Efficient Warm-White Lighting Using Rare-Earth-Element-Free Fluorescent Materials for Energy Saving, Environment Protecting, and Health Caring

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Supplementary Information

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1. Characterization of ZnSe:Mn nanoparticles

In this work, the Mn$^{2+}$-doped ZnSe nanoparticles are prepared by hydrothermal method. Structural characterization of the ZnSe:Mn nanoparticles was performed by X-ray powder diffraction (XRD), as shown in Figure S1. The three peaks located at 27.2°, 45.5°, and 53.7° correspond to the (111), (220), and (311) planes, respectively. They indicate that the hydrothermally prepared ZnSe:Mn nanoparticles are with the zinc blende structure. The average size of ZnSe:Mn nanoparticles can be calculated from Debey-Scherrer’s formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{(Equation S1)}$$

where $D$ is the average particle diameter, $\beta$ is the full width at half maximum (FWHM) in radian of the diffraction peak, $\theta$ is the Bragg’s diffraction angle, and $\lambda$ is the wavelength for the K$\alpha_1$ component of the employed copper radiation.

As we increase the amount of KOH to 0.5 g, 2 g, and 5 g, the FWHM value decreases to 2.36°, 2.06°, and 1.27°, respectively, implying that the ZnSe:Mn NCs become larger with increasing KOH.

2. Optical properties of ZnSe nanoparticles

Figure S2 shows the normalized photoluminescence excitation and emission spectra of ZnSe:Mn nanoparticles at room temperature. The spectrum of the excitation source covers the region from 400 nm to 500 nm with the peak located at 450 nm. The emission is composed of a broad green-orange spectral band (525 nm~650 nm) with
the peak located at 578 nm, which is associated with the Mn$^{2+}$. The color temperature of ZnSe:Mn nanoparticles is low, so it is particularly good for human health.

Figure S1. Optical characterization of ZnSe:Mn nanoparticles. Normalized luminescence excitation and emission spectra of ZnSe:Mn nanoparticles prepared by hydrothermal method.

3. Emission lifetimes calculation

We use a fluorescence lifetime imaging microscopy (FLIM) system to measure the decay curves and lifetimes of ZnSe:Mn nanoparticles with various processes. A standard three-exponential-component model was used to study the recombination dynamics, and thus the decay curves can be described by:

\[
I(t) = A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2) + A_3 \exp(-t / \tau_3)
\]

(Equation S2)

where $A_1$, $A_2$ and $A_3$ are pre-exponential constants and $\tau_1$, $\tau_2$and $\tau_3$ are the decay time of the three exponential components. The emission lifetimes were then determined from the decay time of the three exponential components and the pre-exponential factors using the following relation:

\[
\tau_{avg} = (A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3) / (A_1 + A_2 + A_3)
\]

(Equation S3)
The detailed values of lifetimes associated with various decay processes are presented in Table S1. The sample names “NaOH” and “KOH” imply that the processes include NaOH 4g and KOH 5g respectively, but without dispersion and citric acid. The sample “Dispersion” implies that the process includes KOH 5g and dispersion 5ml. “Citric acid” implies that the process include KOH 5g, 5ml dispersion and 0.1g citric acid.

Table S1 | Lifetimes associated with various decay processes in ZnSe:Mn nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>NaOH</th>
<th>KOH</th>
<th>Dispersion</th>
<th>Citric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_{\text{Av.}} )</td>
<td>0.826 ns</td>
<td>3.789 ns</td>
<td>4.9774 ns</td>
<td>5.048 ns</td>
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</tbody>
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4. EDS spectra for ZnSe:Mn nanoparticles

The EDS spectra with various processes are shown in Figure 4(a-d). The data indicate the similar result. The elemental concentration obtained for the NCs is Mn = 1.5 atom %; Zn = 52.3 atom %; and Se = 46.2 atom %.
b.

cps/eV

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Mn
Zn
Si

b.

c.

cps/eV

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Mn
Zn
Si
Figure S2. EDS spectra of processes with (a) NaOH (b) KOH (c) KOH and
dispersion (d) KOH, dispersion and citric acid.

5. Experimental setup of the photoluminescence system

The experimental setup of system used for measuring the photoluminescence spectra of samples is schematically depicted in the following diagram. A blue LED was employed as excitation sources to measure the photoluminescence properties of the samples. The excitation spectrum spectra of the samples were measured using this photoluminescence system. The measurements were conducted at room temperature.

![Figure S3. Schematic diagram of the photoluminescence system.](image)

6. Measuring method of the quantum efficiency (QE)

In this work, the photon-conversion performance, namely, QE is defined using the following relation:

\[
QE = \frac{\text{number of photons emitted from sample}}{\text{number of photons absorbed by sample}} = \frac{\int \frac{\lambda}{hc} \{I_{em}^\text{sam} - I_{em}^\text{ref} \} d\lambda}{\int \frac{\lambda}{hc} \{I_{ex}^\text{ref} - I_{ex}^\text{sam} \} d\lambda}
\]

(Equation S4)

where \( h \) is Planck’s constant, \( c \) is the speed of light, \( \lambda \) is the wavelength, and \( I(\lambda) \)
is the intensity of PL spectrum at a wavelength of $\lambda$.

![Figure S4 Schematic diagram of absorption (blue) and emission region (orange) for the sample.]

7. Luminous efficacy calculation

The potential luminous efficacy of our phosphors is evaluated using a commercially available blue LED with wall-plug efficiency (WPE) of 83%, meaning 1 watt of electrical power can release 0.83 watts of blue light. The corresponding number of blue photons emitted per second is calculated according to the formula of $\text{WPE} \times \frac{\lambda}{hc}$, where $h$ is the Planck’s constant and $c$ is the speed of light in vacuum. For simplicity of estimation, the emission of LED is just considered at 450 nm. Multiplying the total blue photons by 84.5% (quantum efficiency) gives the number of orange photons. Then, the luminous efficacy is calculated according to the following formula that has taken into account the packaging efficiency.

$$\int \left( \frac{\text{Total number of orange light photons} \times \text{Proportion of orange light photons of each band} \times \text{Lumen to each corresponding band}}{\text{Input Watt}} \right) \times \text{Packaging efficiency}$$

$$= 286 \ (\text{lm/W}) \times \text{Packaging efficiency} \quad \text{(Equation S5)}$$