at 40 °C. The amount of TMPyP in the buffer solution was  $9.46 \times 10^{-3}$ ,  $3.26 \times 10^{-3}$  and  $1.34 \times 10^{-3}$  mmoles for the particles from VTMS : MPTMS = [1 : 1], [1 : 0.75] and [1 : 0.5], respectively. The suspension was stirred for 1 hour to immobilize TMPyP molecules onto the particles, filtered through a membrane filter, and washed with 100 ml of deionized water three times. The sensor particles were dried at room temperature for 2 hours.

*Determination of the immobilized amount of TMPyP molecules onto ORMOSIL-SO<sub>3</sub>H particles*

The immobilized amount of TMPyP molecules was calculated as follows. The filtrate and wash solutions, which contained sensor particles and TMPyP, were collected. Second, the concentration of the combined solution of filtrate and washes was determined by UV-Vis spectroscopy based on a calibration curve constructed with TMPyP solutions of various known concentrations. The amount of unbound TMPyP molecules was obtained using the volume of the combined solution and its concentration. Third, the amount of immobilized TMPyP molecules was obtained by subtracting the measured unbound amount of TMPyP molecules from the initial amount of TMPyP molecules in the mixture solution.

*Colorimetric and spectroscopic observation of ORMOSIL sensor particles in the presence of cadmium ions*

20 ml aliquots of pH 10 buffer solution containing

various concentrations of cadmium ions are added to vials, each containing 4 mg of ORMOSIL sensor particles (TMPyP-ORMOSIL-SO<sub>3</sub>H particles). The mixture in each vial was then stirred at room temperature for 30 minutes, filtered, and dried at room temperature for 2 hours. The color changes of the dried ORMOSIL sensor particles after Cd binding were observed with the naked eyes. For spectroscopic analysis, the dried sensor particles were analyzed by solid state UV-Vis spectroscopy.

*Recovery of TMPyP immobilized ORMOSIL sensor particles by a displacement reaction of Cd ions with EDTA*

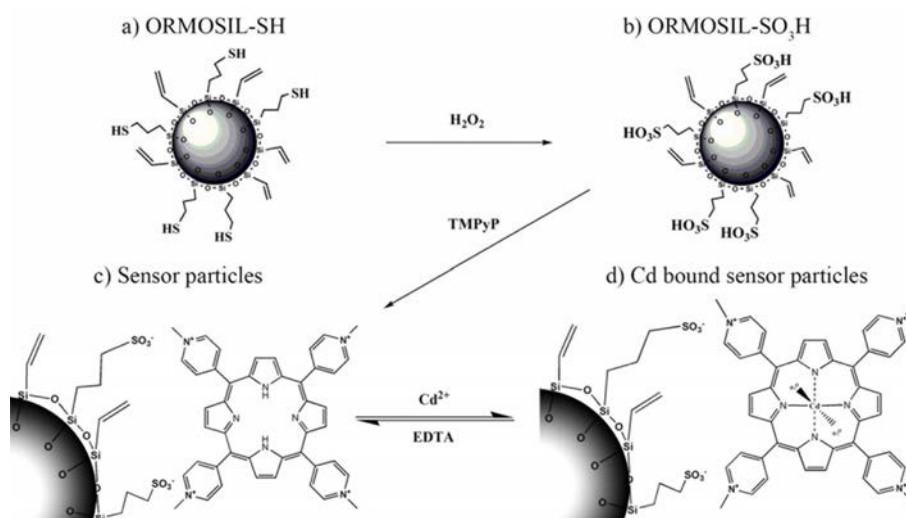
0.01 g of Cd ion bound sensor particles was dispersed in 10 ml of 0.01 M EDTA solution and stirred for 30 minutes to form Cd-EDTA complexes by a displacement reaction. Then, the solution was filtered and washed with deionized water three times to recover the sensor particles by removing Cd-EDTA complexes and unreacted EDTA.

## Characterization

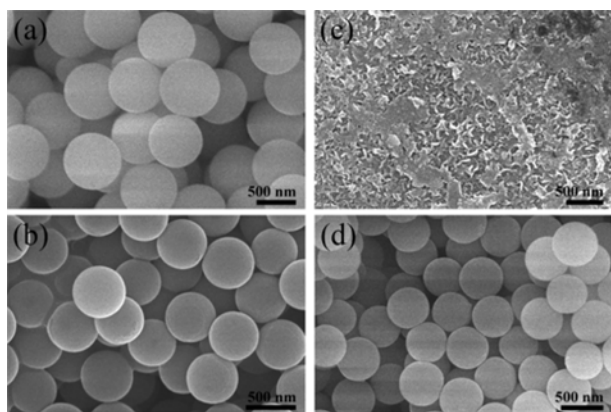
The size and morphology of the prepared particles were analyzed with Field Emission-Scanning Electron Microscopy (FE-SEM, JEOL JEM-6340F). The chemical characterization of the particles was also performed with Fourier Transform-Infrared spectrometry (FT-IR, AAB FTLA2000) and Nuclear Magnetic Resonance spectrometry (Mercury Plus 300 MHz). Liquid and solid state spectroscopic characterization of the TMPyP sensor molecules, ORMOSIL sensor particles, and Cd attached ORMOSIL sensor particles was carried out using Ultraviolet spectroscopy (UV-Vis, Scinco S-4100).

## Results and Discussion

The overall scheme for the preparation of ORMOSIL sensor particles, their detection of cadmium ions, and then the recovery of the sensor particles by EDTA treatment is shown in Fig. 1. In the proposed design of our sensor particles, SH is the key functional group to control the amount of immobilized TMPyP molecules per particle and thus, the sensitivity and detection range of the sensors. Therefore, the first stage, to prepare the ORMOSIL particles with a proper amount of SH groups, is crucial. We prepared the ORMOSIL particles by varying the molar ratio of VTMS to MPTMS in the initial monomer mixture solutions to be 0 : 1, 1 : 1, 1 : 0.75 or 1 : 0.5. The ORMOSIL particles were of spherical shape and similar in size-measuring 540(± 25) nm, 516(± 23) nm, 500(± 28) nm, and 520(± 23) nm in diameter for those prepared with the input molar ratio of 0 : 1, 1 : 1, 1 : 0.75 and 1 : 0.5, respectively. It should be noted that the ORMOSIL particles made of only MPTMS collapsed after the oxidation reaction of SH groups to SO<sub>3</sub>H using hydrogen peroxide. In the meantime, ORMOSIL particles made from mixtures



**Fig. 1.** Preparation of ORMOSIL sensor particles, their detection of cadmium ion, and recovery of the sensor particles by EDTA treatment.



**Fig. 2.** SEM images of ORMOSIL particles prepared with (a) all mercaptopropylsilane, (b) vinyl and mercaptopropyl (1 : 1) silanes, (c) and (d) the particles shown in (a) and (b) after  $H_2O_2$  oxidation, respectively.

containing larger amount of VTMS than MPTMS maintained their integrity after the oxidation reaction, as shown in Fig. 2. Therefore, the ORMOSIL particles obtained from VTMS-MPTMS mixtures with molar ratios of 1 : 1, 1 : 0.75 and 1 : 0.5 were used for further characterization and for preparation of the sensor particles.

The number of TMPyP molecules per g of particles is correlated to the amount of mercaptopropyl groups per g of particles. Therefore, the control of the amount of mercaptopropyl functional groups in ORMOSIL particles—done here by changing the ratio of two organosilanes containing mercaptopropyl groups and vinyl groups in the initial reaction mixture—would be the key factor for preparing a grid sensor with a wide cadmium detection range. The IR spectrum shows C-H stretching vibrational absorption peaks from unsaturated vinyl groups around  $3061\text{ cm}^{-1}$ , those from aliphatic propyl groups between  $2929\text{ cm}^{-1}$  as well as the peak from Si-O-Si around  $1050\text{ cm}^{-1}$  [34]. The solid state  $^{13}\text{C}$  NMR spectrum also shows resonance absorption peaks

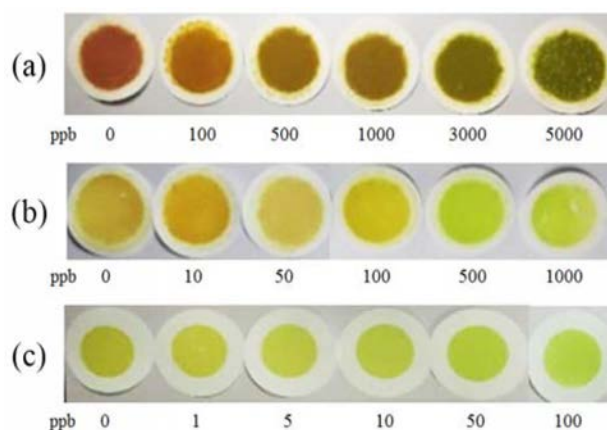
at 130–150 ppm from vinyl groups and those around 20–50 ppm from mercaptopropyl groups [34]. The ratios of mercaptopropyl group to vinyl group in ORMOSIL particles were quantified by analyzing the two absorption bands for mercaptopropyl groups and vinyl groups in FT-IR spectra of ORMOSIL particles—the peak at  $2929\text{ cm}^{-1}$  from a CH stretching vibration for mercaptopropyl groups and the peak at  $3061\text{ cm}^{-1}$  from a CH stretching vibration for vinyl groups. As the input ratio of VTMS : MPTMS for the synthesis of ORMOSIL particles was decreased, the intensity ratio of the two absorption peaks was also decreased. The relative ratios of measured absorption peak intensities in FT-IR spectra between vinyl and mercaptopropyl functional groups were 1.7, 1.4, and 1.0 for the input VTMS : MPTMS ratio of 1 : 0.5, 1 : 0.75, and 1 : 1, respectively.

In the next stage to prepare the ORMOSIL sensor particles, the mercaptopropyl groups in the ORMOSIL particles were oxidized to sulfonic acid groups by aqueous hydrogen peroxide solution and then mixed with an excess amount of TMPyP molecules so as to immobilize TMPyP in the particles. Since the TMPyP binding to the particles is based on the acid-base ion pair interaction between sulfonate anions in ORMOSIL particles and pyridinium groups in TMPyP molecules, the pH of the solution containing TMPyP and ORMOSIL particles may affect the amount of immobilization. In order to find the optimal pH, the pH of the reaction medium was increased to 9, 10, and then 11, which resulted an amount of immobilized TMPyP molecules of 0.38 mg, 2.15 mg, and to 2.95 mg, respectively, per 0.1 g of ORMOSIL particles obtained from mixtures of VTMS and MPTMS with a 1 : 1 molar ratio. While the results show the highest immobilized TMPyP amount for pH 11 (the highest tested pH), pH 10 was selected for the reaction pH because Cd ions tended to form  $\text{Cd}(\text{OH})_2$ , at a pH higher than 10.5, as a precipitate, which interferes the detection experiment. The optimal reaction temperature

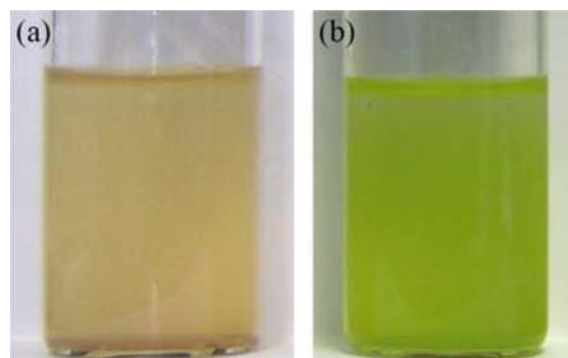
and reaction time for immobilization of TMPyP molecules on ORMOSIL particles were also determined. The amount of immobilized TMPyP molecules increased as temperature increased but reached a plateau at 40 °C and higher. A reaction time of 1 hour was employed to insure complete reaction. Therefore, the optimum conditions for the immobilization of TMPyP molecules in the ORMOSIL particles were set to be 40 °C, pH 10, and 1 hour.

Three different ORMOSIL particles, obtained from VTMS-MPTMS mixtures with molar ratios of 1 : 1, 1 : 0.75 and 1 : 0.5 were fashioned into Cd ion sensors-called sensor particles 1, 2 and 3 respectively-by immobilizing TMPyP molecules under optimum conditions. The amounts of immobilized TMPyP molecules in 0.1 g of ORMOSIL sensor particles were found to be 12.90 mg for sensor particle 1, 4.45 mg for sensor particle 2, and 1.83 mg for sensor particle 3, respectively. It can be noticed that the amount of immobilized TMPyP molecules is not linearly correlated with the relative amount of MPTMS in ORMOSIL particles. The amounts of immobilized TMPyP molecules in the ORMOSIL particles from mixtures of 1 : 0.75 and 1 : 0.5 molar ratios of VTMS:MPTMS are only 34% and 14% of that obtained from the 1 : 1 molar ratio mixture, respectively. This may be caused by the fact that TMPyP molecules bind with sulfonic functional groups through bi-dentate type ligation as shown in Fig. 1. In this instance, two sulfonic groups have to be close to each other for complete ligation. With a low level of sulfonic groups per particle, the chance for two sulfonic functional groups being close enough for bi-dentate type ligation may be significantly reduced, resulting in a significantly low amount of immobilized TMPyP molecules. Moreover, not all the available SH groups may have been converted to SO<sup>3-</sup> groups and some of the TMPyP molecules may bind to the particles by physical adsorption.

Color changes in the presence of the cadmium ion of sensor particles 1, 2 and 3-prepared from mixtures of VTMS : MPTMS with molar ratios of 1 : 1, 1 : 0.75 and 1 : 0.5, respectively-were investigated. The as-prepared sensor particles 1, 2 and 3 take the different color hues-red-orange, orange-yellow and yellow respectively-which indicates loading of different amounts of TMPyP (See the sensors at 0 ppb in Fig. 3). The sensor particles were suspended in aqueous solutions containing various known amounts of Cd ion (0 ~ 5 ppm) and stirred for 30 min. The colors of aqueous suspensions of the sensor particles were observed by the naked eye and then filtered/dried to obtain the dried powder sensors. The color of the dried sensor particles was also observed by the naked eye. We noticed that color changes in the dried sensor particles were more distinguishable than those in the aqueous suspensions, although color changes could be observed for both cases (See Fig. 4 for color changes of aqueous suspension of sensor particle 1 in the



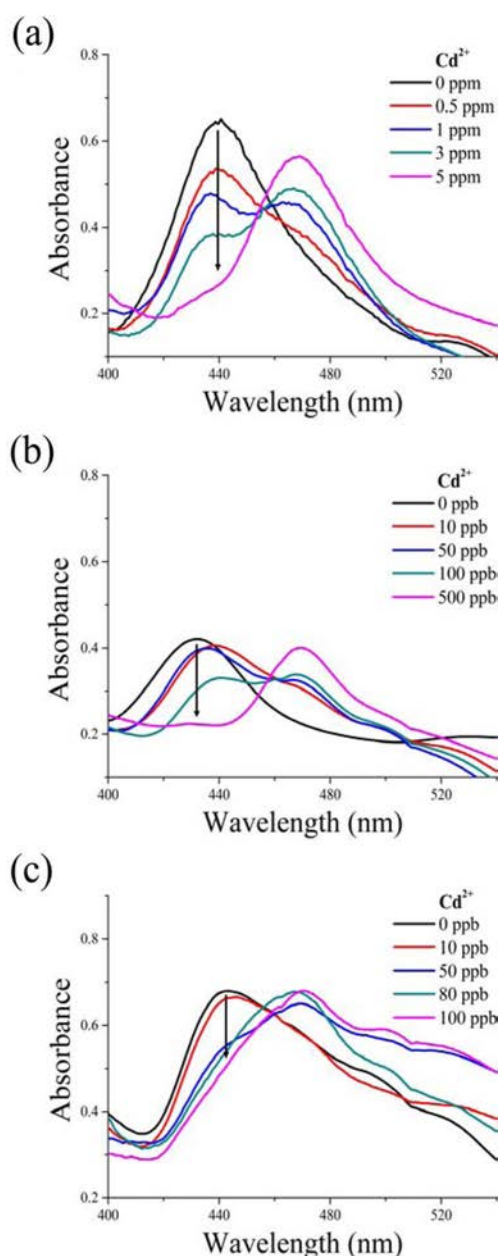
**Fig. 3.** Color changes in ORMOSIL sensor particles with different amount of Cd ion binding. (a) Sensor particle 1; (b) Sensor particle 2; (c) Sensor particle 3.



**Fig. 4.** Color changes in a 10 mL aqueous suspension containing 2 mg ORMOSIL sensor particles 1, with the mole ratio of VTMS to MPTMS being 1 : 1, (a) before (brown) and (b) after (green) Cd ion binding.

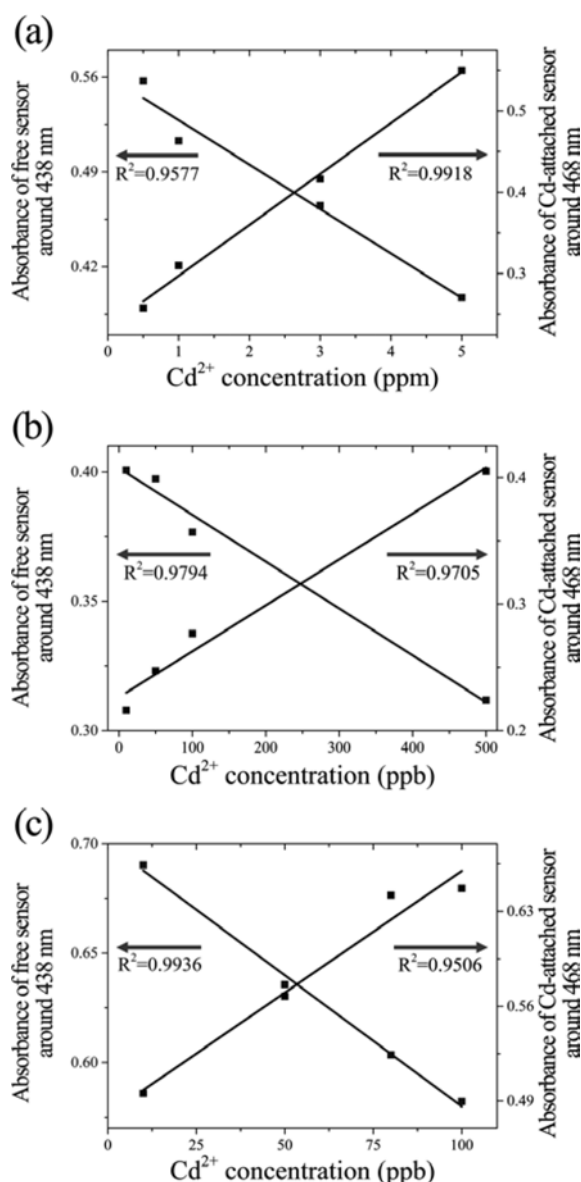
presence of Cd ion).

The colorimetric detection range for each type of sensor particles was found to be different. As shown in Fig. 3a, sensor particle 1 exhibited discernible color changes, from an initial red-orange hued mahogany color at 0 ppm; to an orange-brown hued copper color (0.1 ppm) and golden-brown color at 0.5 and 1 ppm; to yellow-green hued olive color at 3 ppm; and then to a dark olive green color at 5 ppm. When the Cd ion concentration increased to greater higher than 5 ppm, no distinguishable color changes of the sensor particle 1 were recognized. Therefore, sensor particles 1 could be used for the detection range of 0.1 ~ 5 ppm in Cd ion concentration. As can be seen in Fig. 3b, when sensor particle 2 was placed in the presence of Cd ion of 0 ~ 1000 ppb, color of sensor particles 2 varied distinctively from orange-yellow hue, saffron color at 0 and 10 ppb; to orange-yellow hue, arylide yellow at 50 ppb; to a yellow hue, dandelion color at 100 ppb; and then to a yellow-green hue, chartreuse color at 500 and 1000 ppb. The sensor particle 2 did not exhibit any discernible color change when the Cd ion concentration increased from 500 ppb to 1000 ppb and greater. It is noticeable that for Cd ion concentrations between 0.1



**Fig. 5.** Solid state UV-Vis spectra of ORMOSIL sensor particles with variation of Cd ion concentrations; (a) sensor particle 1, (b) sensor particle 2, and (c) sensor particle 3.

ppm and 0.5 ppm, the sensor particles 2 showed more clearly distinguishable color changes than sensor particles 1. By combining these two sensor particles, Cd ion concentrations between 0.05 and 5 ppm can be easily differentiated. For sensor particles 3, the color changes in the Cd ion concentration range between 0 to 100 ppb are shown in Fig. 3c. It shows the distinguishable color changes—from a yellow hue, peridot color at 0 and 1 ppb; to a yellow-green hue, pear color at 5 and 10 ppb; and finally to a yellow-green hue, chartreuse color at 50 and 100 ppb. When a Cd ion concentration higher than 50 ppb was employed, the color of sensor particle 3 became saturated. These results demonstrate that by



**Fig. 6.** Calibration curves of UV-Vis absorbance for three ORMOSIL sensor particles with variation of Cd ion concentrations; (a) sensor particle 1 (b) sensor particles 2, and (c) sensor particles 3.

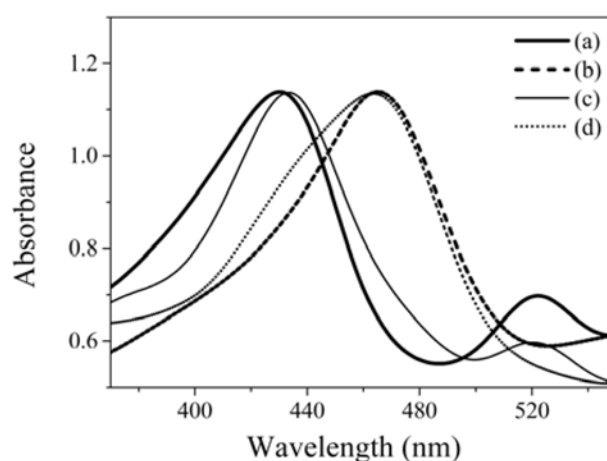
employing sensor particles with variable amount of immobilized TMPyP molecules, the detection ranges and sensitivities for the colorimetric Cd ion detection were easily controlled. Combining these sensor particles in the presence of different Cd ion concentrations leads to formation of a colorimetric sensor grid that has a Cd ion detection range of 10 ppb to 5 ppm.

UV-Vis absorption spectral changes of the three ORMOSIL sensor particles in the presence of different Cd ion concentrations were also studied as shown in Fig. 5. The primary observations from the UV-Vis spectra follow. First, the strong absorption peak, termed the Soret band, of TMPyP molecules immobilized in the ORMOSIL sensor particles initially appeared around 438 nm but red-shifted to 468 nm after binding

with the Cd ion. The observed red shift may be due to the reduced band gap of the Soret band due to additional interaction of TMPyP molecules with  $\text{SO}_3\text{H}$  groups through ion-pair interactions and complex formation with Cd ions. Second, as the complex formation of Cd ion with TMPyP molecules progressed, the intensities of the Soret band from TMPyP molecules decreased; meanwhile those from Cd ion bound TMPyP molecules were increased. For sensor particles 1, the intensity of the absorption peak around 438 nm gradually reduced and the intensity of the 468 nm peak increased with the concentration of Cd ion being increased from 0 to 5 ppm as shown in Fig. 5a. A linear relationship was observed between the intensity of either of the peaks and the Cd ion concentrations in the range of 0 ~ 5 ppm as shown in Fig. 6a. It is evident that changes in the absorption intensity of sensor particles 1 could be clearly differentiated at each ppm level of Cd ion concentration, which is in accord with the colorimetric results shown in Fig. 3c. For sensor particles 2, there were notable spectral changes when the Cd ion concentration changed from 0 to 10 ppb, from 50 to 100 ppb, and then to 500 ppb as can be seen in Fig. 5b. Note that the sensor particles 2 did not show a distinguishable color change when the Cd ion concentrations changed from 0 to 10 ppb. These results suggest that spectral monitoring may serve as a complementary sensing tool to colorimetric sensing. The peak intensity analysis on the two peaks around 438 nm and 468 nm also showed a linear relationship between the Cd concentration and the intensity of either of the peaks (Fig. 6b). For sensor particles 3, the spectral changes were observed as the Cd ion concentration changes from 0 to 100 ppb (Fig. 5c) and a linear dependence of the peak intensity around 438 or 468 nm on the Cd ion concentrations was found (Fig. 6c). The spectroscopic analysis demonstrates the wavelength shifts and intensity changes that accompany the color changes of the sensor particles in the presence of different Cd ion concentrations. This confirms that a sensor grid constructed by combining the three sensor particles 1, 2 and 3 can be an easy and efficient analysis tool for the colorimetric Cd ion detection in the range between 10 ppb and 5 ppm.

ORMOSIL sensor particles, after the first usage for Cd ions detection, were recovered by treating with ethylenediaminetetraacetic acid (EDTA) (Fig. 1). The color of recovered ORMOSIL sensor particles returned back to the original color, indicating that the Cd ions were removed. The recovered ORMOSIL sensor particles were used again to detect Cd ion, showing the same performance as the freshly prepared sensor particles for colorimetric sensing.

Spectroscopic observation was also done for the ORMOSIL sensor particles before and after EDTA-mediated recovery. As can be seen in Fig. 7, a Soret



**Fig. 7.** Solid state UV-Vis spectra of fresh and recycled sensor particle 1; (a) fresh sensor particles, (b) fresh sensor particles after 2 ppm cadmium ion binding, (c) recycled sensor particles, and (d) recycled sensor particles after 2 ppm cadmium ion binding.

band around 438 nm from TMPyP molecules in the sensor particles was shifted to 468 nm upon addition of 2 ppm Cd ions. Then, this absorption band from Cd bound TMPyP molecules moved back to 438 nm by detaching Cd ions through EDTA treatment. Finally, by treating with the same amount of Cd ions, the Soret band of the recovered sensor particles shifted back to 468 nm without any significant changes in intensity and wavelength.

## Conclusions

ORMOSIL sensor particles for colorimetric detection of Cd ions were prepared by chemically immobilizing TMPyP molecules onto ORMOSIL particles containing thiol groups. The immobilization of TMPyP sensor molecules onto ORMOSIL particles was accomplished by the ion pair interaction between pyridinium functional groups in TMPyP molecules and sulfonic groups in ORMOSIL particles which were obtained by oxidation of mercaptopropylsilanes with hydrogen peroxide. By adjusting relative ratio of organosilanes in ORMOSIL particles, the detection range and sensitivity of ORMOSIL sensor particles toward Cd ion detection were easily controlled. A sensor grid was constructed by combining three ORMOSIL sensor particles with different colorimetric detection ranges and sensitivities to serve as an easy and efficient analysis tool for the colorimetric Cd ion detection in the range between 10 ppb and 5 ppm by the naked eye. Spectroscopic analysis confirmed the changes in wavelength and intensity of a Soret band from TMPyP molecules that accompanied the color changes. The ORMOSIL sensor particles prepared in this study are recyclable as demonstrated by EDTA-treated sensor particles exhibiting almost the same performance characteristics as freshly prepared sensor particles.

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