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Sol–gel synthesis and characterization of SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺/Tb³⁺ core–shell structured spherical particles

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Abstract

Nanocrystalline CaWO₄ and Eu³⁺ (Tb³⁺)-doped CaWO₄ phosphor layers were coated on non-aggregated, monodisperse and spherical SiO₂ particles by the Pechini sol-gel method, resulting in the formation of SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺/Tb³⁺ core-shell structured particles. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), photoluminescence (PL), low-voltage cathodoluminescence (CL), time-resolved PL spectra and lifetimes were used to characterize the core-shell structured materials. Both XRD and FT-IR indicate that CaWO₄ layers have been successfully coated on the SiO₂ particles, which can be further verified by the FESEM and TEM images. The PL and CL demonstrate that the SiO₂@CaWO₄ sample exhibits blue emission band with a maximum at 420 nm (lifetime = 12.8 μ s) originated from the WO₄²⁻ groups, while SiO₂@CaWO₄:Eu³⁺ and SiO₂@CaWO₄:Tb³⁺ show additional red emission dominated by 614 nm (Eu^{3+:5}D₀-⁷F₂ transition, lifetime = 1.04 ms) and green emission at 544 nm (Tb³⁺: $^{5}D_{4}-^{7}F_{5}$ transition, lifetime = 1.38 ms), respectively. The PL excitation, emission and time-resolved spectra suggest that there exists an energy transfer from WO_4^{2-} to Eu^{3+} and Tb^{3+} in SiO₂@CaWO₄:Eu³⁺ and SiO₂@CaWO₄:Tb³⁺, respectively. The energy transfer from WO_4^{2-} to Tb^{3+} in SiO₂@CaWO₄:Tb³⁺ is more efficient than that from WO_4^{2-} to Eu^{3+} in SiO₂@CaWO₄:Eu³⁺.

1. Introduction

Recently, considerable efforts have been devoted to the design and preparation of composite particles consisting of a core covered by shells of different chemical composition. The interests in such core-shell materials stem from the fact that

catalytic, etc) can be tailored by their size, morphology, component and structure of the shells or cores [1–6]. Coreshell materials can be used to protect medicine or other materials from dissolving or from hydrolysis [1] and to strengthen polymeric materials [2]. Some magnetic materials have also been designed as core-shell materials to protect

the properties (mechanical, optical, electrical, magnetic and

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them from reaction with various species in the environment [3] and increase their solubility in some solvents [4]. A great number of processes have been developed to prepare core-shell materials, such as intramuscular polymerization [7], template-directed self-assembly [8], precipitation and surface reaction [9], controlled deposition of preformed inorganic colloids [5], layer-by-layer technique [10], and sonochemical methods [11].

The current demand for high-resolution, high brightness and high efficiency in phosphors for cathode ray tubes, field emissive displays and plasma display panel has promoted the development of phosphors. In particular, phosphors with non-agglomerated, monodisperse, spherical ($<2 \mu$ m) morphology are of great interest, because they offer higher packing density, lower scattering of light, brighter luminescent performance, higher definition, and more improved screen packing [12–14]. Nowadays, many synthetic routes have been developed to control the size, morphology and distribution of phosphor particles, such as spray pyrolysis [15, 16] and flux precipitation [17], but it is still difficult to obtain highly monodisperse and spherical phosphor particles from these methods.

It is well known that monodisperse and spherical silica particles from the nanometre to submicron range can be prepared by the hydrolysis and condensation of tetraethoxysilane (TEOS) catalysed by ammonia [18]. If the silica spheres are coated with phosphor layers, a kind of core-shell phosphor material with spherical morphology will be obtained, and the size of the phosphor particles can be controlled by the silica cores. Furthermore, because silica is cheaper than most of the phosphor materials (which often employ expensive rare earth elements as the activators and/or host components), the core-shell phosphor materials will be cheaper than the pure phosphor materials to some extent. As an important blue phosphor and host material, CaWO₄ has been used in x-ray intensified screens, lasers, fluorescence lamps and scintillators in the last few decades [19-22]. Accordingly, in the present work we prepared monodisperse and spherical silica particles, and coated them with CaWO₄, CaWO₄:Tb³⁺ and CaWO₄:Eu³⁺ layers via the sol-gel process to obtain the core-shell structured SiO₂@CaWO₄, $SiO_2@CaWO_4:Tb^{3+} and SiO_2@CaWO_4:Eu^{3+} particles, which showed blue (WO_4^{2-}), green (Tb^{3+}) and red (Eu^{3+}) emission,$ respectively. Detailed characterizations for the structure, morphology and luminescent properties of the samples were performed.

2. Experimental section

2.1. Synthesis of monodisperse SiO₂ particles

Amorphous sub-micrometre spheres of silica with size around 500 nm were synthesized by the well-known Stöber process, i.e., the hydrolysis and condensation of TEOS in an ethanol solution containing water and ammonia [18]. This method yielded a colloidal solution of silica particles with a narrow size distribution in the sub-micrometre range; the particle size of the silica depends on the relative concentration of the reactants. In a typical experiment, 8.5 ml TEOS (99 wt%, analytical reagent, A.R., Beijing Beihua Chemicals Co., Ltd), 18 ml deionized

H₂O, and 98 ml of NH₄OH (25–28 wt%, A.R. Beijing Beihua Chemicals Co., Ltd) were added into 76 ml absolute ethanol and stirred at room temperature for 4 h, resulting in the formation of a white silica colloidal suspension. The silica particles were centrifugally separated from the suspension and then dried at 100 °C for 12 h. In order to compare with the core–shell particles, some of the as-prepared SiO₂ particles were annealed at 800 °C for 2 h.

2.2. Coating of SiO₂ with CaWO₄, CaWO₄: Eu^{3+} and CaWO₄: Tb^{3+}

Core-shell structured SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺ and $SiO_2@CaWO_4:Tb^{3+}$ particles were prepared by the Pechini sol-gel process. Here we take the fabrication of SiO_2 @CaWO₄ as an example to illustrate the process. 0.20 g CaCO₃ (A. R. Beijing Beihua Chemicals Co., Ltd) was dissolved in dilute HNO₃ (A. R. Beijing Beihua Chemicals Co., Ltd) under vigorous stirring, and the superfluous HNO₃ was driven off until the pH value of the solution reached between two and three. The as-prepared $Ca(NO_3)_2$ was mixed with 0.5494 g ammonium (meta) tungstate hydrate $(H_{26}N_6O_{41}W_{12} \cdot 18H_2O, Fluka), 20 \text{ ml water-ethanol} (V/V =$ 15:5) solution containing 0.8406 g citric acid (A.R. Beijing Beihua Chemicals Co., Ltd) as a chelating agent for the metal ions. The molar ratio of metal ions to citric acid was 1:2. As a cross-linking agent, polyethylene glycol (PEG, molecular weight = 10 000, A.R. Beijing Beihua Chemicals Co., Ltd) was added with a final concentration of 0.20 g ml^{-1} . The solution was stirred for 1 h to form a sol, and then the silica particles were added under stirring. The suspension was further stirred for another 4 h, and then the silica particles were separated by centrifugation. The samples were immediately dried at 100 °C for 1 h. Then the dried samples were heated to 500 °C with a heating rate of $1 °C min^{-1}$, and held there for 2 h in air. The above process was repeated four times to increase the thickness of the CaWO₄ shells. After these processes, the sample was heated to 800 °C with a heating rate of $5 \,^{\circ}$ C min⁻¹, and held there for two hours in air. In this way, the core-shell structured SiO₂@CaWO₄ materials were obtained. For the purpose of comparison, the coating sol was evaporated in a water bath at 80 °C to form a gel, which was annealed in a similar process to produce the pure CaWO₄ powder phosphor. The SiO₂@CaWO₄:Eu³⁺ and SiO₂@CaWO₄:Tb³⁺ core-shell particles were prepared in a similar process as above, with a doping concentration of Eu³⁺ and Tb^{3+} of 5.0 mol% in CaWO₄. As the sources of Eu³⁺ and Tb³⁺, Eu₂O₃ (99.99%, Shanghai Yuelong New Materials Co., Ltd) and Tb₄O₇ (99.99%, Shanghai Yuelong New Materials Co., Ltd) were employed (dissolved in dilute HNO₃).

2.3. Characterization

The x-ray diffraction (XRD) was performed on a Rigaku-Dmax 2500 diffractometer using Cu K α radiation ($\lambda = 0.15405$ nm). The Fourier transform infrared spectroscopy (FT-IR) spectra were measured with Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique (resolution: 4 cm⁻¹). The morphology of samples was inspected in a field emission scanning election microscope (XL30, Philips) and transmission electron microscope



Figure 1. XRD patterns of SiO₂ (a), SiO₂@CaWO₄ (b) and CaWO₄ (c) particles annealed at 800 °C as well as the standard data for CaWO₄ (JCPDS No. 41-1413) as a reference.

(JEOL-2010, 200 kV). The photoluminescence (PL) and cathodoluminescence (CL) spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp and 1–6 kV electron beam (self-made electron gun, 10^{-6} Pa vacuum, filament current 102.5 mA) as the excitation source, respectively. Time-resolved spectra and luminescence decay curves were measured on a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using 240 nm laser (pulse width = 4 ns) as the excitation source (Continuum Sunlite OPO). All the measurements were performed at room temperature.

3. Results and discussion

3.1. Formation and morphology of core-shell particles

The formation and morphology of studied core–shell particles were performed representatively on an SiO₂@CaWO₄ sample using XRD, FT-IR, FESEM and TEM techniques, respectively. The results for SiO₂@CaWO₄:Eu³⁺/Tb³⁺ are similar to those of SiO₂@CaWO₄ and will not be shown here.

XRD. Figure 1 shows the XRD patterns of 800 °C annealed bare SiO₂, CaWO₄ and SiO₂@CaWO₄ particles as well as the standard data for CaWO₄ (JCPDS No. 41-1413) as a reference, respectively. For SiO₂ particles annealed at 800 °C (figure 1(a)), no diffraction peak is observed except for a broad band centred at $2\theta = 22.0^{\circ}$, which is the characteristic peak for amorphous SiO₂ (JCPDS No. 29-0085). For the SiO₂@CaWO₄ core-shell sample fired at 800 °C (figure 1(b)), besides the broad band at $2\theta = 22.00^{\circ}$ from amorphous SiO₂, all the diffraction peaks belonging to crystalline CaWO₄ are present, suggesting that the coatings of CaWO₄ have crystallized well on the surfaces of amorphous silica particles. This coincides well with the XRD pattern of pure CaWO₄ particles annealed at 800 °C (figure 1(c)) and the standard data for CaWO₄ (JCPDS No. 72-0257). No other phase has been detected, indicating that no reaction occurred between the core (SiO₂) and the shell (CaWO₄) components. In general, the nanocrystallite size can be estimated from the



Figure 2. FT-IR spectra of SiO_2 (a), $SiO_2@CaWO_4$ (b) and $CaWO_4$ (c).

Scherrer formula: $D_{hkl} = K\lambda/(\beta \cos \theta)$, where λ is the xray wavelength (0.154 05 nm), β is the full-width at halfmaximum, θ is the diffraction angle, K is a constant (0.89) and D_{hkl} means the size along the (*hkl*) direction [23]. Here we take diffraction data in the (101), (112), (200), (204) and (303) planes to calculate the nanocrystallite sizes of CaWO₄ on the surface of SiO₂, and the estimated average crystallite size is 38 nm.

FT-IR spectra. In order to further verify the formation of the core-shell structure of SiO₂@CaWO₄ particles, FT-IR spectra were performed for the 800 °C annealed silica, CaWO₄ and SiO₂@CaWO₄ particles, as shown in figure 2. In figure 2(a) for the SiO₂ particles, the absorption bands due to OH (3442 cm⁻¹), H₂O (1634 cm⁻¹), Si–O–Si (ν_{as} , 1100 cm⁻¹; $\nu_{\rm s}$, 800 cm⁻¹), Si–OH ($\nu_{\rm s}$, 950 cm⁻¹), and Si–O (δ , 470 cm⁻¹) bonds (where v_{as} = asymmetric stretching, v_s = symmetric stretching, δ = bending) are observed [24]. The presence of vibration bands of O-H and H₂O is due to the water absorbed by the samples in air, which can also be observed in the spectra of CaWO₄ and SiO₂@CaWO₄ particles (figures 2(b), (c)). In figure 2(c) for CaWO₄, apart from the vibration peaks from OH and H_2O , a strong absorption peak at 830 cm⁻¹ and a weak one at 442 cm^{-1} are present, which are due to the stretching vibration and bending vibration of the W-O bond (in WO₄ group), respectively [25]. For the SiO₂@CaWO₄ sample (figure 2(b)), all the main characteristic peaks from SiO₂ and CaWO₄ are present, i.e., the peak of Si–O–Si at 1100 cm^{-1} from SiO₂ core and that of W-O at 830 cm⁻¹ from CaWO₄ shell can be observed clearly. Conclusively, the FT-IR spectra further confirm that CaWO₄ has crystallized well on the surface of amorphous SiO₂, which is in good agreement with the XRD results.

FESEM and TEM. Figure 3 shows the FESEM micrographs of the SiO₂ and SiO₂@CaWO₄ (four times coated) particles annealed at 800 °C, respectively. From the FESEM micrograph of figure 3(a), we can observe that the SiO₂ sample consists of non-agglomerated, monodisperse, spherical particles with an average size around 500 nm. After the silica



Figure 3. FESEM micrographs for the as-prepared SiO₂ (a) and core–shell structured SiO₂ @CaWO₄ (b) particles as well as the histograms ((c), (d)) for their size distribution.

(This figure is in colour only in the electronic version)

particles were functionalized by CaWO₄ coatings, the resulting SiO₂@CaWO₄ particles still keep the morphology of the silica particles, i.e., these particles are still non-agglomerated, monodisperse and spherical, with an average size around 600 nm, which is slightly larger than that (500 nm) for the pure silica particles due to the additional layers of CaWO₄ on them, as shown in figure 3(b). Moreover, no separate and irregular fine particles of CaWO₄ can be observed in figure 3(b). This indicates that almost all of the CaWO₄ materials have been coated on the surfaces of silica particles by our experimental process.

A TEM was used to verify the core-shell structure of $SiO_2@CaWO_4$ particles directly. Figure 4 shows the TEM micrographs of bare SiO_2 (a) and $SiO_2@CaWO_4$ samples (four times coated). Only black spheres (500 nm in diameter) were observed for bare SiO_2 particles (figure 4(a)). In contrast, the core-shell structure for the $SiO_2@CaWO_4$ particles (figure 4(b)) can be seen clearly due to the different electron penetrability for the cores and shells. The cores are black spheres with an average size of 500 nm (similar to the pure SiO_2 particles in figure 4(a)), and the shells have a grey colour with an average thickness of 50 nm. The electron diffraction measurement performed in the interface region of the core and shell of a particle (inset of figure 4(b)) shows electron diffraction rings with some disorder, demonstrating



Figure 4. TEM micrographs of SiO_2 (a) and SiO_2 @CaWO₄ (b) particles. The inset in (b) is the electron diffraction pattern of the selected region, as indicated.

the coexistence of crystalline phase $(CaWO_4)$ and amorphous phase (SiO_2) in the interface region of the core–shell particle.

3.2. Luminescence properties

3.2.1. Photoluminescence and kinetic properties. Upon UV light illumination, the core–shell structured SiO₂@CaWO₄,



Figure 5. Excitation ((a), (c), (d), (f)) and emission ((b), (e), (g)) spectra for SiO₂@CaWO₄ ((a), (b)) SiO₂@CaWO₄:Eu³⁺ ((c), (d), (e)) and SiO₂@CaWO₄:Tb³⁺ ((f), (g)).

SiO₂@CaWO₄:Eu³⁺, SiO₂@CaWO₄:Tb³⁺ particles exhibit strong blue, red and green luminescence, respectively. Figures 5(a)–(g) shows the PL excitation and emission spectra of SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺ and SiO₂@CaWO₄:Tb³⁺ particles, respectively. The excitation spectrum for SiO₂@CaWO₄ (figure 5(a)) contains a broad band from 200 to 280 nm with a maximum at 240 nm, which corresponds to the charge transfer transition in WO₄^{2–} groups in which an oxygen (O) 2p electron goes into empty tungsten (W) 5d orbital. The emission spectrum (figure 5(b)) consists of a broad band ranging from 300 to 600 nm with a maximum at 420 nm due to the WO_4^{2-} ion. From the viewpoint of molecular orbital theory, the excitation and emission bands of SiO₂@CaWO₄ can be ascribed to transitions from the ¹A₁ ground state to the high vibration level of ¹B(¹T₂) and from the low vibration level of ¹B(¹T₂) to the ¹A₁ ground state within the WO_4^{2-} ion, respectively [26].

The excitation spectrum (monitored by the $Eu^{3+5}D_0-^7F_2$ transition at 614 nm) for SiO₂@CaWO₄:Eu³⁺ (figure 5(c)) consists of a broad band with a maximum at 240 nm and a group of sharp peaks originating from the Eu³⁺ f-f transition. Monitored by the WO_4^{2-} emission at 420 nm, the excitation spectrum obtained is also composed of a similar band at 240 nm (figure 5(d)). Consequently, the excitation bands can be ascribed to the WO_4^{2-} groups. This means that there exists an energy transfer from the WO_4^{2-} ion to Eu^{3+} in $SiO_2@CaWO_4:Eu^{3+}$ as in bulk and thin film $CaWO_4:Eu^{3+}$ [27]. Excitation into the WO_4^{2-} groups at 240 nm yields the emission spectrum (figure 5(e)), which contains not only the emission of the WO_4^{2-} group, but also the characteristic emission of Eu³⁺, as labelled in the figure. The presence of the strong WO_4^{2-} emission indicates that the energy transfer from WO_4^{2-} to Eu^{3+} is far from complete in the SiO₂@CaWO₄:Eu³⁺ system. The emission of Eu³⁺ is dominated by the red ${}^{5}D_{0}-{}^{7}F_{2}$ hypersensitive transition, which indicates that Eu³⁺ is located at a site without inversion symmetry [27, 28]. Note that weak emission lines from higher excited states of $Eu^{3+}({}^{5}D_{1}, {}^{5}D_{2})$ are present (superimposed on the emission band of WO_4^{2-}) due to the low vibration energy of WO_4^{2-} groups (830 cm⁻¹, as indicated by figure 2) [28]. This also suggests that the high phonon energy of the silica cores (1100 cm^{-1}) has little influence on the emission properties of Eu³⁺ in the core–shell SiO₂@CaWO₄:Eu³⁺ sample.

For the SiO₂@CaWO₄:Tb³⁺ sample, the excitation spectrum (monitored by the Tb^{3+ 5}D₄–⁷F₅ transition at 544 nm, figure 5(f)) consists of a narrow band with maximum at 240 nm due to the WO₄²⁻ group as described above. The f–f transitions within the Tb³⁺ 4f⁸ configuration can hardly be detected because of their weaker intensity. Upon excitation into the WO₄²⁻ at 240 nm, the obtained emission spectrum (figure 5(g)) contains exclusively the characteristic emission of Tb³⁺ with ⁵D₄–⁷F₅ green emission (544 nm) as the most prominent group (other transitions are labelled in the figure). The blue emission from WO₄²⁻ is nearly undetected, suggesting that an efficient energy transfer from WO₄²⁻ to Tb³⁺ has occurred in the SiO₂@CaWO₄:Tb³⁺ sample. Furthermore, the emission from the ⁵D₃ level of Tb³⁺ is much weaker than that from the ⁵D₄ level due to the cross relaxation effect of Tb³⁺ [28].

The PL decay curves for WO_4^{2-} (420 nm) in SiO₂@ CaWO₄, Eu³⁺ (613 nm, ⁵D₀–⁷F₂) in SiO₂@CaWO₄:Eu³⁺ and Tb³⁺ (544 nm, ⁵D₄–⁷F₅) in SiO₂@CaWO₄:Tb³⁺ are shown in figures 6(a)–(c), respectively. The curve in figure 6(a) for WO₄²⁻ emission can be fitted into a single exponential function as $I = I_0 \exp(-t/\tau)$ (I_0 is the initial intensity at t = 0, and τ is the 1/e lifetime) and the lifetime can be determined by the fitting as 12.8 µs. The decay curves for WO₄²⁻ in SiO₂@CaWO₄:Eu³⁺ and SiO₂@CaWO₄:Tb³⁺ are similar to that in SiO₂@CaWO₄ (which also can be fitted into a single exponential function) with lifetimes 10.5 and 8.0 µs respectively, which become shorter than that (12.8 µs) in SiO₂@CaWO₄. The shortening of the lifetime



Figure 6. Decay curves for the luminescence of WO_4^{2-} in SiO₂@CaWO₄ (a), Eu³⁺ in SiO₂@CaWO₄:Eu³⁺ (b) and Tb³⁺ in SiO₂@CaWO₄:Tb³⁺ (c).

is due to an energy transfer from WO_4^{2-} to Eu^{3+} (or Tb^{3+}) in $SiO_2@CaWO_4:Eu^{3+}$ (or $SiO_2@CaWO_4:Tb^{3+}$). The shorter lifetime of WO_4^{2-} in $SiO_2@CaWO_4:Tb^{3+}$ (8.0 μ s) than in $SiO_2@CaWO_4:Eu^{3+}$ (10.5 μ s) also indicates a more efficient energy transfer from WO_4^{2-} to Tb^{3+} in the former than that from WO_4^{2-} to Eu^{3+} in the latter [29].

However, the PL decay curves for Eu³⁺ in SiO₂@CaWO₄: Eu³⁺ (figure 6(b)) and Tb³⁺ in SiO₂@CaWO₄:Tb³⁺ (figure 6(c)) cannot be fitted into a single exponential function, but rather a double exponential function as $I = A_f \exp(-t/\tau_f) + A_s \exp(-t/\tau_s)$ (τ_f and τ_s are the fast and slow components of the luminescence lifetimes, A_f and A_s are the fitting parameters). The average lifetime for Eu³⁺ and Tb³⁺ can be determined by the formula as $\tau = (A_f \tau_f^2 + A_s \tau_s^2)/(A_f \tau_s + A_f \tau_s)$ [30], and the average lifetimes for Eu³⁺ in SiO₂@CaWO₄:Eu³⁺ and



Figure 7. Time resolved PL spectra of SiO₂@CaWO₄:Eu³⁺ ((a) $\lambda_{ex} = 240 \text{ nm laser}$) and SiO₂@CaWO₄:Tb³⁺ ((b) $\lambda_{ex} = 240 \text{ nm laser}$).

 Tb^{3+} in SiO₂@CaWO₄: Tb^{3+} are determined to be 1.04 and 1.38 ms, respectively. The double exponential decay behaviour of the activator is frequently observed when the excitation energy is transferred from the donor [30, 31].

In order to further understand the energy transfer process from WO_4^{2-} to Eu^{3+} and Tb^{3+} in $SiO_2@CaWO_4:Eu^{3+}$ and SiO₂@CaWO₄:Tb³⁺, time resolved spectra have been performed, as shown in figures 7(a) and (b), respectively. For SiO₂@CaWO₄:Eu³⁺, the spectra collected at different delay times exhibit two types of emission, namely, the band emission from WO_4^{2-} and characteristic line emission from Eu^{3+} . The emission band of WO_4^{2-} first increased with the delay time, reaching a maximum at $t = 10 \ \mu s$, then began to decrease and disappeared completely at $t = 100 \ \mu s$. The characteristic emission of Eu^{3+} was not present at t = 1and 2 μ s, began to appear at $t = 5 \mu$ s, then increased with delay time, reaching a maximum at $t = 100 \ \mu s$, then began to decrease and quenched completely at t = 2 ms. The above emission characteristics of WO_4^{2-} and Eu^{3+} as a function of delay time reflect the energy transfer process from WO_4^{2-} to Eu^{3+} in the SiO₂@CaWO₄:Eu³⁺ sample. The lifetime for the luminescence of WO_4^{2-} (12.8 μ s) is much shorter than that of Eu³⁺ (1.04 ms), so within $t < 5 \ \mu s$



Figure 8. Schematic diagram for the energy transfer from WO_4^{2-} to Eu^{3+} and Tb^{3+} as well as the emission process from Eu^{3+} and Tb^{3+} .

(very short time) the excitation energy of WO_4^{2-} has not been transferred to Eu^{3+} . As a result, only the emission of WO_4^{2-} is observed and no emission of Eu³⁺ is observed during this period. With time going on, the excitation energy began to transfer to Eu³⁺, resulting in the appearance of Eu³⁺ emission $(t = 5 \ \mu s)$. When $t = 100 \ \mu s$, most of the excitation energy of WO_4^{2-} nonradiatively transferred to Eu^{3+} , leading to the quenching of the emission of WO_4^{2-} accompanied by that of Eu^{3+} reaching a maximum value. Later on $(t > 100 \ \mu s)$, the emission of Eu³⁺ began to decrease until it disappeared at t = 2 ms due to the depopulation of the excited states of Eu³⁺. The above energy transfer and emission process for WO_4^{2-} and Eu^{3+} in SiO₂@CaWO₄:Eu³⁺ is schematically shown in figure 8 (left) [32]. Upon UV (240 nm) excitation, an electron in the ground state $({}^{1}A_{1})$ is excited into the ${}^{1}B$ $({}^{1}T_{2})$ level of WO₄²⁻, where the electron either relaxes to its lowest excited ¹B ($^{1}T_{2}$) level of WO₄²⁻, producing the emission by the transition to the ${}^{1}A_{1}$ level, or the excitation energy transfers to Eu^{3+ 5}D₃ or higher levels by resonance process, from which the energy nonradiatively relaxes to the ${}^{5}D_{0}$ level by multiphonon relaxation. Then the characteristic emission of ${}^{5}D_{0}-{}^{7}F_{J}$ (J = 0, 1, 2, 3, 4) occurs.

The same situation holds for Tb³⁺ in SiO₂@CaWO₄:Tb³⁺, i.e., the WO_4^{2-} emission first increased with delay time, reaching its maximum at $t = 20 \ \mu s$, then began to decrease and quenched completely at $t = 100 \ \mu s$, while the emission of Tb³⁺ increased with decay time, reaching a maximum at $t = 100 \ \mu s$, and then decreased until it almost disappeared at t = 2 ms. The above process can be explained as those for Eu^{3+} in SiO₂@CaWO₄: Eu^{3+} , and the energy transfer and emission process for WO₄²⁻ and Tb³⁺ in SiO₂@CaWO₄:Tb³⁺ are schematically shown in figure 8 (right). The excitation energy of WO_4^{2-} mainly transfers to 5D_3 or higher levels of Tb^{3+} . The relaxation from 5D_3 to 5D_4 cannot happen by a multiphonon relaxation process due to the large energy difference (5700 cm^{-1}) between these two levels [33]. In view of the high concentration (5 mol%), the relaxation from D_3 to 5D_4 of Tb^{3+} mainly occurred by the cross-relaxation process, as shown in figure 8 (right). For Tb^{3+} , the energy difference between ${}^{5}D_{3}$ and ${}^{5}D_{4}$ is equal to that between ${}^{7}F_{0}$



Figure 9. CL spectra of SiO₂@CaWO₄ (a), SiO₂@CaWO₄:Eu³⁺ (b) and SiO₂@CaWO₄:Tb³⁺ (c) (accelerating voltage = 6 kV).

and ${}^{7}F_{6}$. The emissions from the ${}^{5}D_{3}$ level will be quenched by the cross-relaxation process, i.e., $Tb^{3+}({}^{5}D_{3}) + Tb^{3+}({}^{7}F_{6}) \rightarrow Tb^{3+}({}^{5}D_{4}) + Tb^{3+}({}^{7}F_{0})$, accompanied by the emissions from the ${}^{5}D_{4}$ level [28].

3.2.2. Cathodoluminescence properties. Similar to the emission under UV excitation, the SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺, SiO₂@CaWO₄:Tb³⁺ core–shell particles also exhibit strong blue, red and green luminescence respectively under the excitation of an electron beam. The typical emission spectra under the excitation of electron beam (6 kV) are shown in figures 9(a)–(c), which basically agree with the corresponding PL emission spectra (figures 5(b), (e), (g)). However, for SiO₂@CaWO₄:Eu³⁺, the emission intensity ratio of Eu³⁺ to WO₄²⁻ (0.49) in the CL spectrum (figure 9(b)) is larger than that (0.11) in the PL spectrum (figure 5(b)). For CL, the emission of Eu³⁺ resulted from both the energy transfer



Figure 10. The CL integrated intensity of $SiO_2@CaWO_4$ (a), SiO_2@CaWO_4:Eu³⁺ (b) and SiO_2@CaWO_4:Tb³⁺ (c) as a function of accelerating voltages. The actual intensity of $SiO_2@CaWO_4$:Tb³⁺ (c) is much higher than those shown in the figure if they are taken under same conditions as (a) and (b). The data in (c) were collected with a lower filament current than (a) and (b).

from WO₄²⁻ and the direct excitation of Eu³⁺ by the plasma produced by the incident electrons, while for PL the emission of Eu³⁺ is only from the former. Thus it is understandable that the emission intensity ratio of Eu³⁺ to WO₄²⁻ in the CL spectrum is larger than that in the PL spectrum. Also in the CL spectrum for Tb³⁺ in SiO₂@CaWO₄:Tb³⁺, only the emission from the Tb^{3+ 5}D₄ level is observed due to an efficient energy transfer from WO₄²⁻ to Tb³⁺ as well as the direct excitation of Tb³⁺ by the plasma produced by the incident electrons. The disappearance of WO₄²⁻ emission in the sample can be attributed to the efficient (nearly complete) nonradiative energy transfer from WO₄²⁻ to Tb³⁺, as observed and discussed for the PL spectrum (figure 5(g)).

The CL intensity of SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺, and SiO₂@CaWO₄:Tb³⁺ has been investigated as a function of accelerating voltage, as shown in figure 10. For all the samples, the CL intensity increases with the increase of accelerating voltage from 1 to 6 kV. With the increase of accelerating voltage, more plasma will be produced by the incident electrons, resulting in more WO_4^{2-} and $Eu^{3+}(Tb^{3+})$ ions being excited and thus higher CL intensity. Due to the strong low-voltage CL intensity and excellent dispersing properties of SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺, SiO₂@CaWO₄:Tb³⁺ core–shell phosphors, they are potentially applied in field emission display (FED) devices.

4. Conclusions

A simple and effective sol-gel process has been developed to coat CaWO₄, CaWO₄:Eu³⁺ and CaWO₄:Tb³⁺ phosphor layers on monodisperse spherical SiO₂ particles. The obtained core–shell structured SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺ and SiO₂@CaWO₄:Tb³⁺ phosphors maintain spherical morphology, sub-micrometre size and narrow size distribution. Under UV light and low-voltage electron beam excitation, the SiO₂@CaWO₄, SiO₂@CaWO₄:Eu³⁺ and SiO₂@CaWO₄:Tb³⁺ phosphors show blue, red and green luminescence, respectively. There exists an energy transfer

from WO_4^{2-} to Eu^{3+} in $SiO_2@CaWO_4:Eu^{3+}$ and to Tb^{3+} in $SiO_2@CaWO_4:Tb^{3+}$, respectively. The energy transfer in the latter is more efficient than in the former. The obtained core-shell phosphors have potential applications in FED devices.

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