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Temperature Control of Light Transmission Using Mixed System of Silica Hollow Particles with Nanoparticle Shell and Organic Components

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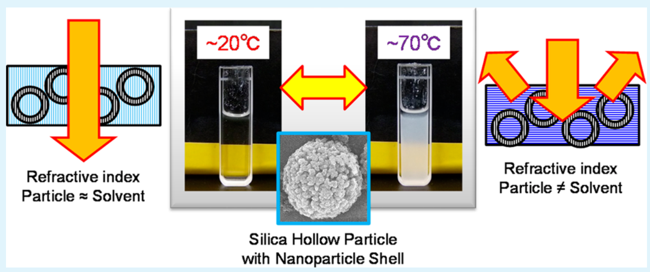
Supporting Information

ABSTRACT: We reported before that a silica hollow particle whose shell consists of silica nanoparticle (**SHP-NP**) has a high light reflection ability to prevent light transmission through the particle, which is caused from the intensive light diffusion by the hollow structure and the nanoparticle of the shell. Since the difference in the refractive indices between silica and air is responsible for the strong light reflection, the mixing of the particle with organic components having refractive indices close to that of silica such as tetradecane produced transparent mixtures by suppression of the light reflection. The transparency of the mixtures thus prepared could be controlled by temperature variation. For example, the mixture of the particle **SHP-NP** with tetradecane was transparent at 20 °C and opaque at 70 °C, while the mixture with *n*-hexyl cyclohexane was opaque at 20 °C and transparent at 70 °C. As the refractive indices of organic components changed with temperature more than 10 times wider than that of silica, the temperature alternation produced a significant change in the difference of the refractive indices between them to achieve complete control of the transparency of the mixtures. This simple control of the light transmission that can automatically regulate sunlight into the room with temperature alteration is expected to be suitable for smart glass technology for energy conservation.



KEYWORDS: *smart glass, light transmission, silica hollow particle, refractive index, temperature change*

1. INTRODUCTION

Reversible control of light transmission is a desirable technology in a number of applications such as display, optical filter, and "smart glass" technology.[1−5] In particular, smart glass technology based on unrestricted control of light transmittance is a current hot topic of environmental technology, because it is considered as a prominent approach for energy conservation of air conditioning.[6−11] There are two main types in smart glass technology: one is the "active type" that controls the transparency of the glass by extraneous stimuli such as electricity,[12−15] and the other is the "passive type" in which the light transmittance is varied spontaneously by the change of external environment such as temperature alternation.[16] This passive smart glass is suitable for conserving energy in air conditioning by controlling solar insolation. For example, when the sunshine is strong, sunlight into the room is blocked preventing elevation of indoor temperature, while gentle sunshine is permitted to pour into the room.[11] Thermochromism materials,[7,9,17] thermotropic liquid crystals,[18,19] and other responsive materials[20,21] are leading technologies of the passive-type smart glass. However, as these approaches generally require complicated systems and equipment, simple and low-cost systems are desired for promoting further development in smart glass technology.

We reported a simple preparation method of silica hollow spherical particles using water/oil/water emulsion, where sodium silicate is employed as a silica source.[22−25] Without any additives to the sodium silicate, silica hollow particles with seamless shell (**SHP-SL**, named after silica hollow particle with seamless shell) are obtained (Figure 1A).[22] On the other hand, addition of the appropriate amount of sodium chloride to the

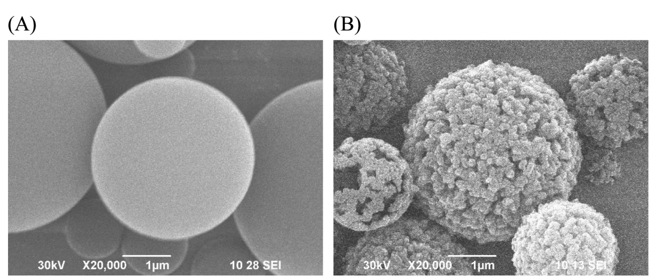


Figure 1. SEM images of silica hollow particles with a seamless shell (A, **SHP-SL**) and nanoparticle shell (B, **SHP-NP**).

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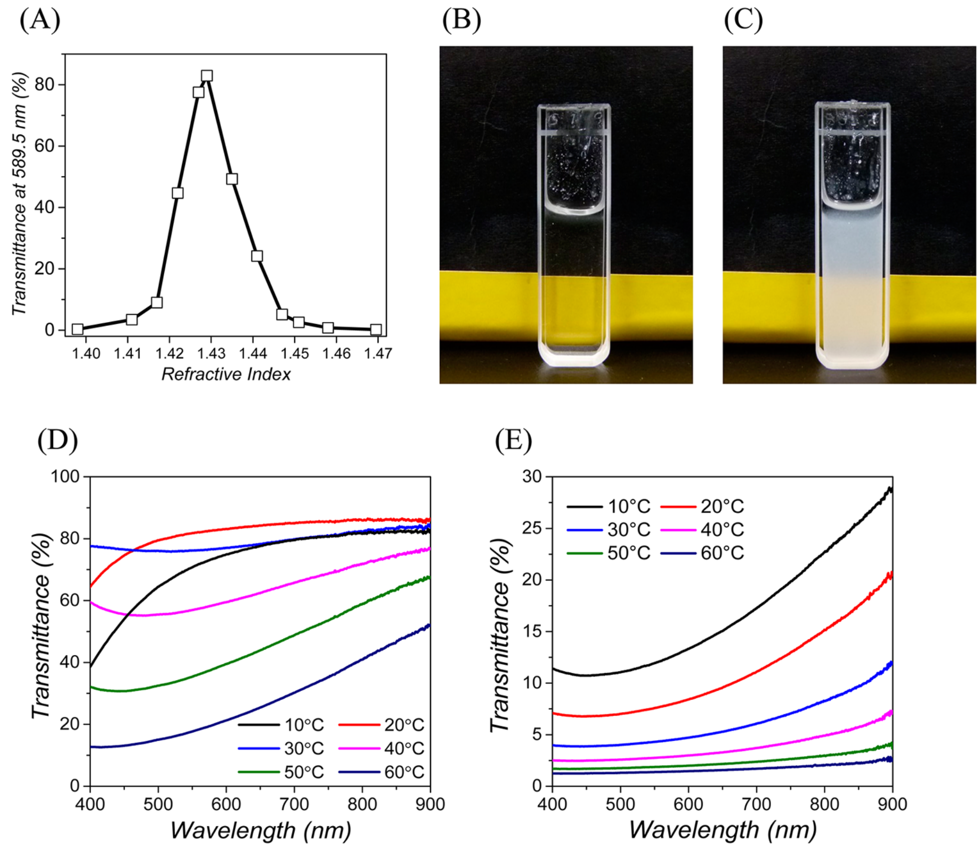

Figure 2. (A) Transmittance of the visible light of 589.5 nm at 20 °C through mixtures of the silica hollow particle **SHP-NP**[25] with hydrocarbon solvents as a function of refractive indices of the solvents listed in Table 1. (B) Picture of a cell containing a mixture of the silica hollow particle **SHP-NP** and tetradecane at 20 °C. (C) Picture of the same cell as B at about 70 °C. (D) Visible light spectra of a mixture of the particle **SHP-NP** with tetradecane at different temperatures. (E) Visible light spectra of a mixture of the particle **SHP-SL**[22] with tetradecane at different temperatures.

sodium silicate produced unique silica hollow spherical particles, whose shells consist of silica nanoparticles of several hundred nanometers as shown in Figure 1B (**SHP-NP**, named after silica hollow particle with nanoparticle shell).[25] In our previous paper,[25] the light reflectance by **SHP-SL**, **SHP-NP**, and common silica gel was compared to find a close correlation between the structures of silica and the light reflection. The reflection of UV and visible light was increased in the order silica gel < **SHP-SL** < **SHP-NP** to reveal the importance of the hollow structure and the silica nanoparticle in the shell.[25] In general, the turbidity of dry silica is caused by the scattering of light due to the difference in the refractive indices between silica and air. On the other hand, when the particle **SHP-NP** is mixed with decane whose refractive index (~1.411) is closer to that of silica (1.4−1.5) than air (~1.0), the light transmittance through the mixture was enhanced considerably.[25] This means that proper selection of the components mixing to the particle **SHP-NP** can control the reflection and transmission of light through the mixtures. In addition, the refractive indices of materials generally change with temperature, whose extents are defined by their thermo-optic coefficient.[26−28] It is known that the thermo-optic coefficients of most organic components are more than 10 times that of silica, and the former is negative, and the latter is positive. For example, while the coefficient (dn/dT) of cyclohexane of main visible light is about -540–560×10^{-6}/K, that of fused silica is 12–14×10^{-6}/K.[26] Therefore, even when the refractive index of an organic component mixed with the particle **SHP-NP** coincides with that of the particle to form the transparent mixture at an initial temperature, the temperature variation produces significant differences in the refractive indices between them to change the light transmittance of the mixture. Although this principle is basically used in the measurement of refractive index by the thermal immersion method,[29] to our knowledge there have been no examples of its application to smart glass technology. In this paper, we present the control of light transmittance observed in the mixture of the silica hollow particle with nanoparticle shell (**SHP-NP**) and organic solvents and polymers, where the temperature alteration changed the transparency of the mixtures reversibly. This simple system of light transmission control consisting of only the silica particle and the organic components will be advantageous to applications to a wide range of smart glass technologies.

2. EXPERIMENTAL SECTION

2.1. Materials. Sodium silicate used for preparation of the silica hollow particles was obtained from Kishida Chemical (water glass No. 3 as Japanese Industrial Standards). Other reagents used for the preparation were purchased from Wako Pure Chemical Industries, Ltd. and Kishida Chemical. All solvents mixed with silica hollow particles were purchased from Tokyo Chemical Industry Co., Ltd., and the refractive indices of these solvents (n20/D values; the refractive indices of a wavelength of 589.3 nm, sodium D line, at 20 °C) for discussion are the standard values of the reagents from Tokyo Chemical Industry. Silicone oil KF-50-300CS and poly(methyl acrylate) (PMA, M_w 40000, 40% toluene solution) were purchased from Shin-Etsu Chemical Co., Ltd. and Sigma-Aldrich Co. LLC, respectively.

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2.2. Preparation of Samples. The silica hollow particles with a seamless shell (**SHP-SL**) and nanoparticle shell (**SHP-NP**) were prepared by the described methods.[22,25] The silica hollow particle **SHP-NP** was prepared using the solution of sodium silicate and NaCl with a weight ratio of 5/1 (g/g). The mixtures of silica hollow particles and organic solvents were obtained from 0.3 g of a silica hollow particle and 0.8 mL of an organic solvent by sufficient mild mixing using a long thin bar for removing air bubbles in borosilicate glass cells (5 mm in light path length), and no other special treatments like sonication were performed. In the case of silicone oil KF-50-300CS as a viscous fluid, the mixture of the silica hollow particle was prepared in a Petri dish of borosilicate glass (27 mm inner diameter) from 0.1 g of the particle **SHP-NL** and 1.5 mL of KF-50-300CS. In the case of poly(methyl acrylate), 3 mL of the toluene solution of PMA was mixed with the silica hollow particle in the Petri dish and toluene was removed by natural evaporation for a few days. The thicknesses of these mixtures in the Petri dishes were fixed to approximately 2 mm. The silica particles in these mixtures were recoverable by solvent washing and filtration.

2.3. Light Transmittance Measurement. The transmittance spectra of UV and visible light through the cells prepared as above were directly recorded by a double-beam spectrometer without any cells in the reference side using a Shimadzu UV-2500PC spectrometer. The temperature of the cells was changed between 10 and 60 °C using a temperature-controlled cell holder (Shimadzu TCC-240A), and spectra were recorded after at least 3 min temperature stabilization. The temperature from 10 to 60 °C is the maximum working range of the apparatus. When a vacant cell was used for the measurement, the light transmittance was approximately 85% in all wavelength regions. On the other hand, when the cells filled with hydrocarbon solvents we used (without silica particle) were employed, the transmittance of light was approximately 90% in all wavelengths. In these all cases, no change of the transmittance with temperature (10−60 °C) was observed. In the cases of silicone oil KF-50-300CS and poly(methyl acrylate), visible spectra were recorded by an Ocean Optics USB2000+ spectrometer using a tungsten lamp of Olympus BX type microscope as the light source. The temperature of the sample was altered with the hot stage of INSTEC Inc., which can control the temperature from 30 to 90 °C. For the pictures of Figure 2A and 2B and Movies 1 and 2 and Figure S3, Supporting Information, the cells were heated at 70 °C in a thermostatic chamber for 30 min which was cooled down in a room air conditioned at 20 °C.

3. RESULTS AND DISCUSSION

3.1. Light Transmission through the Mixture of Silica Hollow Particle with Hydrocarbon Solvents.

As mentioned in our previous paper,[25] the light reflection of the particle **SHP-NP** is caused by the difference in the refractive indices between silica and its surrounding. Then, we measured the light transmittances of mixtures of the particle **SHP-NP** with a variety of hydrocarbon solvents using a simple double-beam spectrometer. Table 1 summarizes the relationship between the transmittance of the visible light of 589.5 nm through the mixtures at 20 °C and the refractive index of each solvent (n20/D). No strong interaction of these hydrocarbon solvents with the surface of the silica particle is advantageous to analyze the light transmittance of the mixtures precisely. Figure 2A is a plot of the transmittance of the visible light of 589.5 nm at 20 °C as a function of the respective refractive indices of solvents from Table 1. This chart clearly indicated that the transparency of the mixture of the particle **SHP-NP** with hydrocarbons depended on the refractive indices of the hydrocarbons mixed. The highest transparency of the mixture was observed when the particle **SHP-NP** was mixed with tetradecane, whose refractive index was approximately 1.429. The transmittance of the visible light of 589.5 nm at 20 °C reached approximately 85% in this case. The light transmittances of a vacant cell and cells filled with these hydrocarbons in the same measuring method were approximately 85% and 90% in all wavelength regions, respectively, where no change of the light transmittance with temperature variation was found. Therefore, this mixture showing 85% of the light transmittance could be regarded as nearly transparent at 20 °C. As the refractive indices of silicon oxides are known to be different by their structure,[30] the refractive index of this silica particle **SHP-NP** was estimated to be around 1.43 at 20 °C. On the other hand, in the cases of undecane and *n*-hexyl cyclohexane with about 1.417 or 1.447 of refractive index, the light transmittances (589.5 nm at 20 °C) were poor (about 9% and 5%, respectively). Thus, the light transmittances of the mixtures of the particle **SHP-NP** with hydrocarbons are controllable by the refractive index of the mixed hydrocarbon.

Table 1. Refractive Indices of Hydrocarbon Solvents and Transmittance of Visible Light of 589.5 nm at 20 °C through Mixtures of the Particle SHP-NP with Solvents

hydrocarbon solvent mixed to the particle **SHP-NP**	refractive index of hydrocarbon solvent (n20/D)[a]	transmittance of 589.5 nm at 20 °C through the mixture (%)
octane	1.398	0.24
decane	1.411	3.41
undecane	1.417	8.99
dodecane	1.422	44.67
cyclohexane	1.427	77.51
tetradecane	1.429	82.90
hexadecane	1.435	49.26
n-butyl cyclohexane	1.441	24.14
n-hexyl cyclohexane	1.447	5.10
n-octyl cyclohexane	1.451	2.54
cyclooctane	1.458	0.75
trans-decahydronaphthalene	1.470	0.18

[a]Intermediate value of the refractive indices (n20/D) noted in specification values of Tokyo Chemical Industry.

The light transmittance through the cells containing the particle **SHP-NP** and hydrocarbons changed with the temperature of the cells. As a prominent example, the nearly transparent cell with tetradecane at 20 °C (Figure 2B) became opaque when the cell was warmed to 70 °C (Figure 2C). In the Supporting Information, the moving image (16 times speed) of the cell during cooling from about 70 to 20 °C is uploaded (Movie 1). In this image, the opaqueness of the mixture in the cell gradually decreased with cooling and finally became transparent at 20 °C. This change of the light transmission was ascertained by the direct transmittance spectra shown in Figure 2D. With increasing temperature, the transmittance decreased to about 20% at 60 °C (the highest temperature of the apparatus we used). The cooling to 10 °C (the lowest temperature) also decreased the transmittance. The difference in the light transmittance between 20 and 60 °C was reached 65%. However, the transmittance of the mixture of the particle **SHP-SL** (silica hollow particles with seamless shell, Figure 1A)[22] with tetradecane was low at 20 °C. Although the transmittance variation of the mixture was also observed as shown in Figure 2E, the transmittance difference of the visible light of 589.5 nm between 10 and 60 °C was only about 10%. Even in the largest change of the transmittance at 900 nm in wavelength, the difference was less than 30%. Thus, the silica hollow particle with nanoparticle shell, **SHP-NP**, leads to the

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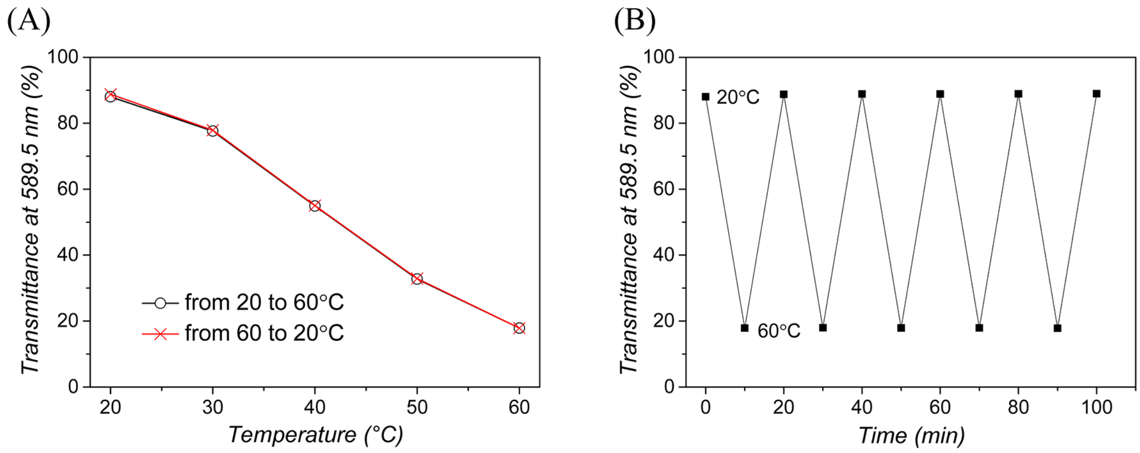

Figure 3. (A) Profiles of the transmittance at 589.5 nm when the cell temperature was changed from 20 to 60 °C and from 60 to 20 °C. (B) Repetitive change of the transmittance of 589.5 nm between 20 and 60 °C. Results in about 10 min after the cell temperature attained each temperature.

largest change of the light transmittance of the mixture with tetradecane by temperature variation.

3.2. Variation of Light Transmittance with Temperature through the Mixture of Silica Hollow Particle with Hydrocarbon Solvents. Figure S1, Supporting Information, shows the transmittance variation of the light at 589.5 nm through the mixture of the particle **SHP-NP** with tetradecane when the temperature of the cell holder was altered from 20 to 60 °C. Although the temperature of the cell holder nearly reached 60 °C in 200 s, the light transmittance was still about 40%, which did not return to the transmittance in Figure 2D (about 18%). However, this gap is considered to result from the fact that the temperature of the mixture did not attain 60 °C in 200 s. After 420 s, the light transmittance became a constant value (approximately 18%) that was identical with that of Figure 2D, showing that the temperature of the whole cell reached 60 °C. In Figure 3A, the light transmittance variation of 589.5 nm after becoming constant is illustrated when the temperature of the cell holder was changed every 10 °C from 20 to 60 °C and from 60 to 20 °C. The complete overlap of the two plots from 20 to 60 °C and from 60 to 20 °C revealed that there is no hysteresis in the light transmittance alteration. In the repeated test shown in Figure 3B, the light transmittance returned to the initial ones at 20 and 60 °C even after five times repetition. Thus, this transparency change was completely repeatable.

Figure 4 summarizes the variations of the transmittances of the visible light at 589.5 nm in mixtures of the particle **SHP-NP** with various hydrocarbons at different temperatures from 10 to 60 °C. In Figure S2, Supporting Information, selected visible light spectra of the mixtures used for Figure 4 are illustrated. In the cases of hydrocarbons whose refractive indices are lower than hexadecane (n20/D: 1.435), the plots are downward sloping, while the plot of hexadecane is convex upward peaking at 40 °C. The reverse changes of the transparency were observed using hydrocarbons whose refractive indices are higher than hexadecane. In the cases of these solvents, *n*-butyl, *n*-hexyl, and *n*-octyl cyclohexane, the plots are upward sloping. In Figure S3, Supporting Information, two images of cells containing a mixture of the particle **SHP-NP** and *n*-hexyl cyclohexane at 20 and 70 °C are shown , and the moving image of the cell during cooling from about 70 to 20 °C is uploaded (Movie 2, Supporting Information). This change of transparency was naturally repeatable for a number of times with temperature as well as tetradecane. Thus, the character of the transmittance variation, becoming transparent or opaque with temperature increase, can be selected by the hydrocarbon solvents mixed with the particle **SHP-NP**. These properties will be advantageous to create different types of smart glasses.

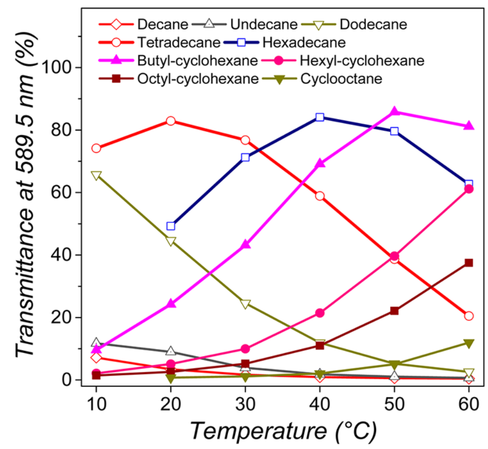

Figure 4. Variation of the transmittance of the visible light at 589.5 nm through the different mixtures of the silica hollow particle **SHP-NP** with hydrocarbon solvents at varied temperatures.

3.3. Consideration of the Variation of Light Transmittance with Temperature. As mentioned in section 3.1, the refractive index of the silica hollow particle **SHP-NP** is assumed to be about 1.43. Then, in Figure 5A, the light transmittance of visible light (589.5 nm) listed in Table 1 is plotted as a function of the difference (in absolute value) in the refractive indices of each hydrocarbon from 1.43. This plot is approximately linear and upward sloping when the transmittance is more than 5%, meaning that the light transmittance has a direct correlation with the difference in the refractive indices between the silica hollow particle and hydrocarbon solvents. The blue line with triangle points in Figure 5B is the plot of the correlation between the transmittance of the visible light of 589.5 nm through the mixture of the particle **SHP-NP** with hexadecane shown in Figure 4A and the refractive indices of hexadecane at from 20 to 60 °C obtained from the literature.[31] This blue plot line is nearly overlapped with the red plot line, which is the same plot of Figure 2A. From the fitting

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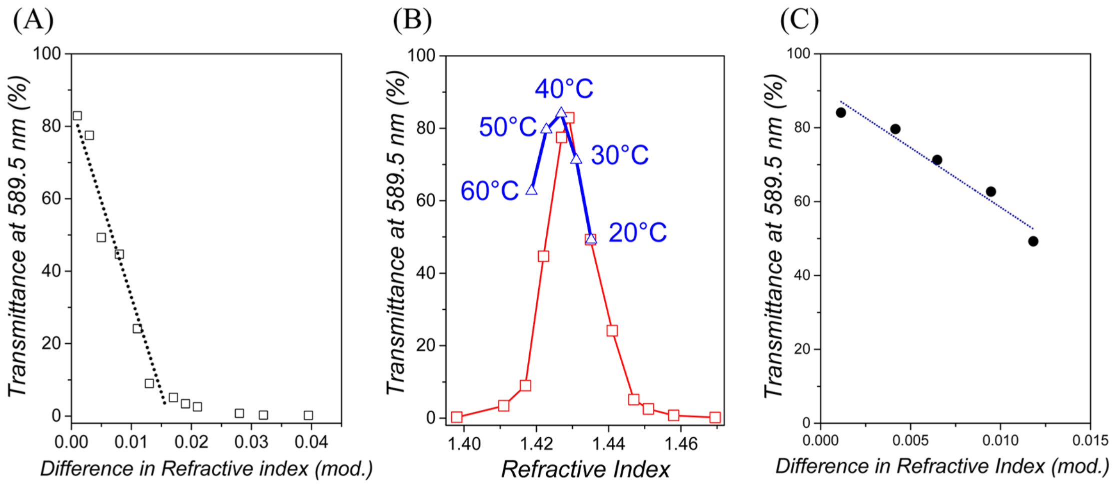

Figure 5. (A) Plot of the light transmittance of 589.5 nm listed in Table 1 as a function of the difference (in absolute value) in the refractive indices of each hydrocarbon from 1.43. (B) Blue line with triangle points is the transmittance of the visible light of 589.5 nm as a function of refractive indices of hexadecane at 20 (RI = 1.4352), 30 (RI = 1.43106), 40 (RI = 1.4269), 50 (RI = 1.42279), and 60 °C (RI = 1.41867).[31] Red line with square points is the same plot of Figure 2A. (C) Plot of the light transmittance of the mixture of the particle **SHP-NP** with hexadecane as a function of the difference (in absolute value) in refractive indices shown in Table S1, Supporting Information.

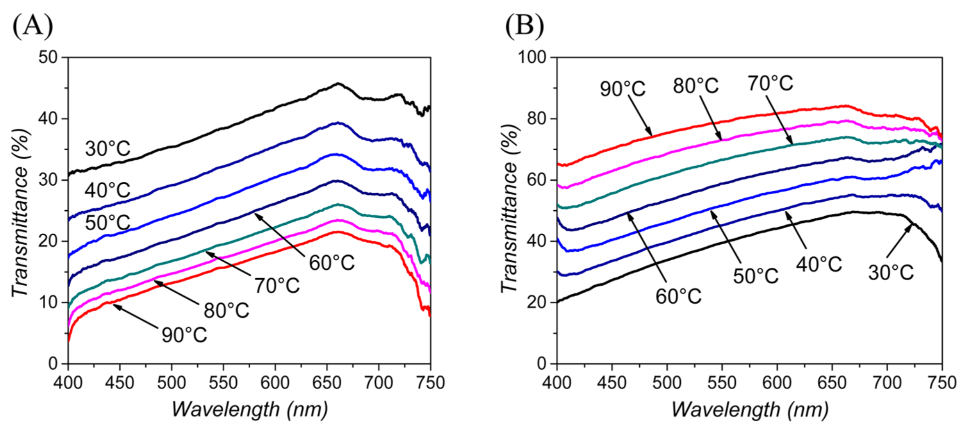

Figure 6. Visible spectra of the mixtures of the silica hollow particles **SHP-NP** with silicone oil KF-50-300CS (A) or poly(methyl acrylate) (B) at different temperatures.

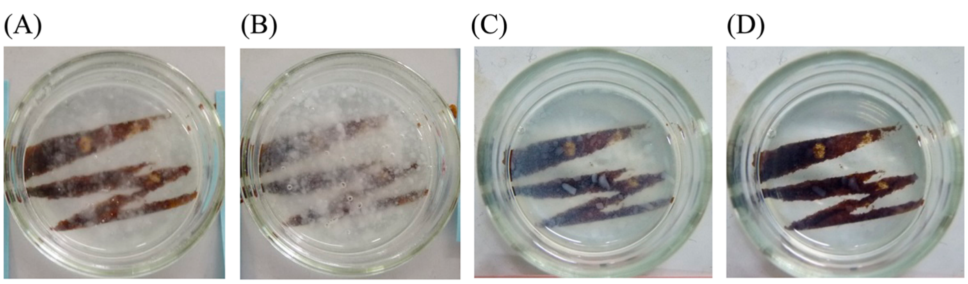

Figure 7. Images of the mixtures of the particle **SHP-NP** with silicone oil KF-50-300CS at 25 (A) and 80 °C (B) and with poly(methyl acrylate) at 25 (C) and 80 °C (D).

curve of the blue plot shown in Figure S4, Supporting Information, the highest transmittance is observed in about a refractive index of 1.426 at approximately 42 °C. Therefore, the refractive index of the particle **SHP-NP** was assumed to be 1.426 at 42 °C. The thermo-optic coefficient of fused silica at 578 nm in wavelength is reported to 11.9×10^{-6}/K.[26,32,33] Table S1, Supporting Information, shows the estimated differences in the refractive indices between hexadecane and the particle **SHP-NP** from 20 to 60 °C and the measured light transmittance at the respective temperature. The plot of the light transmittance as a function of the difference in the refractive indices of hexadecane and silica is also found to be linear as shown in Figure 5C. This observation revealed that the light transmittance is completely controlled by the difference in the refractive indices between the silica hollow particle **SHP-NP** and the hydrocarbon solvents mixed at the temperature.

3.4. Light Transmission through the Mixture of a Silica Hollow Particle with Polymer Materials. Figure 6 shows the visible light spectra of the mixture of the silica hollow particle **SHP-NP** with silicone oil KF-50-300CS or poly(methyl

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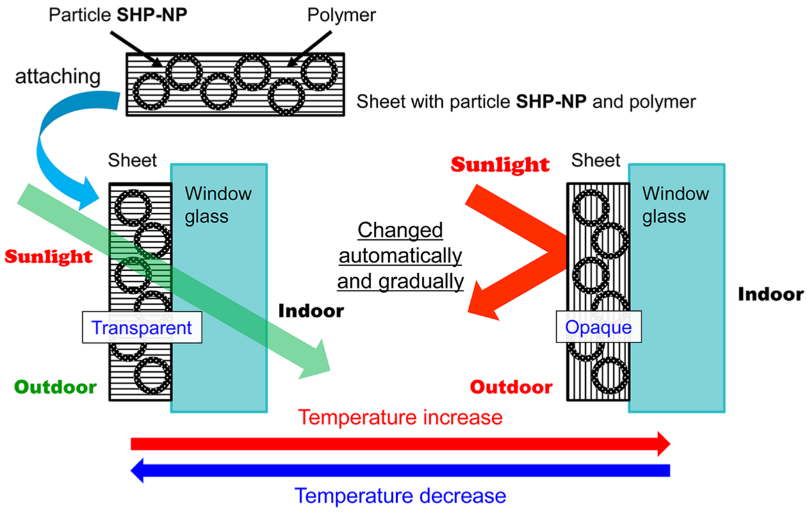

Figure 8. Possible scheme of smart glass technology using the silica hollow particle **SHP-NP**.

acrylate) (PMA, $M_w \approx 40\,000$) at different temperatures. In these cases, as the mixture could not be packed in common cells, these mixtures (0.1 g of **SHP-NL** and about 1.5 mL of a polymer) were prepared in Petri dishes (27 mm inner diameter) with a thickness of approximately 2 mm. In the case of the silicone oil (n25/D: 1.425), the transmittance of the visible light (589.5 nm) was about 42% at 30 °C, which was reduced with temperature elevation to approximately 17% at 90 °C. On the other hand, the mixture with PMA (n20/D: 1.494) became more transparent with temperature increase. About 42% of the transmittance of the visible light at 30 °C increased to 81% at 90 °C. The images of these mixtures at two different temperatures are shown in Figure 7, which demonstrate the clear changes of the transparency with temperature. Thus, the transmittance control of the mixture of the particle **SHP-NP** by temperature was also achieved with the organic macromolecular materials.

3.5. Potential Applications of the Temperature Control of the Light Transmittance. A possible application of this temperature control of the light transmittance using the silica hollow particle with nanoparticle shell (**SHP-NP**) for smart glass technology is exemplified as follows (Figure 8). A gel–sheet material produced from the particle **SHP-NP** and a suitable polymer material having an appropriate refractive index is attached to the outside of the window glass. When the outdoor temperature is comfortable (for example, around 20 °C), the sheet is transparent to introduce sunlight into the room (left state in Figure 8). On the other hand, if is hot outside of the room, the sheet becomes opaque to block the sunlight (right state in Figure 8). This change between the two states (transparent or opaque) occurs automatically and gradually, and an intermediary transparency is also possible. This simple smart glass technology using the gel–sheet is expected to spread easier, because the sheet can be attached to windows of existing buildings and houses. We are now attempting further examination of this approach, which will be reported in our continued report.

4. CONCLUSION

Light transmission of the mixture of the silica hollow particle **SHP-NP** with various hydrocarbon solvents varied with changes in temperature. The transmittance alteration was completely reversible and had no hysteresis. The appropriate selections of the hydrocarbon solvents provided mixtures that were transparent at 20 °C and opaque at 70 °C (for example, with tetradecane) or opaque at 20 °C and transparent at 70 °C (for example, with *n*-hexyl cyclohexane). The polymeric organic materials, silicone oil and poly(methyl acrylate), could be also applied to this light transmittance control with temperature. The mechanism of the transparency variation is the adjustment of the refractive indices of the silica hollow particle and the organic components. As the refractive index alteration of the organic components with temperature is generally 10 times higher than that of silica, the difference in the refractive indices between them induced by the temperature variation changes the transparency of the mixture. This light transmittance control that requires only two components, the silica hollow particle **SHP-NP** and an organic component, will be applied to a number of fields on light controls as smart glass technology.

■ ASSOCIATED CONTENT

Supporting Information

Movies 1 and 2, Figures S1–S4, and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Lee, H.-K.; Kanazawa, A.; Shiono, T.; Ikeda, T. Reversible Optical Control of Transmittance in Polymer/Liquid Crystal Composite Films by Photoinduced Phase Transition. *J. Appl. Phys.* **1999**, *86*, 5927–5934.

(2) Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. Thermal and Light Control of the Sol-Gel Phase Transition in Cholesterol-Based Organic Gels. Novel Helical Aggregation Modes as Detected by Circular

Dichroism and Electron Microscopic Observation. *J. Am. Chem. Soc.* **1994**, *116*, 6664−6676.
(3) Wang, M.; He, L.; Zorba, S.; Yin, Y. Magnetically Actuated Liquid Crystals. *Nano Lett.* **2014**, *14*, 3966−3971.
(4) Mao, Y.; Liu, J.; Ge, J. Tuning the Transmittance of Colloidal Solution by Changing the Orientation of Ag Nanoplates in Ferrofluid. *Langmuir* **2012**, *28*, 13112−13117.
(5) Jochum, F. D.; Theato, P. Thermo- and Light Responsive Micellation of Azobenzene Containing Block Copolymers. *Chem. Commun.* **2010**, *46*, 6717−6719.
(6) Niklasson, G. A.; Granqvist, C. G. Electrochromics for Smart Windows: Thin Films of Tungsten Oxide and Nickel Oxide, and Devices Based on These. *J. Mater. Chem.* **2007**, *17*, 127−156.
(7) Baetens, R.; Jelle, B. P.; Gustavsen, A. Properties, Requirements and Possibilities of Smart Windows for Dynamic Daylight and Solar Energy Control in Buildings: A State-of-the-Art Review. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 87−105.
(8) Gesheva, K. A.; Ivanova, T. M.; Bodurov, G. Transition Metal Oxide Films: Technology and "Smart Windows" Electrochromic Device Performance. *Prog. Org. Coat.* **2012**, *74*, 635−639.
(9) Kamalisarvestani, M.; Saidur, R.; Mekhilef, S.; Javadi, F. S. Performance, Materials and Coating Technologies of Thermochromic Thin Films on Smart Windows. *Renewable Sustainable Energy Rev.* **2013**, *26*, 353−364.
(10) Gao, Y. F.; Luo, H. J.; Zhang, Z. T.; Kang, L. T.; Chen, Z.; Du, J.; Kanehira, M.; Cao, C. X. Nanoceramic VO_2 Thermochromic Smart Glass: A Review on Progress in Solution Processing. *Nano Energy* **2012**, *1*, 221−246.
(11) Ye, H.; Meng, X.; Long, L.; Xu, B. The Route to a Perfect Window. *Renewable Energy* **2013**, *55*, 448−455.
(12) Thakur, V. K.; Ding, G.; Ma, J.; Lee, P. S.; Lu, X. Hybrid Materials and Polymer Electrolytes for Electrochromic Device Applications. *Adv. Mater.* **2012**, *24*, 4071−4096.
(13) Uchida, T.; Shibasaki, M.; Matsuzaki, T.; Nagata, Y. Glare-Tunable Transparent Electrochemical Smart Window Coupled with Transparent Organic Light-Emitting Diode. *Appl. Phys. Express* **2013**, *6*, 041604.
(14) Christie, A. M.; Lilley, S. J.; Staunton, E.; Andreev, Y. G.; Bruce, P. G. Increasing the Conductivity of Crystalline Polymer Electrolytes. *Nature* **2005**, *433*, 50−53.
(15) Llordés, A.; Garcia, G.; Gazquez, J.; Milliron, D. J. Tunable Near-Infrared and Visible-Light Transmittance in Nanocrystal-in-Glass Composites. *Nature* **2013**, *500*, 323−326.
(16) Hendaoui, A.; Émond, N.; Dorval, S.; Chaker, M.; Haddad, E. VO_2-Based Smart Coatings with Improved Emittance-Switching Properties for an Energy-Efficient Near Room-Temperature Thermal Control of Spacecrafts. *Sol. Energy Mater. Sol. Cells* **2013**, *117*, 494−498.
(17) Zhou, J.; Gao, Y.; Zhang, Z.; Luo, H.; Cao, C.; Chen, Z.; Dai, L.; Liu, X. VO_2 Thermochromic Smart Window for Energy Savings and Generation. *Sci. Rep.* **2013**, *3*, 3029.
(18) Kakiuchida, H.; Tazawa, M.; Yoshimura, K.; Ogiwara, A. Thermal Control of Transmittance/Diffraction States of Holographic Structures Composed of Polymer and Liquid Crystal Phases. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 1747−1752.
(19) Cupelli, D.; Nicoletta, F. P.; Manfredi, S.; Marco, M.; Formoso, P.; De Filpo, G.; Chidichimo, G. Self-Adjusting Smart Windows Based on Polymer-Dispersed Liquid Crystals. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 2008−2012.
(20) Kakiuchida, H.; Tazawa, M.; Yoshimura, K. Optical Diffractometry of Highly Anisotropic Holographic Gratings Formed by Liquid Crystal and Polymer Phase Separation. *Phys. Rev. E* **2012**, *86*, 061701.
(21) Bechinger, C.; Ferrere, S.; Zaban, A.; Sprague, J.; Gregg, B. A. Photoelectrochromic Windows and Displays. *Nature* **1996**, *383*, 608−610.
(22) Fujiwara, M.; Shiokawa, K.; Tanaka, Y.; Nakahara, Y. Preparation and Formation Mechanism of Silica Microcapsules (Hollow Sphere) by W/O/W Interfacial Reaction. *Chem. Mater.* **2004**, *16*, 5420−5426.
(23) Fujiwara, M.; Shiokawa, K.; Sakakura, I.; Nakahara, Y. Silica Hollow Spheres with Nano-Macroholes Like Diatomaceous Earth. *Nano Lett.* **2006**, *6*, 2925−2928.
(24) Fujiwara, M.; Shiokawa, K.; Hayashi, K.; Morigaki, K.; Nakahara, Y. Direct Encapsulation of BSA and DNA into Silica Microcapsules (Hollow Spheres). *J. Biomed. Mater. Res., Part A* **2007**, *81*, 103−112.
(25) Fujiwara, M.; Shiokawa, K.; Sakakura, I.; Nakahara, Y. Preparation of Silica Hollow Particles (Microcapsules) with Nano-particled Shells: A Material for High Reflection of UV and Visible Light. *Langmuir* **2010**, *26*, 6561−6567.
(26) Nikogosyan, D. N. *Properties of Optical and Laser-Related Materials*; John Wiley & Sons: New York, 1997. p 169.
(27) Kang, E.-S.; Lee, T.-H.; Bae, B.-S. Measurement of the Thermo-Optic Coefficients in Sol-Gel Derived Inorganic−Organic Hybrid Material Films. *Appl. Phys. Lett.* **2002**, *81*, 1438−1440.
(28) Pokrass, M.; Burshtein, Z.; Gvishi, R. Thermo-Optic Coefficient in Some Hybrid Organic/Inorganic Fast Sol−Gel Glasses. *Opt. Mater.* **2010**, *32*, 975−981.
(29) Danhara, T.; Yamashita, T.; Iwano, H.; Kasuya, M. An Improved System for Measuring Refractive Index using the Thermal Immersion Method. *Q. Int.* **1992**, *13−14*, 89−91.
(30) Skinner, B. J.; Appleman, D. E.; Melanophlogite, A. a Cubic Polymorph of Silica. *Am. Mineral.* **1963**, *48*, 854−867.
(31) Paredes, M. L. L.; Reis, R. A.; Silva, A. A.; Santos, R. N. G.; Santos, G. J. Densities, Sound Velocities, and Refractive Indexes of Tetralin + n-Hexadecane at (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K. *J. Chem. Eng. Data* **2011**, *56*, 4076−4082.
(32) Toyoda, T.; Yabe, M. The Temperature Dependence of the Refractive Indices of Fused Silica and Crystal Quartz. *J. Phys. D: Appl. Phys.* **1983**, *16*, L97−L100.
(33) Malitson, I. H. Interspecimen Comparison of the Refractive Index of Fused Silica. *J. Opt. Soc. Am.* **1965**, *55*, 1205−1208.