

Optical Properties of Nd³⁺ Ion-Doped ZnO Nanocrystals

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Hexagonal Nd³⁺-doped ZnO nanocrystals with multiple luminescent centers were synthesized by means of a facile sol-gel method. The Nd³⁺-doped ZnO nanocrystals were characterized by using the X-ray diffraction, transmission electron microscopy, ultraviolet-visible reflectance spectra, and fluorescence spectroscopy. Host-to-Nd³⁺ energy transfer was observed for the first time in Nd³⁺-doped ZnO nanocrystals. It was found that Nd³⁺ ions can be effectively sensitized by the ZnO nanocrystals, resulting in sharp and intense characteristic Nd³⁺ luminescence. The photoluminescence (PL) and PL excitation spectra of Nd³⁺ ions in the ZnO nanocrystals were investigated in detail. Furthermore, the possible mechanism of host-to-Nd³⁺ energy transfer was also proposed on the basis of the optical properties of Nd³⁺ ions in the ZnO nanocrystals.

Keywords: ZnO, Nd³⁺, Energy Transfer, Photoluminescence, Optical Spectroscopy.

1. INTRODUCTION

In the past decades, rare-earth (RE) ion-doped semiconductors have been the focus of research interest due to their unique optical properties and promising applications in many technological fields.¹⁻¹⁵ By doping with different luminescence centers, the optical properties of RE^{3+} ion-doped semiconductors can be tailored in the visible to infrared region, which is of interest for the promising applications in areas as diverse as optoelectronic devices, flat plane displays, and biological labels. In most of these applications, an efficient energy transfer from the host to RE^{3+} is desired, since the direct excitation of the parity-forbidden f-f transitions of RE ions are usually inefficient compared to the host absorption in the ultraviolet (UV) region. Some wide band gap semiconductors, such as GaN,^{16–18} ZnO,^{3, 19, 20} and TiO_2 ,^{8, 9, 21} have been selected as the host materials to sensitize RE³⁺ ions efficiently and yield the desired luminescence. Among these materials, ZnO, as a well-known wide band gap semiconductor, is considered as a promising host candidate for RE³⁺ ion doping due to its outstanding optical and thermal properties. Recently, many important results for RE³⁺-doped ZnO nano- and microstructures have been reported.^{2,3,10,19,20,22-24} In our recent work, by using a modified sol-gel method, Eu³⁺ ions were successfully incorporated in the ZnO lattices, and multiple sites of Eu³⁺ and host-to-Eu³⁺ energy transfer were observed.^{19,23}

Zeng et al. have also observed similar host-to- Eu^{3+} energy transfer in Eu³⁺ ion-doped ZnO hierarchical microspheres fabricated via a hydrothermal strategy.^{20, 24} Pereira et al. reported that Tb³⁺ ions could be incorporated into ZnO nanocrystals using colloidal synthetic procedures.²² However, the vast majority of research work to date has been concentrated on the emission in the visible range because of potential applications in full-color flat plane displays.^{3, 19, 20, 24} RE³⁺-doped ZnO are also expected to be one of the promising materials for emissions in the near-infrared (NIR) spectral region, particularly in connection with optical fiber telecommunication. Trivalent erbium (Er^{3+}) is of particular interest because of its characteristic NIR emission at 1.54 μ m, which corresponds to the minimum transmission loss region for silica-based glass optical fibers.^{25–27} Similar to the case of trivalent erbium, trivalent neodymium (Nd³⁺) has also several technically important luminescent bands including the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ (a second lasing transition at ~900 nm), ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ (the basis of 1.06 μ m Nd³⁺ lasers) and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$ (the basis of 1.3 μ m Nd³⁺ lasers) transitions, which have attracted much attention at present. However, because of the large mismatch in ionic radius and charge imbalance between Nd³⁺ and Zn²⁺, the successful incorporation of Nd³⁺ ions into the ZnO nanocrystals with a wet-chemical method still remains a great challenge. So far, no detailed optical properties and host-to-Nd³⁺ energy transfer have been reported in Nd³⁺ ion-doped ZnO nanocrystals.

In this work, we report a facile method to incorporate Nd³⁺ ions into hexagonal ZnO nanocrystals. By virtue of

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the optical spectra of Nd³⁺, we can unambiguously prove the existence of multiple luminescence centers of Nd³⁺ in ZnO nanocrystals. The photoluminescence (PL), PL excitation, and ZnO-to-Nd³⁺ energy transfer in ZnO nanocrystals are investigated in detail.

2. EXPERIMENTAL DETAILS

2.1. Nanocrystals Synthesis

Nd³⁺-doped ZnO nanocrystals with the nominal doping concentration of 1 at% were prepared by using a modified sol-gel method.^{28,29} The detailed synthesis procedures were described as follows. In a typical synthesis, 0.01 mol zinc acetate dihydrate (AR) and the required amount of neodymium acetate hexahydrate (99.99%) were dried at 120 °C to remove the water and then transferred into a 250 ml round-bottom flask. After cooling to room temperature (RT) naturally, 100 ml absolute ethanol was by added to the round-bottom flask. The mixture was refluxed under vigorous stirring in an 80 °C water bath for 3 h to obtain a clear precursor solution. The precursor solu- 20 tion was hydrolyzed by the addition of 0.025 mol lithium hydroxide monohydrate powder in an ultrasonic bath for 30 min at 0 °C. The obtained mixture was precipitated by the addition of 300 ml hexane. The resulting precipitates were isolated by centrifugation, washed with ethanol several times, and dried at 40 °C to yield the as-grown samples. Finally, the as-grown samples were further annealed at 400 °C in air for 30 min to obtain the final products. The final products were white powders with a yield of \sim 70% based on the starting materials. For comparison, pure ZnO nanocrystals were also synthesized following the same procedure.

2.2. Measurements

The morphology of Nd³⁺ doped ZnO nanocrystals was investigated by a JEOL-2010 transmission electron microscope (TEM) equipped with the energy dispersive X-ray spectrum. The precise concentration of Nd³⁺ in ZnO nanocrystals was determined by the Ultima2 ICP optical emission spectrometer. Powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO powder diffractometer with Cu K α_1 radiation ($\lambda = 0.154187$ nm). Ultraviolet-visible (UV-vis) diffuse reflectance spectra for pure and Nd³⁺-doped ZnO nanocrystals were measured by a Perkin-Elmer Lambda 900 UV/VIS/NIR Spectrometer using BaSO4 as a reference. Emission and excitation spectra were recorded on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with both continuous (450 W) and pulsed xenon lamps. For low-temperature measurements, samples were mounted on a closed cycle cryostat (10-350 K, DE202, Advanced Research Systems). The line intensities and

positions of the measured spectra were calibrated according to the FLS920 correction curve and standard mercury lamp.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Characterization

The crystallinity and phase purity of the samples were investigated by XRD analysis. Figure 1(a) shows the XRD pattern of Nd³⁺-doped ZnO nanocrystals annealed at 400 °C. For comparison, the XRD pattern obtained from pure ZnO nanocrystals annealed at 400 °C is also presented in Figure 1(b). These XRD diffraction peaks for both pure and Nd³⁺-doped ZnO nanocrystals can be well ascribed to hexagonal ZnO with wurtzite structure (JCPDS No. 36-1451), and be indicative of the presence of highly crystalline ZnO nanocrystals without any other impurity phases. On the basis of the Debye-Scherrer's formula, the average sizes of pure and Nd³⁺-doped ZnO nanocrystals are estimated to be \sim 14 and \sim 12 nm, respectively. Compared with the pure ZnO nanocrystals annealed at 400 °C, the average size of Nd³⁺-doped ZnO nanocrystals decreases slightly, indicating that the incorporation of Nd³⁺ ions in ZnO nanocrystals restrains the nanocrystal growth to some extent.

The morphology of Nd^{3+} -doped ZnO nanocrystals annealed at 400 °C was characterized by TEM. From the representative TEM (Fig. 2(a)) and high resolution TEM (Fig. 2(c)) images, it can be seen that the Nd^{3+} -doped ZnO nanocrystals are irregularly spherical with a diameter of 10–13 nm, which is basically close to that of 12 nm as estimated by XRD. As shown in the high resolution TEM image in Figure 2(c), the d(101) crystalline lattice fringes are very clear, further confirming the high crystallinity of Nd^{3+} -doped ZnO nanocrystals. The selected area electron diffraction (SAED) pattern of Nd^{3+} -doped ZnO nanocrystals (Fig. 2(b)) exhibits the polycrystalline nature, and



Fig. 1. XRD patterns of Nd³⁺-doped (a) and pure (b) ZnO nanocrystals.



Fig. 2. TEM images (a), SAED pattern (b), high-resolution TEM 20 images (c), and EDS pattern (d), of Nd³⁺-doped ZnO nanocrystals.

the rings can be well indexed to diffractions from the (100), (002), (101), (102), (110), (103), and (112) planes of the hexagonal wurtzite structure in turn, in accordance with the above XRD analysis. The elemental components of the samples are investigated by energy-dispersive X-ray spectrum (EDS) as shown in Figure 2(d), which confirms the existence of the Zn, O, and Nd in ZnO nanocrystals. The precise content of Nd³⁺ in ZnO nanocrystals is determined to be 1.05 at% by the Ultima2 ICP optical emission spectrometer.

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3.2. UV-Vis Diffuse Reflectance Spectra

To determine the band gap energy of pure and Nd³⁺-doped ZnO nanocrystals, the RT UV-vis diffuse reflectance spectra for both samples were measured using BaSO₄ plate as a reference. As shown in Figure 3, both samples exhibited a strong absorption onset at \sim 380 nm, which corresponds to the excitonic $1S_{h}\!\rightarrow\!1S_{e}$ transition of ZnO and is well consistent with the absorption onset observed in Eu³⁺-doped ZnO nanocrystals.¹⁹ By virtue of the method proposed by Cao et al.,³⁰ the band gap energies (E_g) of pure and Nd³⁺ doped ZnO nanocrystal were determined to be 3.18 and 3.24 eV (inset of Fig. 3), respectively. In addition to the strong absorption onset around \sim 3.2 eV, some relatively weak absorption peaks centered at 1.40, 1.53, 1.66, 1.79, 2.10, and 2.42 eV were also observed in the RT UV-vis diffuse reflectance for Nd³⁺-doped ZnO nanocrystals (Fig. 3(b)), which correspond to the direct absorption peaks of Nd^{3+} ions from the ground state (${}^{4}I_{9/2}$) to the higher excited states: ${}^{4}F_{2/3}$, ${}^{4}F_{5/2} + {}^{2}H_{9/2}$, ${}^{4}F_{7/2} + {}^{4}S_{3/2}$, ${}^{4}F_{9/2}$, ${}^{2}G/_{7/2} + {}^{4}G_{5/2}$, and ${}^{2}G_{9/2}$, respectively.



Fig. 3. The RT diffuse reflectance spectra of pure (a) and Nd³⁺ (b) doped ZnO nanocrystals. The inset shows the plot of $F(R)^2$ versus photon energy of pure and Nd³⁺ doped ZnO nanocrystals, where $F(R) = (1 - R)^2/2R$, and *R* is the reflectance. Band gap energies of ZnO by nanocrystals can be obtained by extrapolation to F(R) = 0.

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Figure 4 compares the 10 K PL spectra for Nd^{3+} -doped ZnO nanocrystals under different excitation lights. As shown in Figure 4(a), upon direct excitation from the ground state ${}^{4}I_{9/2}$ to the ${}^{4}G_{5/2}$ state of Nd^{3+} at 604 nm, sharp and abundant NIR emission lines of Nd^{3+} were observed with the dominant emission line centered at 898.5 nm. These sharp and resolved emission lines centered at 898.5, 1082.6, and 1373 nm correspond to radiative relaxations from ${}^{4}F_{3/2}$ to its low-lying multiplets ${}^{4}I_{9/2}$, ${}^{4}I_{11/2}$, and ${}^{4}I_{13/2}$, respectively, and indicate a highly crystallized environment around the Nd^{3+} ions in the ZnO nanocrystals. Although the transition from ${}^{4}F_{3/2}$ to ${}^{4}I_{11/2}$ is well known as the strongest transition in Nd^{3+} -doped semiconductors such as GaN, 17,18 the 898.5 nm emission line from ${}^{4}F_{3/2}$ to ${}^{4}I_{9/2}$, shows higher intensity than



Fig. 4. The 10 K NIR emission spectra of Nd^{3+} -doped ZnO nanocrystals under the (a) 604 nm and (b) 370 nm excitation.

the transition from ${}^{4}F_{3/2}$ to ${}^{4}I_{11/2}$. Similar NIR emission patterns have also been observed in Nd³⁺ ion-doped Si nanoclusters, nonetheless only broad emission lines of Nd³⁺ were detected.³¹ Furthermore, such sharp and abundant emission lines resulting from Nd³⁺-doped ZnO nanocrystals have not been reported before. Owing to the time-reversal (Kramers) degeneracy for the f^3 configuration (Nd³⁺), theoretically, five emission lines for the transition of ${}^{4}F_{3/2}$ to ${}^{4}I_{9/2}$ are expected for single Nd³⁺ luminescence center in ZnO nanocrystals at 10 K. However, as clearly shown in Figure 4(a), eight resolved emission lines assigned to the transition from ${}^{4}F_{3/2}$ to ${}^{4}I_{9/2}$, more than theoretical splitting number, are well identified upon the excitation at 604 nm, which suggests that these emission lines very likely resulted from different luminescence centers of Nd³⁺ in ZnO nanocrystals. Because of the lattice distortion arising from the large difference in ionic radius between Nd³⁺ and Zn²⁺, multiple luminescence centers are not unexpected once Nd³⁺ ions are embedded within ZnO nano-lattices. Similarly, multiple sites of Eu³⁺ ions have been revealed in Eu³⁺-doped ZnO nano- and microcrystals fabricated by various methods.^{19, 23, 24} May

Furthermore, upon excitation above ZnO band gap $(\sim 370 \text{ nm})$, much sharper and more abundant emission lines corresponding to the transitions from ${}^{4}F_{3/2}$ to its lowlying multiplets ${}^{4}I_{9/2}$, ${}^{4}I_{11/2}$, and ${}^{4}I_{13/2}$ were also observed in the NIR region at 10 K (Fig. 4(b)). Since there is no direct absorption of Nd^{3+} at ~ 370 nm as observed in Figure 3(b), such emission lines under the indirect excitation indicate that the Nd³⁺ emissions are associated with an energy transfer process from ZnO host to Nd³⁺, which was not previously observed in Nd³⁺-doped bulk or nanocrystalline ZnO. However, it should be noticed that the indirectly excited Nd³⁺ emission pattern is more complicated than that by direct excitation (Fig. 4(a)). A careful comparison of these two PL spectra, as depicted in Figure 4(b), reveals that the relative intensities of several emission lines as marked with rhombus symbols change under different excitation paths. Moreover, several new emission lines marked with star symbols appear in addition to those lines observed under the direct excitation, which may arise from Nd3+ ions located at different crystalfield (CF) environments in ZnO nanocrystals. Different NIR luminescence patterns under indirect or direct excitation paths suggest inhomogeneous CF surroundings for the doped Nd³⁺ ions, and thereby confirm the existence of multiple luminescence centers of Nd³⁺ in ZnO nanocrystals. In addition to the characteristic $4f^{N}-4f^{N}$ emission lines of Nd³⁺ ions in the NIR region, a broad band centered at \sim 585 nm in the visible was observed upon excitation at 370 nm (not shown), which is attributed to the defect states such as interstitial oxygen (O_i) as verified in Eu3+-doped ZnO nano- and microstructures.23, 24 For comparison, the PL properties for pure ZnO nanocrystals were also investigated under the 370 nm excitation. A similar

broad orange band centered at 570 nm was observed (not shown), which is blue-shifted ~ 0.056 eV relative to that of Nd³⁺-doped counterparts.

To better understand the absorption and radiative transition mechanisms responsible for the Nd³⁺ ions emissions in ZnO nanocrystals, the 10 K PL excitation spectra were measured by monitoring the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition of Nd^{3+} at 898.5 nm. As shown in Figure 5(a), the PL excitation spectrum is dominated by an intense UV broad peak starting at 400 nm and centered at \sim 370 nm. This UV broad peak is attributed to the band gap and defects of ZnO nanocrystals and agrees well with the band gap value derived from the UV-vis reflectance spectrum for Nd³⁺-doped ZnO nanocrystals (Fig. 3(b)). A similar excitation broad band was observed in Eu³⁺-doped ZnO nanocrystals^{19,23} and ZnO thin films³² fabricated by the electrodeposition method. Additionally, the shape of the UV excitation peak for Nd³⁺-doped ZnO nanocrystals matches well that of the pure counterpart as shown in Figure 5(b), which further verifies that the Nd³⁺ emissions can be achieved via an efficient nonradiative energy transfer process from ZnO to Nd³⁺ ions. In addition to the broad ZnO band gap excitation peak centered at \sim 370 nm, direct excitation peaks arising from 4f-4f transitions of Nd^{3+} ions were observed as assigned in Figure 5(a). Sharp excitation peaks centered at 440.5, 484, 528, 543, 586, 604, 756, and 810 nm are attributed to the direct excitation of Nd^{3+} from the ground state ${}^{4}I_{9/2}$ to the excited states: ${}^{2}P_{1/2}$, ${}^{4}G_{9/2}$, ${}^{2}G_{9/2}$, ${}^{4}G_{7/2}$, ${}^{4}G_{5/2}$, ${}^{4'}S_{3/2} + {}^{4}F_{7/2}$, and ${}^{4'}F_{5/2} + {}^{2}H_{9/2}$, respectively. Note that the intensity of ZnO band gap excitation peak is stronger than that of direct excitation peaks of Nd³⁺ ions in the PL excitation spectra, which suggests that host sensitization is a more efficient way to excite Nd³⁺ ions than direct excitation of Nd³⁺ in ZnO nanocrystals even at 10 K. Because of the overlap between the emission lines of multiple sites of Nd³⁺ as revealed in Figure 4, no PL excitation spectrum for single

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Fig. 5. The 10 K excitation spectra of (a) Nd³⁺-doped ZnO nanocrystals and (b) pure ZnO nanocrystals.

luminescence center of Nd³⁺ can be selected under current experimental facilities. This is why we observed eight emission lines of ${}^{4}F_{3/2}$ to ${}^{4}I_{9/2}$ transition of Nd³⁺ under the 604-nm excitation.

3.4. Host-to-Nd³⁺ Energy Transfer

The RE³⁺ luminescence sensitized by the ZnO host (i.e., via a host-to-RE³⁺ energy transfer process) is of particular interest for materials applications. In this process, various types of defect states in semiconductors may play an important role.^{1,7,19,33} As illustrated in Eu³⁺-doped ZnO nanocrystals,^{3, 19} ZnO nanorods,³⁴ and nanosheetbased ZnO microspheres,²⁴ the introduction of proper trap centers (intrinsic or extrinsic defects) enables the host-to-RE³⁺ energy transfer. As shown in the excitation spectra (Fig. 5(a)), we observed a broad excitation band centered \sim 370 nm, which is attributed to the band gap and defects of ZnO nanocrystals,^{19,23} suggesting an energy transfer from the ZnO host to Nd³⁺ ions. Based on the PL and PL excitation spectra, a possible mechanism for the energy transfer from ZnO host to Nd³⁺ ions is proposed and schematically depicted in Figure 6. Upon the band gap excitation of ZnO nanocrystals, the absorbed UV photon leads to the formation of electron-hole pair (exciton) in ZnO host. The exciton recombination will transfer its energy to excited states of the defects. Some excited defects may transit its energy nonradiatively to the exited state of ²P_{3/2} of Nd³⁺, followed by nonradiative relaxation to ${}^{4}F_{3/2}$ of Nd³⁺, thereby NIR emissions of Nd³⁺ take



Fig. 6. Schematic illustration of the possible mechanism of energy transfer from ZnO host to Nd^{3+} . VB, CB, and DS were the abbreviations of valence band, conduction band, and defect states, respectively.

place (Fig 4(b)). Meanwhile, the de-excitation of another part of excited defects will result in the broad orange band centered at ~585 nm, which is in competition with the NIR emissions of Nd³⁺ and somewhat limits the energy transfer efficiency of host-to-Nd³⁺ as well as the intensity of NIR emissions of Nd³⁺. Similar defect-mediated energy transfer mechanism was already proposed to illustrate the luminescence of Eu³⁺ sensitized by ZnO¹⁹ nanocrystals and TiO₂⁷ nanostructures.

4. CONCLUSIONS

In summary, owing to different chemical properties between Nd³⁺ and Zn²⁺, the introduction of Nd³⁺ into the lattice of ZnO via the wet chemical method is still a great challenge at present. We have successfully used a modified sol-gel method to dope Nd³⁺ ions into the hexagonal ZnO nanocrystals that exhibit sharp and intense NIR luminescence of Nd³⁺. The optical properties of Nd³⁺ in ZnO nanocrystals were investigated in detail by virtue of fluorescence spectra at 10 K, which provided evidence for the existence of multiple luminescence centers of Nd³⁺ in ZnO nanocrystals. A defect-mediated energy transfer was found to sensitize the Nd³⁺ ions in ZnO nanocrystals and thus resulted in sharp and intense characteristic Nd³⁺ luminescence. Deep insight into optical properties of Nd³⁺-doped ZnO nanophosphors, particularly, the host-to-Nd³⁺ energy transfer, is of great importance to material applications such as optoelectronic devices.

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