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Improved photostability of hydrophobic natural dye incorporated in organo-modified hydrotalcite

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Abstract

The β -carotene and annatto extract are typical carotenoids used as a safe colorant of foods. However, the instability against irradiation limits their wide use. The improvement of the stability was investigated by the intercalation of the dye into the interlayer space of the anion-exchangeable clay, hydrotalcite. The hydrophobic environment was constructed in the interlayer space of the hydrotalcite by the modification with anionic surfactant (dodecyl sulfate and dodecylbenzene sulfonate). The lipophilic β -carotene and annatto dye were successfully incorporated into the organo-modified hydrotalcite, and the incorporated dye exhibited the improved photostability under visible irradiation from a 100 W halogen lamp (190 klux) in the air. The effect of the stabilization on the anionic annatto dye was higher by the incorporation in the modified hydrotalcite than in the modified cation exchangeable clay, suggesting that the polarity of the clay sheet had some influence on the stabilization of the incorporated dye. The stabilization effect of the β -carotene was not so significant as that of the annatto dye, because sufficient intercalation of the non-polar β -carotene may require stronger hydrophobic environment. The π - π interaction between the β -carotene and the benzene ring of the dodecylbenzene sulfonate was found to contribute to the stability enhancement.

KEYWORDS: A. nanostructures, A. organic compounds, C. X-ray diffraction, D. optical properties, D. surface properties.

1. Introduction

Carotenoids are one of naturally occurring pigments and are widely included in plants and animals. They have a long polyene chain as a chromophore, resulting in their generally strong hydrophobicity. More than 700 types of carotenoids have ever been found in nature [1]. Among them, β -carotene is the most typical carotenoid. It is one of the members called carotene, which possesses no other elements than hydrogen and carbon in its composition. The structure of the β -carotene is shown in Figure 1. Two six-membered rings are located at both ends of the polyene chain with 9 alternating single and double bonds. The β -carotene is included in many vegetables and its contribution to the human health is well-known in recent years [2].

The series of compounds without the six-membered rings at the ends of the conjugated double bonds are generally called apocarotenoids. The annatto dye, which is extracted from the seed of *Bixa orellana* L., contains some kinds of apocarotenoid (bixin and norbixin) as the main components [3]. The structures of bixin and norbixin are also shown in Figure 1. The annatto dye, especially containing norbixin as a predominant component, is slightly water-soluble, but it is generally considered rather hydrophobic as the β -carotene is.

The β -carotene and annatto dye are both used widely as non-toxic natural colorants of foods [4, 5]. The oil-soluble nature of the lipophilic dye is suitable for the coloration of processed dairy products or meats [6-8]. However, the instability of the dye limits its more widespread use: the carotenoids easily decompose through oxidation and lose their color [9]. Especially, annatto dye is known to be unstable under visible-light [10, 11]. The improvement of the stability will extend the usage of the carotenoids as a general colorant.

For various purposes, some researchers have reported the improvement of the stability by the incorporation of the carotenoid molecules into other materials such as carbon nanotubes [12],

polyacrylic acid [13] and cyclodextrin [14]. The inclusion of the dye as a guest molecule into inorganic host materials is a promising approach, like the ancient Mayan people who used the composite of indigo and palygorskite clay for their colorant [15, 16]. The intercalation of cationic or anionic dye molecule into the clay interlayer has been carried out to enhance the stability of the dye [17-24]. We have also reported the stability enhancement of the natural dye such as anthocyanin [25] and carmine [26] by the intercalation between the clay layers. However, nonionic hydrophobic dyes are hardly intercalated into the polar clay interlayer space. In fact, we could not intercalate the lipophilic annatto dye between the layers of the anion exchangeable hydrotalcite, although the annatto dye had carboxyl groups in its structure and exhibited anionic nature [26].

The polar and hydrophilic interlayer space of clays can be converted into hydrophobic one by the exchange of the interlayer ions with suitable surfactant molecules. Such modified clays are called organoclays and have an ability to adsorb various organic molecules between the layers by the hydrophobic interaction [27, 28]. The cation-exchangeable montmorillonite has been modified with the cationic alkylammonium surfactants and used for the inclusion of the lipophilic β -carotene into the clay interlayer [29]. We have also been successful to intercalate and stabilize the annatto dye using the montmorillonite modified with the cationic surfactant [30]. Therefore, it can be said that the cation-exchangeable clays can adsorb and stabilize the hydrophobic dye by the proper organo-modification.

Assuming that the stabilization effect comes from the intercalation caused by the hydrophobic interaction, the polarity of the original interlayer space (positive or negative charge of the clay sheet) is not expected to have strong influence on the stability enhancement of the included dye molecules. In this study, we have investigated the possibility for the stabilization of the β -carotene and the annatto dye with hydrotalcite modified with anionic surfactant. The hydrotalcite is a typical anion-exchangeable clay, having a layered structure made of the Mg-Al double hydroxide. It is

often used as an adsorbent or a host material of various anionic compounds [31, 32] including dyes [33-36], and shows different properties from those of the cation-exchangeable montmorillonite. Therefore, the development of the composite with the hydrotalcite may expand the range of application for the dyes as a colorant. In addition, the results obtained here will contribute to the evaluation of the generality of the idea that the intercalation into the clay layers can stabilize the included dye molecules.

2. Experimental

2.1 Materials

The hydrotalcite (denoted as HT) used in this study was supplied from Wako Chemical Co., whose chemical composition and anion exchange capacity (AEC) was $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ and 331 meq/100g-HT, respectively. Silica (SIO) was supplied from Japan Catalysis Society (JRC-SIO-6) and used as a host material of the reference sample. The annatto dye (ANA) and the β -carotene (BC) were both supplied from Wako Chemical and used as received. As the anionic surfactants, sodium dodecyl sulfate (SDS) supplied from Kishida Chem. Co. and sodium dodecylbenzene sulfonate (SDBS) from Tokyo Chemical Industry were employed.

The organo-modification of the HT was carried out by the reconstruction method using the so-called “memory effect”, where the once calcined HT restored the original HT structure when mixed with aqueous solutions, incorporating various anions dissolved in the solutions between the layers [37, 38]. First, 1 g of HT was calcined at 773 K for 2 h in the air. Then, 6.6 mmol (200% vs. AEC) of each anionic surfactant (SDS or SDBS) was dissolved in 100 cm³ of deionized water, and the calcined HT was mixed with the aqueous solution and stirred for 18 h. The mixture was filtered and the sediment was collected to be dried at 343 K for 3 h. Thus obtained organo-modified HT was

denoted as SDS/HT or SDBS/HT.

The composite sample of the dye with the organo-modified HT was prepared by immersing the host materials in the dye solution. The ethanolic solution (40 cm³) containing 20 mg of ANA or 10 mg of BC was mixed with 0.4 g of SDS/HT or SDBS/HT, stirred for 2 h and kept for 24 h in the dark. The amount of the dye dissolved in the solution was 5 wt% (ANA) or 2.5 wt% (BC) to the modified HT. After the adsorption step, the sediment was filtered and the collected solid sample was dried at 323 K under reduced pressure in the dark. The obtained composite sample was represented as ANA/SDS/HT, ANA/SDBS/HT, BC/SDS/HT or BC/SDBS/HT.

As the reference samples, the composites of ANA and BC with SIO were prepared. The SIO was mixed with the solution of ANA dissolved in ethanol or with the solution of BC dissolved in petroleum ether. The dye molecules were forced to be immobilized on the SIO surface by drying up the solvent under the air stream in the dark. The loading amount of the dye was adjusted to 5 wt% (ANA) or 1 wt% (BC). The light absorption of the ANA/SIO was about 20 % of those of the ANA/SDS/HT and ANA/SDBS/HT. This meant that the light absorption by the ANA/SIO was smaller than the ANA/SDS/HT and ANA/SDBS/HT so that the light fastness of the ANA/SIO could be overestimated. On the other hand, the absorption of the BC/SIO was adjusted to be almost the same as those of the BC/SDS/HT and BC/SDBS/HT.

2.2 Measurements

XRD patterns were measured with Rigaku MiniFlex X-ray diffractometer (CuK α , step angle and scan speed 0.05° and 2°/min, 15mA, 30 kV). Transmittance UV-Vis spectra were recorded with Shimadzu UV-1700 spectrophotometer. Diffuse reflectance UV-Vis spectra were collected with JASCO V-550 spectrophotometer with ISV-469 integrating sphere equipped to the spectrometer.

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 loaded in a plastic cell covered with a thin glass, and placed at the position of 1.1 cm from the aperture of the light guide. The light intensity was 190 klux at the sample position. The lamp emitted all the visible wavelength region, so that the colored samples were sufficiently irradiated of the absorbable light. The degree of the color fading was determined by the decrease in the main absorption peak of ANA or BC on the diffuse reflectance spectra of each composite material.

3. Results and discussion

3.1 Organo-modification of the hydrotalcite and incorporation of the dye

Figure 2 illustrates the XRD patterns of the unmodified and organo-modified HT. The d_{003} reflection of unmodified HT was observed at $2\theta = 11.4^\circ$. The basal spacing was given by the d_{003} reflection angle using the Bragg's law, and assuming that the thickness of the HT sheet was 0.48 nm [39], the interlayer distance of HT was calculated to be 0.30 nm. This value was in accordance with that of HT including carbonate ions between the layers.

After the modification with the surfactants, the d_{003} reflection was shifted toward lower angle of $2\theta = 3.2^\circ$ (SDS/HT) and 3.0° (SDBS/HT), indicating the expansion of the interlayer space. The interlayer distance of SDS/HT was calculated to be 2.28 nm. The value of the interlayer distance was close to that reported earlier [40, 41]. On the other hand, the interlayer distance of SDBS/HT was calculated to be 2.47 nm. The increase in the distance was due to the difference in the molecular length: SDBS has a benzene ring in addition to the dodecyl group.

The molecular length of SDS has been calculated to be 2.08 nm [41]. Considering this, the

interlayer distance of SDS/HT was a little large for the monolayer but small for the bilayer formation of SDS in the HT interlayer. Therefore, the alkyl chains of the SDS molecules may form tilted bilayer, or the alkyl chains may be almost perpendicular to the HT sheet and interdigitated each other [40, 42, 43]. The same discussion can be made on the case of SDBS/HT. From these results, we concluded that the alkyl chains of the intercalated surfactant may form tilted bilayer or interdigitated single layer between the HT layers.

The influence of the dye adsorption on the layered structure of HT was investigated. The change in the XRD patterns caused by the dye adsorption was shown in Figure 3. The d_{003} peaks were also observed after the dye adsorption, and the peak position was almost the same as that of SDS/HT or SDBS/HT. Therefore, the layered structures of the SDS/HT and SDBS/HT were maintained during the adsorption process of the dye. However, the peak intensity was obviously reduced, showing that the uniformity of the layered structure was partly lost by the adsorption of the dye. This result suggests that the intercalation of the dye molecules between the layers caused the disorder of the layered structure. In other words, the hydrophobic dye molecules were successfully intercalated in the interlayer space of the organo-modified HT.

3.2 UV-Vis spectra of the adsorbed annatto dye

The UV-Vis spectra of the ANA/SIO, ANA/SDS/HT and ANA/SDBS/HT were represented in Figure 4, together with that of the ethanolic solution of ANA. In the spectrum of the ANA solution, a main peak was observed at 455 nm, with two sub-peaks at 428 nm and 485 nm. The fine structure in the spectra implies that the ANA molecules are highly dispersed in the solution. The ANA/SIO sample lost such a fine structure of the spectrum and exhibited only one broad peaks at 428 nm, as shown in Figure 4 (a). The short wavelength shift of the absorption peak, as well as the

disappearance of the fine structure, suggests the formation of an aggregate of ANA on the SIO surface [30].

On the other hand, both the composite samples of ANA/SDS/HT and ANA/SDBS/HT maintained the fine structure in their spectra, and exhibited three distinguishable peaks at 442 nm, 472 nm and 504 nm, as shown in Figure 4 (c) and (d). The fine structure of the spectra suggests that the ANA molecules are not aggregated but still stay dispersed even when included in the interlayer of SDS/HT and SDBS/HT. The absorption peaks of ANA/SDS/HT and ANA/SDBS/HT appeared at longer wavelength than that of the ANA solution. We can interpret this result as the sign of the change in the orientation of the ANA molecule between the layers. The intercalated ANA molecules are forced to take more planar orientation in the narrow interlayer space than the free state. The planar molecular orientation brings about the expansion of the π -conjugation, which causes the longer wavelength shift of the absorption peak [44].

3.3 Stability improvement of the annatto dye under irradiation

The light endurance of ANA/SDS/HT and ANA/SDBS/HT under visible irradiation was compared with that of ANA/SIO. The result is shown in Figure 5. Evidently the light fastness of SDS/HT and SDBS/HT was superior to that of ANA/SIO. Considering that the ANA molecule on the ANA/SIO sample was simply adsorbed on the external surface of SIO, it can be concluded that the intercalation into the hydrophobic interlayer space of the organo-modified HT enhanced the stability of the intercalated dye. The photostability of ANA in ANA/SDBS/HT was a bit better than that of ANA/SDS/HT, however, the stability was almost at the same level.

On the other hand, the stability enhancement was more considerable in case of ANA/SDS/HT and ANA/SDBS/HT than in the previously reported composite of ANA and organo-modified

montmorillonite [30]: in the composite of ANA and the montmorillonite modified with C₁₂ surfactant, 45% of ANA had been lost during only 1 h irradiation. This may come from the difference in the manner of intercalation of the surfactant between the organo-modified HT and montmorillonite. From the value of the interlayer distance, the alkyl chain of the surfactant in the organo-modified montmorillonite has been supposed to be parallel to the clay sheet surface [30, 45], whereas those in the organo-modified HT was perpendicular to the sheet or formed tilted bilayer, as discussed in section 3.1. This can be rephrased that the density of the alkyl chain in the interlayer space of HT is higher than that of the montmorillonite. The intercalated ANA molecule in the SDS/HT and SDBS/HT might be sufficiently surrounded by the dense alkyl chains of the surfactant in the interlayer. As a result, the dye molecules were shielded against the contact with atmospheric oxygen, so that the color fading caused by the oxidation under irradiation was suppressed in the ANA/SDS/HT and ANA/SDBS/HT samples. Another possible reason is the difference in the polarity of the clay sheet. Contrary to the montmorillonite, the HT is anion-exchangeable and possesses positively charged clay sheet. Therefore, the anionic nature of ANA deriving from its carboxyl groups results in the favorable intercalation and tight fixation of the ANA molecule in the interlayer of HT. Although most of the positive charge in the HT sheet is compensated by the anionic surfactants, the electrostatic interaction between the HT sheet and the carboxyl group of ANA may also contribute to the stabilization of the dye. This means that the anion exchangeable clay is suitable for the intercalation of the anionic ANA, even though the effective adsorption of the dye cannot be achieved without modification of the interlayer space by surfactant due to the hydrophobic nature of the ANA molecule.

The vibrational deactivation of the dye molecule is another possible reason of the photostability enhancement than the protection from the atmospheric oxygen. It is thought that the photoexcited carotenoids can transfer the energy to the surrounding alkyl chains by the vibrational deactivation

due to the twisting motion about the polyene chains. Such an effect is also reported to be one possible reason for the photostabilization of the β -carotene intercalated into the organophilic interlayer space of dialkylammonium montmorillonite [29]. However, we could not fully evidence the reasons for the photostability enhancement in the scope of the present study. More detailed and quantitative investigation will clarify the contribution of the respective causes of stabilization.

3.4 UV-Vis spectra of the incorporated β -carotene

Figure 6 shows the UV-Vis spectra of BC/SIO, BC/SDS/HT and BC/SDBS/HT together with an ethanolic solution of BC. The BC solution gave a spectrum showing a fine structure with 5 peaks at 380, 404, 428, 452 and 479 nm. This means that the BC molecules were dispersed in the solution. The spectra of BC/SDS/HT, BC/SDBS/HT and BC/SIO exhibited a broad peak at around 440 nm, accompanied by a shoulder peak at 550 nm. As the carotenoids are reported to show a red-shifted absorption peaks by some types of aggregate formation [46, 47], the shoulder peak at 550 nm can be assigned to the aggregate of the BC molecule. Both the sign of the aggregation and the disappearance of the fine structure suggested the poor molecular dispersion in each composite samples of BC. The absorption peaks of BC/SDS/HT and BC/SIO appeared at 438 nm, whereas that of BC/SDBS/HT appeared at 454 nm. The slightly longer wavelength shift of the absorption peaks in the BC/SDBS/HT suggests the existence of a little interaction between the BC and SDBS molecules. This interaction is discussed later.

3.5 Stability improvement of the β -carotene under irradiation

The light fastness of the composite samples of BC was shown in Figure 7. Compared to BC/SIO, improved photostability was achieved in the BC/SDS/HT and BC/SDBS/HT samples.

However, the enhancement of the stability was not so drastic as the ANA composites. As described above, the UV-Vis spectra showed that the BC molecule was not dispersed well in the BC/SDS/HT and BC/SDBS/HT samples. This might imply that the BC molecules were not sufficiently intercalated in the interlayer space of the organo-modified HT, but were aggregated, for example, at the site near the edge of the organo-modified HT sheet. As BC is more hydrophobic than ANA, the hydrophobicity of the modified HT may not be enough for BC. Similar difficulty in the intercalation of BC into the clay layers have also been reported in the study of dialkylammonium-modified montmorillonite system [29].

Distinct superiority was found in the photostability of BC/SDBS/HT compared to that of BC/SDS/HT. The same tendency was also observed between ANA/SDS/HT and ANA/SDBS/HT, although the difference in the stability was not so obvious. As described above, the peak shift to the longer wavelength was observed in the spectrum of BC/SDBS/HT, suggesting some interactions between BC and SDBS. Considering these, there may be the π - π interaction between the phenyl group of SDBS and the π conjugation system of the carotenoid molecules, and the interaction may further contribute to the stabilization of the dye intercalated in the HT interlayer. Since the stabilization effect brought about by the intercalation itself was insufficient in the BC composites, the effect of the stability enhancement by the π - π interaction should be more distinctive than that on the ANA composites.

4. Summary

Lipophilic annatto and β -carotene was intercalated between the layers of the organo-modified hydrotalcite. The intercalated dye exhibited improved photostability under visible irradiation from the 100 W halogen lamp (190 klux at the sample position) in the air. The polarity of the clay sheet

had some influence on the incorporation and stabilization of the dye molecule: the dye with an anionic nature favored an anion exchangeable clay, even though the interlayer space was modified with surfactants. As for the β -carotene, the hydrophobicity of the organo-modified hydrotalcite was not enough for the sufficient intercalation in the interlayer. Stability improvement of the β -carotene may require the construction of more hydrophobic environment between the layers, as well as the advances in the method to incorporate the dye.

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References

- [1] H.-R. Sliwka, V. Partali, S.F. Lockwood, in: J.T. Landrum (Ed.), *Carotenoids: Physical, Chemical and Biological Functions and Properties*, CRC Press, 2009, pp. 31-58.
- [2] F. Khachik, *Pure Appl. Chem.* 78 (2006) 1551-1557.
- [3] C. Ulbricht, R.C. Windsor, A. Brigham, J.K. Bryan, J. Conquer, D. Costa, N. Giese, J. Guilford, E.R.B. Higdon, K. Holmes, R. Isaac, S. Jingst, J. Kats, L. Peery, E. Rusie, A. Savinainen, T. Schoen, T. Stock, S. Tanguay-Colucci, W. Weissner, *J. Diet. Suppl.* 9 (2012) 57-77.
- [4] D. Frick, *Rev. Prog. Color. Relat. Top.* 33 (2003) 15-32.
- [5] A. Mortensen, *Pure Appl. Chem.* 78 (2006) 1477-1491.
- [6] J. Paust, *Pure Appl. Chem.* 63 (1991) 45-58.
- [7] S. Zarringhalami, M.A. Sahari, Z. Hamidi-Esfehani, *Meat Sci.* 81 (2009) 281-284.
- [8] E.J. Kang, R.E. Campbell, E. Bastian, M.A. Drake, *J. Dairy Sci.* 93 (2010) 3891-3901.
- [9] J.E.M. Ferreira, D.B. Rodriguez-Amaya, *J. Food Sci.* 73 (2008) C589-C594.
- [10] S.V. Najar, F.O. Bobbio, P.A. Bobbio, *Food Chem.* 29 (1988) 283-289.

- [11] P.G. Prabhakara Rao, T. Jyothirmayi, K. Balaswamy, A. Satyanarayana, D.G. Rao, LWT - Food Sci. Technol. 38 (2005) 779-784.
- [12] K. Yanagi, Y. Miyata, H. Kataura, Adv. Mater. 18 (2006) 437-441.
- [13] L. Cao-Hoang, R. Fougere, Y. Waché, Food Chem. 124 (2011) 42-49.
- [14] L. Szente, K. Mikuni, H. Hashimoto, J. Szejtli, J. Inclusion Phenom. Mol. Recognit. Chem. 32 (1998) 81-89.
- [15] H. Van Olphen, Science. 154 (1966) 645-646.
- [16] E. Fois, A. Gamba, A. Tilocca, Microporous Mesoporous Mater. 57 (2003) 263-272.
- [17] J. Bujdak, N. Iyi, T. Fujita, Colloids Surf. A. 207 (2002) 207-214.
- [18] M. Sumitani, S. Takagi, Y. Tanamura, H. Inoue, Anal. Sci. 20 (2004) 1153-1157.
- [19] L. Latterini, M. Nocchetti, G.G. Aloisi, U. Costantino, F. Elisei, Inorg. Chim. Acta. 360 (2007) 728-740.
- [20] C. Chakraborty, K. Dana, S. Malik, J. Phys. Chem. C. 115 (2011) 1996-2004.
- [21] M. Ogawa, M. Sohmiya, Y. Watase, Chem. Commun. 47 (2011) 8602-8604.
- [22] A.A. Teixeira-Neto, C.M.S. Izumi, M.L.A. Temperini, A.M.D. Ferreira, V.R.L. Constantino, Eur. J. Inorg. Chem. (2012) 5411-5420.
- [23] M. Samuels, O. Mor, G. Rytwo, J. Photochem. Photobiol. B. 121 (2013) 23-26.
- [24] Y.-H. Lin, Y. Hori, S. Hoshino, C. Miyazawa, Y. Kohno, M. Shibata, Dyes Pigm. 100 (2014) 97-103.
- [25] Y. Kohno, R. Kinoshita, S. Ikoma, K. Yoda, M. Shibata, R. Matsushima, Y. Tomita, Y. Maeda, K. Kobayashi, Appl. Clay Sci. 42 (2009) 519-523.
- [26] Y. Kohno, K. Totsuka, S. Ikoma, K. Yoda, M. Shibata, R. Matsushima, Y. Tomita, Y. Maeda, K. Kobayashi, J. Colloid Interface Sci. 337 (2009) 117-121.
- [27] M. Ogawa, K. Kuroda, Bull. Chem. Soc. Jpn. 70 (1997) 2593-2618.
- [28] L.B. de Paiva, A.R. Morales, F.R. Valenzuela Díaz, Appl. Clay Sci. 42 (2008) 8-24.
- [29] N. Kakegawa, M. Ogawa, Appl. Clay Sci. 22 (2002) 137-144.
- [30] Y. Kohno, M. Inagawa, S. Ikoma, M. Shibata, R. Matsushima, C. Fukuhara, Y. Tomita, Y. Maeda, K. Kobayashi, Appl. Clay Sci. 54 (2011) 202-205.
- [31] L. Perioli, V. Ambroggi, C. Rossi, L. Latterini, M. Nocchetti, U. Costantino, J. Phys. Chem. Solids. 67 (2006) 1079-1083.
- [32] V. Ambroggi, L. Perioli, M. Nocchetti, L. Latterini, C. Pagano, E. Massetti, C. Rossi, J. Phys. Chem. Solids. 73 (2012) 94-98.
- [33] U. Costantino, N. Coletti, M. Nocchetti, G.G. Aloisi, F. Elisei, Langmuir. 15 (1999) 4454-4460.
- [34] J. Bauer, P. Behrens, M. Speckbacher, H. Langhals, Adv. Funct. Mater. 13 (2003) 241-248.
- [35] G. Bascialla, A.E. Regazzoni, Colloids Surf. A. 328 (2008) 34-39.

- [36] N. Drici Setti, N. Jouini, Z. Derriche, *J. Phys. Chem. Solids*. 71 (2010) 556-559.
- [37] S. Miyata, *Clays Clay Miner.* 28 (1980) 50-56.
- [38] T. Sato, K. Kato, T. Endo, M. Shimada, *React. Solids*. 2 (1986) 253-260.
- [39] K. Takehira, T. Shishido, *Catal. Surv. Asia*. 11 (2007) 1-30.
- [40] E.L. Crepaldi, P.C. Pavan, J. Tronto, J.o.B. Valim, *J. Colloid Interface Sci.* 248 (2002) 429-442.
- [41] A. Clearfield, M. Kieke, J. Kwan, J.L. Colon, R.C. Wang, *J. Incl. Phenom. Mol. Recognit. Chem.* 11 (1991) 361-378.
- [42] H. He, R.L. Frost, T. Bostrom, P. Yuan, L. Duong, D. Yang, Y. Xi, J.T. Klopprogge, *Appl. Clay Sci.* 31 (2006) 262-271.
- [43] K. Yao, Y. Imai, L. Shi, A. Dong, Y. Adachi, K. Nishikubo, E. Abe, H. Tateyama, *J. Colloid Interface Sci.* 285 (2005) 259-266.
- [44] A.J. Meléndez-Martínez, G. Britton, I.M. Vicario, F.J. Heredia, *Food Chem.* 101 (2007) 1145-1150.
- [45] M. Ogawa, H. Shirai, K. Kuroda, C. Kato, *Clays Clay Miner.* 40 (1992) 485-490.
- [46] H. Auweter, H. Haberkorn, W. Heckmann, D. Horn, E. Lüddecke, J. Rieger, H. Weiss, *Angew. Chem. Int. Ed.* 38 (1999) 2188-2191.
- [47] S. Köhn, H. Kolbe, M. Korger, C. Köpsel, B. Mayer, H. Auweter, E. Lüddecke, H. Bettermann, H.-D. Martin, in: G. Britton, S. Liaaen-Jensen, H. Pfander (Eds.), *Carotenoids*, Birkhäuser Basel, 2008, pp. 53-98.

Figure captions

Figure 1. Molecular structures of (a) norbixin, the main component of the annatto dye, and (b) β -carotene.

Figure 2. XRD patterns of (a) HT, (b) SDS/HT and (c) SDBS/HT.

Figure 3. XRD patterns of the composites of ANA and BC with organo-modified HT. In panel [A], curve (a) represents the spectrum of SDS/HT, (b) ANA/SDS/HT, (c) BC/SDS/HT, and in panel [B] (a) SDBS/HT, (b) ANA/SDBS/HT and (c) BC/SDBS/HT.

Figure 4. Diffuse-reflectance UV-Vis spectra of (a) ANA/SIO, (b) ANA/SDS/HT and (c) ANA/SDBS/HT. The dotted curve indicates the UV-Vis spectrum of the ethanolic solution of ANA.

Figure 5. Changes in the absorption of the composite samples of ANA under visible light

irradiation. Close and open circles indicate those of ANA/SDS/HT and ANA/SDBS/HT, respectively, whereas squares show those of ANA/SIO. The change in the absorption is related to the initial value before irradiation.

Figure 6. Diffuse-reflectance UV-Vis spectra of (a) BC/SIO, (b) BC/SDS/HT and (c) BC/SDBS/HT. The dotted curve indicates the UV-Vis spectrum of the ethanolic solution of BC.

Figure 7. Changes in the absorption of the composite samples of ANA under visible light irradiation. Close and open circles indicate those of BC/SDS/HT and BC/SDBS/HT, respectively, whereas squares show those of BC/SIO. The change in the absorption is related to the initial value before irradiation.

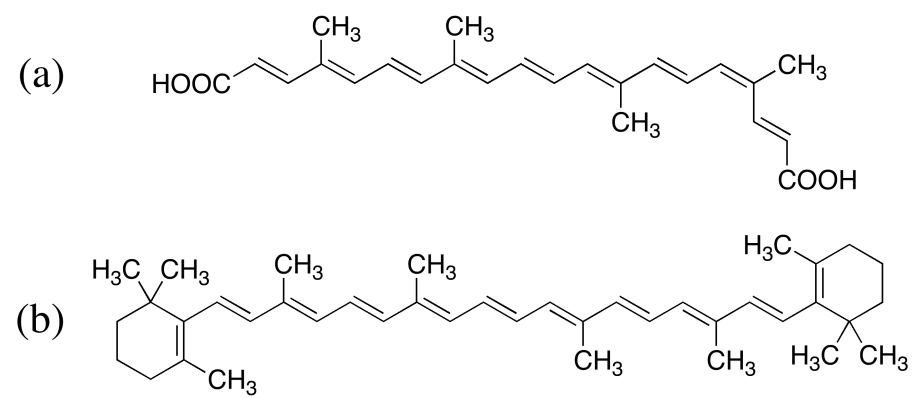


Figure 1

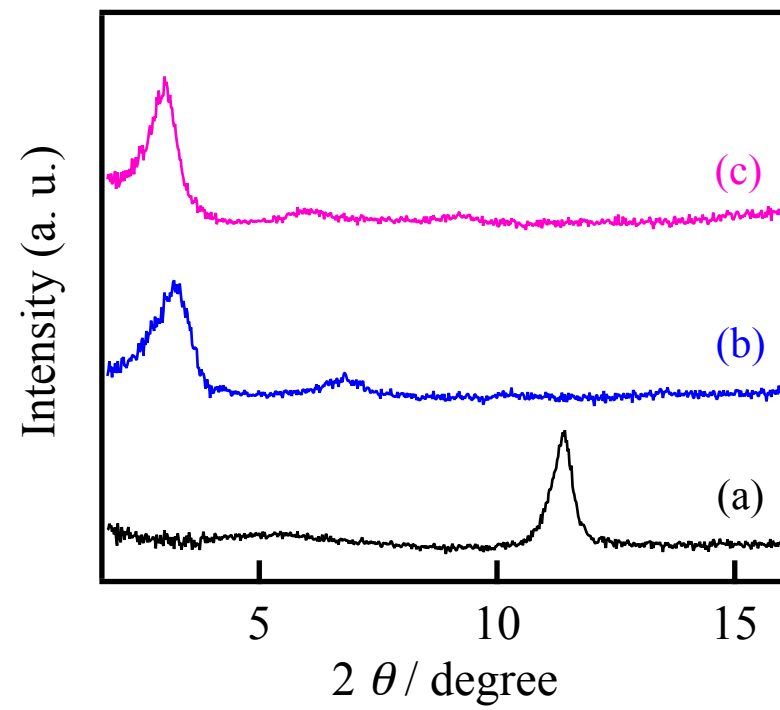


Figure 2 (color version)

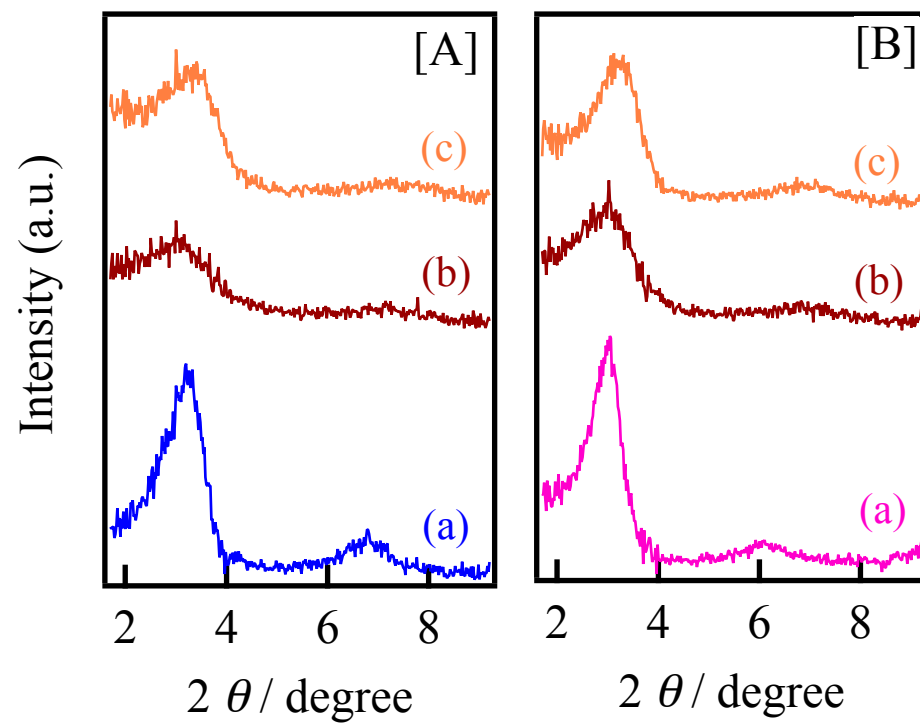


Figure 3 (color version)

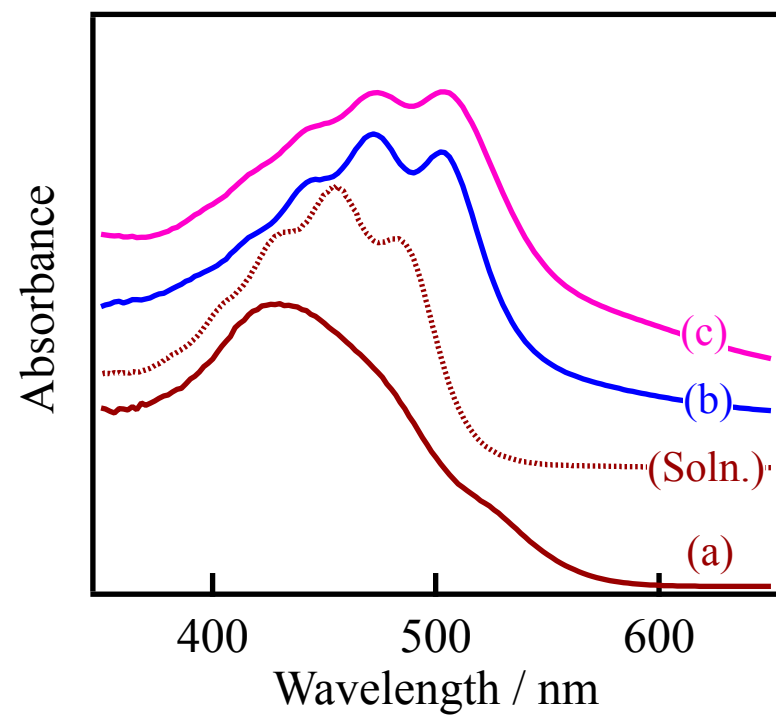


Figure 4 (color version)

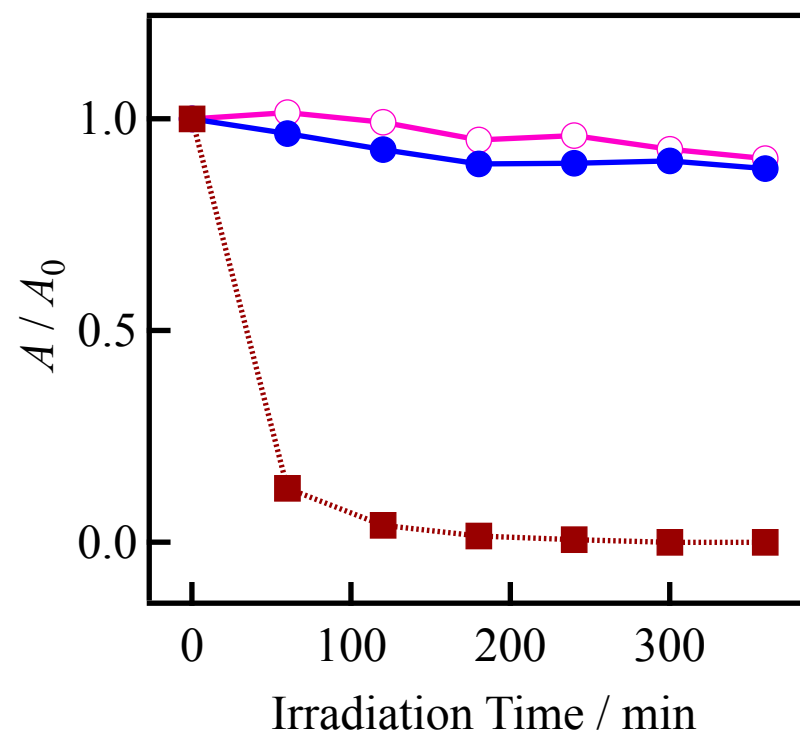


Figure 5 (color version)

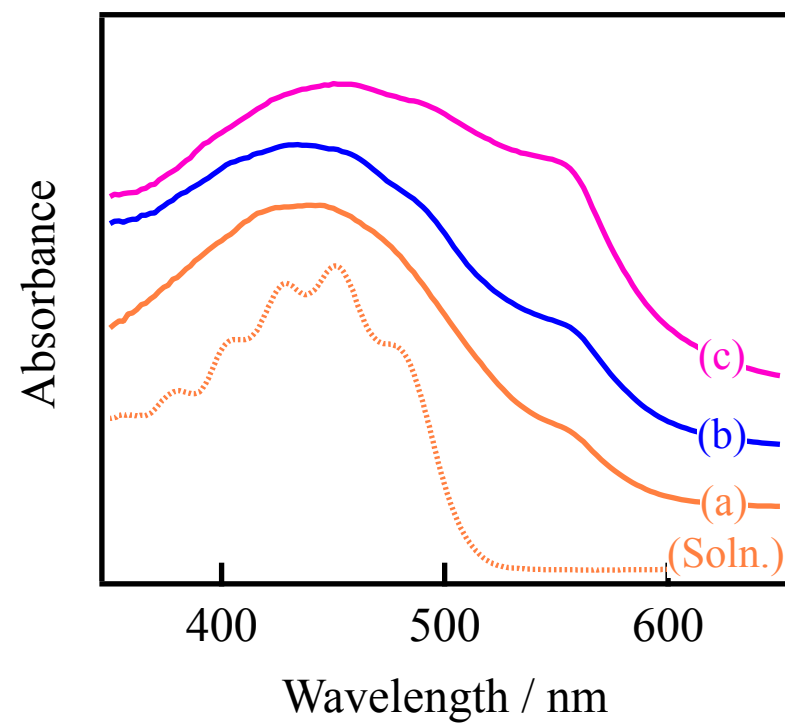


Figure 6 (color version)

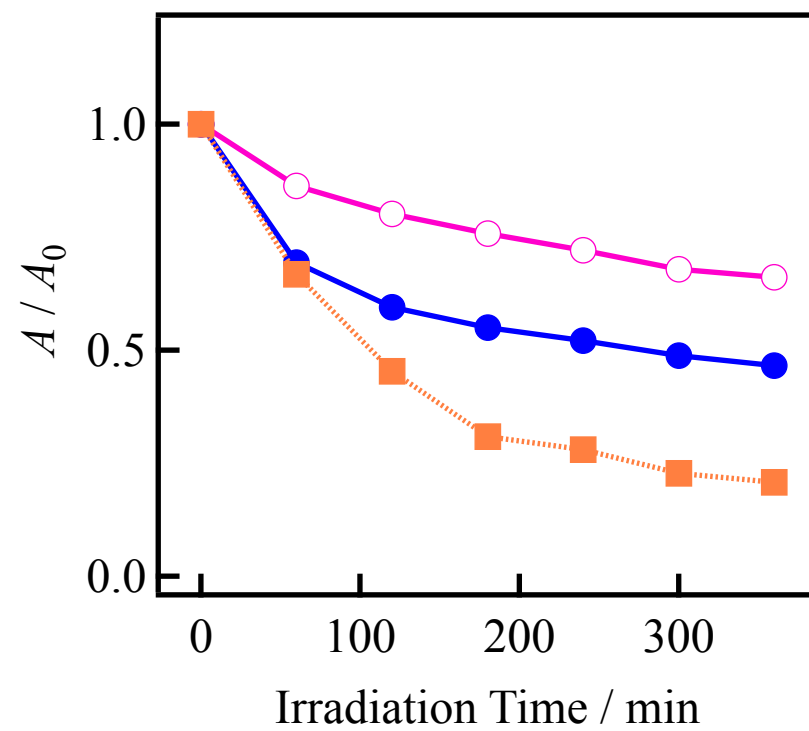


Figure 7 (color version)