

Hydrothermal Synthesis of $\text{GdVO}_4\text{:Ho}^{3+}$ Nanorods with a Novel White-light Emission

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A novel white-light phosphor $\text{GdVO}_4\text{:Ho}^{3+}$ was prepared via a simple hydrothermal reaction route. Under ultraviolet excitation, the as-prepared nanocrystals showed a broad band emission and sharp lines, which are associated with the oxygen vacancies around V^{4+} ions and the typical f-f transitions of Ho^{3+} ions, respectively. The coexistence of broad emission and sharp lines results in the bright white light with a quantum yield of 28%.

White-light phosphors featured by high efficiency, lower energy consumption, and good reliability have found many applications such as in backlight of the liquid-crystal display, automobile light, and solid-state lighting.^{1,2} There have been extensive reports on the methodologies to generate white light. The first approach is previously frequently used, which is based on the combination of blue-light-emitting diode emitting at 460 nm and yellow phosphors such as cerium-doped yttrium aluminum garnet (YAG:Ce).³ However, there still exist serious problems of poor color quality due to the scarcity of red light. An alternative approach is based on the red/green/blue tricolor or single-phased white-light phosphors under the excitation of ultraviolet wavelength. Nevertheless, in the tricolor system, other than the complexity involved in maintaining the appropriate proportions of the individual component in the blend, the blue-emission efficiency is usually poor because of the strong reabsorption effect.⁴ To get rid of these drawbacks mentioned above, the preparation of white-light phosphors with a single-phased structure is essential, which could be regarded as a promising route to fabricate the advanced light-emitting devices.

Till now, most literature works on the fabrication of single-phased white-light phosphors have been concentrated on Eu^{2+} and Mn^{2+} -codoped phosphors,^{5,6} which suffer from the high-temperature disposal and its resulting uncertain phase segregation and uncontrollability of morphology, size distribution, and even chemical composition.^{5,6} Since low-temperature hydrothermal reactions have merits of single-phase formation and homogeneous size distribution and since almost all nanocrystals have abundant surface defects, a combination of surface-defect emission and band-edge emission of hydrothermally prepared nanocrystals is expected to be promising in generating white light as that in CdS nanocrystals.⁷ Here, we explore this strategy to generate white light by taking advantages of the defect state emissions of nanoscale host and the typical transitions of the dopant ions. Since both constituent emissions are critically independent of the particle size, it is highly possible to use a single sample with wide particle size distribution. Moreover, although the defect state emissions are hard to change, the chromaticity can be well tuned by altering the relative proportion of dopant ions. Therefore, this plausible approach of generating novel white light could find many applications.

In this work, we present a facile hydrothermal preparation of $\text{GdVO}_4\text{:Ho}^{3+}$ nanorods which gave white-light emission under UV excitation.

The synthetic procedure for $\text{GdVO}_4\text{:Ho}^{3+}$ can be briefly described as follows. Solutions of $0.095 \text{ mol}\cdot\text{L}^{-1}$ $\text{Gd}(\text{NO}_3)_3$, $0.005 \text{ mol}\cdot\text{L}^{-1}$ $\text{Ho}(\text{NO}_3)_3$, and $0.05 \text{ mol}\cdot\text{L}^{-1}$ EDTA (30 mL) were mixed with the given amount of Na_3VO_4 solution (30 mL) to get a suspension. Then, the pH value was carefully adjusted to 9 by a well-defined NaOH solution to get a clear solution. CTAB (0.06 g) was added to this mixed solution with vigorous stirring. Finally, the clear solution was sealed in 25-mL Teflon-lined stainless steel autoclaves to react at 180°C for 12 h. The obtained product was washed with deionized water and ethanol several times and dried at 80°C for 3 h.

X-ray diffraction pattern (XRD) of the as-prepared $\text{GdVO}_4\text{:Ho}^{3+}$ nanocrystals is shown in Figure 1. It can be seen that all diffraction peaks can be readily indexed according to a hexagonal structure (space group $I4_1/amd$). The lattice constants are $a = 0.7128$ and $c = 0.6349$ nm, which are very close to the standard data for GdVO_4 (JCPDS 17-0260). No impurities were detected. The broad diffraction peaks in Figure 1 indicated the fine nature of the as-prepared samples. Based on the half height width of (020) peak, the particle size was calculated to be around 7.7 nm using the Scherrer formula.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images (Figure 2) indicated that the as-prepared nanocrystals are entirely composed of homogeneous nanorods with an average diameter of about 8 and length of 30–50 nm. The rod diameter was very close to that calculated from XRD data. HRTEM image (inset of Figure 1b) clearly shows that all nanorods were fully crystallized into tiny crystals with an interplanar spacing of about 0.357 and 0.358 nm, which are comparable with that of 0.359 nm for (020) plane.

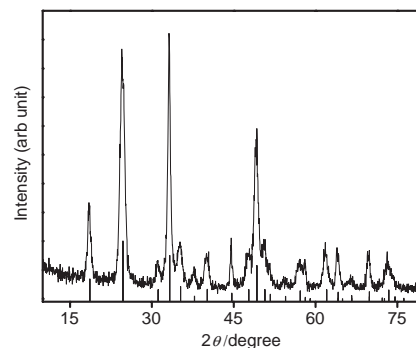


Figure 1. XRD pattern of $\text{GdVO}_4\text{:Ho}^{3+}$ nanocrystals, which was recorded using copper target ($\lambda = 1.5418 \text{ \AA}$). Vertical bars below the pattern denote the standard diffraction data of GdVO_4 .

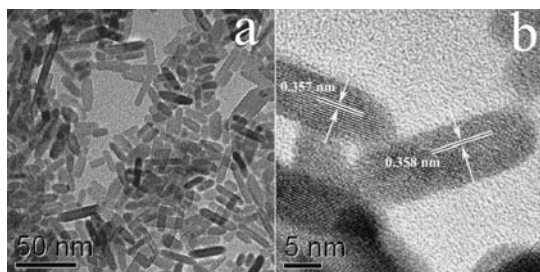


Figure 2. (a) TEM and (b) HRTEM images of $\text{GdVO}_4:\text{Ho}^{3+}$ nanocrystals.

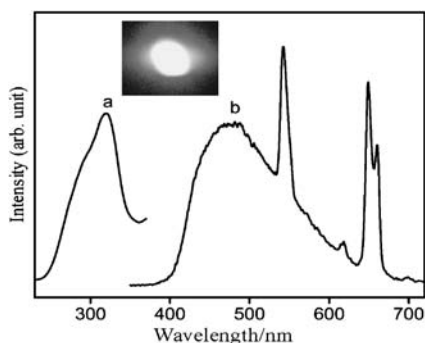


Figure 3. (a) PLE ($\lambda_{\text{em}} = 450 \text{ nm}$) and (b) PL ($\lambda_{\text{ex}} = 320 \text{ nm}$) spectra of $\text{GdVO}_4:\text{Ho}^{3+}$ nanocrystals. Inset presents a direct view photo of the nanocrystals when excited at 320 nm by a continuous Xe lamp.

Figure 3a shows the photoluminescence excitation (PLE) spectrum of $\text{GdVO}_4:\text{Ho}^{3+}$ nanocrystals. As illustrated in Figure 3a, a broad excitation band with a maximum intensity was observed at 320 nm, which is originated from a charge-transfer transition of VO_4^{3-} groups. The corresponding photoluminescence (PL) spectrum is shown in Figure 3b. A series of sharp lines was observed at 542, 616, and 649, 660 nm which are originated from the typical f–f transitions of $^5\text{S}_2\text{--}^5\text{I}_8$, $^5\text{F}_3\text{--}^5\text{I}_7$, and $^5\text{F}_5\text{--}^5\text{I}_8$ of Ho^{3+} ions, respectively. Surprisingly, a broad emission band in the range from 380 to 640 nm was also observed, showing a maximum intensity at 478 nm. A direct view photo of the sample under 320 nm excitation (inset of Figure 3) clearly indicates that the as-prepared $\text{GdVO}_4:\text{Ho}^{3+}$ exhibited a bright white-light emission which is remarkably different from the cyan color of the bulk counterparts (Figures S1 and S2)⁸ prepared by conventional solid-state reactions.

To interpret the origin of the bright white-light emission, we have to take into account the structural factors that are responsible for the luminescence properties. It is verified that under UV excitation, the excitation energy of unactivated YVO_4 crystal will readily migrate through VO_4^{3-} groups to a quenching site and dissipate nonradiatively. The thermally activated energy migration is very efficient so that no visible emission is observed at room temperature.⁹ These considerations lead us to conclude that GdVO_4 nanocrystals essentially do not show any visible emissions under UV excitation. Numerous publications have indicated that the vacancies or interstitial atoms in lattice usually result in the presence of a broad band emission.^{10,11} For instance, ZnS nanotubes exhibit a weak blue emission centered at 439 nm and a strong green emission at 538 nm, which derived from the

stoichiometric defects including self-activated centers, vacancy states, and interstitial states related to the peculiar nanostructures.¹¹ Therefore, it is likely that the broad emission of $\text{GdVO}_4:\text{Ho}^{3+}$ nanocrystals can be originated from the defect centers. Stanbury and co-workers reported on a broad emission at 475 nm in undoped YVO_4 crystals under excitation of 337 nm (N_2 laser), which was attributed to the oxygen vacancies.¹² On the other hand, Garces et al. systematically investigated the defect centers in YVO_4 crystals, such as $[\text{V}^{4+}]_{\text{A}}$, $[\text{V}^{4+}]_{\text{B}}$, and $[\text{V}^{4+}]_{\text{C}}$,¹³ and suggested that the $[\text{V}^{4+}]_{\text{A}}$ center is a V^{4+} ion adjacent to an oxygen vacancy. Moreover, Polosan et al. observed a broad emission centered at 440 nm for $\text{YVO}_4:\text{Ho}^{3+}$ crystals which is assigned to the $[\text{V}^{4+}]_{\text{A}}$ center.¹⁴ Therefore, the broad emission band observed here is probably related to the $[\text{V}^{4+}]_{\text{A}}$ centers in $\text{GdVO}_4:\text{Ho}^{3+}$ nanocrystals.

The quantum yield (QD) was determined by comparison with a standard (Rhodamine B in ethanol, QD = 0.55, as indicated by Kubin and Fletcher¹⁵) according to the method proposed by Donegá et al.¹⁶ It is seen that $\text{GdVO}_4:\text{Ho}^{3+}$ nanocrystals present a QD of 28%, which is related to the quenching effects of surface defects from high surface-to-volume ratio and hydroxy groups covered on the surfaces of nanocrystals.^{17,18}

In conclusion, we developed a novel white-light phosphor with the QD of 28% through a simple hydrothermal treatment. White-light emission can be produced by combination of broad band emission due to $[\text{V}^{4+}]_{\text{A}}$ center and sharp lines of Ho^{3+} transition. This strategy reported here is fundamentally important, which may open the realm of new possibilities for the development of the other kind of single-phased white-light phosphors and bring opportunities to high efficient emitting devices.

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