

Synthesis and characterization of $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors

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$\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors were synthesized via a sol-gel method. The morphology and structure of the $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphor have been investigated by transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FT-IR). The result indicated that TiO_2 layer with 25 nm was uniformly coated over the phosphors surface. Meanwhile, $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors showed obviously thermal stability compared to $\text{CaMoO}_4:\text{Eu}^{3+}$ phosphors, indicating it is an effective way to improve the useful lifetime of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors.

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Molybdates have been found to be excellent and versatile phosphor hosts, owing to their chemical stability, broad and intense charge transfer band (CTB) in the near ultraviolet (NUV) region [1-2]. In order to seek for a highly-efficient red-emitting phosphor, much attention has been paid to Eu^{3+} -activated molybdate phosphors [3-5]. According to the previous literature, $\text{CaMoO}_4:\text{Eu}^{3+}$ has been reported as a potential candidate due to its satisfactory chromaticity coordinates, excellent thermal and chemical stability [6-7]. The study found that $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors prepared by co-precipitation method have better morphology and luminescent properties than that synthesized by traditional solid-state reaction method, but the drawbacks of large luminous decay and instability of particles surface are still far from the ideally phosphors. In order to overcome these drawbacks, a possible way is to coat the surface of $\text{CaMoO}_4:\text{Eu}^{3+}$ phosphor particles with a very thin oxide layer. Several nano oxide layer coating on phosphor had been applied to enhance the chemical stability and improve the luminescence characteristics, for example In_2O_3 , ZnO , Y_2O_3 , and SiO_2 , etc. [8-15]. TiO_2 is expected to be one of the candidates for the coating materials because it is chemically stable, resistance to water. TiO_2 coating could offer stable protection to the phosphor cores from degradation and can passivate surface recombination centers to keep luminescent efficiency, and then improve thermal stability and prolong the lifetime [16-18]. Therefore, $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors should deliver good thermal stability. Especially, the effect of the

TiO_2 layer on the optical properties of $\text{CaMoO}_4:\text{Eu}^{3+}$ phosphor has never been studied.

In this paper, $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors were synthesized via a sol-gel process. Detailed characterizations for the structure, morphology, luminescent properties and thermal stability of the samples were performed.

$\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphor was prepared by co-precipitation method according to the previous literature [19]. Tetra-n-butyl Titanate (A.R.), CH_3COOH (A.R.), $\text{CH}_3\text{CH}_2\text{OH}$ (A.R.) and distilled water were mixed uniformly at volume ratio of 1:1:10:3 and the pH of mixed solution was adjusted with 1mol/l HCl to 5. The obtained solution was heated in 85°C water bath with continuously stirring, until the solution turns into gel. A certain amount of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors were added into the gel with a peristaltic pump (flow 5mL/min). Finally, the phosphors were dried at 120°C for 1h and presintered at 300°C for 2h, and then $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors were obtained.

The surface structure of samples were carried out by Tecnai G2F20 field emission transmission electron microscope. Using X-ray diffraction with Cu $K\alpha$ radiation ($\lambda=0.15405$ nm) to study the effect of coating on the structure of phosphors, and the accelerating voltage and emission current were respectively 40 kV and 30mA. FT-IR spectra were characterized by MAGNA-IR 550 IR spectrophotometer with KBr pellet technique. The composition of phosphors was analyzed by INCA Energy 350 EDS. The photoluminescence was characterized by RF-5301 fluorescence spectrometer with a xenon lamp as

excitation source. All the measurements were performed at room temperature.

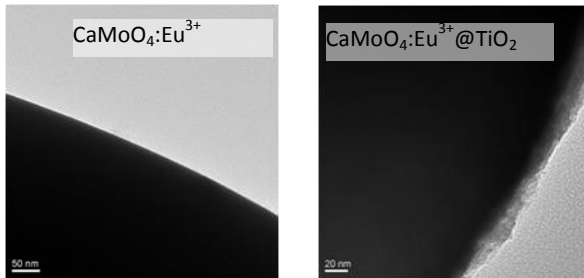


Fig. 1. TEM of $\text{CaMoO}_4:\text{Eu}^{3+}$ and $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2

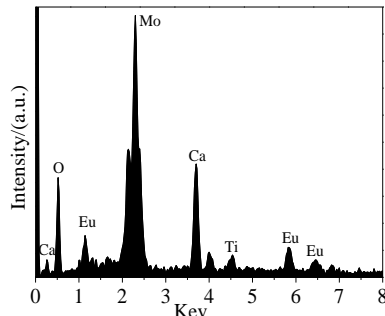


Fig. 2. EDS of $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors

Fig. 1 gives The TEM of $\text{CaMoO}_4:\text{Eu}^{3+}$ and $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 . It shows that the surface of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors is smooth without attachments, while the surface of the $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors has bright gel layer with good continuity and dispersion. The thickness of TiO_2 gel layer is about 25nm. In addition, there are no agglomerated particles of TiO_2 in gel layer [20]. The EDS analysis reveals that the $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors consisted of mainly five elements Ca, Mo, O, Eu and Ti (Fig. 2). It indicated that TiO_2 gel has successfully coated on the surface of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors.

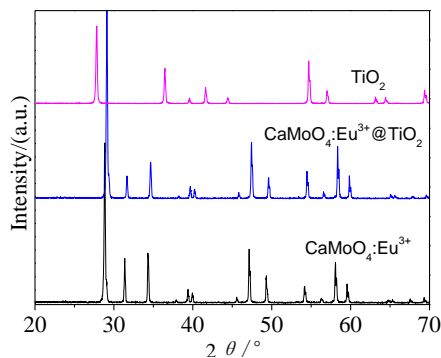


Fig. 3. XRD patterns of $\text{CaMoO}_4:\text{Eu}^{3+}$, $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 and TiO_2

The XRD patterns of $\text{CaMoO}_4:\text{Eu}^{3+}$, $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 and TiO_2 are shown in Fig. 3. The results indicated that $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors are still single tetragonal scheelite structure, which well correspond to the standard file # JCPDS 29-0351 [21]. It can be found that no peak of TiO_2 is detected in the $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 pattern, indicating the TiO_2 coated on the surface of $\text{CaMoO}_4:\text{Eu}^{3+}$ phosphor particle should be amorphous [22].

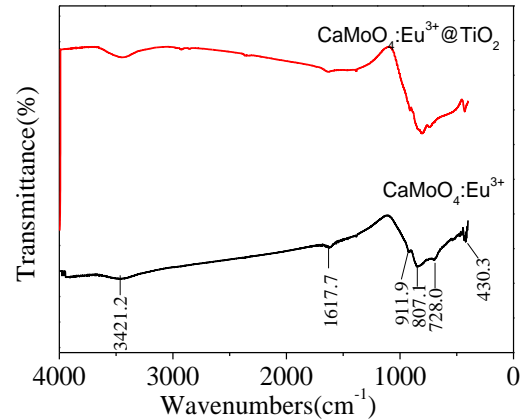


Fig. 4. FT-IR spectra of $\text{CaMoO}_4:\text{Eu}^{3+}$ and $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2

Fig. 4 shows FT-IR spectra of $\text{CaMoO}_4:\text{Eu}^{3+}$ and $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 . With comparison of FT-IR spectra of two samples, it can be obtained that the FT-IR spectra of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors and $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors are similar. It is worth noting that the peak number of $\text{CaMoO}_4:\text{Eu}^{3+}$ @ TiO_2 red phosphors is slightly less than that of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors. Maybe this can be interpreted that coating decreases stretching vibration of O-Mo-O in MoO_4^{2-} tetrahedron, and ν_2 bending vibration of Mo-O [14]. It can indicate that TiO_2 successfully coated on the surface of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors by sol-gel method.

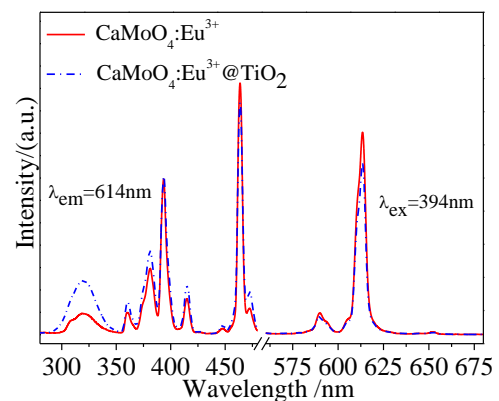


Fig. 5. Excitation and emission spectra of phosphors

Fig. 5 gives the excitation and emission spectra of $\text{CaMoO}_4:\text{Eu}^{3+}$ and $\text{CaMoO}_4:\text{Eu}^{3+}@\text{TiO}_2$. The excitation spectra monitored at 394 nm show that the intensity of excitation peaks increases evidently after coating TiO_2 . The broad band from 290 nm to 350 nm in the excitation spectra is attributed to the charge-transfer band of Eu-O. The narrow peaks ranged from 350 nm to 480 nm are the transitions of Eu^{3+} from the ground state to the excited state of $4f^7$ configuration [23]. The excitation peaks of two samples both are observed at 360nm (${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$), 383nm (${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$), 394nm (${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$), 417nm (${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$) and 465nm (${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$). The excitation peaks of 394nm and 465nm are higher than other peaks from the figure are observed. Thus these phosphors can be well excited by NUV (394 nm) and blue LED chips (465 nm). It is also evident that emission band shapes of the two samples excited by 394 nm at room temperature are similar, and the characteristic emissions of Eu^{3+} in two samples are at ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ (654 nm), ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (614 nm) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (590 nm). It proves that the TiO_2 layer is not affect the luminescent properties of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors. Moreover, the coating layer can passivate the activation of surface defects and remove vacant building, and finally reduce the probability of non-radiation for $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors [24]. The emission intensity of $\text{CaMoO}_4:\text{Eu}^{3+}@\text{TiO}_2$ red phosphors is reduced slightly. However, the slightly decrease of emission intensity is allowed for the application of white LEDs (W-LEDs).

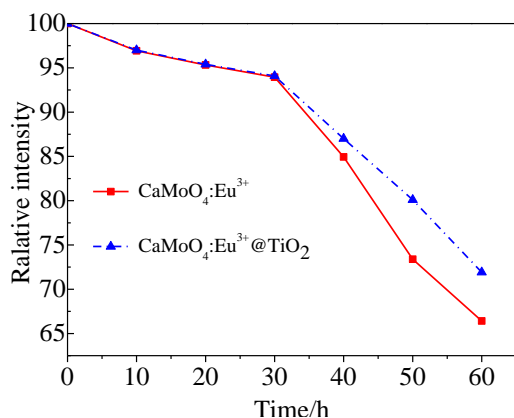


Fig. 6. Thermal stability of phosphors with different heat treatment time at 500 °C

Fig. 6 displays the thermal stability dependences of the relative emission intensity of $\text{CaMoO}_4:\text{Eu}^{3+}$ and $\text{CaMoO}_4:\text{Eu}^{3+}@\text{TiO}_2$ heat treatment at 500 °C with different time. With the increase of heat treatment time, the relative emission intensities of all samples decrease. However, the falling of relative emission intensity for $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors are faster than $\text{CaMoO}_4:\text{Eu}^{3+}@\text{TiO}_2$. The reason is that TiO_2 layers on the surface of $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors not only eliminate the surface defects, but also prevent destruction of external environment. Hence, the coated $\text{CaMoO}_4:\text{Eu}^{3+}$ red

phosphors have great improvement on the thermal stability and the lifetime of W-LEDs is furthermore extended.

$\text{CaMoO}_4:\text{Eu}^{3+}@\text{TiO}_2$ red phosphors were synthesized via a sol-gel method. The amorphous TiO_2 layer is not affected the crystal and luminescent structure of $\text{CaMoO}_4:\text{Eu}^{3+}@\text{TiO}_2$ phosphors. Compared with $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors, the emission intensity of $\text{CaMoO}_4:\text{Eu}^{3+}@\text{TiO}_2$ red phosphors decreases slightly, however, the thermal stability is obviously improved.

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