Enhanced near infrared emission from the partially vitrified Nd$^{3+}$ and silver co-doped zeolite Y

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Near infrared (NIR) emission from the Nd$^{3+}$ doped zeolite Y was strongly enhanced by partially vitrifying the zeolite structure via extra loading silver ions and post annealing. Under the low annealing temperatures at 450 °C and 650 °C, the states of the loaded silver were determined to be the co-existence of the isolated Ag$^{+}$ atoms, the Ag$^{0}$ ions, and the Ag$_{2}^{+}$ dimers. However, there was no enhancement in the NIR emission by the introduction of these small silver clusters. Under higher annealing temperature at 900 °C where the lattice of the zeolite Y was partially collapsed into the amorphous phase, strong NIR emission enhancement at 1064 nm with a factor of 6.8 was observed. The partial vitrification process by the co-loading of silver and post heat-treatment had strong effect on eliminating the H$_{2}$O molecules, which can greatly enhance the NIR emission.

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I. INTRODUCTION

Bioluminescence imaging based on the micro/nano-scale fluorescent materials has advantages like high sensitivity, low cost, high feasibility and flexibility, etc.1–3 Previously, tremendous amount of work has been done on the visible and the near infrared (NIR) (I) (0.65–0.95 µm) “human optical window” up-conversion luminescence under the NIR excitation. Among the above, Er$^{3+}$, Yb$^{3+}$ co-doped NaYF$_{4}$ nano-particles were most intensively investigated for their strong ability of drug storage/release and have been reported to be potentially traceable drug delivery, porous materials in various forms bioluminescence imaging often deals with the luminescence enabled by the low phonon energy of the NaYF$_{4}$ host.4–7 The high up-conversion fluorescence quantum efficiency and the low background fluorescence from the human tissues and the low cost, high feasibility and flexibility, etc.1–3

Lately, a secondary “human optical window” luminescence centered in the 1–1.35 µm NIR range under the NIR excitation has been explored for its promisingly low scattering from the human tissues and the low background fluorescence from the organic medicine molecules or the human tissues.8–11 Since bioluminescence imaging often deals with the luminescence traceable drug delivery, porous materials in various forms are preferred for their strong ability of drug storage/release within the pores or the channels. Recently, self-activated porous silica nano-fibers, Er$^{3+}$, Yb$^{3+}$:NaYF$_{4}$ nano-crystals embedded in the porous silica nano-fibers and the porous Nd$^{3+}$:YAG nano-fibers have been fabricated by electrospinning and exhibited excellent bio-luminescence imaging and drug delivery properties.12–14 Intensity variation of the up- or down-conversion emission has been observed due to the change of the environmental conditions around the luminescent centers. Speaking of the porous materials, zeolite is one of the most famous for its nature-born size, well-defined pores and channels, and actually has been put into practical use in catalysis, molecule sieving, and ion exchanging, etc. Recent research shows that zeolites are excellent luminescence host materials owing to their strong ability of separating the luminescent centers from the aggregation induced quenching.15–18 However, due to the strong and fast non-radiative vibrational de-activation of the luminescent centers from excitation state by water molecules, or -OH bonds, reports on the NIR luminescence in the zeolite matrixes were few. Tuning down the vibrational energy by extra loading the low vibrational organic guests,19,20 or by the separation of the luminescent centers from the water molecules or the detrimental -OH bonds by partially sealing the pores with inorganic clusters,21 have been demonstrated as efficient solutions to ensure the strong NIR emission. Here, in this work, we report the enhanced NIR luminescence from partially vitrified Nd$^{3+}$ doped zeolite Y by co-loading of silver and post heat-treatment. Nd$^{3+}$ was chosen as the luminescent centers because the ~1.06 µm emission from the Nd$^{3+}$: $^{4}F_{3/2}$→$^{4}I_{11/2}$ transition falls well in the second “human optical window” (1–1.35 µm). The Stokes shift between the Nd$^{3+}$ 1064 nm emission and the ~800 nm NIR excitation is beneficial to accurate signal collection. Another advantage of the rare earth luminescence is that once the host matrix is determined, the emission wavelength of is fixed, independent of the excitation power or the excitation wavelength. This is favorable to the stable signal collection or even to the fingerprint identification. It also should be noted that the quantum yield of the rare earth down-conversion luminescence is usually considerably higher than that of the up-conversion process.

II. EXPERIMENTAL

A. Sample preparation

First, Nd(NO$_{3}$)$_{3}$·6H$_{2}$O was weighed and dissolved in de-ionized (DI) water to get a 50 mmol/L solution (40 mL). Then 2 g zeolite Y (SiO$_{2}$/Al$_{2}$O$_{3}$ = 7, Tosoh, Japan) was added into the solution and the suspension was stirred at 80 °C for 36 h. The product was centrifuged and rinsed by DI water and then dried at 80 °C. The powders were annealed from 900 °C to 1200 °C in air. Then, one half of the powders was used in the experiment and the remaining half was stored for further studies.

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annealed at 900°C were stirred in a 250 mmol/L AgNO3 solution (40 mL) at 80°C for 8 h and then the aforementioned, rinsing and drying process was repeated. The dried powders were further annealed at 450°C, 650°C, and 900°C in air. The obtained samples were named as $S_{\text{Nd}}\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\times\time
XRD $\theta$–$2\theta$ scans of the Nd$^{3+}$ and silver co-loaded zeolite Y are given in Fig. 1(b). It can be seen that compared with the untreated pure zeolite Y, the diffraction intensity was decreased for $S_{\text{Nd-900 C, Ag-450 C}}$ and $S_{\text{Nd-900 C, Ag-650 C}}$. While for $S_{\text{Nd-900 C, Ag-900 C}}$, the diffraction intensity from zeolite Y became very weak and a characteristic amorphous broad band turned up. It is interesting that unlike $S_{\text{Nd-1000 C}}$ and $S_{\text{Nd-1100 C}}$ for which the zeolite Y phase was totally sacrificed and the new phase (mullite) turned up instead, while the zeolite Y structure was still partially maintained for $S_{\text{Nd-900 C, Ag-900 C}}$ without showing extra crystalline phases.

Schematic diagram of the ideal zeolite Y structure is presented in Fig. 2. There are a set of well defined sites for the cations in the zeolite Y structure. $S_{\text{I}}$ is located in the center of the hexagonal prism which is inaccessible to the detrimental -OH bonds or the water molecules. $S_{\text{I'}}$ is located in sodalite cage close to the center of the prism-sodalite shared 6-member ring. $\text{Ag}^0_2$ dimers can be formed with one $\text{Ag}^0$ atom occupying the $\text{SI}$ site linked to one $\text{Ag}^+$ occupying the $\text{SI'}$ site. $S_{\text{II}}$ is located in the sodalite cage close to the center of the sodalite self-own 6-member ring. $S_{\text{II}}$ is in the super cage, next to $S_{\text{II'}}$ and in line with $S_{\text{II}}$ and the center of the sodalite self-own 6-ring. Recent study based on PL spectra and high-resolution powder XRD shows that NIR luminescent centers such as Bi$^{3+}$ located in the sodalite cage mainly contribute to emission. $S_{\text{II}^*}$ is located deeper in the super cage and also in line with $S_{\text{II'}}$ and $S_{\text{II}}$. $S_{\text{U}}$ is in the center of the sodalite cage. Thus, the luminescent centers located at the $S_{\text{I}}$, $S_{\text{I'}}$, $S_{\text{II}}$, $S_{\text{II}^*}$, and $S_{\text{U}}$ sites in the sodalite cage and the super cage are vulnerable to be quenched by the existence or the entrance of the water molecules or the highly vibrational -OH bonds.

XPS spectra of silver for all the silver doped samples and $S_{\text{Nd-900 C}}$ were shown in Fig. 3. Except for $S_{\text{Nd-900 C}}$, the two peaks for $\text{Ag 3d}_{3/2}$ and $\text{Ag 3d}_{5/2}$ located at 368.3 eV and 374.3 eV were detected for all the silver doped samples with post heat-treatment. There was a 0.3 eV negative shift each for the $\text{Ag 3d}_{3/2}$ and the $\text{Ag 3d}_{5/2}$ peaks, compared with the counterparts of $S_{\text{Nd-900 C, Ag-untreat}}$ ($\text{Ag 3d}_{3/2}$ @ 368.0 eV and $\text{Ag 3d}_{5/2}$ @ 374.0 eV, respectively). The negative shifts indicated the partial reduction of $\text{Ag}^+$ ions into $\text{Ag}^0$ atoms.
during the post heat-treatment process.\textsuperscript{25} The formation of Ag\textsuperscript{0} atom from Ag\textsuperscript{+} ion can be through the negative charge transfer from the framework \(\text{O}_2^-/\text{C}_0\) or water as the reducing agent.\textsuperscript{26} However, it is not suitable to estimate the ratio of Ag\textsuperscript{0}/Ag\textsuperscript{+}, since it is difficult to distinguish Ag\textsuperscript{0} atoms from Ag\textsuperscript{+} ions in the XPS spectra accurately for quantitative calculation.

The absorption peaks due to the transitions from the Nd\textsuperscript{3+}: 4I\textsubscript{9/2} ground state to the higher energy states have been assigned in Fig. 4(a). Due to the Nd\textsuperscript{3+}/Ag\textsuperscript{+} ion exchanging during the loading of the Ag\textsuperscript{+}, the absorption of Nd\textsuperscript{3+} became lower than that of the Nd\textsuperscript{3+} single doped samples. The absorption spectra in the UV range were presented in Fig. 4(b). For S\textsubscript{Nd-900°C, Ag-untreat}, the absorption of silver was almost negligible. For S\textsubscript{Nd-900°C, Ag-450°C} and S\textsubscript{Nd-900°C, Ag-650°C}, the absorption peak located at 265 nm is assigned to the Ag\textsuperscript{+} ions.\textsuperscript{27} The absorption at 306 nm for S\textsubscript{Nd-900°C, Ag-650°C} was attributed to the 2S\textsuperscript{1/2}→2P\textsuperscript{1/2} transition of the isolated Ag\textsuperscript{0} atom located in the center of the hexagonal prism.\textsuperscript{23,28} For S\textsubscript{Nd-900°C, Ag-900°C} the 265 nm and the 306 nm absorption peaks totally disappeared, and no other new absorption peaks were detected.

To further determine the states of the loaded silver, the emission spectra in the visible range under the 265 nm and the 306 nm excitation were investigated. For S\textsubscript{Nd-900°C, Ag-450°C} and S\textsubscript{Nd-900°C, Ag-650°C}, the strongest emission peaks under the 265 nm excitation was both located at 544 nm (see Fig. 5), which was attributed to Ag\textsuperscript{0} atoms from the Ag\textsuperscript{0}(SI)-Ag\textsuperscript{+}(SI') dimers.\textsuperscript{25} While for S\textsubscript{Nd-900°C, Ag-900°C} under the 265 nm excitation, a new emission peak centered at 394 nm turned up. This emission band may be attributed to the oxygen vacancy defects, since for the untreated pure zeolite Y, a similar emission band with a lower intensity has also been observed. Under the 306 nm excitation, two strong emission peaks located at 494 nm and 544 nm were observed for S\textsubscript{Nd-900°C, Ag-450°C} and S\textsubscript{Nd-900°C, Ag-650°C}. The 494 nm emission was attributed to the emission from the isolated Ag\textsuperscript{0} atom at site SI in the hexagonal prism.\textsuperscript{29} One clear tendency that can be seen is that the intensity of these emissions dropped drastically when annealed at 650°C and 900°C.

![FIG. 5. PL spectra of S\textsubscript{Nd-900°C, Ag-untreat}, S\textsubscript{Nd-900°C, Ag-450°C}, S\textsubscript{Nd-900°C, Ag-650°C}, S\textsubscript{Nd-900°C, Ag-900°C} and S\textsubscript{Nd-900°C, Ag-900°C} under the 265 nm (a) and the 306 nm (b) excitations in the visible range.](image)

![FIG. 6. NIR emission spectra of the Nd\textsuperscript{3+} (and silver) doped zeolite Y samples.](image)

![FIG. 7. FTIR spectra for the pure zeolite Y, S\textsubscript{Nd-untreat}, S\textsubscript{Nd-900°C, Ag-untreat}, S\textsubscript{Nd-900°C, Ag-450°C}, S\textsubscript{Nd-900°C, Ag-650°C} and S\textsubscript{Nd-900°C, Ag-900°C}.](image)
which was in accordance with the absorption spectra and implied that the small silver clusters may turn into large particles or may be incorporated into the amorphous phase at high heat-treatment temperatures. For SNd-900°C, Ag-900°C, there was no emission in the visible range under the 306 nm excitation. The shapes of the emission peaks under the 265 nm and 306 nm excitations for SNd-900°C, Ag-untreat were similar to the counterparts of SNd-900°C, Ag-450°C. However, the emission intensity decreased by ~1 order of magnitude.

Seen from the PL spectra in the NIR range (shown in Fig. 6), there was no emission in the NIR range upon the 803 nm excitation for the untreated pure zeolite Y. The NIR emission for the sample without annealing was the weakest among the Nd³⁺ doped samples. For SNd-900°C, Ag-450°C and SNd-900°C, Ag-650°C, the integrated emission intensity for the 1064 nm emission both dropped about 42.4%, compared with that of SNd-900°C. The possible reason is that these samples got hydrated again to some extent during the silver loading and the second round low temperature thermal treatment at 450°C and 650°C. In addition, Ag⁺ ions, Ag⁰ atoms and Ag⁰(Si)-Ag⁺(Si') dimers were too small to isolate the Nd³⁺ luminescent centers from the -OH bonds and the H₂O molecules, thus made no positive contribution to the NIR emission of Nd³⁺. For SNd-900°C, Ag-900°C, there was a large enhancement with a factor of 6.8 for the integrated 1064 nm emission compared with the counterpart of SNd-900°C. Since there was no absorption around 803 nm from silver in the absorption spectra, the enhanced NIR emission cannot be attributed to the energy transfer from silver to Nd³⁺. It was reasonable that the partially vitrification by annealing the silver co-loaded sample at 900°C made the main contribution to the NIR emission enhancement. In this case, the role of the low vibrational organic compounds (bis(perfluoromethylsulfonyl)amine, PMS-H) in the zeolite framework was so obvious that strong
NIR emission could be observed even for the sample directly dried at 150°C without high temperature annealing, which may be attributed to the strong combination between the PMS-H and the -OH bonds.\textsuperscript{19} FTIR spectra were measured to take a further look at the microstructure evaluation of the zeolite, as shown in Fig. 7. The characteristic absorption bands of the -OH bonds located around 3400 cm\(^{-1}\) to 3600 cm\(^{-1}\) were observed in the FTIR spectra.\textsuperscript{22} For SNd-900\_C, Ag-450\_C and SNd-900\_C, Ag-650\_C, the amount of the -OH bonds did not seem to be reduced at all. For SNd-900\_C, Ag-900\_C, the -OH absorption band became slightly lower, which implied that at 900°C silver had positive effect on eliminating the high vibrational -OH bonds by vitrifying the zeolite Y structure during the postannealing dehydration process. The absorption band located at 1634 cm\(^{-1}\) is attributed to the structural or absorbed H\(_2\)O in the silicates.\textsuperscript{30} For SNd-900\_C, Ag-900\_C, the absorption at 1634 cm\(^{-1}\) was reduced at least 50% compared with other samples. This was believed to be the main reason for the strong enhancement for the NIR emission. For the pure zeolite Y, the sharp absorption peak located at 1400 cm\(^{-1}\) is attributed to NH\(_4\)Br. Since the other samples were ion-exchanged with Nd\(^{3+}\) and Ag\(^{+}\), the absorption by NH\(_4\)Br in the FTIR spectra has been greatly reduced. The intense absorption band around 1100 cm\(^{-1}\) was the characteristic asymmetric Si-O/Al-O stretching vibration.\textsuperscript{16} TEM morphology of the pure zeolite Y clearly exhibits the typical polyhedron profile (Fig. 8(a)). The morphology of SNd-900\_C shown in Fig. 8(b) is similar to that of pure zeolite Y. While for SNd-900\_C, Ag-900\_C, collapse of the polyhedron morphology can be observed in Fig. 8(c). Large silver nano-particles were not observed for SNd-900\_C, Ag-900\_C, which may be attributed to the low doping concentration of silver in the zeolite Y framework. Based on the semi-quantitative calculation from the XPS data, the atomic concentration of silver is \(\sim 1\%\). Small silver cluster like Ag\(_{2}\) dimer whose scale is less than 1 nm, is insensitive to TEM or XRD 0-20 detection but sensitive to optical spectra.

The decay curves of the Nd\(^{3+}\) 1064 nm emission were given in Fig. 9. The decay curves of the Nd\(^{3+}\) 1064 nm emission for SNd-untreat, SNd-900\_C, SNd-900\_C, Ag-untreat, SSNd-900\_C, Ag-450\_C and SNd-900\_C, Ag-650\_C all showed at least two exponential decay features. The mean decay time \((t_m)\) values calculated from the equation \(t_m = \int_0^{\infty} [I(t)/I_0]dt\), where \(I(t)\) is luminescence decay intensity at time \(t\), \(I_0\) is the maximal value of the decay intensity, and \(I_0\) corresponds to the initial time when \(I_0\) occurs, as listed in Table I, were close to the data (22 \(\mu s\)) reported in Ref. 19. The slight drop in the emission lifetime for SNd-900\_C, Ag-650\_C implied that the structure collapse of the crystalline zeolite Y might start. While for SNd-900\_C, Ag-900\_C, the emission decay time rocketed to 237 \(\mu s\), which was close to that of the Nd:YAG single crystal (254 \(\mu s\) for the 0.1 at. \% Nd:YAG).\textsuperscript{31} The strong NIR emission in the NIR (II) range, the large Stokes shift, and the long emission decay time together make the Nd\(^{3+}\) doped zeolite Y with silver as a dehydration catalyst a very promising material for the luminescence traceable drug delivery. For practical bio-application, water solubility is a key issue to be solved, so surface modifications, like ligands exchange,\textsuperscript{32} for instance, will be conducted in order to achieve a hydrophilic surface in our future work.

\section*{IV. CONCLUSIONS}

The 1064 nm NIR emission from the Nd\(^{3+}\) doped zeolite Y has been enhanced by partially collapsing the porous zeolite structure into the amorphous phase with the co-loading of silver and the post heat-treatment. The emission decay time at 1064 nm under the 803 nm excitation reached 237 \(\mu s\), which was close to that of the Nd:YAG laser crystals. The reason for the enhanced emission intensity and the prolonged emission decay time is mainly due to the promoted elimination of the H\(_2\)O molecules from the zeolite Y from framework. The strong NIR emission from the Nd\(^{3+}\) doped zeolite materials may have applications for the luminescence traceable drug delivery.

\begin{table}[h]
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