High Efficiency Near-IR Emission of Nd(III) Based on Low-Vibrational Environment in Cages of Nanosized Zeolites

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Developing a strongly luminescent Nd(III) center in organic media has been an attractive target because of its applicability to organic liquid lasers, optical-fiber polymers, organic electroluminescent devices, and near-IR immunoassays. Strong luminescence of Nd(III) in organic media should be achieved by systems that exclude chemical bonds having low vibration quanta, for example, C-H and O-H, and by separating the distance between the emitting centers for suppression of concentration quenching. On the other hand, a series of zeolites should be one of the most suitable host materials for the efficient near-IR emission of rare earth cations, because their wall consists of Si-O-Al and Si-O-Si framework with low vibration quanta and their pores can be used for separately locating the cations. Here we have succeeded in drastically enhancing the near-IR emission of Nd(III) by ligating it with bis(perfluoromethylsulfonyl)-aminate (PMS) cages of a nanocrystalline, large-pore zeolite (faujasite type, see Figure 1). The nanosized zeolite powder containing the Nd(III)-ligand is stably dispersed in dimethylsulfoxide-d_6 (DMSO-d_6), constituting a transparent dispersion, by which we have achieved the highest quantum efficiency in its emission in organic media.

Synthesis of nanosized faujasite (nano-FAU) was carried out according to a recipe reported in the literature.[1] By the XRD pattern, the formation of FAU zeolite was confirmed. FE-SEM showed the fine structure of the zeolite and that the particle sizes of the crystallites were 50-80 nm. Nd(III) exchanged nano-FAU (Nd-nano-FAU) was prepared by placing the zeolites in $NdCl_3 \cdot 6H_20$ aqueous solution. The ligand PMS was incorporated into the cage from gas phase. Figure 2 shows the emission spectra of Nd(III) exchanged nano-FAU treated with PMS as a powder excited at 585 nm under vacuum. The three peaks in the emission spectrum were attributed to the f-f transitions.[2] In contrast to the poor emission of Nd-exchanged nano-FAU treated only with D_2O, Nd-nano-FAU treated with PMS showed remarkably strong emission. The observation has led us to a conclusion that ligation of Nd(III) with PMS in the cages of nano-FAU enhances the emission. To characterize Nd-nano-FAU powder treated with PMS, the powder was dispersed in DMSO-d_6.[3] The transparent dispersion showed the seven peaks in absorption spectrum, which were attributed to the typical transitions of Nd(III). Using the peak intensity at 526 nm as a standard because of its insensitiveness to the environment, the apparent concentration of Nd(III) cations was determined to be 8.5 mM in the DMSO- d_6 dispersion. The transparent dispersion of Nd-nano-FAU treated with PMS showed remarkable emission when excited at 585 nm (Figure 3), while the dispersion of Nd-nano-FAU without the treatment with PMS gave no detectable emission. The quantum yield for the emission of Nd-nano-FAU treated with PMS was determined to be 9.5 % under excitation at 585 nm. This is the highest value ever observed for Nd(III) emission in organic media. The time decay of the emission seemed to consist of the two components at least, but was fitted by one-main-component exponential. The lifetime was determined as 22 μs (Figure 3, inset). Interestingly, dynamic light scattering (DLS) analysis of the Nd-nano-FAU treated with PMS dispersion revealed that the Nd-nano-FAU treated with PMS particles aggregate to some extent, giving the particle size distribution ranging between 100 and 175 nm. This fact indicates that 2-3 particles of Nd-nano-FAU treated with PMS aggregate in DMSO- d_6 without undergoing cross relaxation of the excited states of Nd(III).

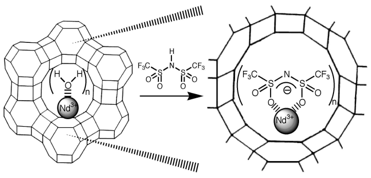

Figure 1. The conceptual process of this research.

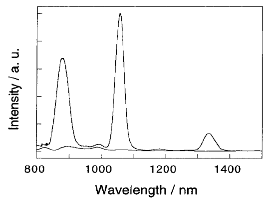

Figure 2. Emission spectra of Nd-nano-FAU treated with PMS (above) and Nd-nano-FAU treated with D_2O alone (below) measured by a reflectance method of their powders under vacuum. The samples were excited at 585 nm.

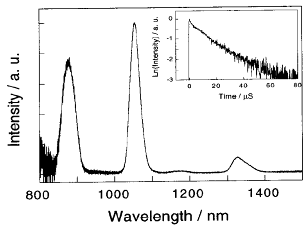

Figure 3. Emission spectrum of the dispersion of Nd-nano-FAU treated with PMS in DMSO-d_6. The sample was excited at 585 nm. The inset is emission decay curve.

1) Zhu, G.; Qui, S.; Yu, J.; Sakamoto, Y.; Xiao, F.; Xu, R.; Terasaki, O. *Chem. Mater.* **1998**, *10*, 1483-1486.
2) Ryo, M.; Wada, Y.; Okubo, T.; Nakazawa, T.; Hasegawa, Y.; Yanagida, S. *J. Mater. Chem.* **2002**, 12, 1748.
3) Wada, Y.; Okubo, T.; Ryo, M.; Nakazawa, T.; Hasegawa, Y.; Yanagida, S. *J. Am. Chem. Soc.* **2000**, *122*, 8583.