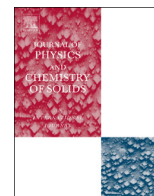




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Adsorption behavior of natural anthocyanin dye on mesoporous silica

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ABSTRACT

Because of its non-toxicity, naturally occurring anthocyanin is potentially suitable as a colorant for foods and cosmetics. To the wider use of the anthocyanin, the immobilization on the inorganic host for an easy handling as well as the improvement of the stability is required. This study is focused on the adsorption of significant amount of the natural anthocyanin dye onto mesoporous silica, and on the stability enhancement of the anthocyanin by the complexation. The anthocyanin has successfully been adsorbed on the HMS type mesoporous silica containing small amount of aluminum. The amount of the adsorbed anthocyanin has been increased by modifying the pore wall with *n*-propyl group to make the silica surface hydrophobic. The light fastness of the adsorbed anthocyanin has been improved by making the composite with the HMS samples containing aluminum, although the degree of the improvement is not so large. It has been proposed that incorporation of the anthocyanin molecule deep inside the mesopore is required for the further enhancement of the stability.

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1. Introduction

Anthocyanins are one of the naturally occurring dyes found in many flower petals and fruits [1,2]. The structure of the typical anthocyanin is shown in Fig. 1. Anthocyanins are non-toxic and used as a colorant of foods and cosmetics [3]. In order to use the anthocyanin more widely, investigations have been made so far in regard to the improvements of the properties of the dye. For the benefit of the ease in handling, and for the increasing affinity to various media, immobilization onto the solid matrices is one of the steps required for the wider practical use of the anthocyanin. In addition, the instability of the anthocyanin is another reason for the limited use: the anthocyanin generally loses its color easily at elevated temperature, neutral to basic pH conditions, and especially under visible-light irradiation [4]. The enhancement of the color stability is essential for practical use of the anthocyanin [5]. The immobilization of the anthocyanin on the solid host materials is also one promising approach to improve the stability [6–8].

In this study, we try to immobilize the anthocyanin on mesoporous silicates. Since the mesoporous silicates are known to have an overwhelming large surface area, they expectedly have potential to

adsorb enough amounts of various organic molecules including dye [9–12]. Among many type of mesoporous silicates, an HMS type one is characteristic of rather mild preparation condition that it can be prepared at room temperature in an aqueous solution using neutral alkyl amines as a structure-directing agent [13]. We have previously reported that Al-containing HMS type mesoporous silica adsorbs sufficient amount of the flavylium, a model synthetic dye having the same molecular skeleton as the natural anthocyanin (Fig. 1) [14], and that the incorporated flavylium exhibits enhanced stability against visible light irradiation [15,16]. It has also been reported by other groups that the incorporation into the mesoporous silicate stabilizes other dye molecules [17–19]. In our case, it has been found that the solid acidity caused by the Al³⁺ site on the HMS surface plays an important role in the adsorption and stabilization of the incorporated flavylium.

The present study aims to find the method to let the anthocyanin be adsorbed efficiently on the mesoporous silica without any severe color turn and loss of stability. The effect of the solid acidity on the adsorption behavior and the stability was investigated by adding Al³⁺ to the HMS. In addition, the effect of the hydrophobicity in the pore environment was examined by modifying the inner pore wall of the HMS by alkyl chain groups. Photofading of each sample was measured under visible light irradiation to check whether the stability of the anthocyanin was influenced by the modification of the HMS to increase the amount of the adsorbed dye.

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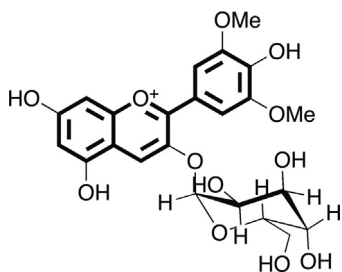


Fig. 1. Typical structure of anthocyanin (Malvidin-3-glucoside). The thick line indicates the flavylium skeleton.

2. Experimental

2.1. Materials

Anthocyanin (AN) was purchased from Kanto Chemical as “Grape Skin Color” and used as received.

The HMS type mesoporous silica was synthesized following the method described elsewhere [15,16]. Briefly, tetraethoxysilane and dodecylamine, both supplied from Wako Chemical, were used as a silicon source and a structure-directing agent, respectively. An aqueous ethanolic solution of the dodecylamine (0.91 g in 40 cm³ water/5 cm³ ethanol) was mixed with tetraethoxysilane (4.6 g) at 333 K and stirred for 1 day. The resulting sediment was collected by filtration and calcined at 903 K for 6 h under air stream. To prepare the Al-containing HMS, 0.12 g of Al(NO₃)₃·9H₂O supplied from Wako Chemical was blended to the solution of dodecylamine before mixing with tetraethoxysilane. The HMS samples containing aluminum are denoted as Al-HMS. The introduced amount of Al³⁺ was 1.5 mol% to Si⁴⁺. The BET surface area of typical samples was greater than 800 m²/g, and the samples had a narrow pore size distribution with the mean pore diameters in the range between 2.8 and 3.0 nm.

Part of the obtained HMS samples was made hydrophobic by modifying the inner pore wall with *n*-propyltriethoxysilane, in a similar manner described in the literature [20]. Thus, 0.5 g of the HMS or Al-HMS was previously dried in an oven at 393 K. The dried HMS or Al-HMS was mixed with 5 cm³ of toluene containing 0.10 g of *n*-propyltriethoxysilane, and then the mixture was refluxed for 6 h under nitrogen stream. The resulting sample was filtered, washed with toluene and acetone, and then dried under reduced pressure for 2 h. Thus obtained hydrophobic HMS and Al-HMS are denoted as HMS(A) and Al-HMS(A), respectively.

2.2. Sample preparation

The synthesized HMS, Al-HMS, HMS(A) and Al-HMS(A) were all used as the host materials for the adsorption of AN. The composite of AN and each host materials were prepared as follows. The aqueous methanolic solution (water:methanol=7:3 v/v) was used as a solvent of AN. The host material weighed 100 mg was mixed with 100 cm³ of the aqueous methanolic solution containing 20 mg of AN, and then maintained at 278 K in the dark. After 3 days the mixture was filtered and the resulting sediment was dried in the air. The obtained composite sample is denoted as AN/HMS, AN/Al-HMS, AN/HMS(A) or AN/Al-HMS(A).

2.3. Measurements

The structure of the synthesized host materials was assured by XRD measurements. The XRD patterns were measured with Rigaku MiniFlex X-ray diffractometer (CuK α , step angle and scan speed 0.05 and 2 deg/min, 15 mA, 30 kV).

The amounts of the adsorbed anthocyanin on each sample were estimated from the optical absorption of the dye in the diffuse reflectance UV–vis spectra. The UV–vis spectra were collected with JASCO V-550 spectrophotometer equipped with ISV-469 integrating sphere.

To investigate the light endurance of the composite samples, the color fading caused by visible light irradiation was evaluated from the decrease in the absorption in the diffuse reflectance spectra. A 100 W halogen lamp (Schott Megalight 100) equipped with a 30 cm length flexible light guide was used as a visible light source. The powder sample was loaded in a plastic cell covered with a thin glass, and placed at the position of 2 cm from the aperture of the light guide.

3. Results and discussion

3.1. Structure of the synthesized mesoporous silica

Fig. 2 illustrates the XRD patterns of the HMS and Al-HMS samples. A peak at around $2\theta=2^\circ$ was observed in both samples, indicating that the samples possessed the wormhole type mesopore, as described in the literature [21]. The formation of the uniformed mesopore was thought to be partially obstructed by the addition of heterogeneous atoms (Al³⁺), because the peak intensity of Al-HMS was a little weaker than that of HMS. The loss of the regularity in the mesostructure by the addition of Al³⁺ has also been reported on other mesoporous silicas such as MCM-41 [22] and FSM-16 [23]. However, as the decrease in the peak intensity was small, the extent of the loss of regularity was expected to be negligible in the following experiments.

3.2. Adsorption of anthocyanin onto the mesoporous silica

Fig. 3 illustrates the diffuse-reflectance UV–vis spectra of the composite samples. As shown in Fig. 3(a), the spectrum of AN/HMS has very low absorption peak at 530 nm. This means that the AN/HMS sample only exhibited extremely pale color and that the amount of adsorbed AN was small on the pure HMS. On the other hand, the addition of Al³⁺ to the HMS made the color of the sample strong, as shown in Fig. 3(b). Therefore, the addition of Al³⁺ was found to be beneficial for the better adsorption of AN on HMS. It has been known that the addition of small amount of Al³⁺ to mesoporous silicas results in the formation of an acidic site, because the shortage of electric charge is caused by the partial substitution of Si⁴⁺ by Al³⁺ in the silica framework [23]. We have

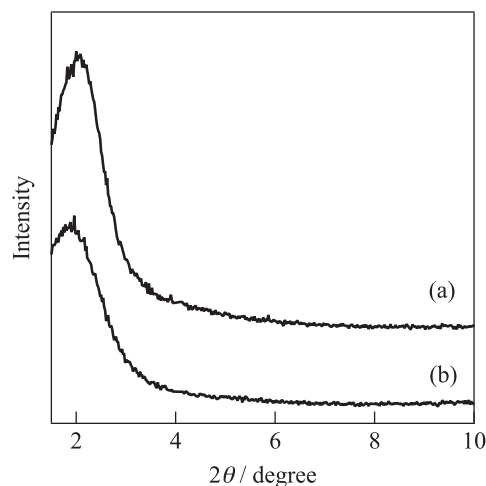


Fig. 2. XRD patterns of the (a) HMS and (b) Al-HMS samples.

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