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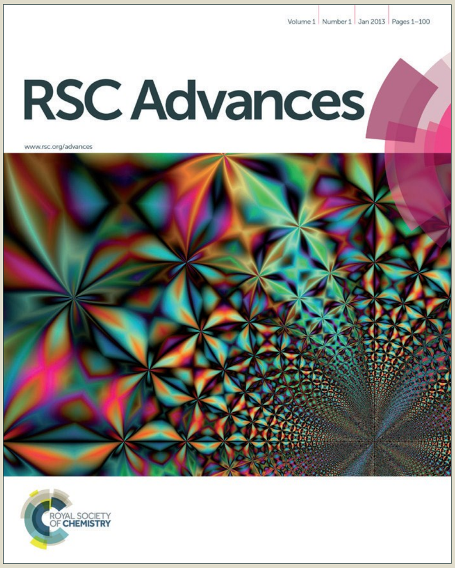

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ARTICLE

Photoinduced adsorption of spiropyran into mesoporous silicas as photomerocyanine

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By UV irradiation to a toluene solution of a spiropyran containing suspended mesoporous silica particle, the photochemically formed photomerocyanine was adsorbed into mesoporous silica to give a red-colored product, which is very stable for a long time at room temperature. The red color was faded out by visible light irradiation, indicating that the photomerocyanine desorbed from mesoporous silica to give toluene solution of spiropyran. The bistability was achieved by the presence two different chemical environments for the photochromic molecules: toluene, which stabilizes organophilic spiropyran and mesoporous silica does hydrophilic photomerocyanine.

Introduction

Photochromism is a phenomenon on reversible photochemical reactions which accompany reversible color change.[1] Active researches have been done on ohotochromic molecule that changes its color upon irradiation and the photochemically generated species can be converted back to the original species either thermally or by subsequent irradiation with a specific wavelength of light. There is potential of photochromism for such applications as optical switching and information storage.[1] Accordingly, the construction of photoresponsive supramolecular systems containing photochromic moiety has actively been conducted,[2,3] in addition to the designing new photochromic compounds.[4]

Host-photochrmoic guest complexes have been synthesized previsouly in order to control the photochromic reaction by the hosy-guest interactions.[2,3] As a host of photochromoic molecules, mesoporous silicas has such advantages as their well-defined and size controllable nanospaces for efficient adsorption and the photochemical transformation of the accommodated molecules. Furthermore, the useful functions of mesoporous materials are expected to be modified by external stimuli using attached photochromic moiety. The introduction of photochromic molecules into mesoporous silicas has been reported so far.[5-7] One of the earliest investigation on this topic is the introduction of cationic azobenzene into mesoporous silica film containing controlled amount of acidic site on the pore surface through electrostatic interactions, and, thanks to the mesopore, the azo dye effectively photo-isomerized even at low temperature.[8] Later on, the introduction of various photochromic molecules into mesoporous silicas has been done by simple impregnation as well as by covalent bonds (grafting or co-precipitation using silane coupling agents with covalently attached photochromic moieties).[9-17]

Here, we report an unique photochromic behavior of a spiropyran (1',3',3'-trimethyl-6-nitrospiro[1(2H)-benzopyran-2,2'-indoline]; hereafter abbreviated as SP) in toluene solution containing suspended mesoporous silica particle. SP was not adsorbed into mesoporous silica. By the UV light irradiation for toluene solution of SP, SP transformed photochemically into a merocyanine (MC) and the formed photomerocyanine was spontaneously adsorbed into mesoporous silica due to the interactions between mesoporous silica and merocyanine. By subsequent visible light irradiation, the MC is converted back to SP and dissolved into toluene phase. This “photoinduced adsorption/desorption” is a newly found phenomenon and is achieved when SP was dissolved in organic solvent (SP is more stable in organic solvent) in the presence of hydrophilic silica (polar merocyanine is stable when adsorbed in mesoporous silica). In addition, the photochemically formed merocyanine adsorbed in mesoporous silica is very stable at room temperature and come back to the original SP only when visible light is irradiated into the suspension.

Experimental

Materials

Tetraethoxysilane (TEOS), hexadecyltrimethylammonium chloride (C16TAC), dimethyloctadecylchlorosilane, resorcinol, n-octadecyldimethylchlorosilane and 1',3',3'-trimethyl-6-nitrospiro-[1(2H)-benzopyran-2,2'-indoline] (spiropyran; SP) were obtained from Tokyo Kasei Kogyo Co. Ltd. Formaldehyde aqueous solution (36-38 wt%), ammonia aqueous solution (28-30 wt%), hydrochloric acid aqueous solution (35-37 wt%), methanol, ethanol and toluene were obtained from Kanto Chemical Co., Inc. Poly(ethylene glycol)-

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block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic, P-123) were obtained from Sigma-Aldrich Co. Ltd. Ethanol was distilled before use. Other chemicals were used without further purification.

Sample preparation

The mesoporous silica spherical particle was prepared by the method described in our previous report.[18] C16TAC (0.211 g), deionized water (17.7 g), methanol (100 mL), and 28% aqueous ammonia solution (7.2 g) were mixed in a sealed PP vessel (vol. 250 mL) and the solution was shaken for 15 seconds at room temperature. To which solution was added TEOS (0.368 mL) and the mixture was shaken for 3 seconds at room temperature. After aging the mixture at room temperature for 20 h, the solid product was separated by centrifugation (3,500 rpm for 10 min), washed with methanol and dried at 60 °C for a day. Surfactant was removed by the calcination of the as-prepared sample in air at 550 °C for 10 h to obtain nanoporous silica spherical particle.

Hollow aggregates of SBA-15 was prepared by the deposition of SBA-15 precursor on the monodispersed spherical particle of the resorcinol-formaldehyde resin (RFS), which was synthesized from resorcinol and formaldehyde solution by the reported method.[19] 28% ammonia aqueous solution (0.8 mL) was mixed with a solution containing anhydrous ethanol (64 mL) and deionized water (160 mL), then the mixture was magnetically stirred for 10 min. Subsequently, resorcinol (1.2 g) was added with continuous stirring for 15 min. Then, an aliquot of 36 % formaldehyde aqueous solution (1.6 mL) was added to the solution and the solution was magnetically stirred for 24 h at 30 ℃. Then, the solution was hydrothermally treated for 24 h at 100 ℃ under a static condition in a Teflon-lined autoclave. After cooling, the resulting solid product was recovered by centrifugation (3,500 rpm for 10 min) and dried at 60 ℃. Deposition of SBA-15 precursor onto RFS was conducted as follows; P123 (5.0 g), deionized water (130 g) and 12 M hydrochloric acid aqueous solution (25 mL) were mixed in a sealed PP vessel (vol. 250 mL). After stirring for 30 min, RFS (500 mg) was added and ultrasonicated for 10 min. To which suspension, TEOS (10.7 g) was added under vigorous stirring at 35 ℃, and aged at at the same temperature for 24 h with magnetic stirring. The mixture was heated for 48 h at 100 ℃ in a Teflon-lined autoclave. After the hydrothermal reaction, the product was separated by centrifugation (3,500 rpm for 10 min) and dried at 60 ^{o}C. The core (RFS) and the surfactant (P123) were removed by calcination in air at 550 °C for 6 h to obtain hollow SBA-15 aggregate (hereafter designated as hollow SBA-15).

Octadecylsilyl group modified mesoporous silica was prepared as follows; 1.0 g of the mesoporous silica was dispersed in the toluene solution (30 mL) of n-octadecyldimethylchlorosilane and the mixture was heated at 60 °C for 72 h. Then, the solvent was removed by evaporation and the solid product was washed with toluene.

Photochemical reactions

Mesoporous silica (50 mg) was suspended in the solution (50 mL), which contains spiropyran (2 or 10 mg/50 mL). The mixture was vigorously mixed for 2 h under dark, and subsequently UV and visible light irradiation (150 W Xe lamp (Ushio Inc.)) were conducted sequentially. The photochromic reactions were followed by naked eye observation as well as by UV-Vis spectra. A part of the mixture was separated by centrifugation (3,500 rpm for 10 min) in every 30 min, in order to determine the amount of the adsorbed photomerocyanine from the absorbance of spiropyran in the supernatant by UV spectra.

Characterization

The nitrogen adsorption/desorption isotherms of the porous silicas were measured at 77 K on a BELSORP mini instrument (BEL Japan, Inc.). Prior to the measurement, the samples were heated at 120 °C for 3 h under nitrogen flow. Thermogravimetric and differential thermal analysis (TG-DTA) curves were recorded on a Rigaku TG8120 at a heating rate of 10 ℃ min^{-1} under air using α-Al_2O_3 as the standard material. The adsorbed amount of spiropyran (SP) was determined by the change in the concentration of SP in solutions before and after the reactions with mesoporous silicas. The concentration of SP was determined by the change in the absorbance at 334 nm using Shimadzu UV-3100PC spectrophotometer.

Results and Discussion

Upon UV irradiation for the toluene solution of SP (concentration of 0.12 mM), SP changed its color from colorless to blue, due to the formation of photomerocyanine. The blue color faded out immediately when the irradiation was stopped.[20] The color change is seen from the photographs of the solution before and just after the irradiation. (Figure 1(A) inset). On the other hand, when mesoporous silica spherical particle, which was prepared according to the previous report,[18] was suspended in the toluene solution of SP (0.12 mg / L), red-color was developed upon UV irradiation. The photographs of the suspension before and after the UV irradiation are shown in Figure 1(B) inset. The red color is due to the protonated form of photomerocyanine, which was suggested by the previous paper.[21] Since the two states (both colorless and red) are stable under the given conditions, red solid was isolated by centrifugation after the UV irradiation for the suspension. The solid thus collected was red and the color was difficult to be faded out. These observations confirmed the red form in mesoporous silica. In the present system, the protonated photomerocyanine is though to form by the interactions of the photomerocyanine with silanol group on the mesopore surface. Thus, the state of the photochemically formed merocyanine was affected by the presence of the mesoporous silica.

Insert Figure 1

The changes in the UV-Visible absorption spectra of the solution (with and without mesoporous silica spherical particle) are also shown in Figure 1. It should be noted here that, in all systems reported in the present paper, the color is simple red or blue and two color mixture was never seen. The photochemical reaction of SP was affected by the presence of the mesoporous silica even though the dye was dissolved in toluene.

The stability of the photochemically formed compounds is a very important topic of photochromism in order to achieve optical recording and various photo-responsive supramolecular systems.[1,2] As described previously and also as reported extensively in literatures,[1] the blue photomerocyanine was not stable and came back to the colorless spiropyran immediately after the UV irradiation was stopped. Whereas, the red-color observed for the SP solution containing suspended mesoporous silica was very stable in the dark. The red color did not fade out when the sample was stored in the dark for several days at room temperature.

Thanks to the very stable photomerocyanine, the mesoporous silica was separated from the suspension, after the irradiation, by centrifugation (3,500 rpm for 10 min). Red-colored mesoporous silica was obtained as precipitate and the supernatant was transparent. These observations confirmed the photomerocyanine was stabilized by the interactions with mesoporous silica. The amount of the photomerocyanine adsorbed on mesoporous silica was determined by subtracting the concentration of SP in the supernatant from the initial SP concentration (0.12 mM). The concentration was derived from the UV spectra (the absorption maximum of SP at 334 nm). The amounts of the adsorbed SP (photochemically formed merocyanine) as a function of the irradiation time are shown in Figure 2. The amounts of the adsorbed merocyanine increased as a function of the irradiation time, and decreased when the UV irradiated sample was subsequently irradiated by visible light. There are several reports on the photoirradiation triggered adsorption/ desorption of molecules,[22-24] where photochromic units were immobilized on the entrance of the mesopore or in the interlayer space of layered compounds. The photochemical reactions of the immobilized molecules induced the adsorption/desorption of photochemically inert target molecules (toxic organic and drug) into the nanospaces from/to external environments, toward controlled release application. On the contrary, the phenomenon observed in the present study is the adsorption/desorption of a photochromic molecule (spiropyrane) from/to mesopore. To the best of our knowledge, there is no report on the photoinduced adsorption of photochromic molecule into mesoporous silica, and the phenomenon has a different impact and possibility for applications of photochromisms of organic molecules.

Insert Figure 2

When the photochemical reaction was conducted using concentrated SP solution (0.60 mM) in the presence of the mesoporous silica, similar color change from colorless to red was seen, while the red-color is dense. The largest amount of the adsorbed merocyanine achieved so far was 160 mg/(g of silica) (the experimental conditions were irradiation for 30 min and the initial SP concentration of 0.60 mM). The pore volume of the mesoporous silica used in the present study was 0.50 cm^3/(g of silica) as derived from the nitrogen adsorption isotherm. Considering the density, the adsorbed dye amount, and the pore volume, it was thought that 48 % of the pore was occupied by the photomerocyanine. The large pore volume (0.50 cm^3/(g of silica)) of the mesoporous silica contributed to the efficient transformation through the adsorption for the large amount of photochromic molecule, which was thought to lead the clearer color change.

In order to confirm the above idea on the mechanism of the presently observed photoinduced adsorption, mesoporous silica with larger pore size (hollow SBA-15) was used. The scanning electron micrographs of the hollow SBA-15 is shown in Figure 3 together with that of the mesoporous silica sphere. The effects of the chemical nature of the pore surface were examined using hollow SBA-15 before and after the pore surface modification with dimethyloctadecylchlorosilane. The successful formation of hollow SBA-15 and the attachment of the octadecyl group on the hollow SBA-15 pore surface was shown by the nitrogen adsorption isotherms from which average pore size and pore volume were derived to be 7.8 to 7.2 nm and 1.0 to 0.70 m^3/(g of silica) for the sample before and after the modification, respectively. The nitrogen adsorption/desorption isotherms of the hollow SBA-15 before and after the grafting are shown in Figure 4, together with those of the nanoporous silica spherical particle. The BJH pore size distribution derived from the adsorption isotherms are shown in Figure 5.

Insert Figures 3, 4 and 5

When the octadecyl group modified mesoporous silica (octadecylsilylated SBA-15) was used instead of the pristine mesoporous silica (hollow SBA-15), the color change from colorless to red was also observed, while the adsorbed amount was very small (the color change is less visible if compared with the experiment when pristine hollow SAB-15 was used). The amounts of the adsorbed photomerocyanine for hollow SBA-15 and octadecylsilylated SBA-15 were 2.5 and 1.2 mg/(g of silica), respectively, when the photo-irradiation was conducted at the initial SP concentration of 0.12 mM and the duration for 30 min. This difference was thought to be due to the difference in the available hydrophilic nanospace for the hydrophilic merocyanine molecule to be stabilized. Thus, the hydrophilic nanospace of mesoporous silica played important roles to stabilize photochemically formed merocyanine by the hydrogen bonding. Since the degree of the modification may also affect the reaction efficiency, further experiments are being done in our laboratory to tune the reaction more quantitatively by applying differently hydrophilic materials and the results will be reported subsequently.

Insert Table 1

By the visible light irradiation for the red-colored powder product (after the separation by centrifugation), the color faded out. Upon subsequent thermal treatment in dark, the red-color regenerated. Such reverse photochromism has been observed previously for the SP molecules occluded in hydrophilic environments.[25] For the photochromism of the powder product, the color fading was followed by naked eye observation and diffuse reflectance spectra, which were not quantitative. We are investigating the reversible photochromism using mesoporous silica film for detailed quantitative and kinetic study and the results will be reported subsequently. As an application of the present phenomena (photoinduced adsorption/desorption), we will investigate the hybrid systems composed of hydrophilic and hydrophobic parts as thin film or core-shell particle as a solid-state sample for possible optical device application..

Conclusions

In conclusion, photoinduced adsorption of merocyanine into mesoporous silica was shown for the first time, by the UV irradiation of toluene solution of spiropyran containing suspended mesoporous silica particles. The photochemically formed photomerocyanine in mesoporous silica was very stable at room temperature, suggesting possible application for optical recording. The hydrophilic nanopore of mesoporous silica was thought to play an important role to stabilize photochemically formed merocyanine as a protonated form. The reaction yields varied depending on the pore size and surface modification, confirming the mechanism of the optical bistability mentioned above and suggesting possible further optimization using mesoporous silica with different pore size and surface chemistry.

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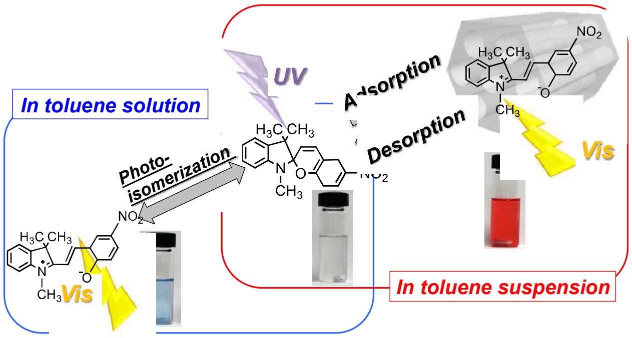

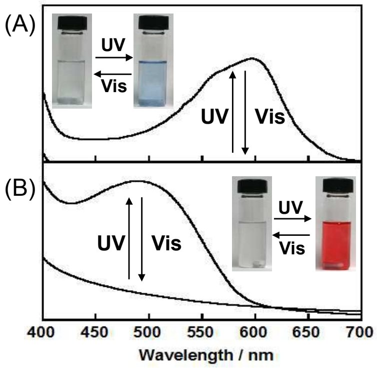

Figure 1. UV-visible absorption spectra of the spiropyran toluene solution (A) and the spiropyran toluene solution containing suspended mesoporous silica particle (B) before and after the UV irradiation. Insets show the photographs of the samples before and after the irradiation.

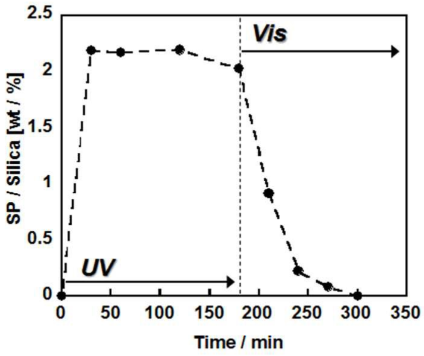

Figure 2. The change in the amounts of the adsorbed spiropyran as photochemically formed merocyanine by the UV irradiation.

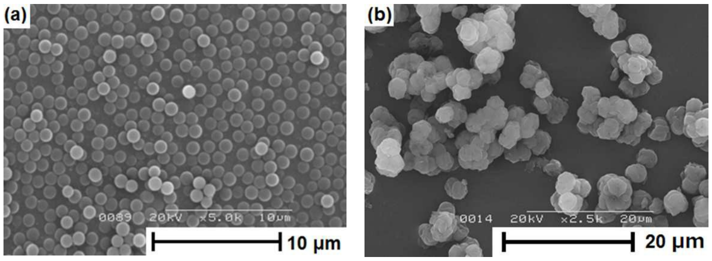

Figure 3. Scannnig electron micrographs of (a) the spherical mesoporous silica and (b) hollow SBA-15

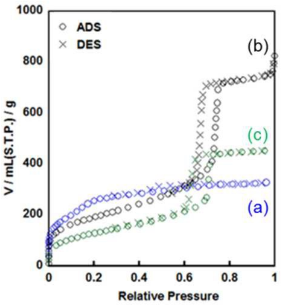

Figure 4. Nitrogen adsorption/desorption isotherms of (a) the spherical mesoporous silica and (b,c) hollow SBA-15 before (b) and after (c) the modification with octacdecyl group

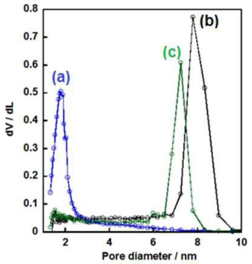

Figure 5. BJH pore size distribution of (a) the spherical mesoporous silica and (b,c) hollow SBA-15 before (b) and after (c) the modification with octacdecyl group

Table 1. Characteristics of mesoporous silicas and their adsorption properties for spiropyrane (SP).

Sample	BJH pore size[a] [nm]	Pore volume[a] [cm^3/g]	SP in the initial solution [mM]	SP / Silica [wt%]	SP / nanopore [volume%][b]
Mesoporous silica sphere	1.9	0.50	0.12	2.4	7.2
	1.9	0.5	0.60	16	48
Hollow SBA-15	7.9	1.0	0.12	2.5	3.8
Hollow SBA-15	7.9	1.0	0.60	4.9	7.4
Octadecylsilylated SBA-15	7.2	0.70	0.12	1.2	2.6

[a] Derived from the nitrogen adsorption isotherm.

[b] Calculated based on the pore volume and the assumption that the volume of spiropyran single molecule is 0.83 nm^3.