Electronic Supplementary Information

Improved sensitization efficiency in Er$^{3+}$ ions and SnO$_2$ nanocrystals co-doped silica thin films

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1. An estimation on the average sizes of SnO$_2$ NCs with the increasing annealing temperature according to the excitation peaks’ position.

As shown in Fig.4, the redshifts of the excitation from band-to-band transition of SnO$_2$ nanocrystals (NCs) can be explained as the enlargement of the average sizes with the increasing annealing temperatures. Based on these excitation peaks, we also estimated the average size of SnO$_2$ NCs using the effective mass theory.$^{[1]}$

$$E_g(R) = E_g(R \to \infty) + \frac{\hbar^2}{8R^2} \times \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\varepsilon_0 R} + \text{smaller terms},$$

where $E_g(R)$ is the band gap energy of SnO$_2$ NCs, $R$ is the average radius of SnO$_2$ NCs, $E_g(R \to \infty)$ is the band gap energy of SnO$_2$ bulk materials and $\varepsilon$ is the relative dielectric constant. $m_e^*$ and $m_h^*$ stand for the effective mass of an electron and a hole, respectively. For SnO$_2$ NCs,

$$E_g(R \to \infty) = 3.60 \, eV, \quad \varepsilon = 14, \quad \varepsilon_0 = 8.85 \times 10^{-12} F/m,$$

$$m_e^* = 0.35 \, m_0, \quad m_h^* \gg m_e^*,$$

where $m_0$ stands for the free electron mass. Meanwhile, $E_g(R)$ can be calculated as follows,
\[ E_g(R) = \frac{1240}{\lambda_{exc}} \]

where \( \lambda_{exc} \) stands for the excitation peak from band-to-band transition of SnO\(_2\) NCs.

As shown in Table 1, it is found that the average sizes of SnO\(_2\) NCs with different annealing temperatures are consistent with the TEM observations.

Table 1S. Band gaps and average sizes of SnO\(_2\) NCs after annealing at different temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature / °C</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>Bulk materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{exc} ) / nm</td>
<td>293</td>
<td>300</td>
<td>322</td>
<td>—</td>
</tr>
<tr>
<td>Band gap / eV</td>
<td>4.23</td>
<td>4.13</td>
<td>3.85</td>
<td>3.60</td>
</tr>
<tr>
<td>Average size / nm</td>
<td>2.92</td>
<td>4.22</td>
<td>5.12</td>
<td>—</td>
</tr>
</tbody>
</table>

2. XRD patterns of samples after annealing at 1000°C.

In order to characterize further the formation of SnO\(_2\) NCs, the aged gels were annealed at 1000 °C and then milled into powers for the X-ray diffraction (XRD, using 0.1540562 nm Cu Ka radiation) test.

XRD pattern for corresponding sol-gel powers containing with 20% Sn after annealing at 1000°C is demonstrated in Fig. 1S(a). The pattern shows all the diffraction peaks assigned to tetragonal rutile crystalline phase of the SnO\(_2\) NCs (JCPDS No. 41-1445), which is consistent with the TEM observation results. As shown in Fig. 1S(b), the related XRD spectra express a slight shifting, revealing the fact that Er\(^{3+}\) ions should be very likely incorporated in the D\(_{2h}\) lattice site of Sn\(^{4+}\).
Fig.1S (a) XRD pattern of the 20% Sn doped SiO$_2$ powder samples after annealing 1000 °C. (b) Comparison of XRD spectra of pure and Er$^{3+}$-doped SnO$_2$ NCs silica thin films.

Reference