



Fixation and stability enhancement of beta-carotene by organo-modified mesoporous silica



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ABSTRACT

β -carotene is one of naturally occurring dyes, and has been used as a colorant because of its nontoxicity and biological functions. However, the color stability of the β -carotene is not sufficient. The aim of this study is to enhance the stability of the β -carotene by incorporation into the pore of mesoporous silica. Although the highly lipophilic β -carotene does not generally meet rather hydrophilic inner pore space of mesoporous silica, the modification of the inner pore by alkyl chains enables the incorporation of the β -carotene into the mesopore. The incorporated β -carotene is successfully stabilized against visible light irradiation. Also improved is the durability of the dye in the composite sample against elution to the solvent. The effect of the complexation on the stability enhancement depends on the affinity of the lipophilic β -carotene to the organo-modified inner pore space.

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1. Introduction

Carotenoids are one of the groups of naturally occurring dyes. They are found in many vegetables and fruits, and very common to the human life. Among them, the carotenoids that are made only of carbon and hydrogen are called carotenes. β -carotene is a typical compound belonging to carotenes, and is known as a precursor of vitamin A [1].

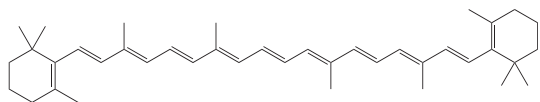
The most characteristic structure of the β -carotene is its highly conjugated double bonds with a center of symmetry (Scheme 1). Due to this hydrocarbonaceous structure, the β -carotene has a very high hydrophobic nature and an affinity to the hydrocarbon tails of surfactants [2]. The highly conjugated polyene structure is also responsible for the yellow to orange color of the β -carotene deriving from the light absorption of visible region. In addition, the β -carotene is known to show some important biological functions such as antioxidant properties and inhibition of cancer [3–5]. Because of its nontoxicity, as well as its color and biological functions, the β -carotene has been widely used as a food colorant [1].

However, the conjugated π -bonding is generally reactive and not so resistant to the oxidation. Like other compounds with the highly conjugated double bonds, the β -carotene easily loses its color by oxidative degradation in the air, especially under illumination [6,7]. Therefore, the improvement of the color stability is a requisite step for the extensive use of the β -carotene as a general colorant [8].

The composite of various dye molecules and inorganic host materials is one of the promising technique to acquire the improved stability, and various inorganic materials, such as clay, zeolite and mesoporous silica, have been found to be effective for this purpose [9–15]. Among those inorganic host materials, silica-based one possesses non-acidic or non-basic nature and can be adopted for more general usage. In addition, the mesoporous structure provides the large surface area including inner pore space, which may result in a more dye adsorption and a vivid color. We have reported that the natural anthocyanin [16–18] or its model compounds, flavylium [19,20], can be stabilized by the incorporation into the pore of mesoporous silica. Although the dyes with a hydrophobic nature is not suitable for the adsorption to the surface of the mesoporous silica or clays [21], it has been reported that the modification of the clay interlayer spaces with the alkyl chains of surfactants (organo-modified clays) enables the

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Scheme 1. Chemical structure of β -carotene.

adsorption and stabilization of the hydrophobic natural dyes [10,22–24]. The hydrophobic environment can also be achieved in the pore of the mesoporous silica by the modification of the side-wall inside the mesopore with the alkyl chains [17]. Since several research groups reported the stability enhancement of the β -carotene using hydrophobic host materials such as carbon nanotubes [25] or organo-modified clays [22], the stabilization of the β -carotene can be expected through the incorporation into the organo-modified mesoporous silica.

Here, we report the possibility to improve the stability of the β -carotene using the mesoporous silica as an inorganic host material. As the mesoporous silica samples, we used the MCM-41 and HMS type ones, which possessed the straight and wormhole-like mesopore, respectively [26,27]. In order to give the hydrophobic nature to the mesopore space, the inner surface of the mesoporous silica was modified with the alkyl chains using alcohols (organo-modification). The shape of the mesopore and the length of the alkyl chains may have some effects on the light fastness of the dye and its resistance to the elution. Since the β -carotene is highly lipophilic, nonaqueous solvents are usually required to dissolve and disperse the β -carotene molecules before adsorption onto the inorganic hosts. However, from the environmental point of view, the use of organic solvents is not favorable. Therefore, in this study we employed a simple method to obtain the composite materials: mixing both the β -carotene and the mesoporous silica in a solid state. This physically mixing technique is superior to the adsorption from the dye solution, because the mixing of the powdery crude materials is an easy operation as a dry process. The light fastness and the resistance to the elution of the obtained composite samples were investigated.

2. Experimental

2.1. Sample preparation

The HMS type mesoporous silica was prepared in the manner described in the literature [20]. Dodecylamine (Wako Chemical Co., 0.91 g) was dissolved in 5 cm³ of ethanol and mixed with 45 cm³ of water. Tetraethoxysilane (TEOS, Wako Chemical Co., 4.60 g) was dropped to the solution slowly, and the mixture was kept at 333 K for 22 h. The resulting sediment was collected by filtration and calcined at 903 K for 6 h under dry air stream. After grinding in mortar, the powdered HMS sample was obtained.

The MCM-41 type mesoporous silica was prepared by the conventional method described elsewhere [16]. Briefly, hexadecyltrimethylammonium chloride (HDTMA, Tokyo Chemical Co.) was used as a structure-directing agent. The aqueous solution of the HDTMA (2.66 g/44.29 cm³ H₂O) was mixed both with the aqueous NaOH solution (0.58 g/6.3 cm³) and with TEOS (10.29 g) under vigorous stirring. The mixture was then subjected to the hydrothermal synthesis at 413 K for 48 h. The resulting sediment was filtered and calcined at 873 K for 6 h under dry air stream. After grinding in mortar, the powdered MCM-41 sample was obtained.

The organo-modification of the inner pore of the mesoporous silica was carried out using 1-butanol and 1-octanol as a modifying reagent. According to the literature, the fixation of the alkoxy groups is expected through the condensation between the alcohol and the surface hydroxyl groups located on the silica surface

[28,29]. Prior to the experiment, the HMS or MCM-41 (1 g) was dried at 393 K for 24 h in the air. The dried mesoporous silica sample was mixed with 40 cm³ of the 1-butanol or 1-octanol (Wako Chemical Co.), which was previously dehydrated by the dried Molecular Sieves 3A. The mixture was refluxed (~423 K) under nitrogen atmosphere for 6 h, followed by filtration. The resulting sediment was washed with 50 cm³ of acetone for 1 h, and finally dried at 353 K under reduced pressure, and the organo-modified HMS or MCM-41 was obtained. In the following, the HMS and MCM-41 modified with 1-butanol are denoted as C4-HMS and C4-MCM-41, respectively. Similarly, the samples modified with 1-octanol are denoted as C8-HMS and C8-MCM-41, respectively.

As reference samples, non-mesoporous conventional silica (JRC-SIO-6, supplied from the Catalysis Society of Japan) was employed (SIO). The organo-modified C4-SIO and C8-SIO were prepared using SIO by the same procedure as the mesoporous silica described above.

The composite samples between the β -carotene (supplied from Wako Chemical Co., denoted as BC) and various inorganic host materials were prepared by mixing the two powdery components physically. Prior to the preparation of the composites, the inorganic hosts were dried at 393 K in an oven in the air for 24 h. The BC (1.5 mg) was mixed with 200 mg of each host materials (HMS, MCM-41, SIO and respective organo-modified ones) in a mortar with a pestle for 10 min in the air. Then, the colored composite samples (BC/HMS, BC/C4-HMS, BC/C8-HMS, BC/MCM-41 and so forth) were obtained.

2.2. Measurements

XRD patterns were recorded using Rigaku MiniFlex X-ray diffractometer (CuK α , step angle and scan speed 0.05° and 2°/min, 15 mA, 30 kV).

Nitrogen adsorption experiments were carried out with Shimadzu TriStar 3000 apparatus. The specific surface area and pore volume/size distribution of each mesoporous samples were evaluated by the BET and BJH methods, respectively.

FTIR spectra of the organo-modified mesoporous silica were collected in the transmission mode with JASCO FT/IR 550 Fourier transformed infrared spectrometer. Each mesoporous silica sample weighed 6 mg was mixed with 300 mg of KBr (Kishida Chemical Co.), and the mixture was pressed to form a self-supporting disk ($\phi = 1$ cm) at a pressure of 10 MPa for 1 min.

Diffuse reflectance UV–Vis spectra were collected using JASCO V-550 spectrophotometer with ISV-469 integrating sphere. On measuring spectra, the powdery samples were loaded in a plastic cell covered with a thin glass. Transmission spectrum of the BC hexane solution was collected with Shimadzu UV-1700 spectrophotometer.

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 powdery 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 54 klux. The degree of the color fading was determined by the decrease in the main absorption peak of the BC on the diffuse reflectance spectra of each composite material.

To examine the durability of the composite samples against elution to the solvent, 100 mg of each composite sample was dispersed in 25 cm³ of ethanol and stirred for 30 min. Then the sample was filtered and the sediment was dried at 313 K under reduced pressure. The durability against elution was evaluated by

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