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A Simple Method to Make Composites of Hydrophobic Plant-Derived Dye with Organo-Modified Hydrotalcite

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Abstract

The stability of naturally occurring dyes can be improved by incorporation into various inorganic host materials. In this study, we try to insert hydrophobic plant-derived dye between the layers of hydrotalcite. Prior to the complexation with the hydrophobic dye, the hydrotalcite is modified with anionic surfactant to make the interlayer space more hydrophobic. By simply mixing the powdery dye and the organo-modified hydrotalcite, the dye molecules can be incorporated into the interlayer of the hydrotalcite by a hydrophobic interaction. The intercalated dye shows an improved stability against visible light irradiation. On the other hand, rather hydrophilic dye shows less effect on the stability improvement by the complexation, although it has a similar molecular skeleton as the hydrophobic dye.

Key-words*: Naturally occurring dye, Hydrotalcite, Intercalation, Organo-modification, Stability enhancement*

1. Introduction

Many naturally occurring dyes used in our daily life are derived from plants. Because those plant-derived dyes are generally safe and non-toxic, they are widely used as a colorant of foods and cosmetics. However, while the safety is superior, the stability of most plant dyes is low, so that the wider use of the natural dyes is limited.

The stability of the dye can be improved by making composites with various inorganic host materials[1-3]. In particular, the incorporation into the interlayer space of the clay is one promising method to improve the stability of the dye, and has been extensively studied so far[4-8]. The clay has a layered structure, and exchangeable ions exist between the layers to compensate the permanent electric charge of the clay sheet. The net charge of the clay sheet also causes an electrostatic field in the interlayer, which is the reason why the interlayer space of the clays is compatible with an ionic or a hydrophilic dye molecule. On the other hand, if the interlayer space is organically modified with proper surfactants by ion exchange, a hydrophobic molecule can also be inserted between the clay layers[9-12]. We have also reported the preparation of composites between several hydrophobic dyes and corresponding organo-modified clays by adsorption from the dye solution using organic solvents[13-15]. Several investigations[16,17] as well as ours[13,14] have shown that hydrophobic organic molecules exhibit enhanced stability when inserted between the organo-modified interlayers.

However, from the viewpoint of environmental concerns the use of organic solvents is not favorable. In addition, the use of solvents requires separation and drying, both of which are energy-consuming processes. Therefore, we focused on the possibility that the hydrophobic natural dye can be intercalated in the organo-modified clays by hydrophobic interaction in a solid phase.

In this study, hydrotalcite was used as a host material for the intercalation. The hydrotalcite is one of the so-called layered double hydroxides (LDH) which can also be found as a mineral in nature. It has a positively charged layered structure made of the mixed hydroxide of aluminum and magnesium, and exchangeable anions exist between the layers. The interlayer space of the hydrotalcite can be modified to be hydrophobic by anion exchange with proper anionic surfactant. The organo-modified hydrotalcite has an ability to load hydrophobic organic molecules including dyes[10,14]. In other words, hydrophobic interaction between the organo-modified hydrotalcite and several hydrophobic dyes can be expected.

The plant-derived dyes used in this study were curcumin, β-carotene and crocin. Their structures are shown in **Fig. 1**. Curcumin is a hydrophobic natural dye which derives from *Curcuma longa*, and commonly used as a food colorant. β-carotene is the most familiar carotenoid dye and is found in many vegetables and fruits, whose character is highly lipophilic as expected from its molecular structure. Crocin