Photosensitization of europium ions by silver clusters in zeolite

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A B S T R A C T

Photosensitization of europium (Eu) ions by silver (Ag) clusters was achieved by simultaneously doping Eu and Ag in zeolite cages. The photoluminescence (PL) due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu ions at 613 nm is significantly increased by the presence of Ag clusters. The excitation wavelength dependence of the PL intensity coincided well with the absorption spectrum of Ag clusters, indicating that Eu ions are excited by the energy transfer from Ag clusters.

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1. Introduction

Rare-earth (RE) ions are well-known phosphorescent materials, which are practically used for many kinds of commodities, such as lighting, display, and laser [1–5]. They show sharp luminescence arising from the intra-4f shell transitions. Since the 4f shell of RE ions is shielded by outer shells, the luminescence is little affected by their surrounding environment, and thus highly efficient in a variety of host materials [6,7]. Recently, Eichelbaum and Rademann [8] reported that PL of RE ions in silicate glasses were significantly enhanced by metal clusters precipitated by synchrotron X-ray irradiation. The enhancement was found to be caused by energy transfer from metal clusters to RE ions. Their results indicate that metal clusters have a great potential to enhance the effective excitation cross section of RE ions, which is intrinsically small due to the dipole forbidden process.

In this work, we focus on zeolite as a host material to study the photosensitization effect of metal clusters. Zeolite, possessing a cage structure consisting of orthosilicate ion $\left(SiO_4^{4-} \right)$ and orthoaluminate ion $\left(AlO_4^{5-} \right)$ structural units, is one of the most suitable host materials for the formation of metal clusters [9–12]. Metal clusters are known to be chemically stable in the nano-sized pores in the cage, and can be formed by a simple ion exchange process followed by a thermal treatment [13–16]. In this paper, the effect of Ag clusters on the PL properties of Eu ions in zeolite was investigated for the first time. We show that PL of Eu ions in the visible region can be significantly increased by Ag clusters in zeolite, due

to the photosensitization effect. The results suggest that zeolite is a promising host material for the sensitization of RE ions by metal clusters.

2. Experimental procedure

Eu and Ag doped zeolite was prepared by an ion exchange process. The NH$_4$ form of faujasite-type zeolite (zeolite Y, SiO$_2$/Al$_2$O$_3$ = 7) was purchased from Tosoh Co. Japan. The average diameter of particles zeolite is about 800 nm. The zeolites were stirred in the aqueous solution of EuCl$_3$·6H$_2$O at room temperature for 24 h. The products were filtered, washed with deionized water, and dried in air at 100 °C. To activate the PL of Eu ions, the Eu doped zeolite (zeolite:Eu) was annealed in air at 800 °C for 2 h. The crystalline structure of zeolite Y is not destroyed at this temperature as confirmed by a XRD measurement [17]. For Ag doping, zeolite:Eu was stirred in aqueous solution of Ag(NH$_3$)$^{2+}$ at 70 °C for 24 h. Ag(NH$_3$)$^{2+}$ was prepared by reaction of silver nitrate with aqueous ammonia [10]. After 24 h of stirring, Eu and Ag codoped zeolites (zeolite:Eu, Ag) were filtered, washed and dried in air at 100 °C for 24 h. The co-doped zeolite powders were then annealed at 350 °C for 1 h in air. This low temperature annealing forms Ag clusters in the cages of zeolite [13,18]. As a reference sample, Ag singly doped zeolites (zeolite:Ag) were also prepared. The concentrations of Eu and Ag in zeolites were determined by energy-dispersive X-ray spectroscopy (EDS). Concentration of doped Ag was varied from 4.7 to 6.8 at.% by changing Ag concentration in doping solutions. The concentration of Eu was varied from 1.0 to 2.0 at.%, which was also controlled by changing Eu concentration in doping solutions. The samples were kept in air. PL spectra were measured

by a spectrophotometer (Horiba Jobin Yvon, Flourolog). The diffuse reflectance spectra were measured by a UV–VIS–NIR spectrophotometer (Shimadzu, Solid Spec-3700) and the data were converted using the Kubelka–Munk function. Morphologies of the samples were studied by a field emission scanning electron microscopy (FE-SEM) (JEOL, JSM-7001F). The external quantum efficiency (EQE) was determined by an integrating sphere method [19].

Time resolved PL spectra were measured by a monochromator equipped with a charge-coupled device with an image intensifier (ICCD) (princeton instrument, PI-Max). The third harmonic of a Nd:YAG laser (355 nm, pulse width 5 ns, repetition frequency 20 Hz) was used as the excitation source. The ICCD array was gated by a trigger signal from the exciting laser. The time resolution of the measurement system is 5 ns. For these optical measurements, the powder was put in a sample holder loosely. All the measurements were carried out at room temperature.

3. Result and discussion

The ultraviolet (UV) to visible diffuse reflectance spectra plotted as the Kubelka–Munk function (F) of the reflectance (R) of zeolite:Eu(1.0), zeolite:Ag(4.8), zeolite:Eu(1.0), Ag(4.7) and zeolite:Eu(1.0), Ag(6.1) are shown in Fig. 1(a). The numbers in the parentheses represent the Eu and Ag concentration (at.%). Zeolite:Eu(1.0) has a weak absorption band below 300 nm due to the charge transfer state of O^{2-} to Eu^{3+} [4]. Zeolite:Ag(4.8) and zeolite:Eu(1.0), Ag(4.7) exhibits a broad strong UV absorption around 310 nm. This peak is very similar to that reported for Ag clusters in hydrated zeolite Y. In the report [16], Ag_2 has been proposed as the possible origin of the absorption. In other reports [13,20], Ag_3 has been also proposed as possible Ag clusters in hydrated zeolite Y. Even the cluster size seems still controversy, it is generally accepted that the absorption arises from Ag clusters. Note that Ag ions in hydrated zeolite Y show the absorption only below
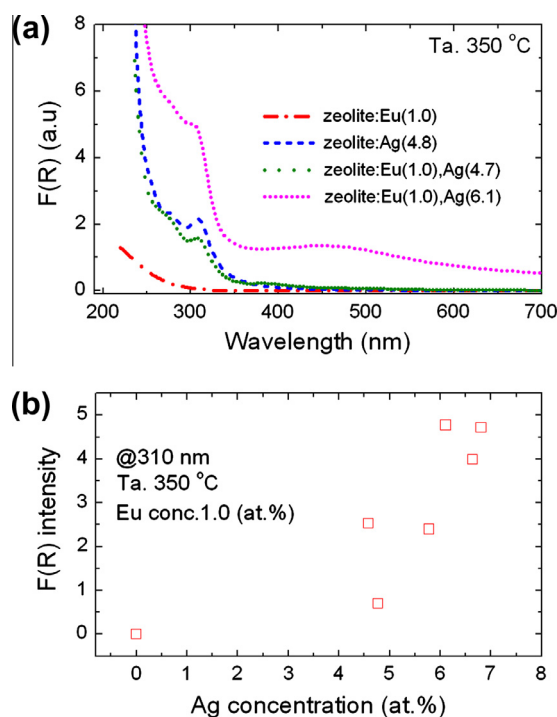
250 nm, which is quite different from that observed in the work [21,22]. Thus Ag ions are not considered to be the origin of the absorption. In addition to the 310 nm peak, the high concentration sample zeolite:Eu(1.0), Ag(6.1) has a broad absorption band around 450 nm, which can be assigned to the surface plasmon resonance of Ag nanoparticles [23,24]. Note that the Ag nanoparticles (NPs) were formed not inside the cages but on the surface of the zeolite crystals, confirmed by a FE-SEM measurement (Fig. S2). In Fig. 1(b), the values of $F(R)$ at 310 nm are plotted as a function of the Ag concentration. While the Eu concentration is fixed to 1.0 at.%, we can see the increase of the $F(R)$ value with increasing the Ag concentration.

Fig. 2(a) shows the PL spectra of the zeolite:Eu, Ag. The Eu concentration is fixed at about 1.0 at.%, and the Ag concentration is changed from 0 to 6.8 at.%. The excitation wavelength is 350 nm. The PL of the sample without Ag doping zeolite:Eu(1.0) is enlarged in the inset of Fig. 2(a), together with that of zeolites as a reference. The zeolites show weak and broad PL centered around 570 nm, which probably arises from oxygen-vacancies in the zeolite [25]. In addition, zeolite:Eu(1.0) shows a sharp PL peak around 613 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions (Eu-PL). In zeolite:Eu, Ag samples, a broad PL centered at 550 nm is observed and the intensity increases with increasing Ag concentration. To confirm the PL band (Ag-PL) arises from Ag clusters, we measured
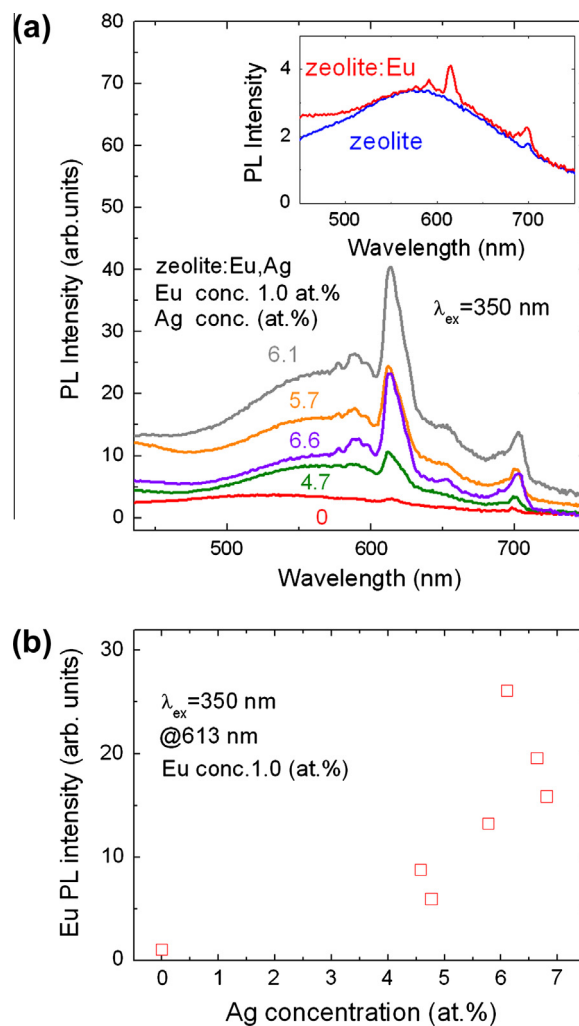

Fig. 1. (a) Diffuse reflectance ultraviolet to visible spectra, plotted as the Kubelka–Munk function (F) of the reflectance (R) of zeolite:Eu(1.0), zeolite:Ag(4.8) and zeolites:Eu, Ag. (b) $F(R)$ intensity (absorption optical intensity) versus plotted as a function of Ag concentration of zeolite:Eu, Ag.

Fig. 2. (a) PL spectra of zeolites, zeolite:Eu and zeolite:Eu, Ag of various Ag concentrations. The inset of the figure is enlarged PL spectra of zeolite and zeolite:Eu. (b) Ag concentration dependence of Eu-PL intensity.