Preparation of magnetic MOF particles using holmium as a metal species

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Abstract

Holmium (Ho) is one of the lanthanides with the high magnetic moment. Ho-MOF particles were prepared using isophthalic acid as an organic linker and Ho as a metal species. The obtained Ho-MOFs were spherical or petal-like and showed high magnetic properties. In addition, Ho-MOF particles dispersed in water were easily magnetically separated and recovered after adsorption of dye.

1. Introduction

In the past few decades, metal-organic framework (MOF) has received much attention due to their high porosity and large surface area[1)]. As a precise porous material, functions such as gas storage and separation can be realized. One of the important uses of MOF materials is in magnetic applications. Magnetic MOF materials have been reported in which iron oxide (Fe_3O_4) magnetic nanoparticles, which are typical magnetic particles, were used as cores and their surfaces were coated with various MOF[2)].

Lanthanide elements originate from 4f orbitals shielded by 5d orbitals and exhibit various luminescence and magnetic behavior. We have reported the preparation of magnetic colloidal materials in which holmium (Ho) was supported on a polymeric scaffold[3, 4)]. Almost all metal ions in the periodic table can be used to compose MOFs, and research on MOFs using lanthanides, an f-block element, as a metal species has been also advanced.[5)]. Recently, spherical MOF particles have also been developed. Developing magnetic colloidal MOF particles with controlled shapes and particle sizes is an attractive issue for practical use.

Herein, we demonstrated the preparation of magnetic colloidal particles based on a MOF using Ho as a metal, namely Ho-MOF particles (**Fig. 1**). By systematically controlling the synthetic conditions of Ho-MOF particles, we investigated the conditions related to particle size and morphology, especially the effects of reaction temperature and reaction time. We also investigated the adsorption of dyes on Ho-MOF particles and their collection by magnetic field.

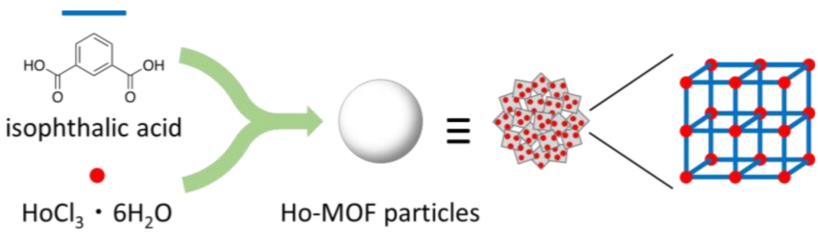

Fig. 1 Schematic illustration of the preparation of Ho-MOF particles.

2. Experiment

Ho-MOF particles were prepared by heating a mixture of isophthalic acid and $HoCl_3 \cdot 6H_2O$ at an arbitrary time and temperature. Dye adsorption tests were carried out by dispersing the prepared Ho-MOF particles in dye solution. The morphology of the particles was measured by SEM observation, the amount of dye adsorption was measured by UV-VIS spectrum.

3. Results and discussion

SEM images of Ho-MOFs prepared under various conditions are shown in **Fig. 2**. Ho-MOF particles were obtained in approximately 30-50% yield under 8 conditions (filled in green) of high temperature and short time, and further reaction gave Ho-MOF in the form of petal-shape (filled in yellow). Subsequent experiments were carried out using the particles prepared under the condition at 180°C for 2 h where relatively monodisperse Ho-MOF particles were obtained.

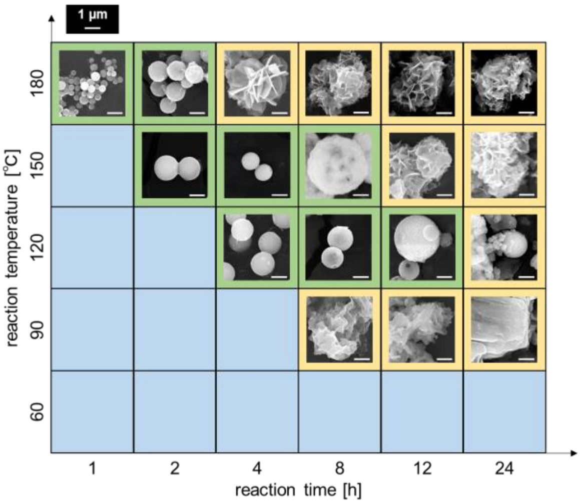

Fig. 2 SEM images of Ho-MOFs prepared under various conditions.

The magnetic response of the prepared Ho-MOF particles was investigated. When a neodymium magnet (0.5 T) was brought closer to powder sample of Ho-MOF particles, the sample was shown to be attracted and respond to the bulk magnet (**Fig. 3a**). The placement of the magnet on the side of a glass tube, which contained the aqueous dispersion of Ho-MOF particles, gradually attracted the particles to the magnet, and almost all particles were attracted after 30 min (**Fig. 3b**). We also investigated the dye adsorption capacity of Ho-MOF particles. When the adsorption of methylene blue (MB) and direct red 80 (DR80) was evaluated, the adsorption equilibrium was reached in 10 min for both samples. Since the adsorption of dyes did not affect the magnetic response behavior (**Figs. 3c** and **3d**), we succeeded in producing MOF particles that have both adsorption and magnetic properties.

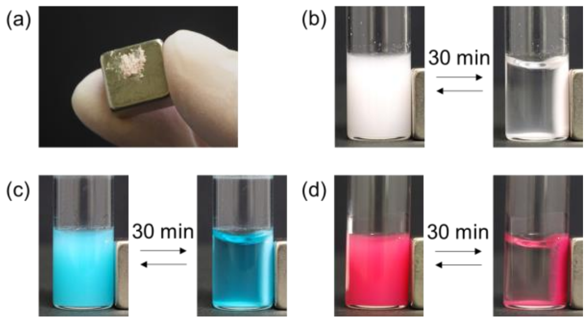

Fig. 3 Photograph of the magnetic response behavior of (a) Ho-MOF particle powders and (b) aqueous dispersion of Ho-MOF particles (0.5 wt%). Magnetic response behavior of the aqueous dispersion of Ho-MOF particles adsorbed by (c) MB and (d) DR80.

4. Conclusions (or Summary)

In conclusion, we succeeded in the preparation of magnetic colloidal particles based on Ho-MOF. When the reaction was carried out at 180°C for 2 h, spherical and relatively monodispersed Ho-MOF particles were obtained. Obtained Ho-MOF particles were well dispersed in water and exhibited excellent responsiveness to the magnet. Additionally, the Ho-MOF particles were able to adsorb the dye in the solution and collect it with a magnet. Ho-MOF based colloidal particles that have both magnetic responsiveness and adsorption properties will allow the development of new classes of functional materials.

References

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