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Preparation of Composite Comprising Anthocyanidin Dye and HMS-Type Mesoporous Silica and its Color Properties

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Abstract

A method for preparation of a composite comprising an anthocyanidin (aglycone of anthocyanin) dye and HMS-type mesoporous silica under neutral conditions was developed and the colorant properties of the composite as a red pigment were investigated.

HMS containing a small amount of Al in the synthesis step (Al-HMS) effectively adsorbed anthocyanidin dye to generate a red composite. However, the color of the composite shifted from red to purple as the Al content of Al-HMS increased. This phenomenon was not observed for the composite comprising Al and MCM-41-type mesoporous silica (Al-MCM-41) synthesized under strongly basic conditions. Washing with dilute $NaOH_{(aq)}$ was effective for resolving this issue. Superficial Al species external to the silica framework were removed, and the resulting composite exhibited a vivid red color, even when the Al concentration was high.

Minimal elution of the dye from the Al-HMS composite was observed in water and the composite exhibited higher photo-stability than the Al-MCM-41 composite.

Key-words: *Anthocyanidin, Mesoporous silica, HMS, Light Fastness, Liquid Dissolution*

1. Introduction

Anthocyanins are natural colorants that exhibit several different colors in plants[1]. Anthocyanins are non-toxic and are used as natural colorants in food. However, because of their poor stability in basic solution, under irradiation, and at high temperature[2,3], the application of anthocyanins as natural red pigments for cosmetics and jet printing ink is limited.

These stability problems become more pronounced when anthocyanins are dissolved in water. Hence, our research has focused on the application of aglycones of anthocyanin (anthocyanidins) that are insoluble in water as colorants.

Because anthocyanidins are less stable than anthocyanins, they are preferably utilized as composites with inorganic host materials for practical purposes. These host materials include montmorillonite[4], hydrotalcite[5], clays[6], and mesoporous silica[7-11], which are reported to enhance the stability of natural dyes. Among these host materials, mesoporous silica is favored as it is readily dispersed in water as well as non-aqueous solvents.

In a previous paper, we reported the development of a composite comprising an anthocyanidin and Al-containing MCM-41 type mesoporous silica (Al-MCM-41)[9]. As a cationic dye, the anthocyanidin was adsorbed on the cationic exchange site of Al-MCM-41 formed by Al, and the resulting red composite showed high stability against visible irradiation compared to the non-treated dye. Moreover, elution of the anthocyanidin from the composite into either water or ethanol was limited, demonstrating the high elution resistance.

MCM-41 is one of the most popular materials among various types of mesoporous silica. However, MCM-41 is synthesized under strongly basic conditions and requires a large amount of deionized water for rinsing in order to bring the pH of the supernatant to neutral, given that the color of anthocyanidins or anthocyanins easily fades under basic conditions. This is one of the most serious drawbacks of MCM-41 for practical use as a dye host material. On the other hand, HMS-type mesoporous silica can be synthesized under neutral conditions and Al-containing HMS (Al-HMS) also possess a cationic exchange site on which the cationic dye can be adsorbed[8].

The aim of this study is to develop a vivid red composite comprising anthocyanidin extracted from grape skins and Al-HMS by synthesis under neutral conditions. In this study, we investigate the synthesis and post-synthesis treatment of Al-HMS and estimate the color properties, photo-stability, and elution resistance of the obtained composites.