Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

A general strategy via charge transfer sensitization to achieve efficient NIR luminescence in lanthanide-doped $NaGdS_2$ nanocrystals

- Supporting Information

Shiteng Wang,[abc] Chunguang Zhang,[a] Wei Zheng,*[acd] Zhongliang Gong,[a] Ping Huang,[ad] Jin Xu,[ad] Youyu Liu,[a] Renfu Li[ad] and Xueyuan Chen*[abcd]

[a]*CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Key Laboratory of Nanomaterials, and State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.*

[b]*School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China.*

[c]*University of Chinese Academy of Sciences, Beijing 100049, China.*

[d]*Fujian Science and Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, China.*

Fax: +86-591-63179421; Tel: +86-591-63179421; E-mail: zhengwei@fjirsm.ac.cn; xchen@fjirsm.ac.cn

Table S1. Effective photoluminescence (PL) lifetimes (τ_{eff}) and PL quantum yields (QYs) of $NaGdS_2$:0.5%Yb^{3+} nanocrystals (NCs) with different sizes by monitoring the Yb^{3+} emission at 991 nm. τ_{eff} was calculated by

$$\tau_{eff} = \frac{1}{I_{max}} \int_0^\infty I(t)dt ,$$

where $I(t)$ denotes the PL intensity as a function of time t, and I_{max} is the maximum PL intensity.

Size (nm)	τ_{eff} (μs)	PLQY
14.7	327	9.9%
20.1	348	14.0%
27.8	421	16.4%
36.7	562	21.2%

Table S2. Effective PL lifetimes (τ_{eff}) of 36.7-nm $NaGdS_2$:*x*%Yb^{3+} NCs with different Yb^{3+} concentrations (C (Yb^{3+})) by monitoring the Yb^{3+} emission at 991 nm.

C (Yb^{3+}) / mol%	τ_{eff} (μs)
0.02	263
0.10	357
0.30	456
0.50	494
1.00	388
3.00	264

Table S3. Temperature-dependent effective PL lifetimes (τ_{eff}) of $NaGdS_2$:0.5%Yb^{3+} NCs (size: 36.7 nm) in the temperature range of 10-300 K by monitoring the Yb^{3+} emission at 991 nm.

T / K	τ_{eff} (μs)	T / K	τ_{eff} (μs)
10	483	160	509
30	509	190	512
50	508	220	509
70	497	250	486
100	471	280	469
130	494	300	427

Table S4. Effective PL lifetimes of Yb^{3+} (τ_{eff}^{Yb}) and Er^{3+} (τ_{eff}^{Er}) in $NaGdS_2$: 0.5%Yb^{3+}/*x*%Er^{3+} NCs with different Er^{3+} concentrations (*C* (Er^{3+})) by monitoring the Yb^{3+} and Er^{3+}emissions at 991 nm and 1545 nm, respectively. The efficiency of energy transfer (η_{ET}) from Yb^{3+} to Er^{3+} was calculated by

$$\eta_{ET} = 1 - \frac{\tau_x^{Yb}}{\tau_0^{Yb}} \ ,$$

where $\boldsymbol{\tau_0^{Yb}}$ and $\boldsymbol{\tau_x^{Yb}}$ represent the effective PL lifetime of Yb^{3+} in $NaGdS_2$: 0.5%Yb^{3+}/*x*%Er^{3+} NCs with 0 and *x* mol% of Er^{3+}, respectively.

C (Er^{3+}) / mol%	τ_{eff}^{Yb} (μs)	τ_{eff}^{Er} (ms)	η_{ET} (%)
0	494	0	0
0.02	401	11.3	18.8
0.10	392	10.2	20.6
0.30	377	7.8	23.7
0.50	349	6.6	29.4
1.00	277	4.7	43.9
2.00	184	2.6	62.8

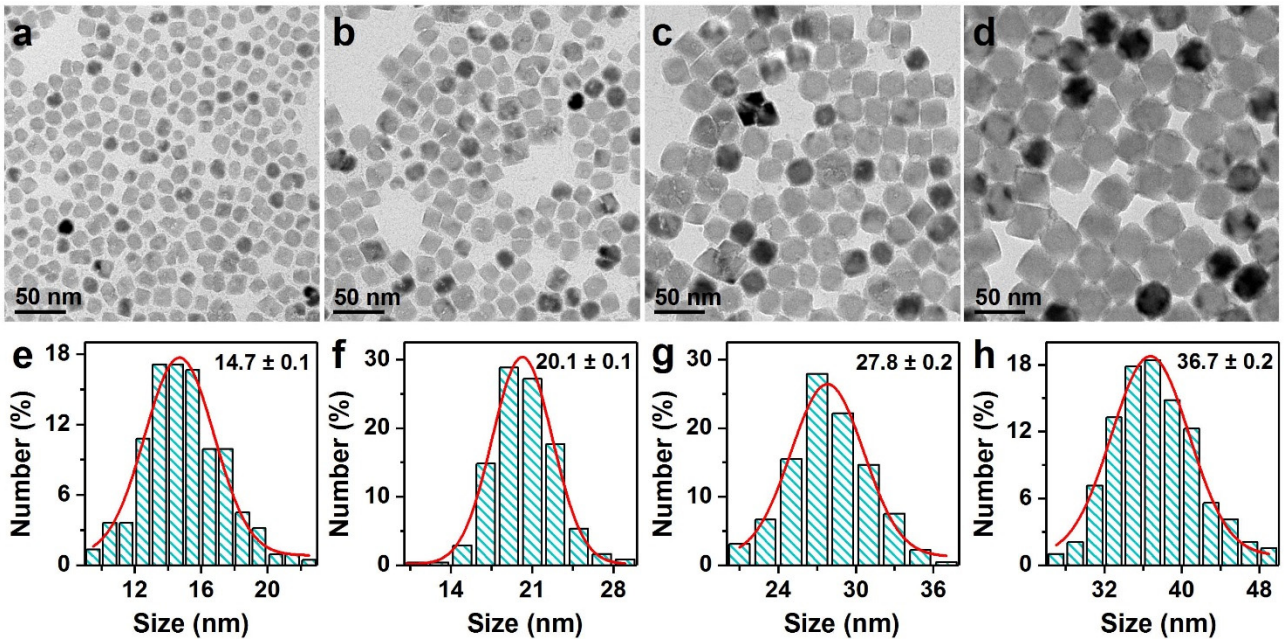

Figure S1. TEM images and size distributions of $NaGdS_2$:0.5%Yb^{3+} NCs synthesized at 265 °C for (a,e) 5 min, (b,f) 10 min, (c,g) 30 min, and (d,h) 60 min. The size distributions of the NCs were obtained by randomly calculating 200 particles in the TEM images.

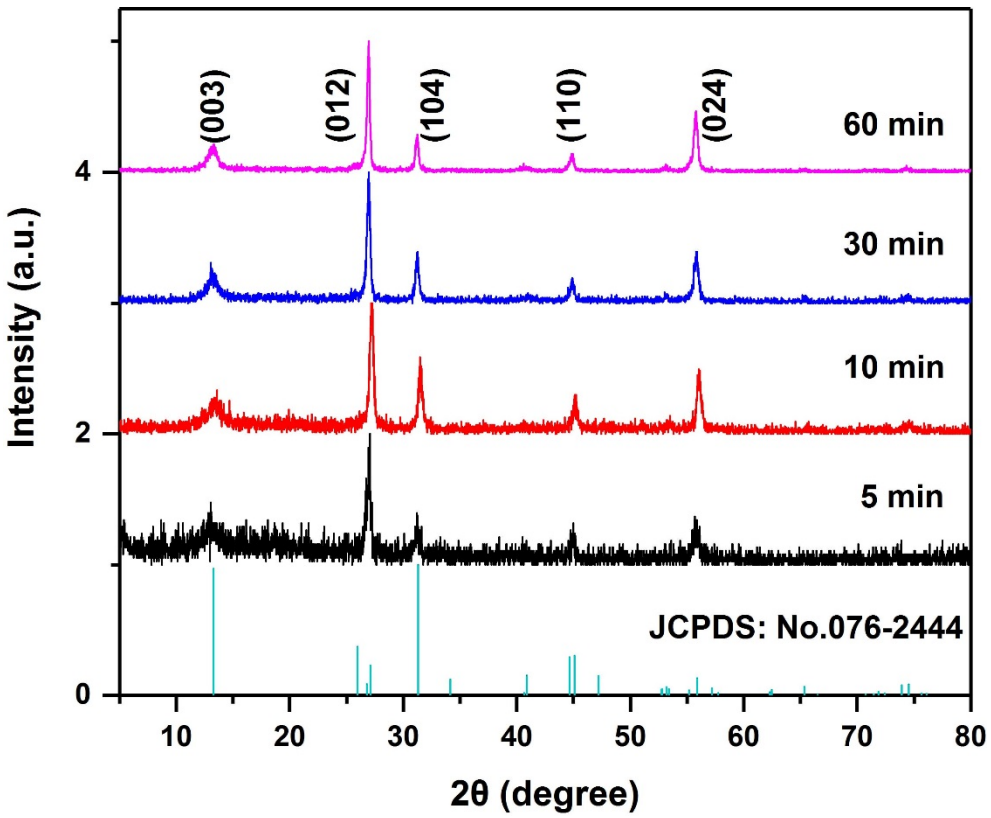

Figure S2. XRD patterns of $NaGdS_2$:0.5%Yb^{3+} NCs synthesized at 265 °C for 5, 10, 30, and 60 min, respectively. The positions of all diffraction peaks match well with the standard pattern of rhombohedral $NaGdS_2$ (JCPDS no. 076-2444). No additional diffraction peaks of impurities such as γ-Gd_2S_3 and Gd_2O_2S are observed in XRD patterns, indicating pure phase and high crystallinity of the resulting NCs. Note that the diffraction peak intensities of the NCs deviate from those of the standard JCPDS pattern, due to the preferred orientation growth of the NCs along the (012) plane, as also observed in $KLuS_2$ and $RbGdS_2$ crystals previously reported.[1, 2]

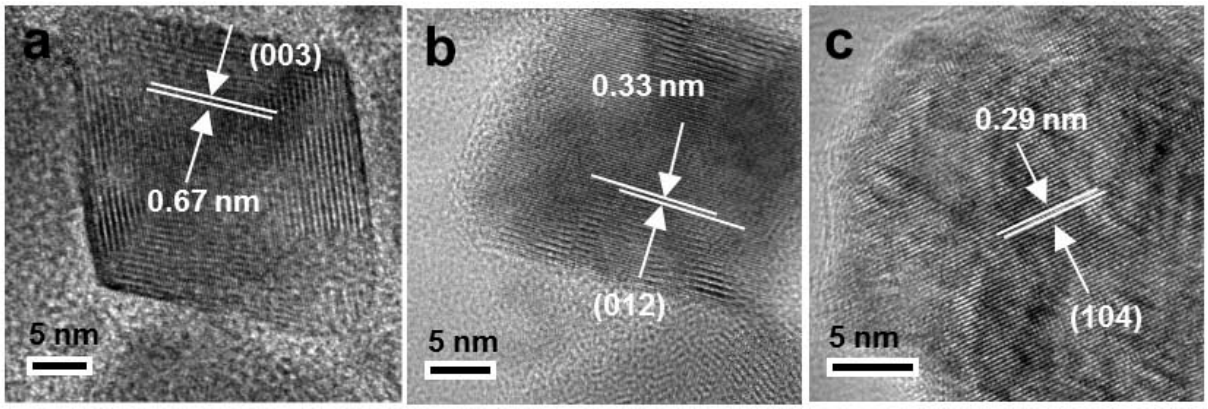

Figure S3. Representative high-resolution TEM (HRTEM) images of $NaGdS_2$:0.5%Yb^{3+} NCs, showing clear lattice fringes with calculated *d* spacings of (a) 0.67, (b) 0.33 and (c) 0.29 nm, which match well with the lattice spacings of the (003), (012) and (104) planes of rhombohedral $NaGdS_2$, respectively.

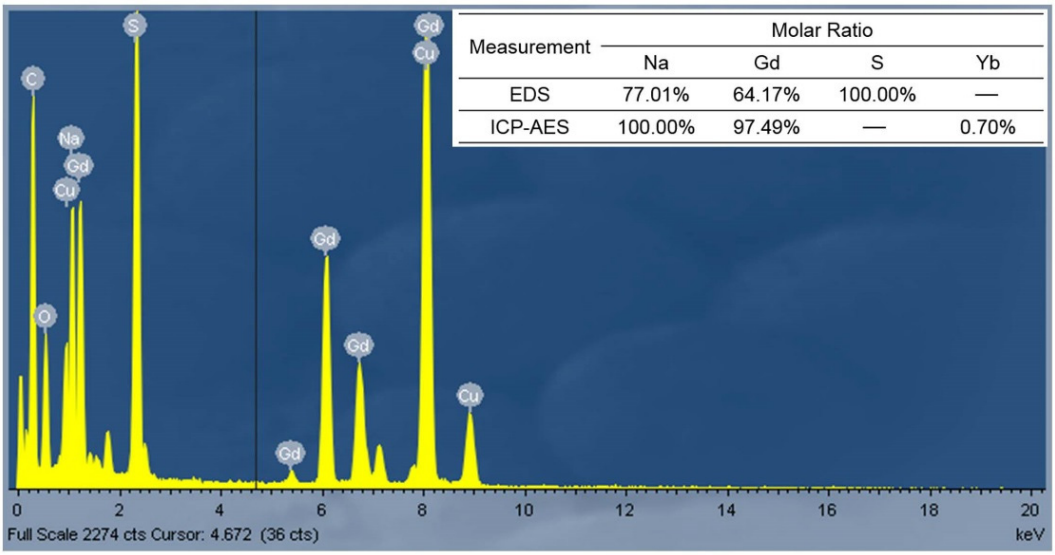

Figure S4. Energy dispersive X-ray (EDX) spectrum of $NaGdS_2$:0.5%Yb^{3+} NCs synthesized at 265 °C for 60 min, showing the elements of Na, Gd and S in the NCs. Yb^{3+} ion was not detected because of its low doping level (0.5 mol%). The insets show the chemical compositions of the NCs determined by EDX spectrum and inductively coupled plasma-atomic emission spectroscopy (ICP-AES), revealing the successful doping of Yb^{3+} in the NCs.

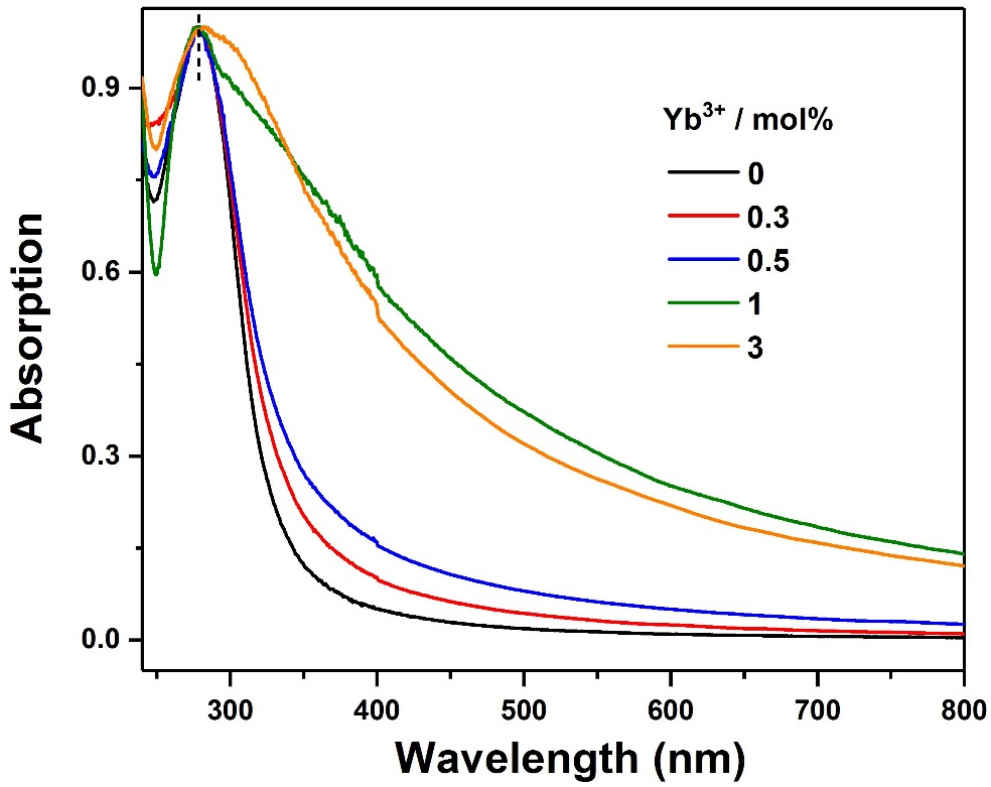

Figure S5. Optical absorption spectra of $NaGdS_2$:*x*%Yb^{3+}NCs with different Yb^{3+} concentrations synthesized at 265 °C for 60 min. All NCs exhibit a strong absorption band at around 279 nm (4.44 eV), which agrees well with the host absorption of $NaGdS_2$ previously reported.[3] Besides the host absorption, an additional absorption band at around 351 nm was observed in Yb^{3+}-doped NCs, with an intensity increased with increasing Yb^{3+} concentration. This absorption band can be assigned to the S^{2-}-to-Yb^{3+} ligand-to-metal charge transfer transition, as previously reported by G. Blasse *et al.* in $NaYS_2$:Yb^{3+}/Er^{3+} bulk crystals.[4]

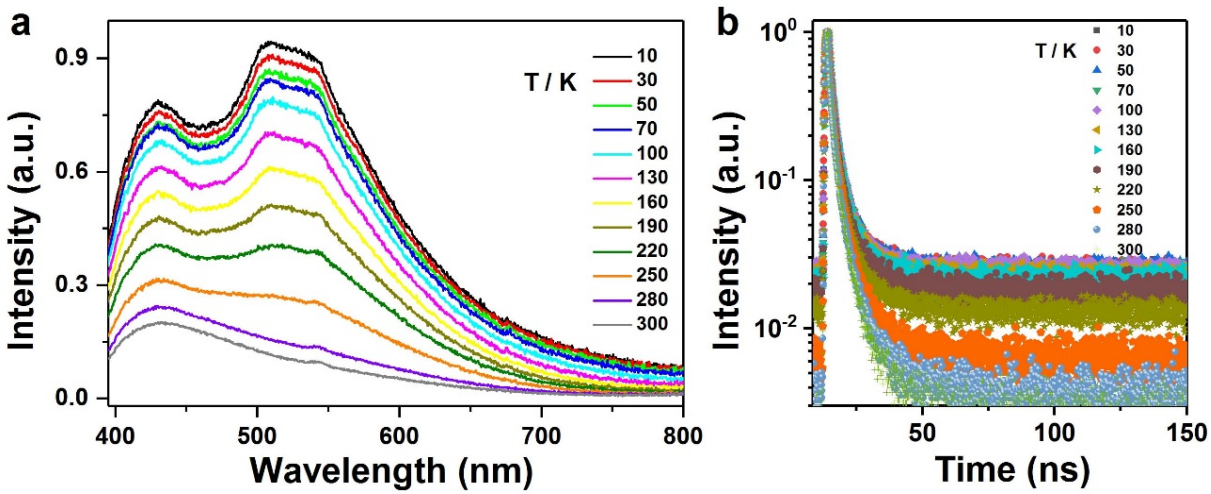

Figure S6. Temperature-dependent PL emission spectra (λ_{ex} = 370 nm) and PL decay curves (λ_{em} = 512 nm) of $NaGdS_2$:0.5%Yb^{3+} NCs. The NCs exhibited two broad emission bands covering from 400 nm to 750 nm, which were also observed in the undoped $NaGdS_2$ (Fig. S6) and can be ascribed to the defect emissions related to S^{2-} deficiency in the NCs.[5, 6] The PL intensities and PL lifetimes (6.8-2.4 ns) of the defects decreased significantly with the temperature rise due to thermal quenching.

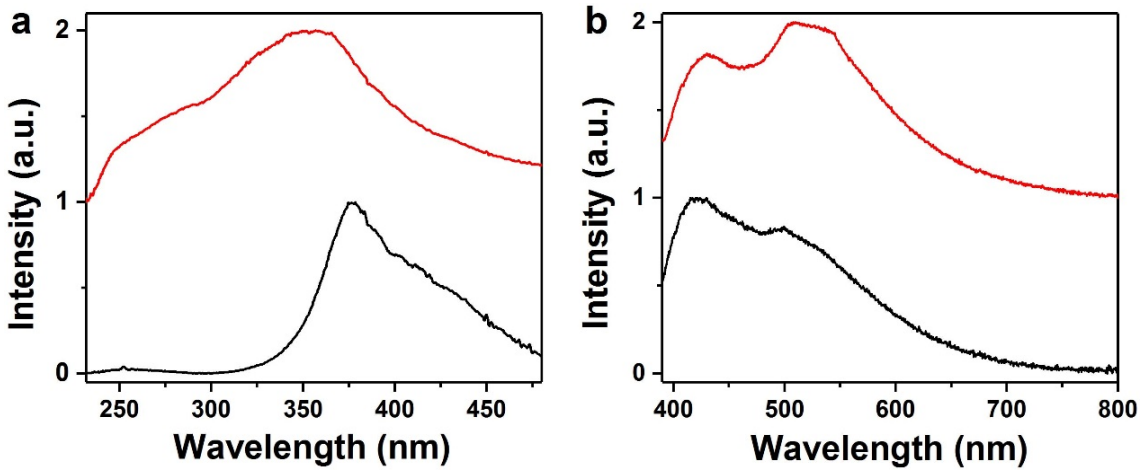

Figure S7. (a) PL excitation spectra of $NaGdS_2$:0.5%Yb^{3+} NCs by monitoring the defect emission at 512 nm (black curve) and the Yb^{3+} emission at 991 nm (red curve). (b) 10 K PL emission spectra of (black curve) the undoped and (red curve) 0.5 mol% Yb^{3+} doped $NaGdS_2$ NCs upon excitation at 370 nm. The different PL excitation spectra for the defect and Yb^{3+} emissions, the similar emission bands in the undoped and Yb^{3+}-doped NCs, and the nanosecond PL lifetimes (2.4-6.8 ns) confirmed that the visible emissions under 370-nm excitation was ascribed to the defect emission related to the S^{2-} deficiency in the NC host rather than the charge transfer luminescence of Yb^{3+}.[7] This indicates an extremely low quenching temperature (<10 K) for the charge transfer luminescence of Yb^{3+} in $NaGdS_2$:0.5%Yb^{3+} NCs.

Reference:

1. V. Jary, L. Havlak, J. Barta, E. Mihokova and M. Nikl, *Chem. Phys. Lett.*, 2013, **574**, 61-65.
2. V. Jary, L. Havlak, J. Barta, E. Mihokova and M. Nikl, *Opt. Mater.*, 2013, **35**, 1226-1229.
3. V. Jary, L. Havlak, J. Barta, M. Buryi, E. Mihokova, M. Rejman, V. Laguta and M. Nikl, *Materials*, 2015, **8**, 6978-6998.
4. P. Gerner and H. U. Güdel, *Chem. Phys. Lett.*, 2005, **413**, 105-109.
5. L. Havlak, V. Jary, M. Rejman, E. Mihokova, J. Barta and M. Nikl, *Opt. Mater.*, 2015, **41**, 94-97.
6. Y. Gao, R. F. Li, W. Zheng, X. Y. Shang, J. J. Wei, M. R. Zhang, J. Xu, W. W. You, Z. Chen and X. Y. Chen, *Chem. Sci.*, 2019, **10**, 5452-5460.
7. L. van Pieterson, M. Heeroma, E. de Heer and A. Meijerink, *J. Lumin.*, 2000, **91**, 177-193.