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Strong white photoluminescence from annealed zeolites

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ABSTRACT

The optical properties of zeolites annealed at various temperatures are investigated for the first time. The annealed zeolites exhibit strong white photoluminescence (PL) under ultraviolet light excitation. With increasing annealing temperature, the emission intensity of annealed zeolites first increases and then decreases. At the same time, the PL peak red-shifts from 495 nm to 530 nm, and then returns to 500 nm. The strongest emission appears when the annealing temperature is 500 °C. The quantum yield of the sample is measured to be ~10%. The PL lifetime monotonously increases from 223 μs to 251 μs with increasing annealing temperature. The origin of white PL is ascribed to oxygen vacancies formed during the annealing process.

1. Introduction

White light-emitting phosphors have been attracting significant attention due to their potential applications in many fields, such as devices indicators, back lights, automobile headlights, and general illumination [1–4]. In general, to obtain white light emission, two or three colors must be combined, i.e., a high-energy emitter (e.g., blue) and a relatively low-energy emitter (e.g., green/red) [5]. Doping multi-type rare-earth ions in various host materials is the most widely used method to achieve white light generation [6]. However, fabrication process of such materials is very complicated in which the ratio of each rare-earth ions must be well controlled, and these rare-earth ions are usually expensive and toxic [7]. An alternative approach is generation of white light emission from a single material, which have advantages such as high stability, easy fabrication, and low cost. For instance, Green et al. prepared white phosphors from a silicate-carboxylate sol–gel precursor [8]. They ascribed the origin of white luminescence to carboxylic acids trapped in silicates. Exploring of novel materials which have broad emission covering the whole visible region is strongly demanded.

Zeolites are microporous crystalline aluminosilicates with nanosized pores. Their framework is composed of SiO_4 and AlO_4 tetrahedra units by sharing oxygen between every two consecutive units, and cations located inside channels or cavities to balance negative charges in the framework. For a long time, zeolites played indispensable roles in many technological and economical applications, such as catalysis, ion exchange, and separations [9, 10]. Recently, zeolites acting as host materials of optically active guests have attracted much attention for constructing novel materials designed at nanosized levels, because of their low-frequency vibrational framework, regularly spaced nanochannels and nanopores, and inexpensive price [11–17]. Up to now, various fluorescent materials, such as metal nanoparticles, quantum dots, organic dyes and rare-earth ions, have been encapsulated within the pores and channels to create advanced composite materials [18–21]. It is imaginable that the fully understanding of the optical properties of zeolites host is an important work for practical applications.

In this work, we systematically studied the photoluminescence (PL) behavior of annealed zeolites for the first time, by diffuse reflectance, emission and excitation spectra, and the decay curve. The annealed zeolites exhibit bright visible emissions, which appear white to the naked eye under ultraviolet (UV) light excitation. The absorption and emission are very sensitive to annealing temperature, and the PL is enhanced as large as 62 times by annealing. On the other hand, the lifetime shows little dependence on annealing temperature. The quantum yield is evaluated, and the origin of the white emission is discussed.

2. Experimental

2.1. Sample preparation

The NH_4 form of faujasite (FAU) type zeolite was purchased from Tosoh Co. Japan (Zeolite Y, $SiO_2/Al_2O_3=7$, grain size 700–1000 nm). The zeolites were used directly without further purification. They were calcined at 100–700 °C for 30 min in air. The samples are denoted as Z-*x* °C, where *x* is annealing temperature.

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2.2. Characterization

The structural properties of prepared products were characterized by an X-ray diffractometer (Rigaku-TTR/S2, $\lambda = 1.54056$ Å) and a field emission scanning electron microscopy (FE-SEM). Diffuse reflectance spectra of the products were measured by a UV–vis–NIR spectrometer (V-570, JASCO, Japan) equipped with an integrating sphere. PL measurements were carried out with the excitation of 325 nm light from a He–Cd laser. The signal was analyzed by a single grating monochromator and detected by a liquid–nitrogen-cooled CCD detector. PL excitation spectrum was obtained by a Horiba NanoLog spectrophotometer equipped with a monochromated Xe lamp and a liquid N_2 cooled photomultiplier tube (Hamamatsu, R5509-72). Time-resolved luminescence measurements were performed by detecting the modulated luminescence signal with a photomultiplier tube (Hamamatsu, R943-02), and then analyzing the signal with a photon-counting multichannel scaler. A Quantaurus-QY Absolute PL Quantum Yield Spectrometer (Hamamatsu, C11347-11) was used for the quantum yield measurement.

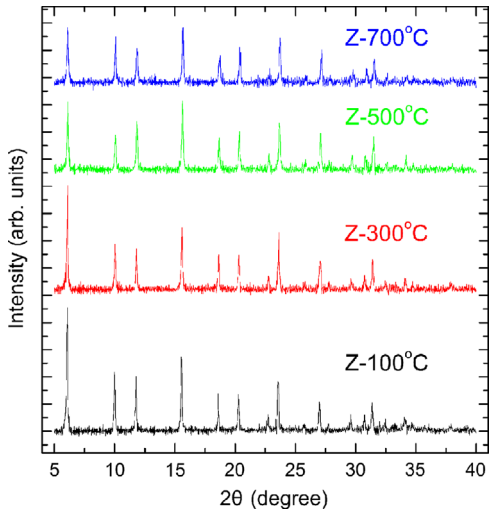

Fig. 1. X-ray diffraction patterns of zeolites annealed at (a) 100, (b) 300, (c) 500, and (d) 700 °C in air.

3. Results and discussion

Fig. 1 shows the XRD patterns of Z-100 °C, Z-300 °C, Z-500 °C, and Z-700 °C samples. The data of the diffraction peaks agree well with the standard values for the Zeolite Y (JCPDS no. 45-0112), indicating that the obtained samples have a single phase after thermal treatment. It also indicates that the diffraction intensity of zeolites is gradually decreased by the increase of the annealing temperature, which reveals the degradation of the crystallinity. The FE-SEM images of corresponding samples are shown in Fig. 2 (a–d). It can be seen that the particle size is in the range of 0.7–1 μm, and the morphology and monodispersity of these samples remain almost unchanged after various temperatures annealing.

It is interesting to mention that, the sample color depends on annealing temperature; when the annealing temperature increases from 100 °C to 500 °C, the color of powder gradually changes from white to gray, and further increase of the annealing temperature to 700 °C results in the recovery to white.

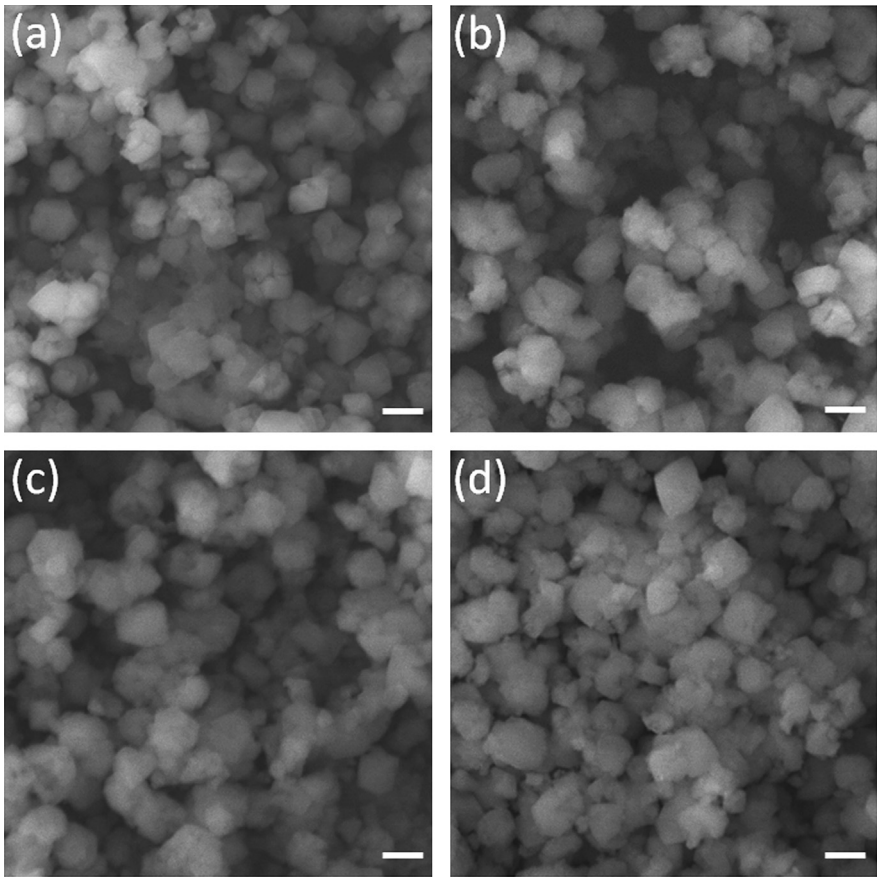

Fig. 2. FE-SEM images of zeolites annealed at (a) 100, (b) 300, (c) 500, and (d) 700 °C in air. Scale bars: 1 μm.