Preparation and Properties of Carbon Dot-Grafted CaAl$_{12}$O$_{19}$:Mn$^{4+}$ Color-Tunable Hybrid Phosphor

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A series of carbon dots (CDs) grafted CaAl$_{12}$O$_{19}$:Mn$^{4+}$ (CAO) color-tunable hybrid phosphors have been synthesized via a facile sol-gel method. Through the hydrolysis and condensation reactions of the silica precursor, CDs can be incorporated into highly flexible hybrid materials through combining with a CaAl$_{12}$O$_{19}$:Mn$^{4+}$ phosphor within silica gel networks for the fabrication of flexible displays and multicolor luminescent materials. By tuning the mass ratio of CDs/CAO and by adjusting the excitation wavelength, the color of the luminescence can be systematically tailored from purplish-red (0.504, 0.250) to greenish-blue (0.238, 0.192). Furthermore, the temperature-dependent luminescence properties of the CDs/CAO phosphors make them suitable as thermometers with a wide linear temperature sensing range from 80 to 300 K.

1. Introduction

Multicolor luminescent materials have attracted increasing attention because of their potential applications in flexible full-color displays, multiplexed biological labeling, and next-generation lighting sources. The use of these materials has been focused on generating low-cost and energy-saving light sources.$^{[1]}$ It is of great benefit to be able to acquire tunable colors from the same luminescent component under a single wavelength excitation. In recent years, many multicolor luminescent materials have been developed, including rare-earth metal based nanoparticles,$^{[2]}$ semiconductor quantum dots (QDs),$^{[3]}$ polymer dots,$^{[4]}$ molecular nanomaterials,$^{[5]}$ and organic fluorescent dyes.$^{[6]}$ However, the low-emission quantum yields (QYs), poor water solubility, potential for photobleaching, and complicated preparation procedures have hampered the practical applications of these materials.$^{[2-6]}$ Therefore, finding environmentally friendly and low-toxicity materials with the right properties for applications in multicolor luminescence devices is still required.

Temperature is a fundamental thermodynamic parameter that affects chemical and biological processes. There are many methods for measuring the temperature, fluorescence-based temperature measurements have attracted much attention because of the merits of being non-invasive, giving a fast response, and being robust even under strong electromagnetic fields.$^{[7]}$ Fluorescence-based measurements using luminescent materials activated with semiconductor nanocrystals,$^{[8]}$ carbon dots,$^{[9]}$ or rare-earth ions$^{[7]}$ are commonly based on the decrease in the emission intensity with increasing temperature by the thermal activation of non-radiative deactivation pathways.$^{[10]}$ Compared to single-intensity-based measurements, fluorescence ratiometric methods are more robust and convenient for actual applications. This is because of the built-in calibrations provided by the simultaneous detection of two signals under a single wavelength excitation, thus overcoming the inaccuracy of the probe concentration and that of small changes in the optoelectronics system, such as that from the used lamps and detectors.

Fluorescent carbon dots (CDs), which comprises a fascinating class of fluorescence-based nanoparticles, have been explored as an outstanding substitute to traditional metal-based QDs thanks to their excellent properties, such as their high biocompatibility, low cytotoxicity, chemical inertness, and attractive photoluminescence (PL) properties.$^{[11,12]}$ They show strong absorption in the near-UV spectral region and efficient blue-light emission, which makes them suitable as blue-emitting components for multicolor luminescence.$^{[1-3]}$ Recently, excitation-dependent PL has been shown for CDs$^{[13]}$ making them promising candidates for multicolor sensing. However, the realization of highly efficient, solid-state, light-emitting materials remains a challenge because of the PL quenching of luminophores that are transferred from their parent colloidal solutions into the solid-state matrices. This is mainly caused by the aggregation of the CDs.$^{[14,15]}$ Thus, it is of great importance to embed the CDs in a proper solid matrix or prepare them in solid-state architectures. Generally, CDs can be dispersed in a polymer matrix to realize luminescent films or composite monoliths. Liang and co-workers incorporated CDs into sodium borosilicate networks and observed a red-shifted emission and enhanced quantum efficiency with increasing doping concentration of the CDs.$^{[16]}$ Organically modified silicates and silica gels are generally superior matrix materials owing to their inherent stability and non-toxicity, which would allow a direct incorporation of the CDs into an existing lighting format.$^{[17]}$

CDs have been suggested as phosphors for white light-emitting diodes (WLEDs)$^{[16]}$ These could be achieved by a
combination of CDs with red-emitting phosphors, whose high luminance and satisfactory chromaticity are required to generate colorful luminescence. Liu’s group firmly embedded Sr₂Si₅N₈:Eu²⁺ phosphors in a cellulose matrix, and it was shown that the particles were well dispersed. The CaAl₁₂O₁₉:Mn⁴⁺ phosphor (CAO) has been regarded as a candidate for the red-emitting component in multicolor luminescence, owing to its high brightness, satisfactory chromaticity, and low cost. Conventional phosphors are generally synthesized using rare-earth raw materials. The price of a CAO phosphor is much cheaper than that of rare-earth based phosphors, meaning that it is more suitable for commercial applications. In this work, we incorporated CDs within the CAO phosphor (CDs/CAO) by hydrolyzing and co-condensing with a silica precursor. By tuning the mass ratio of CDs/CAO and adapting the excitation wavelength, the color of the luminescence can be systematically tailored and even white-light emission can be obtained. Furthermore, thanks to the temperature-dependent luminescent behavior, the CDs/CAO material could possibly be used as a thermometer with a wide linear temperature range from 80 to 300 K.

2. Results and Discussion

The CDs used herein were synthesized on the basis of a previously reported method, including the decomposition and pyrolysis of anhydrous citric acid accompanied by the surface passivation reaction of the amine groups of 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPMS) with the carboxyl groups driven from the pyrolyzed species. These CDs emitted strong blue light under UV excitation with a solution photoluminescence quantum yield (PL QY) of 51%. The obtained CDs comprised a large amount of methoxysilane groups, which led to highly reactive intermediates responsible for bonding with silanols and hydroxyl groups. Thus, these CDs can be further fabricated into silica-encapsulated nanoparticles by hydrolyzing and co-condensing with silica precursors. We then fabricated the CDs grafted CaAl₁₂O₁₉:Mn⁴⁺ phosphor by a facile one-step sol-gel method through the hydrolysis of tetraethyl orthosilicate (TEOS). As illustrated in Figure 1b, the hydrolysis and condensation reactions of TEOS led to the formation of an inorganic silica framework for the sol-gel process. The produced hydration silicon dioxides or low polymeric hydration silicon dioxides will adsorb -OH on the surface of the phosphor and start precipitating to form precipitation nuclei. More SiO₂ will then precipitate on these nuclei so that a new silica layer will continuously be formed. At the same time the CDs are further embedded into the silica layer around the phosphors. The FTIR spectra of the CDs and of the CDs/CAO phosphors are shown in Figure 2a, the characteristic peak at 1635 cm⁻¹ could be assigned to the stretching vibration of the C=O groups from the C=ONH units of the CDs. The formation of the silica layer was confirmed by the presence of the Si-O-Si asymmetric stretching peak at 1116 cm⁻¹. Figure 2b shows the scanning electron microscopy (SEM) image of the synthesized CAO phosphor. It is clear that the sample shows a particle size dispersion in the range of 2 to 4 µm. Typical transmission electron microscopy (TEM) images of the CDs/CAO composite are presented in Figure 2c–e. It can clearly be seen that a transparent silica layer coating has been deposited on the surface of the CAO in which the CDs are distributed evenly.

Figure 1. a) Schematic drawing of a carbon dot with its multiaminosilane-functionalized surface. b) Schematic illustration of the preparation of CDs/CAO through sol-gel processing.
verifying the successfully grafting of the CDs. A high crystallinity with a lattice fringe distance of 1.09 nm can be observed in the inset in Figure 2d, corresponding to that of the (002) facet of CAO. By increasing the magnification we can see that the CDs are well dispersed in the silica layer of CAO with average sizes of around 8 nm. An even closer observation (inset in Figure 2e) reveals a high crystallinity with a lattice fringe distance of 0.21 nm, corresponding to that of the (100) facet of graphitic carbon.\(^{[23]}\) The X-ray photoelectron spectroscopy (XPS) results are demonstrated in Figure 2f. Although the C 1s peak is an inevitable pollution peak for the CAO, the N 1s peak can still clearly be observed at 403 eV and the carbon content has increased for the CDs/CAO, verifying again that the CDs were successfully grafted on the CAO surface.

Figure 3a shows the X-ray diffraction (XRD) patterns of the CDs, CDs/CAO, and CAO materials. For the CDs, one broad peak was observed around \(2\theta = 20^\circ\), indicating that the CDs are amorphous as has been reported before in the literature.\(^{[24]}\) For the CDs-CAO, a broad band centered at \(2\theta = 20^\circ\) was found, which could be ascribed to the amorphous phases of the CDs and that of \(\text{SiO}_2\) (JCPDS No. 29–0085), and the other peaks could be indexed to CAO (JCPDS No. 84–1613), indicating that the crystal form of CAO was retained.

Figure 3b shows that the absorption and emission spectra of the CAO and CDs solution partly overlap, indicating that a slight fluorescence resonance energy transfer (FRET) process from the CDs donor to the CAO acceptor might occur. Figure 3c shows the decay lifetimes for CD emission of the CDs@\(\text{SiO}_2\) and CDs/CAO materials monitored at 450 nm. The decay curves could be well fitted to a second-order exponential equation as follows:

\[
I(t) = I_0 + A_1 \exp\left(-t/\tau_1\right) + A_2 \exp\left(-t/\tau_2\right) \quad (1)
\]

where, \(I(t)\) is the luminescence intensity at time \(t\) and \(I_0\) is the background luminescence intensity, \(A_1\) and \(A_2\) are constants, \(\tau_1\) and \(\tau_2\) are the lifetimes of the exponential components. In addition, the average lifetime constant \(\tau\) could be calculated by:\(^{[25]}\)

\[
\tau = \frac{(A_1\tau_1^2 + A_2\tau_2^2)}{(A_1\tau_1 + A_2\tau_2)} \quad (2)
\]

the average decay time of CDs@\(\text{SiO}_2\) was calculated to be 11.64 ns, and that for CDs/CAO was calculated to be 7.62 ns. Due to the electronic transitions in the CDs, the emission decay of CDs-doped samples are composed of two processes: a short-lived component \(\tau_1\) (1–4 ns) and a long-lived component \(\tau_2\) (7–11 ns), indicating the strong coupling between the core and the surface states of the CDs, which is similar to that of luminescent Si nanoparticles.\(^{[26]}\) The PL lifetime of the CDs donors in the CDs/CAO compound was smaller than that of CDs in a silica matrix. Therefore, we recorded the PL decay curves of the CAO, CAO@\(\text{SiO}_2\), and CDs/CAO to analyze the lifetime of CAO (Figure 3d). The decay curves could be fitted well by the following single-exponential equation:

\[
I(t) = I_0 + A \exp\left(-t/\tau\right) \quad (3)
\]

where, \(I(t)\) is the luminescence intensity at time \(t\) and \(I_0\) is the background luminescence intensity, \(A\) is a constant, and \(\tau\) is the lifetime of the exponential components. According to the fitting results, the decay times of CAO@\(\text{SiO}_2\), CAO, and CDs/CAO were calculated to be 0.90, 0.96, and 0.98 ms, respectively. Compared to pure CAO, the decay time of CAO in a silica matrix decreased slightly, but in combination with CDs the decay time of CAO increased slightly. This relatively small change was due to the weak red emission of the CDs.
Theoretically, if an energy-transfer process occurs between the CDs and CAO, the decay lifetime of the CDs donors decreases and that of the CAO acceptors increases. Our results thus indicate that there is a small amount of energy transfer occurring between the CDs and CAO. Although the intrinsic optical characteristics of the original CDs and CAO did not greatly influence each other, these small changes are still beneficial for the adjustment of the relative emissions intensities of the CDs and CAO in the CDs/CAO compound.

Figure 4a shows the excitation-wavelength-dependent PL spectra of the CDs with the strongest emission peak at 450 nm under excitation at 360 nm. The excitation-wavelength-dependent PL emission of the CDs is a simple consequence of the lowered excitation energy, leaving the various higher emission energy levels inaccessible and increasing the associated energy for the Stokes shift in each case. We could thus easily control the emission wavelength of the CDs, which led to more relative emission intensities of the CDs/CAO compound. Figure 4b shows the normalized fluorescence spectra of CDs, CAO, and CDs/CAO (mass ratio: 0.04). The CDs exhibited an emission peak located at 450 nm under 360 nm excitation. The CAO material exhibits three emission bands under 330 nm excitation: namely at 643 nm, 657 nm, and 667 nm, that were related to the \(^{2}E \rightarrow ^{4}A_{2}\) transition of Mn\(^{4+}\). As expected, the CDs/CAO compound displayed both the characteristic emissions of CDs and those of CAO under a single excitation wavelength of 365 nm. The characteristic emission of the CDs was hereby red shifted, which might be due to the self-absorption in the CDs due to the relatively high content. This would mean that the emission from smaller dots was consecutively absorbed and re-emitted by larger dots.

As demonstrated in Figure 4c, the characteristic emission intensity of both CDs and CAO changed systematically when the excitation wavelength of the CDs/CAO was tuned from 320 nm to 400 nm in intervals of 10 nm. In accordance with the CIE chromaticity coordinates in Figure 4d, the color footprints ran across the white-light emission region from (0.339, 0.366) to purplish-pink (0.352, 0.219). This finding revealed that white-light emission could indeed be obtained by varying the excitation wavelength. Furthermore, we expected that the emissions could be easily tuned by adjusting the relative concentration of the CDs and the CAO. As shown in Figure 5a, the emission spectra of CDs/CAO with different relative concentration (mass ratio: 0.01, 0.02, 0.04, 0.10, 0.20) under 365 nm excitation exhibited the characteristic emission of both the CDs and the CAO. As shown in Figure 5a, the emission spectra of CDs/CAO with different relative concentration (mass ratio: 0.01, 0.02, 0.04, 0.10, 0.20) under 365 nm excitation exhibited the characteristic emission of both the CDs and the CAO. As shown in Figure 5a, the emission spectra of CDs/CAO with different relative concentration (mass ratio: 0.01, 0.02, 0.04, 0.10, 0.20) under 365 nm excitation exhibited the characteristic emission of both the CDs and the CAO. As shown in Figure 5a, the emission spectra of CDs/CAO with different relative concentration (mass ratio: 0.01, 0.02, 0.04, 0.10, 0.20) under 365 nm excitation exhibited the characteristic emission of both the CDs and the CAO. As shown in Figure 5a, the emission spectra of CDs/CAO with different relative concentration (mass ratio: 0.01, 0.02, 0.04, 0.10, 0.20) under 365 nm excitation exhibited the characteristic emission of both the CDs and the CAO. As shown in Figure 5a, the emission spectra of CDs/CAO with different relative concentration (mass ratio: 0.01, 0.02, 0.04, 0.10, 0.20) under 365 nm excitation exhibited the characteristic emission of both the CDs and the CAO. As shown in Figure 5a, the emission spectra of CDs/CAO with different relative concentration (mass ratio: 0.01, 0.02, 0.04, 0.10, 0.20) under 365 nm excitation exhibited the characteristic emission of both the CDs and the CAO.
could be tuned from red to blue in accordance with the different proportions of red and blue emission, respectively.

Apparently, as the concentration of CDs increased the emission band of the CDs became broader. This process was likely driven by consistent self-absorption, where each Stokes shift from the previous emission progressively reduced the highest accessible energy level for the next absorption. Nevertheless, a wide span of energy levels allowed this progressive down shift to continue smoothly over a wide energy range leading to a red shift. The corresponding CIE chromaticity diagram of the different CDs/CAO samples under 365-nm excitation is shown in Figure 5b. The samples numbered from 1 to 5 correspond to different relative concentrations of CDs/CAO (mass ratio: 0.01, 0.02, 0.04, 0.10, 0.20, respectively). The color could thus systematically be tuned from purplish-red (0.504, 0.250) to purplish-pink (0.438, 0.223) and from white (0.281, 0.213) to greenish-blue (0.238, 0.192), as shown in Table 1. Photographs of the corresponding phosphors excited under a 365-nm UV lamp are shown on the right-hand side of Figure 5b. The color composition could thus be regulated by changing the content of the CDs in the CDs/CAO phosphors to meet specific requirements. These optical properties indicate that the CDs/CAO phosphors have a great potential in the fabrication of phosphor-based LEDs. Figure 5c shows the electroluminescence (EL) spectrum from a white-light LED device at an optimized current of 30 mA (ca. 3.2 V), with two emission bands: one broad band at 450 nm and another characteristic peak at 657 nm with corresponding CIE coordinates of (0.334, 0.360), which are very close to ideal white (0.333, 0.333). The device was made by coating CDs/CAO (mass ratio: 0.04) as phosphors encased in an epoxy resin on a prototype solid-state lighting unit comprised of a light-emitting chip with an excitation wavelength of 375 nm. We could therefore conclude that our CDs/CAO phosphors are promising candidates for practical light-emitting applications.

The dual emission spectrum of the CDs/CAO also makes it an excellent candidate for self-referencing luminescent thermometers, which are expected to be more accurate than single-parameter temperature sensors because they provide self-calibrated results by two readouts. To illustrate the potential application of our CDs/CAO compounds as luminescent thermometers, we measured the temperature-dependent emission spectra of CDs/CAO from 80 to 300 K under a single excitation wavelength of 365 nm. These spectra are shown in Figure 5d. The CDs/CAO exhibited a temperature-dependent luminescent behavior with respect to the emission of the CDs at 450 nm and that of the CAO at 652 nm. The luminescent intensities decreased gradually with increasing temperature. The enhanced non-radiative recombination may play an important role in the PL thermal quenching due to the activation of non-radiative recombination centers with increasing temperature. The enhanced non-radiative recombination may play an important role in the PL thermal quenching due to the activation of non-radiative recombination centers with increasing temperature. The enhanced non-radiative recombination may play an important role in the PL thermal quenching due to the activation of non-radiative recombination centers with increasing temperature. The emission peak of the CDs at 450 nm was found to red shift towards a lower energy, which was mainly due to the strong phonon scattering at higher temperatures.280
The intensity ratio of two emissions is commonly used as the thermometric parameter in ratiometric luminescence temperature sensing. For our CDs/CAO, this parameter can be defined by using the ratio of the intensity of the CAO at 652 nm and that of the CDs at 450 nm ($F_{652}/F_{450}$). The temperature-dependence of the $F_{652}/F_{450}$ ratio is plotted in Figure 5e, a good linearity was obtained in the range of 80 to 300 K, which can be described as:

$$T = 1248.13 - 549.45F_{652}/F_{450}$$  \hspace{1cm} (4)

with a correlation coefficient of 0.9818, where $T$ is the temperature of the CDs/CAO phosphors system (K). For a ratiometric luminescent temperature sensor, the relative sensitivity can be determined as:

$$S = \frac{\partial (I_1 / I_2)}{\partial T} \frac{I_1}{I_2}$$  \hspace{1cm} (5)

where $I_1$ and $I_2$ are the two luminescence intensities of the dual emission.[29] Herein, the sensitivity of the CDs/CAO thermometer achieved a maximum value of 0.18% K$^{-1}$ at 300 K. A linear response was clearly found for the CDs/CAO thermometer from cryogenic temperature up to room temperature, which

Table 1. CIE coordinates for CDs/CAO with different relative concentration excited at 365 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (Mass ratio)</th>
<th>CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>(0.504, 0.250)</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>(0.438, 0.223)</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>(0.364, 0.221)</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>(0.281, 0.213)</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>(0.238, 0.192)</td>
</tr>
</tbody>
</table>

Figure 5. a) Emission spectra of CDs/CAO samples with different mass ratios: 0.01, 0.02, 0.04, 0.10, and 0.20. All samples were excited at 365 nm. b) CIE chromaticity diagram for a CDs solution, a CAO phosphor, and CDs/CAO samples with different mass ratios, whereby samples 1 to 5 correspond to mass ratios of 0.01, 0.02, 0.04, 0.10, 0.20, respectively. All samples were excited at 365 nm. The photographs of the corresponding samples excited under a 365 nm UV lamp are shown on the top right of the picture. c) Electroluminescence spectrum of a white LED lamp fabricated using a 375-nm chip combined with a white-emitting CDs/CAO (mass ratio: 0.04) phosphor. d) Temperature-dependent emission spectra of CDs/CAO (mass ratio: 0.04) recorded every 20 K from 80 to 300 K. The material was excited at 365 nm. e) Temperature-dependent intensity ratio of CAO (652 nm) to CDs (450 nm) and the fitted curve for the phosphors.
makes this material a more reliable and useful luminescent thermometer.

3. Conclusions
A simple and effective strategy has been carried out for incorporating carbon dots (CDs) into a CaAl$_2$O$_{19}$:Mn$^{4+}$ phosphor (CAO) by a facile one-step sol-gel method through the hydrolysis of tetrathyl orthosilicate (TEOS). The CDs benefit from surface methoxysilyl groups after using an organosilane as the coordinating solvent, which are highly reactive intermediates responsible for bonding with the silanols and hydroxyl groups of the silica-coated CAO. The emission trajectory of the CDs/CAO can be tuned by carefully optimizing their concentration and their excitation wavelength. The CDs/CAO phosphors show great potential in multicolor displays, LEDs, and temperature sensors. We propose that this research could promote the practical application of CDs/CAO in solid-state luminescence related fields.

4. Experimental Section

Synthesis of CAO: CaAl$_2$O$_{19}$:Mn$^{4+}$ phosphors were prepared by a conventional solid-state reaction. According to the literature,[19] Mn ions were added in the form of MnCO$_3$. Ca$_2$F and MgF$_2$ were also added to serve as a flux. Commercially available high-purity reagents (99.9–99.999%) of CaO, Al$_2$O$_3$, CaF$_2$, MgF$_2$, and MnCO$_3$ were used throughout the procedure. Each sample weighed a total of 500 g, including 0.1 mol% MnCO$_3$, and they were mixed using an alumina mortar and pestle. The mixed batches were fired in a platinum crucible at 1923 K, for 3 h in air. The fired specimens were then ground into powders and separated with a 400 mesh sieve for further use.

Synthesis of CDs: The CDs were synthesized according to a reported method.[20] Briefly, 3-(2-aminoethylamino)propyltrimethoxysilane (AEPMS) (10 mL) was placed into a 100 mL three-necked flask, and degassed with nitrogen for 15 min. Heat was applied, until the temperature reached 240 °C, then anhydrous citric acid (0.4 g) was added quickly under vigorous stirring. After 5 min, the reaction stopped. Then the flask was left to cool down to room temperature. Then the product was purified by precipitation with petroleum ether three times.

Preparation of CDs/CAO: For the preparation of the CDs/CAO compound, the CaAl$_2$O$_{19}$:Mn$^{4+}$ phosphor (0.5 g) was put into a hydrolyzed sol (8 mL), whose molar ratio of the constituents was TEOS/ETOHand/H$_2$O = 1:4:0.25. The CDs (mass ratio of the CDs solution to CAO phosphor: 0.01, 0.02, 0.04, 0.10, 0.20) were put into ethanol (1 mL) and the pH was adjusted to 6.5 by adding hydrochloric acid. The CDs solutions were then added into the above CAO mixture and kept under stirring at room temperature until a uniform gel formed. The derived gel was dried under vacuum at 80 °C for 12 h. Then the xerogel was ground into a powder to obtain the final CDs/CAO compound. The CDs-embedded silica nanoparticles (CDs@SiO$_2$) (mass ratio: 0.04) were prepared in the same way but without the addition of CAO. The silica-coated CAO compounds (CAO@SiO$_2$) (mass ratio: 0.04) were also prepared in the same way but without the addition of CDs.

Fabrication of LEDs: For the fabrication of LEDs, a UV-LED chip with an emission peak wavelength centered at 375 nm was used. In a typical preparation, a mixture of transparent silicon resin and CDs/CAO (mass ratio: 0.04) phosphors were integrated on the UV-LED chip. The ratio of phosphors retained in the silicon gel was 10 wt%. The phosphors and silicon gel mixtures were cured at 80 °C for 30 min.

Characterization: X-ray photoelectron spectroscopy (XPS) was carried out on an AXIS ULTRA DLD, Kratos. The FT-IR spectra were recorded on a Nicolet Avatar 360 Fourier transformation infrared spectrophotometer. Transmission electron microscopy (TEM) images were recorded with a FEI Tecnai 12 transmission electron microscope and the high-resolution TEM (HRTEM) images were recorded using a JEO-L2010 electron microscope. The scanning electron microscopy (SEM) images were recorded using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). UV-vis absorption spectra were recorded using an ultraviolet-visible spectrophotometer (UV-2550, Shimadzu). Photoluminescence spectra were recorded with a fluorescence spectrophotometer (F-7000, Hitachi). The absolute PL quantum yields (QYs) were measured with the same spectrometer using an integrating sphere with its inner face coated with BAF325. Temperature-dependent photoluminescence emission spectra were conducted by combining a heating apparatus (Oxford Instruments) with the same Hitachi F-7000 fluorescence spectrophotometer. The decay lifetimes were recorded on a spectrophotometer (HORIBA, Jobin Yvon FL3–21). The XRD patterns were recorded using powder X-ray diffraction (MSAL XD-2, Beijing, China) with Cu Kα (Kα1 = 0.15405 nm) irradiation and operating at 36 kV and 30 mA with a scanning step of 0.02° (2θ) and a scanning speed of 8° min$^{-1}$.

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