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Enhanced stability of natural anthocyanin incorporated in Fe-containing mesoporous silica

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Abstract

Anthocyanin is known as a safe coloring material although its poor stability often limits more extended use. In this study, we tried the enhancement of the photostability of the anthocyanin by the incorporation into the pore of HMS type mesoporous silica containing various metal

ions. The anthocyanin was adsorbed on the HMS by pouring a highly concentrated anthocyanin solution to the dried HMS, urging the incorporation of the dye into the mesopore by a capillary condensation. Improved stability of the anthocyanin against visible irradiation was achieved by the adsorption onto the HMS containing Fe^{3+} , although other metal ions in the HMS showed less effect on the stabilization. From the UV-Vis spectroscopy, the Fe^{3+} species effective for the stabilization of the anthocyanin was found to be the tetrahedral one highly dispersed in the silica framework. The decrease in the absorptivity of the anthocyanin on the Fe-HMS compared to other metal-containing HMS suggested that the Fe-HMS promoted the aggregate formation of the anthocyanin molecules. The highly dispersed Fe^{3+} species had an ability to gather the anthocyanin molecule close to itself, resulting in tight incorporation of the dye inside the mesopore. The incorporation and aggregate formation of the anthocyanin was expected to contribute to the improvement of the stability against irradiation.

Keywords:

Naturally occurring dye; Adsorption; Photostability; Mesoporous silica; HMS

1. Introduction

From the viewpoint of safety, natural dyes are generally superior to the synthetic ones. Therefore, they are suitable for the use as a colorant of foods and cosmetics, where direct contact with human body cannot be avoided [1, 2]. In addition, the naturally occurring dyes are better than the synthetics in regard to the consumer perception because they are not artificial materials. Among the natural dyes, anthocyanin is one of the most common dyes and generally found in the body of many plants [3]. The anthocyanin, having the structure with the flavylium ring [4], is thought to be definitely nontoxic compound since it has been used as a colorant of foods for a long time [5]. In fact, the anthocyanin is one of the most used natural food additives in the present days, and the importance is growing further. In addition, anthocyanin is known to show bioactivities such as anticancer and antioxidant properties, mainly due to its quenching effect of reactive oxygen species [6].

However, the natural dyes are commonly poor in the stability [7]. Especially, the anthocyanin easily loses its color under neutral to slightly basic conditions or under irradiation [8]. The instability hinders more extensive use of the natural dyes [9].

Incorporation of organic molecules into inorganic host materials is known as a promising method to improve the stability of the organic molecules [10]. For instance, inclusion of dyes into the clay interlayers [11-13], zeolites [14, 15], and mesoporous silicates [16-18] have been reported to enhance the stability of the guest materials. The ancient Maya Blue is also a good example of the composite materials, where the guest indigo dye is greatly stabilized by the incorporation into the channel of the palygorskite clay [19-23]. In addition, the inorganic host has also been used as a vessel for the photochemical conversion system between the chalcone

and the flavylium dye [24, 25], which is a model compound of the natural anthocyanin with the same chromophore (see Scheme 1).

We have investigated the stability enhancement of various natural dyes by making composites with nontoxic inorganic host materials. In a previous report, we showed that the anthocyanin was successfully intercalated and stabilized in the interlayer space of the cation-exchangeable clay (montmorillonite) since the anthocyanin was a cationic dye [26]. The synthetic flavylium dye was also stabilized by the incorporation into the pore of the mesoporous silicates containing metal ions such as Al^{3+} [27, 28]. However, the natural anthocyanin itself was not significantly adsorbed onto the HMS type of the mesoporous silica without metal addition, and only a limited enhancement of the stability was observed by the incorporation of the natural anthocyanin into the Al-containing HMS [4].

In this study, we report the methods and conditions to enhance the stability of the natural anthocyanin by the incorporation into the pore of the mesoporous silica. The HMS type of the mesoporous silica is used as a host material, because the preparation is relatively easy under mild conditions [29]. The effect of the incorporation on the stability of the anthocyanin is investigated in detail using the HMS containing several metal ions. The stabilization effect is evaluated from the light fastness of the dye under visible light irradiation.

2. Experimental

2.1 Materials

Anthocyanin was purchased from Kanto Chemical as “Grape Skin Color”. The as-received

anthocyanin dye was purified by a similar method described earlier [26, 30] using an adsorption column XAD-7. Briefly, the dye was dissolved in a 5 % aqueous solution of formic acid and passed through the column. The eluate was concentrated and mixed with an excess amount of diisopropyl ether to precipitate the purified dye. The precipitate was air-dried at room temperature. Thus purified anthocyanin was denoted as AN.

HMS was prepared based on the literature [31]. Dodecylamine weighed 0.91 g (Wako Chem.) was dissolved in 5 cm³ of ethanol, mixed with 45 cm³ of water, and heated up to 333 K. Tetraethoxysilane (Wako Chem., denoted as TEOS) weighed 4.6 g was dropped to the solution, and the mixture was kept at 333 K for 22 h. The sample was filtered, washed with water, dried in an oven and calcined at 903 K for 6 h under dry air stream. The molar composition of the source materials was 1.0 dodecylamine / 4.5 TEOS / 511 water / 17 ethanol.

To prepare the Al- and B-containing HMS, aluminum isopropoxide and boric acid, (Wako Chem.) were used as the source of Al³⁺ and B³⁺, respectively. The nitrate salts of Ni²⁺ (Ni(NO₃)₂·6H₂O, Kishida Chem.), Mg²⁺ (Mg(NO₃)₂·6H₂O, Wako Chem.), Ga³⁺ (Ga(NO₃)₃·nH₂O, Wako Chem.) and Fe³⁺ (Fe(NO₃)₃·9H₂O, Wako Chem.) were used as the sources of each metal-containing HMS. As for the Fe-containing HMS, tris(2,4-pentanedionato)iron(III) purchased from Dojindo Chem. (denoted as Fe(acac)₃) was used as well as the above-mentioned iron(III) nitrate.

The preparation method of the HMS containing various metal ions is as follows. Unless otherwise noted, the amount of the metal ions was adjusted to 1.0 mol% toward Si in the crude mixture. On using the boric acid or nitrate salts as a metal ion source, given amount of the source compound was dissolved in 5 cm³ of water, and the solution was added dropwise

to the dodecylamine solution with TEOS by turns. On the other hand, when the aluminum isopropoxide or $\text{Fe}(\text{acac})_3$ was used as a metal source, it was dissolved in 3 cm^3 of ethanol, mixed with TEOS, and then poured onto the dodecylamine solution. After mixing the source compounds, the preparation procedure was the same as that of pure HMS described above. In the following, the metal-containing HMS is denoted as M-HMS ($\text{M} = \text{Al}, \text{B}, \text{Ni}, \text{Mg}, \text{Ga}, \text{Fe}$). The FeHMS is referred to as $\text{Fe}(\text{Nx})\text{HMS}$ or $\text{Fe}(\text{Ax})\text{HMS}$, where N and A denotes the Fe sources (N: $\text{Fe}(\text{NO}_3)_3$, A: $\text{Fe}(\text{acac})_3$), and x represents the Fe/Si molar ratio of the starting mixture expressed in percentage.

The HMS and M-HMS powder samples were characterized by XRD and nitrogen adsorption isotherm (see supplementary data). In the XRD pattern, all the samples showed a single reflection peak at around $2\theta = 2^\circ$. The BET specific surface area of the samples was fairly large (681 to $1075 \text{ m}^2/\text{g}$). In addition, the samples exhibited a narrow pore size distribution with the mean pore diameter between 2.8 and 3.2 nm. These results showed that the samples had a mesoporous structure.

The composite materials of each M-HMS and AN were prepared by mixing the AN solution and the M-HMS. The AN weighed 0.6 mg was added to 0.075 cm^3 of methanol, mixed with 0.075 cm^3 of 5 % formic acid aqueous solution, and dissolved by ultra-sonication for 20 min. The AN solution looked strongly dark-red because of the high concentration. Meanwhile, the M-HMS powder was dried at 393 K for 24 h in an oven before mixing with the AN. Then, all of the prepared AN solution (0.15 cm^3) was added dropwise to the previously dried M-HMS powder (100 mg) using a micropipette. This preparation method was expected to promote the incorporation of AN into the mesopore by the capillary condensation. The mixture was dried for 2 h at 313 K under reduced pressure. Thus-obtained

composite samples were denoted as AN/M-HMS.

2.2 Measurements

Diffuse reflectance UV-Vis spectra were collected with JASCO V-550 spectrophotometer with ISV-469 integrating sphere equipped to the spectrometer. Sodium sulfate was used as a reference material. On measuring spectra, the powder samples were loaded in a plastic cell covered with a thin glass.

To investigate the light endurance of each sample, visible light was irradiated to the samples under ambient temperature and pressure. 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 samples were held in the same cell as that used for the UV-Vis measurement, and placed at the position of 1.0 cm from the aperture of the light guide. The light intensity at the sample position was adjusted to 210 klux. The degree of the color fading was determined by the decrease in the main absorption peak of the AN on the diffuse reflectance spectra of each composite material.

To investigate the effect of various metal ions on the AN molecule in the solution, an aqueous ethanolic solution (1:1 v/v, 10 cm³) containing 5.2 mg of AN was mixed with 20 μmol of the nitrate salt of each metal ion. The pH of the solution was adjusted to 1.4 by HCl. The influence of the added metal ions on the AN was evaluated by the change in the transmittance UV-Vis spectra collected with Shimadzu UV-1700 spectrophotometer. To determine whether the Fe²⁺ ion was produced in the mixture or not, 1,10-phenanthroline was used as an indicator.

3. Results and discussion

3.1 UV-Vis spectra of the composite materials

Figure 1 illustrates the diffuse reflectance UV-Vis spectra of various AN/M-HMS samples. A single peak at around 540 nm was assigned to the AN in the composite sample. The peak was observed at 538 nm in the AN/HMS sample without metal ions. Since the AN solution gave the absorption peak at almost the same wavelength of 536 nm (see first row of Table 1), it can be said that the interaction between the AN and the HMS was weak. Meanwhile, the AN/M-HMS samples showed an absorption peak between 536 to 546 nm. Therefore, the absorption peak did not show any significant shift by the existence as well as the kind of the metal ions included in the HMS. This result does not imply the formation of any complexes between the AN and the metal ions in the M-HMS, because the metal complexation of the anthocyanin generally causes some spectral shifts [32, 33].

In Figure 1(e), the baseline of AN/FeHMS slanted up to the short wavelength region. This slope was due to the strong absorption of the Fe^{3+} , as described later in Section 3.3, and did not reflect any difference in the state of the AN incorporated in the M-HMS.

3.2 Light endurance of the composite materials

The stability of the AN incorporated in various M-HMS samples was evaluated by the light fastness under visible irradiation. Figure 2 shows the spectral change of the AN/HMS

sample during visible irradiation by the 100 W halogen lamp for 240 min. Monotonous decrease in the absorption was observed without change in the shape of the band, indicating simple decomposition of the AN molecule caused by the irradiation. Other AN/M-HMS samples also showed similar monotonous decrease in the absorption during irradiation.

Figure 3 shows the change in the absorption value of AN during irradiation of various AN/M-HMS samples. As described above, gradual decrease in the absorption of AN was observed along with the irradiation time in every samples. In the samples other than AN/Fe(N1.0)HMS, the ratio of the remaining absorption of AN after 240 min irradiation was between 24 % and 42 % of the initial absorption. Therefore, the degree of the degradation was not so different from each other, except for Fe(N1.0)HMS. However, as shown by the closed circle symbols in Figure 3, the ratio of the AN absorption after irradiation stayed at 78 % of the initial value in the AN/Fe(N1.0)HMS, indicating that the light endurance of the AN/Fe(N1.0)HMS sample was significantly higher than the others.

Several reasons can be supposed for this unusually high stability of AN in the AN/Fe(N1.0)HMS sample. Firstly, there is a possibility that the acidic property of the host material enhances the stability of the anthocyanin, because the anthocyanin is generally stable only under acidic conditions [34]. The mesoporous silicates containing B^{3+} , Al^{3+} or Ga^{3+} as well as Fe^{3+} is reported to show definite acidity due to the trivalent cation substituting Si^{4+} in the tetrahedral silica framework [27, 35-37]. However, in the present case, only Fe(N1.0)HMS showed the stabilization effect on the adsorbed AN and other metal-containing HMS did not. As the acidity of the Fe-containing HMS is not the strongest among them [35], we can exclude the possibility that the adsorbed AN was mainly stabilized by the acidity derived from the trivalent metal containing HMS.

The formation of some complexes between the metal ion and the dye molecule can be another possible reason for the stabilization. It has been reported that the naturally occurring anthocyanins are often stabilized in the flower petals by forming complexes with some metal ions such as Fe^{3+} , Al^{3+} and Mg^{2+} [8]. At the same time, the formation of metal complexes has more or less influences on the visible absorption of the anthocyanins [33], which can be the main cause of the blue color exhibited by the anthocyanins [38, 39]. However, as the adsorption of AN on Fe(N1.0)HMS did not cause significant UV-Vis spectral shift compared with other composite samples (see Figure 1), the present experimental results did not support the formation of the complex compounds between AN and Fe^{3+} by the adsorption on the Fe(N1.0)HMS. Therefore, the stabilization caused by the formation of metal complexes can also be eliminated.

The degradation of the AN was thought mainly due to the oxidation caused by the atmospheric oxygen activated to the singlet state under irradiation of AN. From this point of view, the effect of the singlet oxygen quencher can be a candidate of the reason for the stabilization [40]. As a quencher of the singlet oxygen, the Ni^{2+} complex is reported to be effective [41]. However, the stability of AN in AN/NiHMS was not so high as that of AN/Fe(N1.0)HMS. This result suggests that the stability enhancement was not mainly caused by the quenching effect of the singlet oxygen by the metal complexes.

Considering these, the stabilization effect on the adsorbed AN was something like a special property caused by the Fe(N1.0)HMS sample itself. Therefore, we investigated the effect of Fe^{3+} on the adsorbed AN more in detail.

3.3 Dependency of the stabilization effect on the amount of Fe^{3+}

We investigated whether the amount of the Fe^{3+} in the FeHMS influenced the stability of the adsorbed AN or not. Figure 4 shows the diffuse-reflectance UV-Vis spectra of the FeHMS samples with various amounts of Fe^{3+} from the two different source materials. Although the indicated amount of Fe^{3+} was not the absolute value incorporated in the FeHMS but the introduced amount of the crude material at the preparation step, it can be said that the amount of the crude metal compound may reflect that of the incorporated Fe^{3+} . In every FeHMS samples, an absorption peak at around 250 nm was observed, which was assigned to 4-coordinated highly dispersed Fe^{3+} species [42-44], although the possibility of the higher coordinated one could not be fully excluded [45-47]. The relationship between the absorption at around 250 nm and the amount of introduced Fe^{3+} is illustrated in Figure 5. The absorption value increased along with the amount of the introduced Fe^{3+} . However, the tendency of the increase differed corresponding to the Fe^{3+} source materials: the Fe(A)HMS showed more larger absorption value than Fe(N)HMS at the same amount of the introduced Fe^{3+} . As the Fe^{3+} complex with a bulky ligand was used as a source material of the Fe(A)HMS sample, the Fe^{3+} species tend to be highly dispersed in the silica framework of HMS, especially in the mesoporous silica [46]. On the other hand, the iron species not incorporated in the silica framework formed the oligomeric iron oxide with the 6-coordinated octahedral Fe^{3+} species, which was detected in Figure 4(a-c) by the broadening of the absorption band at around 350 to 400 nm [46-48]. In the Fe(N)HMS, the formation of the oligomeric iron species disturbs the proportionality of the absorbance of the highly dispersed Fe^{3+} towards the amount of the introduced Fe^{3+} , as seen in Figure 4(a-c). All these results were consistent with our previous report [28].

The light fastness of the AN in the AN/FeHMS was enhanced along with the increase in the amount of the introduced Fe^{3+} . It should be mentioned that the stability of the AN in the Fe(A)HMS surpassed that of the AN/Fe(N)HMS at any amounts of the introduced Fe^{3+} . The relationship between the stability and the absorption of FeHMS samples at around 250 nm is shown in Figure 6. As described above, the absorption value reflects the amount of the tetrahedral Fe^{3+} dispersed in the silica framework. Therefore, we can see that the stability was in proportion to the amount of the highly dispersed Fe^{3+} species. This proportionality had no relationship with the source materials of Fe^{3+} . From this, we concluded that the stability enhancement of the AN in the AN/FeHMS samples was due to the existence of the highly dispersed tetrahedral Fe^{3+} species.

On the other hand, the absorbance of the AN adsorbed onto the FeHMS was in inverse proportion with the amount of the highly dispersed Fe^{3+} species, as shown in Figure 7. This inverse proportionality had, again, no relationship with the source of Fe^{3+} . Considering that the amount of the adsorbed AN was strictly the same because all of the added AN was adsorbed on the FeHMS at the preparation step, this result seems strange at a glance. Two possible reasons can be proposed: the AN was decomposed by the highly dispersed Fe^{3+} , or the absorptivity of the AN was reduced by the highly dispersed Fe^{3+} species. As for the former hypothesis, it would be possible that the Fe^{3+} ions urge the degradation of the organic dye molecule by its oxidative property. However, considering that the degradation of the AN under irradiation was not accelerated but suppressed, the degradation promoted by the Fe^{3+} is not plausible. Therefore, we accept the latter possibility that the absorptivity, *i.e.*, the absorption coefficient of the AN was changed by the Fe^{3+} species.

3.4 Interaction between the anthocyanin molecules and the Fe^{3+} ions

As described in Section 3.3, we tentatively built up the hypothesis that the existence of the Fe^{3+} ions had some influences on the visible absorptivity of the AN. This can be rephrased that the absorption cross-section of the AN molecules was reduced due to the change in the state of AN caused by the Fe^{3+} ions. Therefore, we investigated the interaction of the AN molecules in solutions with several metal ions including Fe^{3+} . Table 1 shows the spectral properties of AN solutions mixed with various metal ions. In all mixtures, the amount of the dissolved AN was the same, and the λ_{max} was observed at almost the same wavelength around 536 nm. However, the color of the AN solution faded on mixing with Fe^{3+} , and the absorbance of the AN in the solutions with Fe^{3+} became significantly lower than the others. If the color loss was due to the oxidative decomposition of the AN by the Fe^{3+} , the Fe^{3+} ions should become the Fe^{2+} after the decoloration reaction of AN. As the Fe^{2+} ions are known to cause the coloration with phenanthroline, we tried to detect the formation of the Fe^{2+} by the phenanthroline test. However, the mixture of the AN solution with the Fe^{3+} was negative toward the phenanthroline test, indicating that the color loss was due not to the decomposition of the AN molecule by the oxidation with the Fe^{3+} . Consequently, the color loss was thought to come from the decrease in the absorption cross-section derived from the aggregation of the AN molecules under the interaction with the Fe^{3+} . In practice, the precipitation of the AN aggregate was observed on adding excess amount of the Fe^{3+} . Moreover, it has been reported that the aggregate of the AN was formed not by the existence of the Al^{3+} but by the Fe^{3+} , although both ions has the ability to form complexes with the AN molecules [49]. These results and report further support the idea that the Fe^{3+} has a special character to promote the

formation of the AN aggregate.

Considering the above results, we concluded that the stability enhancement of the AN incorporated in the FeHMS was due to the formation of an aggregates by the influence of the highly dispersed Fe^{3+} species. It has been reported that the ordered molecular association of the anthocyanins causes the spectral shift as well as the stabilization [50]. As the spectral shift was not observed by the aggregation of AN in the AN/FeHMS, it was suggested that the AN molecules formed an aggregate with a disordered orientation of the dipolar moment.

3.5 Enhanced adsorption and stabilization of the anthocyanin

As described in Section 3.4, the interaction with the Fe^{3+} in the HMS helped the aggregation and stabilization of the AN molecules. The degree of the stabilization was in proportion to the amount of the highly dispersed tetrahedral Fe^{3+} species, and the octahedrally coordinated bulk iron oxide had no relationship with the stabilization. Therefore, the highly dispersed Fe^{3+} species was thought to be the adsorption site of the AN molecules. It is suggested that the *d*-orbital of the Fe^{3+} ion, as well as the acidic property of the Fe^{3+} dispersed in the silica framework, may have some influence on the adsorption and aggregation of the AN molecules. Since the ligand-to-metal charge transfer (LMCT) between the anthocyanin and the transition metal ions including Fe^{3+} has been reported [51], it is possible to think that such kinds of electron transfer interaction may affect the tendency for the AN molecules to form an aggregate. However, we could not determine what sort of interaction really contributed to the aggregation of the AN.

In the previous study, we reported that the AN molecules adsorbed on the AlHMS did not

show enough stability against irradiation, perhaps because they were not effectively incorporated in the mesopore of the AlHMS [4]. On the other hand, it is found in this study that the highly dispersed Fe^{3+} species tend to gather the AN molecules around itself and urges to form an aggregate. In other words, it can be said that the Fe^{3+} ion has stronger effect to adsorb the AN molecules than Al^{3+} , which is in consistent with the previous report concerning the anthocyanidin without sugar moiety [52]. Since the Fe^{3+} ions are widely distributed in the sidewall of the mesopore in the HMS, it is expected that the AN molecules are drawn inside by the Fe^{3+} and tightly incorporated into the mesopore. As the diffusion of the atmospheric oxygen molecule inside the pore is slow, the AN molecules adsorbed inside is shielded from the oxidation under irradiation, as suggested by the results in our previous studies [27, 28]. In addition, the aggregation also contributes to the stability enhancement, because the contact area with the oxygen per one AN molecules decreases by the formation of the aggregate. We concluded that these two factors contributed to the stability enhancement of the AN incorporated in the FeHMS.

In conclusion, not a bulk but a highly dispersed Fe^{3+} species had the effect to adsorb the AN molecules inside the mesopore, and to urge the formation of a randomly oriented aggregate. In the inner pore space, the diffusion of the oxygen molecule was slow, resulting in the suppression of the oxidative degradation of the AN molecule under irradiation. The formation of the aggregate also contributed to the enhancement of the stability.

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Figure captions:

Figure 1. Diffuse-reflectance UV-Vis spectra of several AN/M-HMS composite samples. (a) AN/HMS, (b) AN/AlHMS, (c) AN/MgHMS, (d) AN/NiHMS and (e) AN/Fe(N1.0)HMS.

Figure 2. Change in the diffuse-reflectance UV-Vis spectra of AN/M-HMS composite samples during visible irradiation for 240 min. The spectra were collected at every 30 min.

Figure 3. Changes in the absorption value at $\lambda_{\max}$ of each AN/M-HMS samples during visible irradiation for 240 min. The legend of each marker is displayed inside the figure.

Figure 4. Diffuse-reflectance UV-Vis spectra of several FeHMS samples with different Fe^{3+} sources and amounts. (a) Fe(N0.1)HMS, (b) Fe(N0.5)HMS, (c) Fe(N1.0)HMS, (d) Fe(A0.5)HMS and (e) Fe(A1.0)HMS.

Figure 5. Relationship between the absorption at around 250 nm in the UV-Vis spectra of FeHMS and the amount of introduced Fe in relation to that of Si. The shape of the symbols indicates the difference in the Fe^{3+} source. Square: Fe(N)HMS, Circle: Fe(A)HMS.

Figure 6. Relationship between the absorption at around 250 nm and the retention ratio in the absorption of AN in the AN/FeHMS samples with various Fe^{3+} amounts before and after irradiation for 240 min. The shape of the symbols indicates the difference in the Fe^{3+} source. Square: Fe(N)HMS, Circle: Fe(A)HMS.

Figure 7. Relationship between the absorption at around 250 nm due to highly dispersed Fe^{3+} and the absorption at around 540 nm due to AN in the AN/FeHMS samples with various Fe^{3+} amounts. The shape of the symbols indicates the difference in the Fe^{3+} source. Square: Fe(N)HMS, Circle: Fe(A)HMS. The amount of the loaded AN was the same through all the samples.

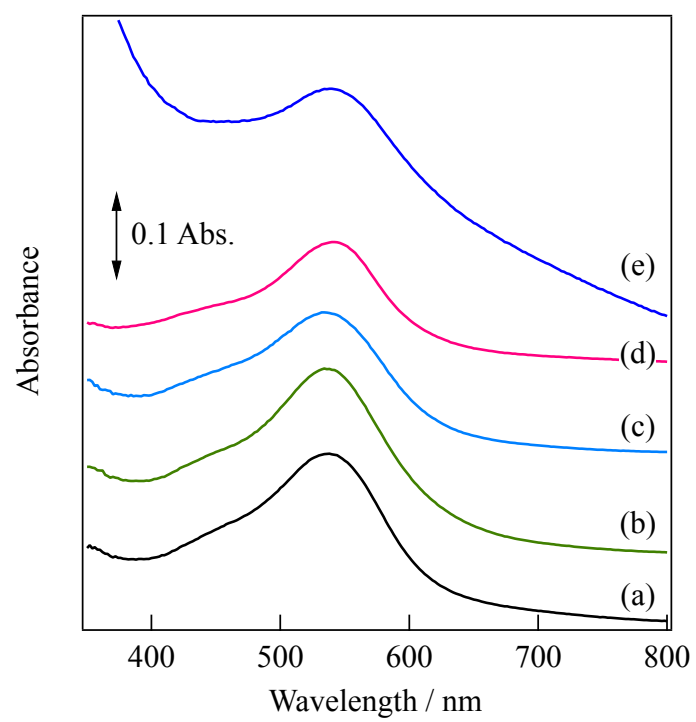


Figure 1.

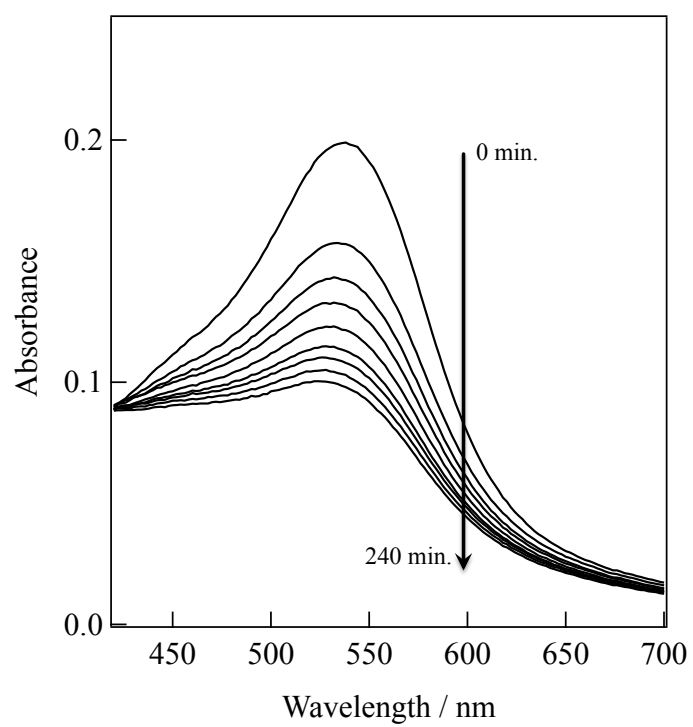


Figure 2.

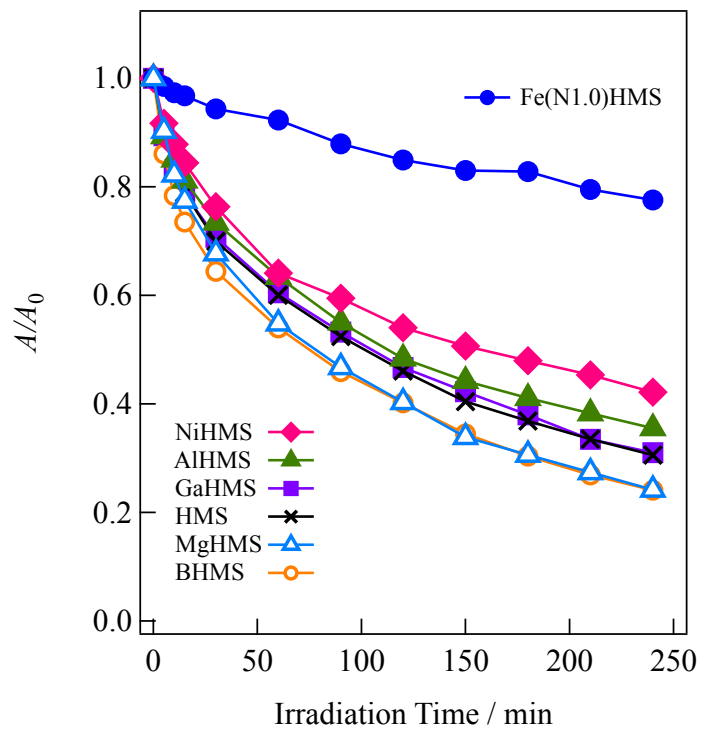


Figure 3.

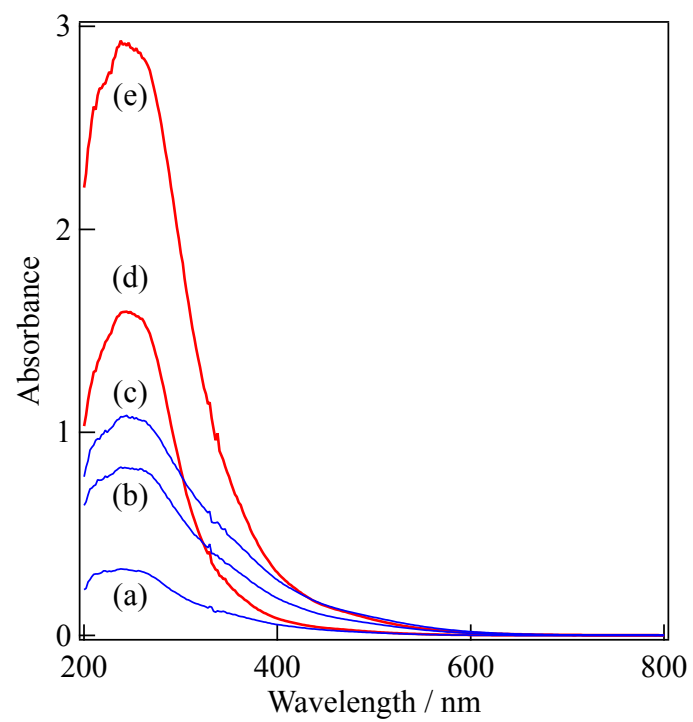


Figure 4.

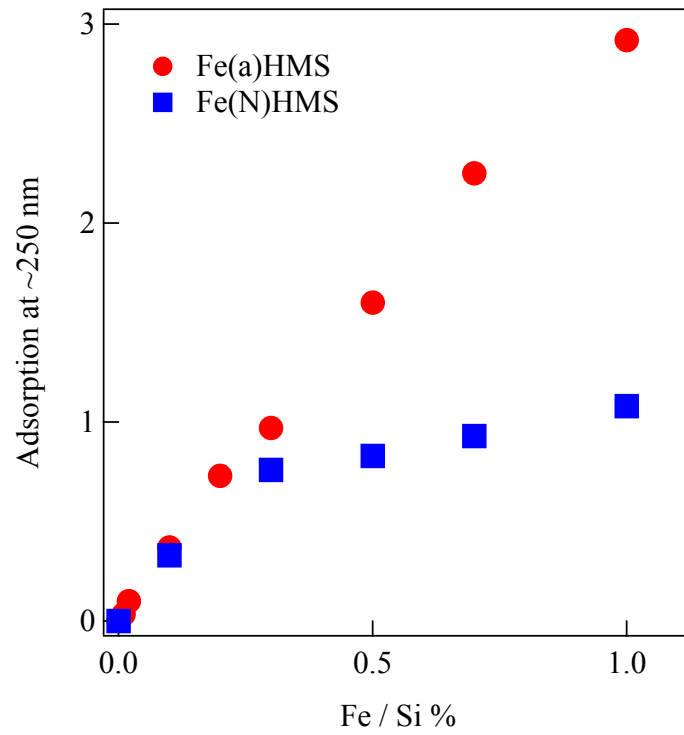


Figure 5.

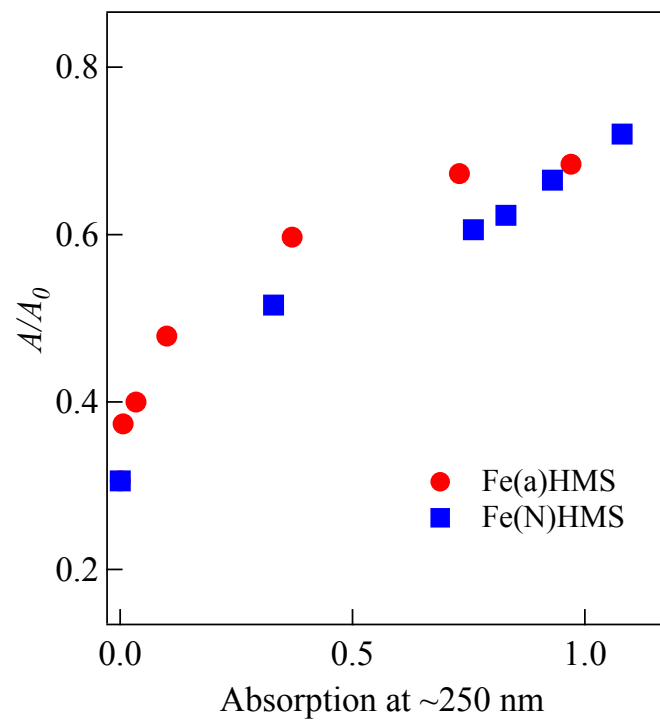


Figure 6.

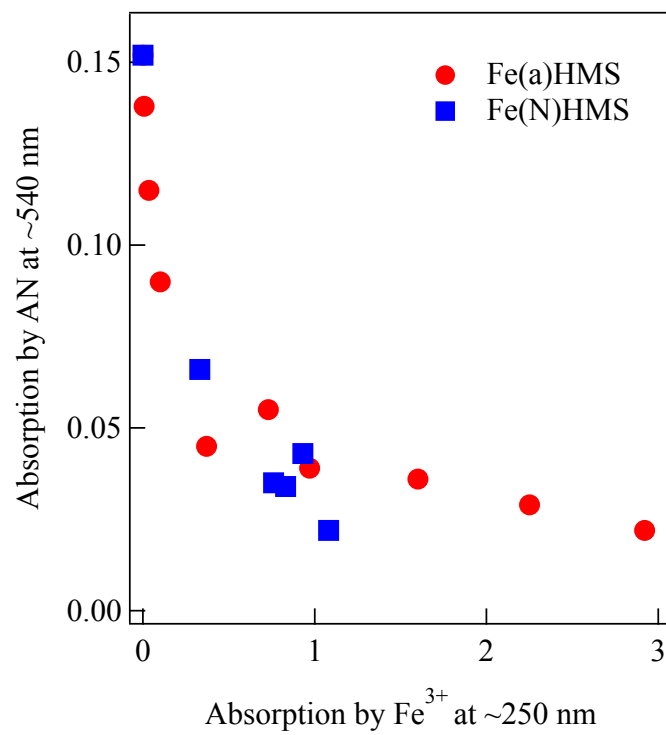


Figure 7.

Table 1. Spectral properties of AN solutions with various metal ions.^a

Added metal ions ^b	λ_{max} / nm	Absorbance
None	536	0.19
Al ³⁺	536	0.18
Ga ³⁺	537	0.18
Mg ²⁺	536	0.18
Ni ²⁺	536	0.18
Fe ³⁺	534	0.03

^a An aqueous methanolic solution (1:1 v/v) of AN was used. The pH of the solution was adjusted to 1.4 by adding HCl.

^b Nitrate salt of each metal was added to the solution.