Photochromism of 2-Hydroxy-4'-Methoxychalcone Adsorbed on Mesoporous Silicate

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Abstract

2-Hydroxy-4'-methoxychalcone (HMC), a synthetic anthocyanin dye, has the same molecular skeleton as plant pigments and is promising as a safe and environmentally friendly photochromic material. With the objective of using the HMC dye under dry conditions, a composite of Al containing mesoporous silica (Al-MPS) and HMC dye was prepared, and its photochromic properties were investigated. The composite of Al-free MPS had a vivid yellow appearance; the color disappeared within seven days on storage in darkness at 313 K and 95 % RH. Its color strength recovered to 50 % of the initial value on UV-A irradiation, demonstrating the coloring-discoloring process. Incorporation of Al into MPS increased the quantity of HMC dye adsorbed onto it; however, the discoloring process from the FV+ form (yellow) to the t-C form (non-color) of the dye occurred with some difficulty.

Key-words: 2-Hydroxy-4'-methoxychalcone, Mesoporous silica, Photochromism, Composite

1. Introduction

Organic photochromic dyes such as azobenzene, fulgide, spiropyran, and diarylethene have applications in rewritable paper, electronic recording materials, and automatic light-control materials^{1,2)}. Among these photochromic dyes, the synthetic anthocyanin 2-hydroxy-4'-methoxychalcone (HMC dye), which has the same molecular skeleton as plant pigments, is believed to be a photochromic material that is safe (in terms of its effect on human health) and has a low environmental impact³⁻⁵⁾. Therefore, this dye can potentially be used in products such as inkjet printer ink, cosmetics, garments, and toys.

HMC dye exhibits photochromic and thermochromic properties when dissolved in an ethanol solution. Irradiation with UV-A turns the solution yellow, and subsequent irradiation with UV-C^{3,4)} or heating at 353 K⁶⁾ turns the solution colorless. Although the HMC dye has considerable potential as an eco-friendly photochromic material, it has two major shortcomings: its light stability and heat stability are inferior to those of other photochromic dyes and it shows optical coloration and decoloration only in solution. In order to enable industrial applicability of the HMC dye, several attempts have been made to surmount these shortcomings. HMC dye conjugated with inorganic host materials such as zeolite, clay, or mesoporous silica has been reported to show improved lightfastness⁶⁻⁸⁾. The photochromic properties of HMC dye derivatives dispersed in organic materials such as agarose gel or polyvinyl alcohol film

have also been investigated⁹⁻¹²⁾.

We are aiming to obtain photochromic and thermochromic materials that can be used under dry conditions (i.e., not in an aqueous solution) by combining the HMC dye with inorganic host material, namely porous silica and silicate. In the previous paper, we reported that HMC dye adsorbed onto silica gel exhibited a coloring-decoloring cycle (coloring by UV-A irradiation, decoloring over time, and recoloring by UV-A reirradiation)¹³⁾.

In this study, we adopted mesoporous silica (MPS) as the host of the dye. MPS possesses a large surface area of over 1000 m²/g and uniform pore size distribution similar to the size of the dye molecule¹⁴⁾. In addition, the introduction of Al into the framework of MPS creates acidic sites in the pores¹⁵⁾. These properties are expected to increase the color strength of the dye composite and improve the color recovery by UV-A irradiation.

2. Experimental

2.1 Synthesis and characterization of mesoporous silica

Mobil Composition of Matter (MCM) No.41 MPS was synthesized in the similar way described in the literature^{16,17)}. All materials in this study were analytical grade from Wako Chemical and used as received. Hexadecyltrimethyl ammonium bromide (C16TMABr, 2.28 g) and given amount of sodium aluminate (Al/SiO₂ wt % = 0, 0.5, 0.7, 1.0, 3.0) was dissolved in 44.3 g of purified water and stirred at 313 K for 1 h. NaOH (0.58 g) dissolved in 6.3 g of purified water and tetraethyl orthosilicate (10.29 g, TEOS) were alternatively

added dropwisely into the solution containing C16TMABr within 15 min while the mixture was vigorously stirring at room temperature. After stirring for additional 2 h, sample temperature was increased to 413 K and kept static for 48 h. The obtained MPS was recovered, washed until pH became *ca.* 8, dried overnight at 333 K under reduced pressure and then calcined at 873 K for 6 h under air blasting condition.

Thus obtained samples are denoted as Al(*x*)-MPS, where *x* indicates the quantity of added Al (Al/SiO₂ wt %).

Nitrogen sorption measurement was performed on Shimadzu Tristar 3000. Surface area was calculated by the Brunner-Emmett-Teller (BET) method. Pore size and pore volume were determined by Barrett-Joyner-Halenda (BJH) method using the peak of desorption branch. The content of aluminum in MPS was estimated by inductively coupled plasma emission spectrometry (ICP; Horiba, JY238ULTRACE).

2.2 Preparation of 2-hydroxy-4'-methoxychalcone/mesoporous silica composites

HMC dye was synthesized at Shizuoka University following procedures provided in the literature¹⁸⁾. HMC dye was dissolved in EtOH using ultrasonic cleaning equipment, and then mixed with an acetic acid buffer solution (pH 4.3). The weight ratio was HMC dye : EtOH : buffer solution = 0.001 : 14 : 129. Next, 100 mL of the HMC solution was irradiated with a UV-A lamp (352 nm, Toshiba FL10BLB). The illuminance was set to 320 lx, and the irradiation time was 15 min. Finally, MPS (0.29 g) was added to the obtained solutions. All mixtures were kept at 298 K for 20 h, after which the sediment was separated by filtration and dried at 313 K for 1 h under reduced pressure.

2.3 Storage of the HMC dye/MPS composite

The HMC dye/MPS composites were spread in approximately 1-mm-thick layers on glass trays. The sample was irradiated with UV-A at an illuminance of 750 lx for 15 min. This illuminance level is required minimum for HMC dye in the composite to be changed from t-C form to FV+. After the initial recording of the diffuse reflectance spectra, samples were placed in sealed plastic containers. The inner condition was controlled to be 313 K and 95 % RH using thermostats and a saturated K₂SO₄ aqueous solution. The containers were placed in the dark for seven days. After storage, the diffuse reflectance spectra of the samples were recorded, and then the sample was again irradiated with UV-A.

2.4 Spectral measurements

The diffuse reflectance spectra of HMC dye/MPS composites were recorded with a JASCO V-650 spectrometer equipped with an integrating sphere ISV-722. The color strength of the composite was calculated from the ratio of the reflected absorption at 440 nm to that at 520 nm ($A = I_{440}/I_{520}$).

The quantity of HMC dye adsorbed onto MPS was calculated from the ratio of the absorbance of the HMC dye solutions before adsorption to that after adsorption.

3. Results and Discussion

3.1 HMC dye adsorption onto MPS

The characterization of synthesized MPS with various Al content is presented in Table 1. The pore diameter of all samples was approximately 2.8 nm and the surface area was around 1000 m²/g, which are typical values of Al containing MPS. From the ICP analyses, the Al/SiO₂ ratio of the obtained MPS samples was almost equivalent to the ratio of the initial gel before the hydrothermal treatment.

The relation of the Al content of MPS with the quantity of HMC dye adsorbed onto MPS is shown in Table 2. The quantity of HMC dye in the Al(0)-MPS composite (Al free) was 0.18 wt % and it showed a vivid yellow color. The quantity of dye was approximately twice that of silica gel¹³⁾. The quantity of the adsorbed HMC dye increased with the addition of a small quantity of Al to MPS (Al(0.5)-MPS); the yellow color of the composite became more intense. Further increase in the Al content up to 3 % led to a gradual increase in the quantity of HMC dye, but it was not as pronounced as that between Al(0)-MPS and Al (0.5)-MPS. We deduced that the coloration of all composites obtained had reached a desirable level for practical application as color materials.

At the preparation of the composite, most of HMC in the solution was FV+ form (cationic form) as UV-A had been irradiated. We assume the adsorption of HMC dye (actually FV+) onto MPS proceeded by two mechanisms. One is the attachment of the dye molecule onto a silanol group on the negatively charged surface of the silica. The surface area of MPS is more than twice that of silica gel, so Al(0)-MPS composite contains more dye than silica gel. The other is the adsorption onto the cation site (negatively charged) produced by Al in the silica framework. For this effect Al(0.5)-MPS contains more dye than Al(0)-MPS does. The reason why the further addition of Al (over 0.5 %) does not increase the dye amount effectively is not yet clear; one possibility is that 0.5 % of Al is the

Table 1 Characterization of mesoporous silica.

Code	BET Surface Area / m ² /g	Pore Diameter / nm
Al(0)-MPS	1139	2.7
Al(0.5)-MPS	1076	2.8
Al(0.7)-MPS	1041	2.6
Al(1.0)-MPS	1080	2.8
Al(3.0)-MPS	938	2.9

Table 2 Quantity of HMC dye in the composites.

	HMC dye amount in composite (%)
Al(0)-MPS	0.18
Al(0.5)-MPS	0.27
Al(0.7)-MPS	0.27
Al(1.0)-MPS	0.28
Al(3.0)-MPS	0.29

Scheme 1 Several forms of 2-hydroxy-4'-methoxychalcone (HMC dye).

Fig. 1 a) Changes in the color values of Al(0)-MPS composites over time. b) Recovery of the color values of Al(0)-MPS composites by UV-A reirradiation after storage. A: color strength of the composite ($I_{440\text{ nm}}/I_{520\text{ nm}}$), A0: initial A value.

limit of the incorporation into the silica framework.

3.2 Photochromic properties of HMC dye and Al-free MPS

The process of structural change of HMC dye has been investigated previously and is shown in **Scheme 1**. HMC dye is known to exist in the following four forms: trans-2-hydroxychalcone (t-C), cis-2-hydroxychalcone (c-C), flav-3-en-ol (FV), and flavylium cation (FV+)¹⁹⁻²¹. Only FV+ is yellow; the other forms are colorless. Therefore, the conversion of FV+ to the other forms is a decoloration process, whereas the reverse is a coloration process. Among the four forms, t-C is the most thermodynamically stable form except under strongly acidic condition. An HMC dye of FV+ is known to convert to t-C over time under light shielding conditions.

In a previous paper, we reported that the speed of decoloration tended to be higher at 313 K than at 298 K and that humidity affected decoloration: the color of the sample disappeared more rapidly when stored under high humidity (95 % RH) than when stored under low humidity (15 % RH)¹⁸. In this experiment, we stored the samples at 313 K and 95 % RH in a light-resistant container.

The optical coloring-decoloring profile of the Al(0)-MPS composite is shown in **Fig. 1**.

Fig. 2 Diffuse reflectance UV-Vis spectra of Al(0)-MPS composite. Solid line: initial stage, dashed line: storage for seven days, dotted line: after reirradiation with UV-A.

In the initial stage (after the first UV irradiation), the composite exhibited vivid yellow color. On storage in a dark place, the samples gradually decolored and became slightly pale green. On irradiation with UV-A after the storage period of seven days, the sample turned yellow again, and the color strength recovered to half of its initial value. This suggests that HMC dye/MPS composite exhibits a coloring-decoloring cycle (coloring by UV-A irradiation, decoloring over time, and recoloring by UV-A reirradiation), although perfect recovery could not be achieved.

The UV-Vis absorption spectra of the Al(0)-MPS composites in the initial stage, after storage for seven days, and reirradiation with UV-A are shown in **Fig. 2**. The absorption peaks at 440 nm and 350 nm correspond to FV+ and t-C, respectively. The broad band from 250 to 300 nm indicates the existence of FV or c-C.

In the initial stages, the composite mainly shows only a 440-nm absorption peak indicating that FV+ (yellow) exists as the main form in the composite. The absorbance at 440 nm fell drastically after the seven-day storage period (dashed line in **Fig. 2**). Additionally, a broad band at 250 ~ 300 nm became stronger and a new absorption peak formed at 620 nm. The latter peak has not been identified so far; it may be analog of green species of 2-hydroxychalcone which is observed as an intermediate between monomer (yellow) and dimer (red)^{22,23}. Longer storage periods of up to one month scarcely changed the UV-Vis spectra (data not shown). These results show that FV+, which is the main form of the initial composite, has since converted over time to FV, c-C, and t-C, all of which are colorless.

After the storage period of seven days, the sample was reirradiated with UV-A. The peak at 350 nm corresponding to t-C became weaker, and contrastingly, the magnitude of the peak corresponding to FV+ increased on reirradiation (dotted line in **Fig. 2**). The strength of the FV+ peak (color strength) recovered to approximately 50 % of that in the initial stage. In contrast, the shape and strength of the band at 250 ~ 300 nm corresponding to FV and c-C scarcely changed with UV-A

Fig. 3 Diffuse reflectance UV-Vis spectra of Al(0.5)-MPS composite. Solid line: initial stage, dashed line: storage for seven days, dotted line: after reirradiation with UV-A.

Fig. 5 Diffuse reflectance UV-Vis spectra of Al(1.0)-MPS composite. Solid line: initial stage, dashed line: storage for seven days, dotted line: after reirradiation with UV-A.

Fig. 4 Diffuse reflectance UV-Vis spectra of Al(0.7)-MPS composite. Solid line: initial stage, dashed line: storage for seven days, dotted line: after reirradiation with UV-A.

Fig. 6 Diffuse reflectance UV-Vis spectra of Al(3.0)-MPS composite. Solid line: initial stage, dashed line: storage for seven days, dotted line: after reirradiation with UV-A.

reirradiation, indicating that the ratio of c-C and FV to FV+ did not change.

The ideal photochromic behavior of HMC dye is that FV+ (yellow) converts to t-C (colorless), reversibly and completely, on storage at 313 K and subsequent UV-A irradiation. In a solution of HMC dye, 100 % reversible conversion between FV+ and t-C occurred. In the solution, the peaks corresponding to the intermediate forms (c-C and FV) were scarcely observed. We presumed that the stable existence of FV and c-C in the composite is one of the reasons why the color strength (deriving from FV+ amount) did not recover to its initial level.

3.3 Photochromic specificity of aluminum containing MPS composite

There are two purposes for introducing Al, which is known to act as a cation site (negatively charged) in MPS. One is that a large quantity of HMC dye (especially FV+) can be adsorbed on to the cationic sites on MPS (the result is given above). The other is that FV+ (partially positively charged) is expected to become more stable than FV and c-C by the effect of a cation site. We expected that on incorporation of Al, the equilibrium of c-C, FV and FV+ inclines toward FV+, improving the ratio of color recovery on UV-A reirradiation.

UV-Vis spectra of the Al(0.5)-MPS composite are shown in

Fig. 3. The features of the spectra are very similar to those of the Al(0)-MPS composite. Further addition of Al to MPS gradually changed the UV-Vis spectra. **Fig. 5** shows the spectra of the Al(1.0)-MPS composite. The intensity of the FV+ peak decreased after storage for seven days. However, unlike Al(0)-MPS, the FV+ peak was still distinct and the color of the composite was faint yellow. The spectrum pattern of Al(0.7)-MPS was intermediate of those of Al(0.5)-MPS and Al(1.0)-MPS (**Fig. 4**). This indicates that the transformation of FV+ into other forms over time becomes more difficult or slows down on incorporation of Al into MPS.

By reirradiation with UV-A, the peak of FV+ increased again and was accompanied by a decrease in the t-C peak. However, contrary to our prediction, 100 % color recovery by UV-A irradiation could not be achieved. This is because after storage, FV and c-C yields did not change to FV+ on irradiation, analogously to the Al(0)-MPS composite. The spectra of the Al(0.7)-MPS composite indicate intermediate features between Al(0)- and Al(1.0)-MPS composites.

These findings suggest two trends. One is that the incorporation of Al inhibits the decoloration process by stabilizing FV+. The second is that FV or c-C is still stable despite incorporation of Al; in other words, conversion of t-C to FV+ does not occur

readily. The first trend was more remarkable when the content of Al increased to 3 %. In the Al(3.0)-MPS composite, FV+ scarcely changed to other forms after storage at 313 K, 95 % RH; the composite remained vivid yellow even after storage for seven days (Fig. 6).

4. Conclusion

A composite with vivid yellow color was obtained by using mesoporous silica as the host of HMC dye. Its color strength was high enough for its practical application as a color material. The color of the composite disappeared within seven days when stored at 313 K, 95 % RH, and its color strength recovered to 50 % of the initial value by UV-A reirradiation, demonstrating the coloring-decoloring process.

The incorporation of Al into MPS increased the quantity of HMC dye adsorbed onto it; however, the decoloring process from FV+ to t-C did not occur readily.

We assume that disturbing the stable existence of the intermediate forms (FV and c-C) may be necessary to achieve 100 % color recovery by UV-A irradiation.

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メソポーラスシリカに吸着した2-ヒドロキシ-4'-メトキシカルコンのフォトクロミック特性

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要 旨

合成アントシアニン色素である2-ヒドロキシ-4'-メトキシカルコン (HMC) は植物色素と同様の骨格を有しており、安全で環境負荷の少ないフォトクロミック材料として期待されている。本論文ではHMCをドライ条件で活用することを目的に、Al含有メソポーラスシリカ (MPS) とHMCの複合体を調製してそのフォトクロミック特性を検討した。

Alを含まないMPSの複合体では、313 K, 95 % RHの遮光条件に7日間保管することで鮮やかな黄色が消色した。またUV-A光の照射によって初期の50 %の着色度まで回復した。一方、MPSにAlを含有させることによってHMCの吸着量を増加させることが可能であった。しかしながら、Alの含有は色素のFV+型 (黄色) からt-C型 (無色) への変換を起さにくくすることが明らかになった。