

Electronic supplementary information

Enhanced upconversion luminescence of BiOCl:Yb³⁺,Er³⁺ nanosheets via carbon dots modification and its optical temperature sensing

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Experimental Section

Chemicals and materials

$C_3H_6N_6$ (Aladdin, 99%), Er_2O_3 (Aladdin, 99.99%), Yb_2O_3 (Aladdin, 99.99%), $Bi(NO_3)_3 \cdot 5H_2O$ (A. R., Shanghai, China), and $NaCl$ (A. Tianjin, China) were used as starting materials. $Er(NO_3)_3$ and $Yb(NO_3)_3$ were prepared by dissolving the corresponding rare earth oxide in HNO_3 under heating.

Synthesis

All chemicals were used as purchased without any further purification. Melamine powder (10 g) was heated to 550 °C at a heating rate of 5 °C/min in a porcelain boat for 4 h. Then ground the reacted bulk sample into powder, a pale yellow bulk g- C_3N_4 solid powder was obtained.¹ Synthesis of CDs/BiOCl: Yb^{3+} , Er^{3+} composite. The sample was synthesized through a typical hydrothermal and subsequent heat treatment method. The specific process is as follows: A certain amount of g- C_3N_4 were ultrasonical immersed in 30 mL deionized water for 24 h and defined as solution A. After that, stoichiometric amounts of Yb_2O_3 (10.0 mol%) and Er_2O_3 (1.0 mol%) were dissolved in an appropriate amount of concentrated nitric acid at 200 °C and 5 mmol $Bi(NO_3)_3 \cdot 5H_2O/NaCl$ was added to 50 mL of deionized water with continuous stirring to obtain solution B. The solution B was dropwise added into solution A under stirring. After being stirred for 1h, the suspension was added into 100 mL Teflon-lined autoclave and subsequently heated at 160°C for 24 h. The reactor was then allowed to cool to room temperature naturally and the precipitate was collected and washed with deionized water and ethanol for six times, and the

final products dried at 60°C for 24 h. The added contents of g-C₃N₄ in the g-C₃N₄/BiOCl materials were 2, 4, 6, and 8 wt %, respectively. As a comparison, a sample without g-C₃N₄ was also prepared according to the above method. Subsequently, the prepared precursor was placed in a quartz crucible and heat-treated at 500°C for 2 hours in a muffle furnace with air atmosphere and thus the final phosphor was obtained. According to the compound amount of g-C₃N₄, the samples after heat treatment are named BYE, 2 CDs/BYE, 4 CDs/BYE, 6 CDs/BYE, 8 CDs/BYE, respectively.

Characterization

The crystalline structures of the samples were characterized by powder X-ray diffraction (XRD) (Bruker D8 Advance diffractometer using Cu K α (λ = 1.5406 Å) radiation). The morphology of the obtained samples was investigated by using scanning electron microscopy (SEM, Hitachi SU-8010) with an acceleration voltage of 25 kV accompanied with energy dispersive spectroscopy (EDS) to examine the chemical composition. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) of the samples were conducted using a TecnaiG2 TF30 electron microscope. The UV-Vis-NIR absorption spectra of the samples were obtained using a Hitachi UV-4100 spectrophotometer. The X-ray Photoelectron Spectroscopy spectrum (XPS) (Thermo Fisher Scientific, US) was carried out to analyze the surface elemental composition analyses. The FT-IR spectra were obtained using a German Bruker ALPHA infrared spectrometer. The UC luminescence spectra and lifetimes were recorded using an Edinburgh Instruments

FLS980 spectrofluorometric equipped with both continuous and pulsed xenon lamps and a 980 nm laser diode (LD) as excitation sources. The samples were placed inside a temperature-regulated chamber purged with N₂ gas (Linkam DSC 600 stage system) for obtaining the temperature-dependent spectra. The temperature of the chamber was varied from 293 to 573 K.

The photocurrents were measured using an electrochemical workstation (Bio-Logic SP-300) with a standard three-electrode system with a Pt wire as the counter electrode, saturated Hg/Hg₂Cl₂ (in saturated KCl) as the reference electrode, and Na₂SO₄ (0.5 M) aqueous solution as the electrolyte. Xenon lamp (power 300W) loaded with 420 nm filter as visible light source and a 980 nm laser diode was utilized as the light source. The transient photocurrent responses with time (I-t curve) of the working electrodes were measured at a bias potential of 1.5 V during repeated on/off illumination cycles under continuous irradiation.

Results Section

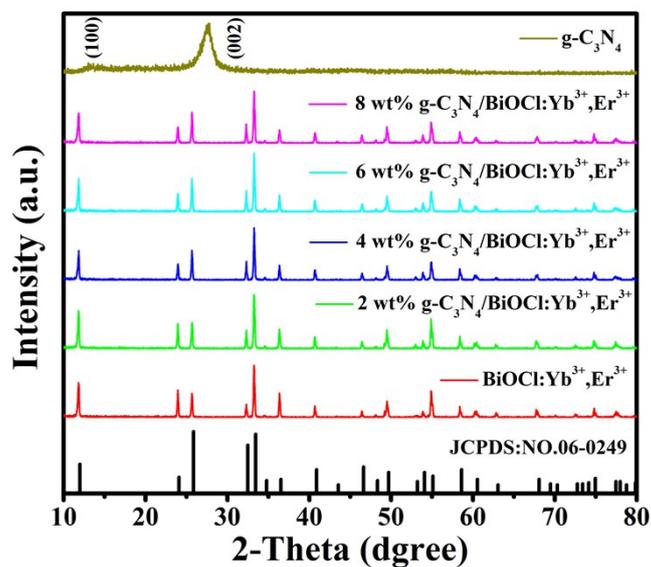


Figure S1. XRD of pure $\text{g-C}_3\text{N}_4$, BiOCl:Yb^{3+} , Er^{3+} and BiOCl:Yb^{3+} , Er^{3+} samples with different weight percentage of $\text{g-C}_3\text{N}_4$ in the composites before annealing.

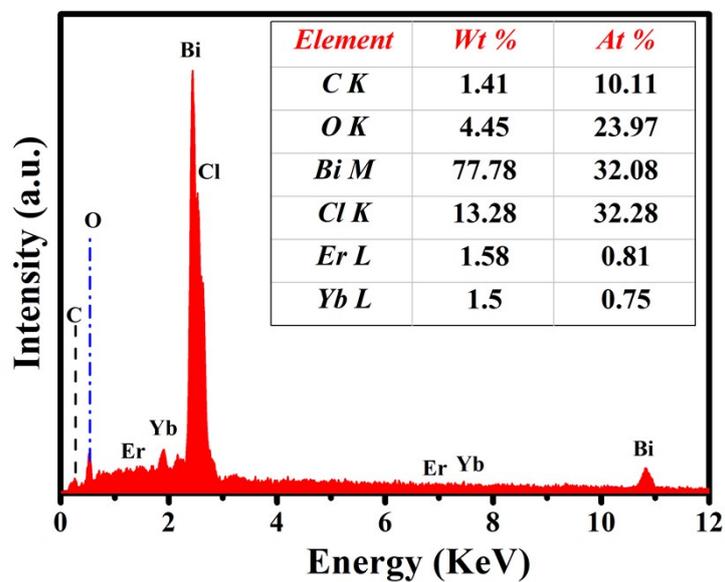


Figure S2. EDS spectrum of the 6CDs/BYE sample.

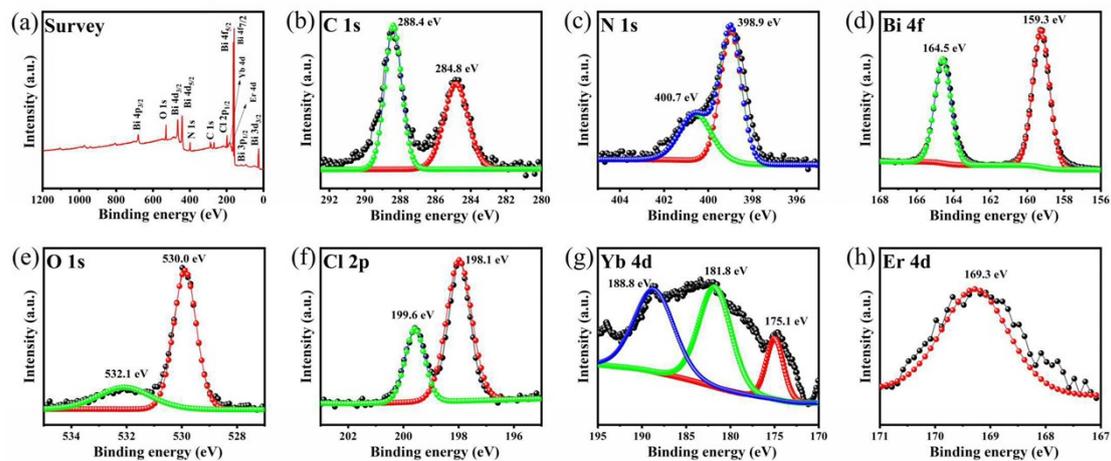


Figure S3. X-ray photoelectron spectroscopy (XPS) spectra of the 6CDs/BYE composite before heat treatment: (a) Survey, (b) C 1s, (c) N 1s, (d) Bi 4f, (e) O 1s, (f) Cl 2p, (g) Yb 4d, (h) Er 4d.

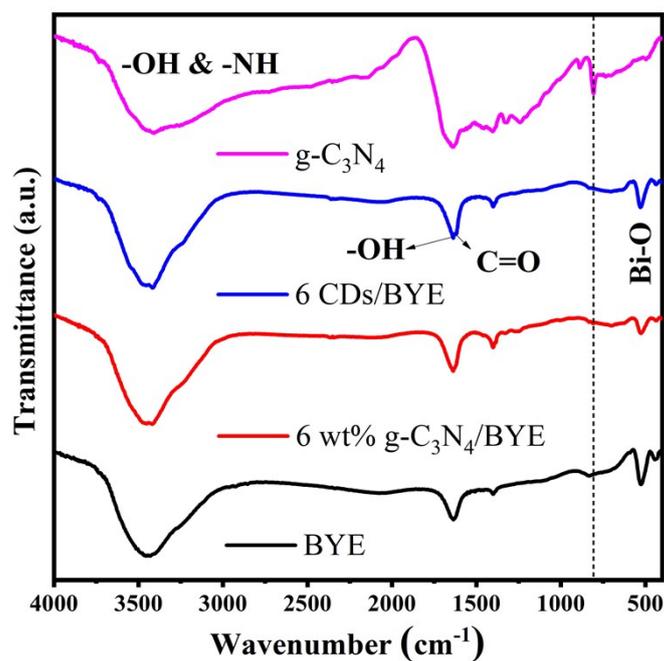


Figure S4. FT-IR spectra for the BYE , 6wt% g-C₃N₄/BYE, 6CDs/BYE, g-C₃N₄ samples.

In terms of g-C₃N₄, the broad peaks between 3000 and 3400 cm⁻¹ correspond to the stretching vibrational modes of N-H and O-H groups, respectively, which are associated with uncondensed amino groups and surface adsorbed H₂O molecules.² In addition, the characteristic vibration of thiazine rings at 806 cm⁻¹ is also observed.² The characteristic peak of BiOCl is observed at 528 cm⁻¹, which refers to the stretching vibration of Bi-O bond.¹ As for the g-C₃N₄/BYE hybrids, the peaks of g-C₃N₄ and BiOCl co-exist in the as-prepared g-C₃N₄/BYE nanocomposite and no other new phases are observed, manifesting that the g-C₃N₄/BYE composite nanosheets are successfully synthesized. After heat treatment, it is worth noting that the characteristic vibration peak of g-C₃N₄ disappeared, and the C=O bond vibration peak appeared at 1620 cm⁻¹.³

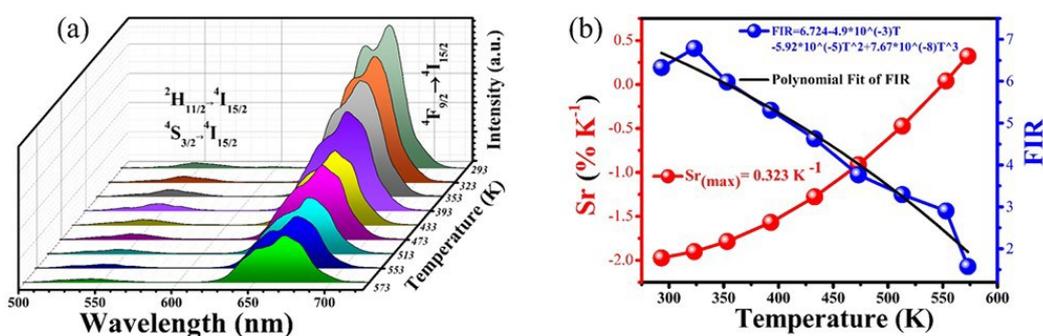


Figure S5. (a) Temperature-dependent photoluminescence spectra of the 6CDs/BYE nanosheets. (b) the temperature-dependent luminescent behaviors of $I_{\text{red}}/I_{\text{green}}$ as a function of temperature and relative sensitivities of S_r , respectively, with the excitation wavelength at 980 nm.

Compared with TCLs, the NTCLs have a variety of horizontal combinations for

the temperature sensing, which may be an effective method to obtain higher sensitivity. Greater flexibility in practical applications such as temperature range selection, excitation mode (wavelength/power), and detection method (UV-vis-NIR)⁴. Therefore, we investigated the temperature dependence of the red and green light energy levels of Er³⁺ ions under 980 nm excitation as shown in Fig. S5(a). Due to the traditional FIR (Eq. (4)) is not suitable for the NTCL, the experimental FIR can be fitted by polynomial function:

$$FIR = \frac{I_{red}}{I_{green}} = C_1 + B_1T + B_2T^2 + B_3T^3 \quad (1)$$

where I_{red} and I_{green} are the integrated intensities of the red and green light levels, respectively, C_1 , B_1 , B_2 , and B_3 are adjustable constants, T is the absolute temperature.

Thence, the relative sensitivity can be described as:

$$S_r = \frac{1}{FIR} \frac{dFIR}{dT} = \frac{1}{FIR} (B_1 + 2B_2T + 3B_3T^2) \quad (2)$$

The evolutions of FIR and S_r values as a function of temperature are shown in Fig.S4(b). The maximum sensitivity of this optical thermometer is determined to be 0.32% K⁻¹ at 573 K based on ⁴F_{9/2}(red emission) and ²H_{11/2}, ⁴S_{3/2}(green emission) levels. Therefore, the present phosphor can be used as an excellent material for optical thermometer with high sensitivity.

References

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