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## ARTICLE

# Multi-color Luminescence of Uniform CdWO<sub>4</sub> Nanorods through Eu<sup>3+</sup> Ion Doping

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Uniform Eu<sup>3+</sup> doped CdWO<sub>4</sub> nanorods were prepared via a simple hydrothermal method and characterized by X-ray diffraction, transmission electron microscopy, photoluminescence (PL) spectroscopy and PL lifetime measurement. The results indicate that the obtained Eu<sup>3+</sup> doped CdWO<sub>4</sub> nanorods have monoclinic phase structure, and the phase structure can be retained at Eu<sup>3+</sup> doping concentrations of 0.4%~4.0%. The diameter of nanorods decreases from 27 to 15 nm with an increase in the doping concentrations, and the morphology becomes irregular at the Eu<sup>3+</sup> doping concentration of 6.5%. Under the excitation of ultraviolet light, the relative intensities of blue-green emission ascribed to WO<sub>4</sub><sup>2-</sup> and red emission from Eu<sup>3+</sup> can be tuned through doping Eu<sup>3+</sup> ions into the CdWO<sub>4</sub> nanorods and thus altering the energy transfer between WO<sub>4</sub><sup>2-</sup> and Eu<sup>3+</sup>. Hence, the multi-color luminescence in a same host under single excited wavelength can be realized simply by altering the doping concentration of Eu<sup>3+</sup>. These luminescent nanomaterials may have potential applications in displays, light sources, bio-imaging and so on.

## Introduction

Metal tungstates have been widely investigated because of their potential applications in various fields, such as sensors, photonics, magnetic devices, photocatalysis, etc.<sup>1-8</sup> As one typical example among them, CdWO<sub>4</sub> has been considered to be a conventional functional material due to its high average refractive index, low radiation damage and excellent X-ray absorption coefficient.<sup>9</sup> To date, most efforts for the preparation of CdWO<sub>4</sub> have mainly been devoted to the forms of single crystals, powders and films, and accordingly the functional properties such as photocatalytic activity have been studied systematically.<sup>10-12</sup> For example, monoclinic and tetragonal structured CdWO<sub>4</sub> nanocrystals can be effectively synthesized by hydrothermal method, and the monoclinic CdWO<sub>4</sub> nanocrystal exhibited a much higher photocatalytic performance than the tetragonal one for degrading methyl orange under ultraviolet (UV) light illumination.<sup>13</sup> Furthermore, reduced graphene oxide (RGO) hybridized CdWO<sub>4</sub> shows much higher photocatalytic activity than pure CdWO<sub>4</sub> for methylene blue degradation, because the RGO can attract the photo-generated electrons and thus help to reduce the recombination rate of photo-generated charges.<sup>14</sup> Ye et al found that Eu<sup>3+</sup>-doped CdWO<sub>4</sub> could enhance photocatalytic activity in the photodegradation of methyl orange.<sup>15</sup> Recently, Eu<sup>3+</sup>-doped CdWO<sub>4</sub> nanocrystals have been synthesized as red phosphor for white-LED,<sup>16</sup> and Dai et al have investigated the surface defects and their influence on the structural and PL properties of CdWO<sub>4</sub>:Eu<sup>3+</sup> nanocrystals.<sup>17</sup> However, there are few papers reported on the

synthesis of uniform rare-earth ion (RE<sup>3+</sup>) doped CdWO<sub>4</sub> nanorods, and the energy transfer between CdWO<sub>4</sub> host and the doping RE<sup>3+</sup> has not investigated systematically. Moreover, the multi-color luminescence in CdWO<sub>4</sub> host through doping RE<sup>3+</sup> has not yet been reported. The intrinsic emission of CaWO<sub>4</sub> phosphor has been confirmed to present a broad emission band centred at ~420 nm due to electronic transitions of the charge-transfer type between oxygen and W<sup>6+</sup> within the anion complex WO<sub>4</sub><sup>2-</sup>, and CaWO<sub>4</sub>:Tb<sup>3+</sup> particles exhibit bright green emission arising from the efficient energy transfer from WO<sub>4</sub><sup>2-</sup> groups to Tb<sup>3+</sup> ions.<sup>18</sup> Similarly, RE<sup>3+</sup> doped CdWO<sub>4</sub> nanorods could exhibit a broad emission band of WO<sub>4</sub><sup>2-</sup> groups and line emissions corresponding to f-f transitions of RE<sup>3+</sup>, and the efficient energy transfer from WO<sub>4</sub><sup>2-</sup> groups in CdWO<sub>4</sub> nanorods to doping RE<sup>3+</sup> ions might be occurred as well.<sup>19,20</sup> The luminescent properties, such as multi-color luminescence and emission intensity of CdWO<sub>4</sub>:RE<sup>3+</sup> nanorods could possibly be controlled through altering the doping concentration and kinds of RE<sup>3+</sup> ion, and affecting the efficiency of energy transfer from WO<sub>4</sub><sup>2-</sup> groups to RE<sup>3+</sup>.

In this work, Eu<sup>3+</sup> doped CdWO<sub>4</sub> nanorods were successfully synthesized through a simple hydrothermal method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), PL and lifetime techniques. The obtained CdWO<sub>4</sub>:Eu<sup>3+</sup> nanorods are uniform and the diameter of these nanorods can be controlled by altering the doping concentrations of Eu<sup>3+</sup> ions. Furthermore, the luminescent color of CdWO<sub>4</sub> nanorods

can be tuned from blue-green to white and red emissions through altering the doping concentrations of  $\text{Eu}^{3+}$ . The multi-color luminescence of the same host under single excited wavelength can be realized by simply changing the doping concentrations of  $\text{Eu}^{3+}$ . These  $\text{CdWO}_4:\text{Eu}^{3+}$  nanorods with uniform size and prominent luminescence properties show promise for various applications in the fields of displays, bio-imaging and white-LEDs.

## Experimental

### Synthesis

All chemicals were used directly without further purification.  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (99.99%, analytical grade reagents, A. R.) and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  ( $\geq 99.0\%$ , A. R.) were obtained from Sinopharm Chemical Reagent Co., Ltd.  $\text{Eu}(\text{NO}_3)_3$  solution was prepared by dissolving  $\text{Eu}_2\text{O}_3$  (99.99%) in diluted nitric acid.  $\text{CdWO}_4$  nanorods were prepared by hydrothermal technique. Typically, 10.0 mL of 0.25 mol/L  $\text{Na}_2\text{WO}_4$  was added to 10.0 mL of 0.25 mol/L  $\text{Cd}(\text{NO}_3)_2$  aqueous solution and the mixture was continuously stirred for 0.5 h. The obtained suspension was then transferred into a Teflon bottle held in a stainless steel autoclave, which was sealed and hydrothermally treated at 160 °C for 22 h. After the autoclave was cooled to room temperature naturally, the precipitates were separated by centrifugation, washed with ethanol and distilled water twice respectively, and dried at 50 °C for 24 h to obtain the sample. Additionally,  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  samples with different dopant concentrations ( $x = 0.4, 1.2, 2.0, 4.0, 6.5$ ) were selected in order to investigate the effects of doping concentrations on the luminescent properties, morphology and phase structure. The synthesis procedure was similar to that mentioned above except that 10.0 mL of 0.25 mol/L  $\text{Na}_2\text{WO}_4$  was added to the mixed solutions of  $\text{Cd}(\text{NO}_3)_2$  and  $\text{Eu}(\text{NO}_3)_3$  with a desired molar ratio, and the other conditions were identical.

### Characterization

Phase structure was characterized by a Bruker D8 Advance X-ray diffractometer (XRD) with Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The accelerating voltage and emission current were 40 kV and 40 mA, respectively. The TEM image, selected area electron diffraction (SAED) pattern and energy dispersive X-ray spectrum (EDS) were obtained on a JEOL-2010 transmission electron microscope and JEOL-2100F scanning transmission electron microscope (STEM) equipped with an Oxford INCA x-sight EDS Si (Li) detector at an accelerating voltage of 200 kV. PL spectra and lifetime test were carried out using an FLS920P Edinburgh Analytical Instrument apparatus equipped with a 450 W Xenon lamp and a  $\mu\text{F}900\text{H}$  high-energy microsecond flash lamp as the excitation sources. Quantum yields of the samples were measured using a  $\text{BaSO}_4$ -coated integrating sphere of diameter 15 cm in FLS920 based on the absolute method. Excitation 290 nm and emission at 475 or 615 nm were selected. The slit widths for the excitation and emission tests were fixed at 5.0 and 0.2 nm, respectively. The step size was 0.2 nm and the integration time was 0.3 s. All of the measurements were performed at room temperature.

## Results and discussion

The phase structure of undoped and  $\text{Eu}^{3+}$  doped  $\text{CdWO}_4$  nanorods were analyzed by XRD technique. Fig. 1a shows the XRD patterns of  $\text{CdWO}_4:\text{Eu}^{3+}$  nanorods with the doping concentrations of 0%, 0.4%, 1.2%, 2.0%, 4.0% and 6.5%. When the doping concentration of  $\text{Eu}^{3+}$  was less than 6.5%, all the diffraction peaks in the patterns matched well with the standard data for the monoclinic structure of bulk  $\text{CdWO}_4$  (JCPDS No. 14-0676) with the space groups of P2/c. No peaks corresponding to any other phases or impurities were detected, suggesting the high purity of these samples within the doping concentration range from 0.4% to 4.0%. In this phase structure, each W is surrounded by four nearest oxygen ions and two more distant ones in approximately octahedral coordination to form a  $\text{WO}_6^{6-}$  molecular complex.<sup>13</sup> However, when increasing the  $\text{Eu}^{3+}$  doping concentration to 6.5%, several weak diffraction peaks marked as star were present, which is identified to the monoclinic phase of  $\text{Eu}_2\text{O}_3$  (JCPDS No. 34-0072). Fig. 1b shows the (-111) and (111) diffraction peaks of  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  in the measured range of  $2\theta = 28^\circ\sim 31^\circ$ , and the diffraction peaks of  $\text{CdWO}_4$  are shifted slightly to the higher angle with an increase in  $\text{Eu}^{3+}$  doping concentration. The ionic radii of  $\text{Cd}^{2+}$  with 6 CN (CN = coordination number) in monoclinic phase is 0.95 Å, which is slightly larger than that of the corresponding  $\text{Eu}^{3+}$  ion (0.947 Å).<sup>21,22</sup> Hence, it is reasonable to observe the peak shift towards higher  $2\theta$ , and to some extent the results might imply that  $\text{Eu}^{3+}$  is homogeneously incorporated into the lattice of  $\text{CdWO}_4$  and occupied the sites of  $\text{Cd}^{2+}$ . Due to the close ionic radii of  $\text{Cd}^{2+}$  and  $\text{Eu}^{3+}$  ions, the values of the calculated lattice parameters and unit cell volume of  $\text{Eu}^{3+}$  doped  $\text{CdWO}_4$  nanorods are very similar to those of the undoped sample, as listed in Table 1. When  $\text{Eu}^{3+}$  ions are doped into the  $\text{CdWO}_4$  host lattice, they would chemically non-equivalently substitute the  $\text{Cd}^{2+}$  sites, thus an excess of positive charge in the lattice must be compensated. One possible way is that two  $\text{Eu}^{3+}$  ions replace three  $\text{Cd}^{2+}$  ions to balance the charge of this compound, which creates two  $\text{Eu}_{\text{Cd}}^{\circ}$  positive defects and one  $\text{V}_{\text{Cd}}^{-}$  negative defect as follows:<sup>20,23</sup>



The oxygen adjacent to the  $\text{Cd}^{2+}$  might slightly deviate the original lattice site, which probably leads to the distortion of the  $\text{WO}_6^{6-}$  molecular complex in order to accommodate the positive and negative defects.

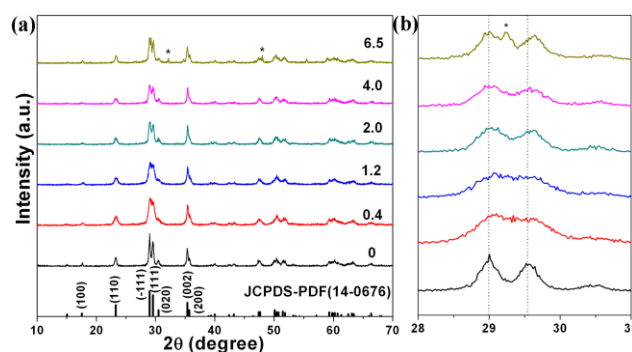


Fig. 1 (a) XRD patterns of  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  with different concentrations ( $x = 0, 0.4, 1.2, 2.0, 4.0, 6.5$ ) and the standard data for bulk  $\text{CdWO}_4$  (JCPDS card No. 14-0676); (b) Diffraction peak positions of  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  in the range of  $2\theta = 28^\circ$  to  $31^\circ$  (The secondary phase marked by “\*”).

Table 1 Lattice parameters and unit cell volume of  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  with different concentrations ( $x = 0, 0.4, 1.2, 2.0, 4.0, 6.5$ )

Samples	Lattice parameters			unit cell volume( $\text{\AA}^3$ )
	a (nm)	b (nm)	c (nm)	
$\text{CdWO}_4$	0.5017	0.5852	0.5067	148.77
$\text{CdWO}_4:0.4\%\text{Eu}^{3+}$	0.5038	0.5836	0.5074	149.14
$\text{CdWO}_4:1.2\%\text{Eu}^{3+}$	0.5035	0.5849	0.5071	149.31
$\text{CdWO}_4:2.0\%\text{Eu}^{3+}$	0.5046	0.5859	0.5079	150.11
$\text{CdWO}_4:4.0\%\text{Eu}^{3+}$	0.5022	0.5845	0.5060	148.47
$\text{CdWO}_4:6.5\%\text{Eu}^{3+}$	0.5018	0.5852	0.5073	148.92

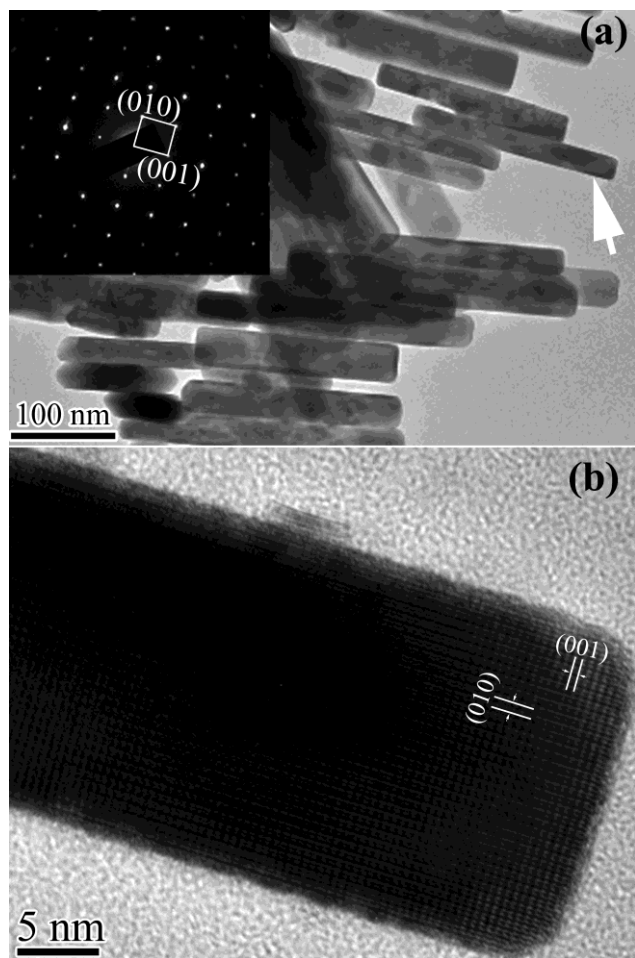


Fig. 2 (a) TEM and (b) HRTEM images of  $\text{CdWO}_4$  nanorods (Inset is the SAED of the single nanorod).

Fig. 2 shows typical TEM images of undoped  $\text{CdWO}_4$  nanorods. It can be clearly seen from Fig. 2a that the obtained sample is composed of uniform nanorods with the diameter of  $\sim 27$  nm and the

length of  $\sim 200$  nm. The SAED pattern (Fig. 2a, inset) taken from the upper single nanorod can be indexed to the (010) and (001) planes of  $\text{CdWO}_4$  single crystalline with the monoclinic phase structure. These findings are consistent with the XRD result as above illustrated. The HRTEM image (Fig. 2b) of the single  $\text{CdWO}_4$  nanorod marked as an arrow in Fig. 2a displays single crystalline nature. The values of interplanar spacing of  $\text{CdWO}_4$  nanorod are 0.586 and 0.507 nm, which is identical to the (010) and (001) facet distance of bulk  $\text{CdWO}_4$  powders, respectively. The growth direction of  $\text{CdWO}_4$  single crystalline nanorod is along the direction perpendicular to (001) plane.

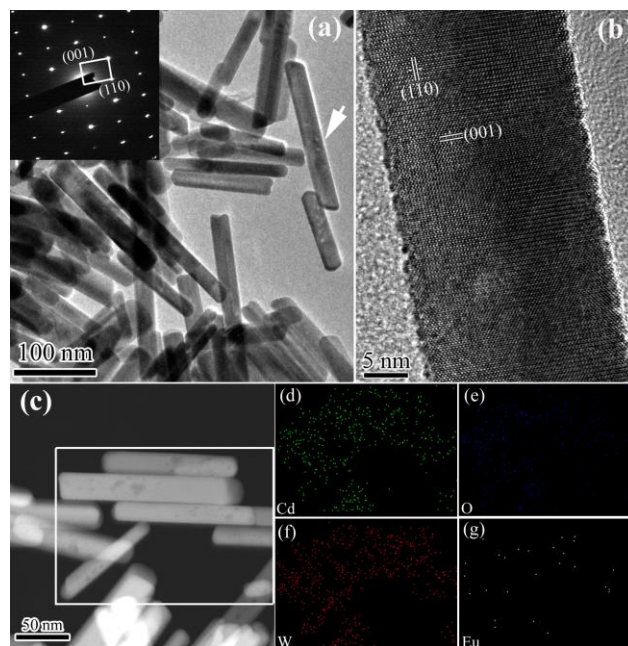


Fig. 3 (a) TEM and (b) HRTEM images of  $\text{CdWO}_4:2.0\%\text{Eu}^{3+}$  nanorods (Inset is the SAED of the single nanorod); (c) STEM-HAADF image of  $\text{CdWO}_4:2.0\%\text{Eu}^{3+}$  nanorods, and (d–g) EDS element mappings for Cd, O, W and Eu of the nanorods shown in (c) respectively.

The morphology of  $\text{CdWO}_4$  nanorods is not changed prominently when the doping concentration of  $\text{Eu}^{3+}$  is at a relatively low concentration range of 0.4%  $\sim$  4%. Fig. 3 shows typical TEM images and EDS element mappings of  $\text{CdWO}_4:2.0\%\text{Eu}^{3+}$  nanorods. It can be seen that the morphology of  $\text{CdWO}_4:2.0\%\text{Eu}^{3+}$  is similar to that of the undoped sample, composed of nanorods with the diameter of  $\sim 25$  nm and the length of  $\sim 150$  nm. The SAED pattern (Fig. 3a, inset) taken from a single nanorod can be indexed to the (110) and (001) planes of  $\text{CdWO}_4$  single crystalline with the monoclinic phase structure. From the HRTEM image of a single  $\text{CdWO}_4:2.0\%\text{Eu}^{3+}$  nanorod, it can be measured that the interplanar spacing is about 0.507 nm and 0.382 nm, corresponding to the (001) and (110) planes of  $\text{CdWO}_4$ , respectively, and the growth direction of the single crystalline  $\text{CdWO}_4:2.0\%\text{Eu}^{3+}$  nanorod is along the direction perpendicular to (001) plane as well. Fig. 3c shows the morphology of  $\text{CdWO}_4:2.0\%\text{Eu}^{3+}$  nanorods acquired in STEM-HAADF (high angle annular dark field) topology mode. The EDS element

mappings of Cd (Fig. 3d), O (Fig. 3e), W (Fig. 3f) and Eu (Fig. 3g) elements show that the nanorods are composed of Cd, O and W elements with doped Eu randomly. It indicates that the  $\text{Eu}^{3+}$  doping at relatively low concentrations has little effect on the phase structure, single crystalline feature and the growth direction of  $\text{CdWO}_4$  nanorods. However, the values of the width and length of  $\text{CdWO}_4$  nanorods showed a decrease trend when increasing  $\text{Eu}^{3+}$  doping concentrations, and the morphology of  $\text{CdWO}_4$  nanorods became irregular when the  $\text{Eu}^{3+}$  doping concentration was increased up to 6.5%, as shown in Fig. S1 (ESI<sup>†</sup>). The reason that the size of nanorods gradually decreases with an increase in doping concentration may be partly attributed to the strong effect of the dopant ion on the crystal growth rate through surface charge modification.<sup>24</sup> This size evolution trend of nanorods is consistent with previous reports on the  $\text{Gd}^{3+}$  or  $\text{Eu}^{3+}$  doped  $\text{NaYF}_4$  and  $\text{Ce}^{3+}$  doped  $\text{LaPO}_4$  nanorods.<sup>24-26</sup>

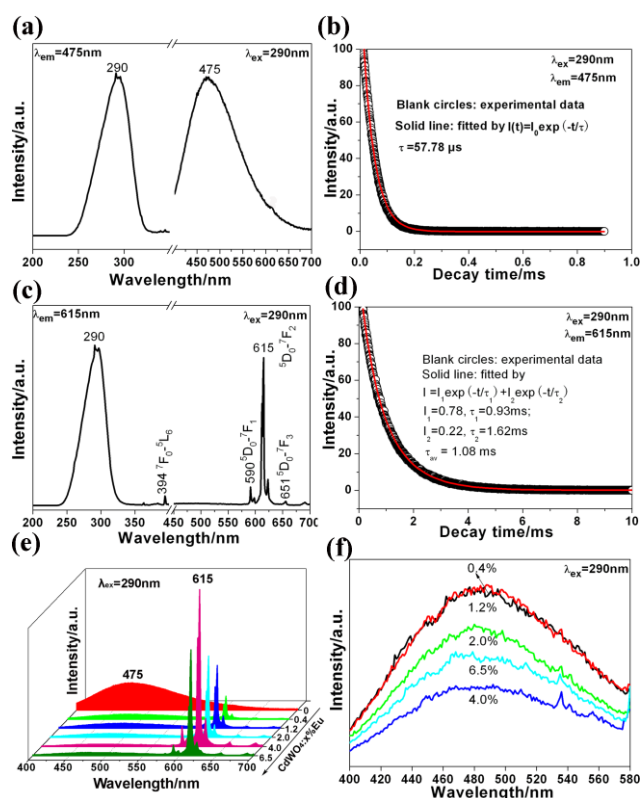


Fig. 4 (a) PL excitation and emission spectra and (b) luminescent decay curve of  $\text{CdWO}_4$  nanorods, (c) PL excitation and emission spectra and (d) luminescent decay curve of  $\text{CdWO}_4:4.0\%\text{Eu}^{3+}$  nanorods, and (e, f) PL emission spectra of  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  samples with different doping concentrations.

The luminescent properties of the undoped and  $\text{Eu}^{3+}$  doped  $\text{CdWO}_4$  samples were investigated by PL spectra and decay curves. In Fig. 4a (left), an intense excitation band from 230 to 350 nm with a maximum at 290 nm is observed, which is attributed to the charge transfer transition from the oxygen (O) 2p orbits to one of the empty tungsten (W) 5d orbits within the  $\text{WO}_4^{2-}$  groups.<sup>27,28</sup> Excited by 290 nm UV light,  $\text{CdWO}_4$  nanorods exhibit a blue-green emission band in the range of 400~700 nm with the emission peak centred at 475

nm, as shown in Fig. 4a (right). The PL decay curve of  $\text{CdWO}_4$  nanorods (Fig. 4b) can be well fitted into a single exponential function as

$$I(t) = I_0 \exp(-t/\tau) \quad (2)$$

where  $I_0$  is the initial intensity at  $t = 0$ ,  $\tau$  is the  $1/e$  lifetime of the lanthanide ions. The lifetime ( $\tau$ ) of  $\text{CdWO}_4$  nanorods is determined to be 57.78  $\mu\text{s}$ .

Fig. 4c (left) shows the excitation spectrum of  $\text{CdWO}_4:4.0\%\text{Eu}^{3+}$  nanorods. Similarly, the excitation spectrum monitored at 615 nm shows a broad excitation band at the range of 230~350 nm with the peak at 290 nm, which is assigned to the  $\text{O} \rightarrow \text{W}$  ligand-to-metal charge transfer from  $\text{WO}_4^{2-}$  groups.<sup>29,30</sup> Meanwhile, the excitation peak at around 394 nm is assigned to the  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  transitions of  $\text{Eu}^{3+}$  ions. The emission spectrum (Fig. 4c, right) is mainly composed of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  ( $J = 1, 2, 3$ ) emission lines of  $\text{Eu}^{3+}$  ions from 550 to 700 nm. Compared with the emission peaks of  $\text{Eu}^{3+}$ , the intrinsic blue-green emission from  $\text{WO}_4^{2-}$  groups is very weak, suggesting the existence of an efficient energy transfer from  $\text{WO}_4^{2-}$  groups to the doping  $\text{Eu}^{3+}$ . It is known that the relative intensities of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  emissions are very sensitive to the detailed nature of ligand environment.<sup>31,32</sup> On a site without inversion symmetry, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  electric dipole transition is strongest. The electric dipole transition is allowed only under the condition that the  $\text{Eu}^{3+}$  ion occupies a site without an inversion centre.<sup>33</sup> In the  $\text{CdWO}_4:4.0\%\text{Eu}^{3+}$  nanorods, the  $\text{Eu}^{3+}$  ions occupy the  $\text{Cd}^{2+}$  ions lattice at a site without inversion symmetry in  $\text{CdWO}_4$  matrix, therefore the dominated emission centred at 615 nm corresponds to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  electric dipole transition.<sup>34</sup>

The luminescent decay curve of  $\text{CdWO}_4:4.0\%\text{Eu}^{3+}$  nanorods (Fig. 4d) can be well fitted into the following double exponential function instead of a single exponential function.

$$I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \quad (3)$$

where  $I_1$  and  $I_2$  are the intensities at different time interval, while  $\tau_1$  and  $\tau_2$  are their corresponding lifetimes. For solid-state luminescent materials in which there exists energy transfer process, when the host materials or sensitizers are excited (indirect excitation), some luminescence decay curves from the rare-earth activator could follow non-exponential function (eq. 4) in the case of  $\text{GdPO}_4: \text{Tb}^{3+}/\text{Ce}^{3+}$ ,  $\text{CaMoO}_4: \text{Tb}^{3+}$ ,  $\text{LaVO}_4: \text{Eu}^{3+}$ , etc.,

$$I = I_0 e^{-(t/\tau - Dt^{0.5})} \quad (4)$$

where  $D$  is related to diffusion and energy transfer.<sup>22,35</sup> At the same time, there are other luminescence decay curves that obey double exponential function in many luminescence materials, such as rare earth tungstate and molybdate compounds, lanthanide-doped upconversion nanoparticles, and so on.<sup>36</sup> It should be denoted that the luminescence decay behavior might simultaneously follow the double exponential function and non-exponential function even for the same luminescent materials (like  $\text{CaMoO}_4: \text{Tb}^{3+}$  nanoparticles), except for the slight difference of the parameter goodness.<sup>35a</sup> As for  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  nanorods, there exists an energy transfer from

WO<sub>4</sub><sup>2-</sup> to Eu<sup>3+</sup> excitation at 290 nm, and this is followed by the luminescence decay from <sup>5</sup>D<sub>0</sub> level of Eu<sup>3+</sup>. It can be seen from Fig. S2 (ESI†) that all luminescent decay curves of CdWO<sub>4</sub>:x%Eu<sup>3+</sup> (x = 0.4, 1.2, 2.0, 4.0, 6.5) can be well fitted into the double exponential function, and the goodness of parameter is found to be 0.9997, 0.9993, 0.9995, 0.9995 and 0.9995, respectively. These values of the parameter goodness are well enough and the double exponential fitting is satisfying, although the luminescent decay curves of CdWO<sub>4</sub>:x%Eu<sup>3+</sup> might follow the non-exponential behavior as well. Parchur *et al.*<sup>35a,37</sup> reported that if the particles are spherical, the sphere can be divided into two shells of equal volume. Inner shell ions have a longer lifetime than outer shell ions. Based on this, the average lifetime  $\tau_{av}$  can be calculated using the following equation:

$$\tau_{av} = (I_1\tau_1^2 + I_2\tau_2^2)/(I_1\tau_1 + I_2\tau_2) \quad (5)$$

However, for the luminescent materials with non-spherical morphology such as CdWO<sub>4</sub>:Eu<sup>3+</sup> nanorods in this work, the average lifetime  $\tau_{av}$  can be determined by the formula as<sup>38</sup>

$$\tau_{av} = \sum A_i\tau_i/A_i = (I_1\tau_1 + I_2\tau_2) / (I_1 + I_2) \quad (6)$$

The energy transfer from WO<sub>4</sub><sup>2-</sup> groups to the doping Eu<sup>3+</sup> in CdWO<sub>4</sub>:Eu<sup>3+</sup> nanorods can be used to change the relative intensity of blue-green emission (WO<sub>4</sub><sup>2-</sup>) and red emission (Eu<sup>3+</sup>), and hence multi-color luminescence is realized. The effect of Eu<sup>3+</sup> doping concentrations on the relative intensity of blue-green (WO<sub>4</sub><sup>2-</sup>) and red emissions (Eu<sup>3+</sup>) in CdWO<sub>4</sub>:Eu<sup>3+</sup> samples is shown in Fig. 4e. With increasing Eu<sup>3+</sup> doping concentrations from 0.4% to 6.5%, the emission intensity of Eu<sup>3+</sup> at 615 nm increases gradually until a maximum emission is reached at 4.0%, and then decreases at 6.5%. The decrease in emission intensity of Eu<sup>3+</sup> is mainly due to the known concentration quenching effect at higher Eu<sup>3+</sup> doping concentration. Correspondingly, the emission intensity of WO<sub>4</sub><sup>2-</sup> groups at 475 nm decreases gradually, reaches a minimum value at 4.0%, and then increases at 6.5%, as shown in Fig. 4f. The contrary changes in the relative intensity between blue-green and red emissions as a function of Eu<sup>3+</sup> concentration increase also suggests the existence of energy transfer from WO<sub>4</sub><sup>2-</sup> groups to the doping Eu<sup>3+</sup>. It should be denoted that the multi-color luminescence properties for CdWO<sub>4</sub>:Eu<sup>3+</sup> nanorods could be further improved via optimizing the Eu<sup>3+</sup> doping concentration.

In order to further prove the energy transfer between WO<sub>4</sub><sup>2-</sup> groups and Eu<sup>3+</sup>, the luminescence decay curves for <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> emission (615 nm) of CdWO<sub>4</sub>:x%Eu<sup>3+</sup> samples excited at 290 and 394 nm were measured, respectively. As mentioned above, when the WO<sub>4</sub><sup>2-</sup> groups was excited with 290 nm UV light, all luminescence decay curves of CdWO<sub>4</sub>:x%Eu<sup>3+</sup> samples can be fitted into a double exponential behavior (For comparison, the luminescence decay curves and the fitted results of CdWO<sub>4</sub>:0.4%Eu<sup>3+</sup> and CdWO<sub>4</sub>:4.0%Eu<sup>3+</sup> were also given in Fig. S3 (a) and (c), ESI†). The values of the average lifetime determined by Eq. (6) were listed in Table S1 (ESI†). However, when the doping Eu<sup>3+</sup> ions were excited with 394 nm UV light, all luminescence decay curves of these samples can be fitted into a single exponential function as Eq. (2),

and the decay curves, the fitted results and the lifetimes were given in Fig. S3 (b, d) and Table S1 (ESI†), respectively. The decay behaviors at different excitation wavelength also indicate the existence of energy transfer between WO<sub>4</sub><sup>2-</sup> groups and Eu<sup>3+</sup> in CdWO<sub>4</sub>:Eu<sup>3+</sup> samples. It is observed from Table S1 (ESI†) that the lifetime values increase when changing Eu<sup>3+</sup> doping concentrations up to 4.0%, similar to the observation on the emission spectra of the samples under 290 nm excitation.<sup>39</sup> Moreover, the lifetime values measured under 394 nm excitation is shorter than those under 290 nm excitation. The obtained results here are consistent with the previous reports.<sup>40</sup>

The luminescence decay curves of host materials in the Eu<sup>3+</sup> doped samples ( $\lambda_{ex} = 290$  nm,  $\lambda_{em} = 475$  nm) can also be well fitted into a single exponential function (Fig. S3 e and f) (ESI†), similar to that of the undoped CdWO<sub>4</sub> nanorods. However, it is noticeable that the lifetime values of CdWO<sub>4</sub>:x%Eu<sup>3+</sup> (x = 0.4, 1.2, 2.0, 4.0 and 6.5) are shorter compared to undoped CdWO<sub>4</sub> nanorods in Table 2. It is apparent that the energy transfer is occurred from WO<sub>4</sub><sup>2-</sup> groups to Eu<sup>3+</sup>. Using these lifetime values, a simple operational definition of energy transfer efficiency ( $\eta_{ET}$ ) and energy transfer rate ( $\omega_{ET}$ ) of WO<sub>4</sub><sup>2-</sup>-Eu<sup>3+</sup> can be determined by<sup>41</sup>

$$\eta_{ET} = 1 - \frac{\tau_s}{\tau_{s0}} \quad (7)$$

$$\omega_{ET} = \frac{1}{\tau_s} - \frac{1}{\tau_{s0}} \quad (8)$$

where  $\tau_s$  and  $\tau_{s0}$  are the lifetimes of WO<sub>4</sub><sup>2-</sup> with doped and undoped Eu<sup>3+</sup> respectively. The values of  $\eta_{ET}$  and  $\omega_{ET}$  are summarized in Table 2.

Table 2 Luminescence lifetime ( $\tau$ ), energy transfer efficiency ( $\eta_{ET}$ ) and energy transfer rate ( $\omega_{ET}$ ) of CdWO<sub>4</sub>:x%Eu<sup>3+</sup> (x = 0, 0.4, 1.2, 2.0, 4.0 and 6.5) with  $\lambda_{ex} = 290$  nm and  $\lambda_{em} = 475$  nm.

Sample	$\tau/\mu\text{s}$	$\eta_{ET}$	$\omega_{ET}/\text{s}^{-1}$
CdWO <sub>4</sub>	57.78		
CdWO <sub>4</sub> :0.4%Eu <sup>3+</sup>	15.16	73.8%	$4.86 \times 10^4$
CdWO <sub>4</sub> :1.2%Eu <sup>3+</sup>	15.01	74.0%	$4.93 \times 10^4$
CdWO <sub>4</sub> :2.0%Eu <sup>3+</sup>	15.92	72.4%	$4.55 \times 10^4$
CdWO <sub>4</sub> :4.0%Eu <sup>3+</sup>	15.16	73.8%	$4.86 \times 10^4$
CdWO <sub>4</sub> :6.5%Eu <sup>3+</sup>	11.72	79.7%	$6.81 \times 10^4$

The energy transfer process in CdWO<sub>4</sub>:Eu<sup>3+</sup> is shown in Fig. 5. When excited by UV at 290 nm, electrons in the ground state (<sup>1</sup>A<sub>1</sub>) are excited into the <sup>1</sup>B (<sup>1</sup>T<sub>2</sub>) level of WO<sub>4</sub><sup>2-</sup>. The electrons in excited state can either relax to the lowest excited <sup>1</sup>B (<sup>1</sup>T<sub>2</sub>) level of WO<sub>4</sub><sup>2-</sup>, producing the emission through the transition to the <sup>1</sup>A<sub>1</sub> level, or transfer the excited energy to the level of <sup>5</sup>D<sub>3</sub> or higher levels in Eu<sup>3+</sup> through a resonance process.<sup>19</sup> The energy nonradiatively relaxes from these high energy levels to the <sup>5</sup>D<sub>0</sub> level by multiphonon relaxation. Then the characteristic emissions of Eu<sup>3+</sup> due to <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>J</sub> (J = 1, 2, 3, 4) transitions are occurred.<sup>42-44</sup>

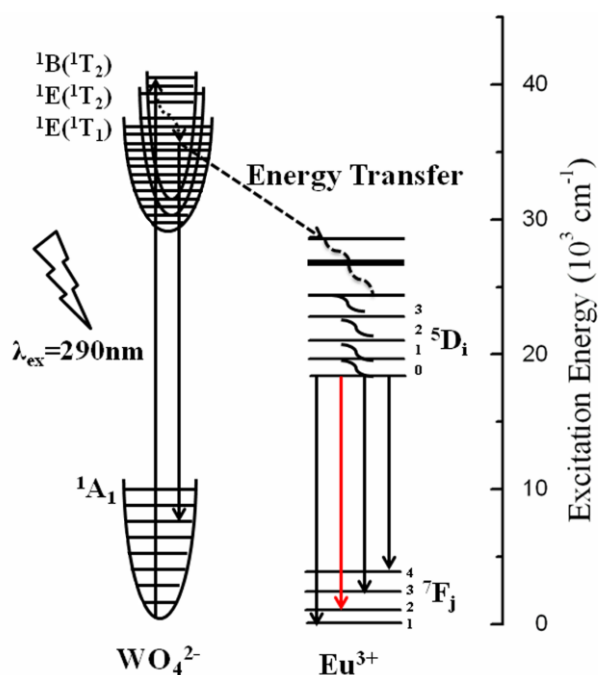


Fig. 5 Energy level scheme for  $\text{WO}_4^{2-}$  group and the energy transfer process from  $\text{WO}_4^{2-}$  to  $\text{Eu}^{3+}$  as well as the emission process from  $\text{Eu}^{3+}$ .

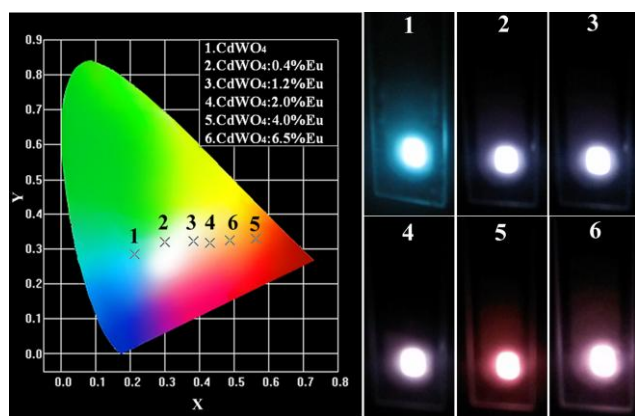


Fig. 6 CIE chromaticity diagram and luminescence photographs of  $\text{CdWO}_4:\text{Eu}^{3+}$  with different doping concentrations (0%, 0.4%, 1.2%, 2.0%, 4.0%, 6.5%).

The CIE diagram of the  $\text{CdWO}_4$  with different  $\text{Eu}^{3+}$  doping concentrations is shown in Fig 6 (left). It can be seen that  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  ( $x = 0, 0.4, 1.2, 2.0, 4.0, 6.5$ ) can emit blue-green, white, white, light red, bright red and dark red, respectively.  $\text{CdWO}_4:4.0\%\text{Eu}^{3+}$  nanorods show bright and high color saturation because the  $^5\text{D}_0\text{-}^7\text{F}_2$  transition of  $\text{Eu}^{3+}$  increases to the maximum at the doping concentration of 4.0%. The PL quantum efficiency of the  $\text{CdWO}_4$  host,  $\text{CdWO}_4:0.4\%\text{Eu}^{3+}$  and  $\text{CdWO}_4:4.0\%\text{Eu}^{3+}$  nanorods are 30.35%, 2.07% and 9.75%, respectively. Fig. 6 (right) gives the emitting photographs of  $\text{CdWO}_4:x\%\text{Eu}^{3+}$  samples under the irradiation of 290 nm UV light, corresponding to the sample points as shown in CIE chromaticity diagram.

## Conclusion

In summary, uniform undoped or  $\text{Eu}^{3+}$  doped  $\text{CdWO}_4$  nanorods have been prepared by a simple hydrothermal method and further characterized by various techniques of structure and luminescence. The  $\text{CdWO}_4$  based samples have monoclinic phase structure at the doping concentrations of 0.4%~4.0%, and the nanorod-like morphology can be maintained when the doping concentration is lower than 6.5%. Due to the combination of the relative intensities from blue-green emission in intrinsic  $\text{WO}_4^{2-}$  complex and red emission in doping  $\text{Eu}^{3+}$  ions, the multi-color luminescence can be realized in the same  $\text{CdWO}_4$  host under single excited wavelength simply via altering  $\text{Eu}^{3+}$  doping concentration. These luminescent nanomaterials may have a potential for the applications in displays, light sources, bio-imaging and so on.

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## Notes and references

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†Electronic Supplementary Information (ESI) available: [TEM images of  $\text{CdWO}_4$ ,  $\text{CdWO}_4:2.0\%\text{Eu}^{3+}$ ,  $\text{CdWO}_4:4.0\%\text{Eu}^{3+}$  and  $\text{CdWO}_4:6.5\%\text{Eu}^{3+}$  samples, luminescence decay curves and lifetimes]. See DOI: 10.1039/b000000x/

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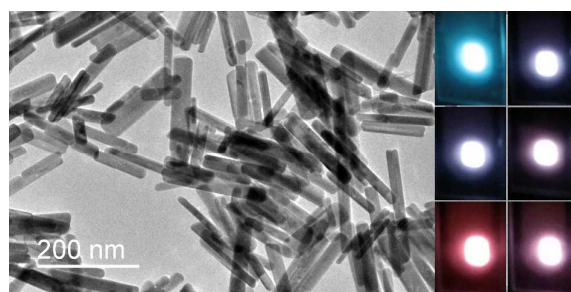


## Multi-color Luminescence of Uniform CdWO<sub>4</sub> Nanorods through Eu<sup>3+</sup> Ion Doping

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Lin Jin,<sup>a</sup> Yurong Shi,<sup>a</sup> Zhenling Wang,<sup>\*,a</sup> Jianhua Hao<sup>\*,d</sup>

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Multi-color luminescence of uniform CdWO<sub>4</sub>: Eu<sup>3+</sup> nanorods can be realized only through altering the doping concentration of Eu<sup>3+</sup> ions.



TOC Figure