Supporting Information

Perceiving Linear-Velocity by Multiphoton Upconversion

Hai Huang[a,c,d], Feng Huang[a,c,d, *],Lin Lin[a,c,d], Zhuohong Feng[a,c,d], Yao Cheng[b], Yuansheng Wang[b], Daqin Chen[a,c,d,*]

[a] College of Physics and Energy, Fujian Normal University, Fujian Provincial Key Laboratory of Quantum Manipulation and New Energy Materials, Fuzhou, 350117, China

[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

[c] Fujian Provincial Engineering Technology Research Center of Solar Energy Conversion and Energy Storage, Fuzhou,350117, China

[d] Fujian Provincial Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen, 361005, China

[*] Corresponding authors.

E-mail: fengh@fjnu.edu.cn (F. Huang); dqchen@fjnu.edu.cn (D. Q. Chen)

Supplementary Note 1: establishment and analytical solutions of rate equations

To idealize the multi-photon pumping process, we assumed that the energy of excitation photon is matched with the gap between adjacent levels. Therefore, the change of population on each level includes three terms: 1. the supplement from lower level; 2. the loss which is pumped to the higher level; 3. the consumption for yielding radiation. The following formula is a typical expression describing the change of population (dN_x/dt, x>0) on a single level, taking these three terms into account:

$$\frac{dN_x}{dt} = wc_{x-1}N_{x-1} - wc_xN_x - A_xN_x$$

where w is the power of the excitation, A_x are the radiative transition rates of corresponding energy levels, c_x are the absorption cross-section of each level. As for the ground state (N_0), we should consider the loss which is pumped to the higher level as well as the supplement from the radiation transitions of all the other excited levels. Then the equation should be written as:

$$\frac{dN_0}{dt} = -wc_0N_0 + A_1N_1 + A_2N_2 + A_3N_3......$$

Consequently, the simultaneous equations:

$$\frac{d}{dt}\begin{pmatrix} N_0 \\ N_1 \\ N_2 \\ N_3 \\ \vdots \end{pmatrix} = \begin{pmatrix} -wc_0 & A_1 & A_2 & A_3 & \vdots \\ wc_0 & -wc_1 - A_1 & 0 & 0 & \vdots \\ 0 & wc_1 & -wc_2 - A_2 & 0 & \vdots \\ 0 & 0 & wc_2 & -wc_3 - A_3 & \vdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}\begin{pmatrix} N_0 \\ N_1 \\ N_2 \\ N_3 \\ \vdots \end{pmatrix}$$

where w is the power of the excitation, A_1, A_2, A_3……. are the radiative transition rates of corresponding energy levels, c_0, c_1, c_2…… are the absorption cross-section of each level.

Analytical solutions of the rate equations, established according to **Figure 1a**, can be expressed as follow:

$$\begin{pmatrix} N_0 \\ N_1 \\ N_2 \\ N_3 \\ \vdots \end{pmatrix} = \begin{pmatrix} d_{11} d_{12} d_{13} & \vdots & \vdots \\ d_{21} d_{22} d_{23} & \vdots & \vdots \\ d_{31} d_{32} d_{33} & \vdots & \vdots \\ \cdots\ \cdots\ \cdots & \ddots & \vdots \\ \cdots\ \cdots\ \cdots & \cdots & \ddots \end{pmatrix}\begin{pmatrix} e^{-\lambda_0 t} \\ e^{-\lambda_1 t} \\ e^{-\lambda_2 t} \\ e^{-\lambda_3 t} \\ \vdots \end{pmatrix}$$

where d_{11}, d_{12}, d_{13} …… are the elements of the eigenvectors belonging to the characteristic matrix of the rate equations, while λ_1, λ_2, λ_3 …… are the eigenvalues of the characteristic matrix.

Accordingly, the fluorescence intensity ratio between different levels calculated as follow:

$$\text{FIR}=\frac{I_x}{I_{x+1}} \approx \frac{N_x}{N_{x+1}} = \frac{\sum_i d_{xi} e^{-\lambda_{i-1} t}}{\sum_j d_{(x+1)j} e^{-\lambda_{j-1} t}}$$

Obviously, it is hard to obtain a simplified analytical expression about FIR versus v. To analyze our experimental data, we turn to adopt Taylor expansion, regarding the FIR as a function of velocity (FIR= f(v)), thus expressing the FIR as follow:

$$\text{FIR}=f(v) = f(0) + f'(0)v + \frac{1}{2}f''(0)v^2 + \ldots + \frac{1}{n!}f^{(n)}v^n$$

In other words, we addressed FIR approximatively as a polynomial of velocity. And according to the result of our experimental measurement, it seems that the term higher than quadratic can be ignored, matching the quadratic polynomial. This part of discussion has been added in the revised supporting information.

Supplementary Note 2：synthesis of core-shell UCNCs

A multi-step thermal co-precipitation method is applied to synthesize the $NaYF_4$/$NaGdF_4$ core-shell NCs. Typically, to synthesize the core, 0.8 mmol $GdCl_3 \cdot 6H_2O$ or $YCl_3 \cdot 6H_2O$ was dissolved in 1 mL aqueous solution, and then was added to a 100 mL flask containing 8 mL OA. The mixture was heated at 150 ^oC for 30 min to remove water from the solution. Then 12 mL ODE was quickly added to the flask and the resulted mixture was heated at 150 ^oC for another 30 min to form a clear solution, and then cooled down to room temperature. Afterwards, 10 mL methanol solution containing NH_4F (3 mmol) and NaOH (2 mmol) was added and the solution was stirred at 50 ^oC for 30 min. After the methanol was evaporated, the solution was heated at 80 ^oC for 5 min, and further heated at 280 ^oC under N_2 for 90 min and then cooled down to room temperature. The products were precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol for several times, and finally re-dispersed in 6 mL cyclohexane. The modification of the core size is achieved by controlling NH_4F content and reaction temperature/time.

For the growth of shell, similar procedure was performed. Merely one more step was inserted. That is, before the addition of NH_4F and NaOH, the pre-prepared core NCs dispersed in 6 mL cyclohexane was added to the above solution and kept at 110 ^oC for 30 min.

The doping of Yb, Er, Tm ions into the core or shell was achieved by introducing designed amounts of $YbCl_3 \cdot 6H_2O$, $TmCl_3 \cdot 6H_2O$ and $ErCl_3 \cdot 6H_2O$ into the $GdCl_3$ or YCl_3 aqueous solution.

Supplementary Note 3：characterizations

XRD analysis was carried out using a powder diffractometer (MiniFlex600 RIGAKU) with Cu K_α radiation (λ= 0.154 nm) operating at 40 kV. Microstructure observations of the core-shell NCs were carried out on a JEOL JEM-2010 TEM operated at 200 kV accelerating voltage. STEM images were taken on a FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope operated on a HAADF mode. The fluorescence spectra were obtained from a Horiba Jobin Yvon Fluorolog 3-22 spectrophotometer. Temporal response curves were measured by a FLS 920 spectrofluorometer equipped with a 980 nm laser pumps modulated with an impulse generator (square wave is generated with the pulse width ranging from 50 μs~500 μs, and the pulse edge being 10 μs).

Supplementary Movies

Movie 1: A video documenting the luminescent chromatic phenomenon of the UCNCs coated turnplate during an acceleration and deceleration cycle.

Figure S1-S7

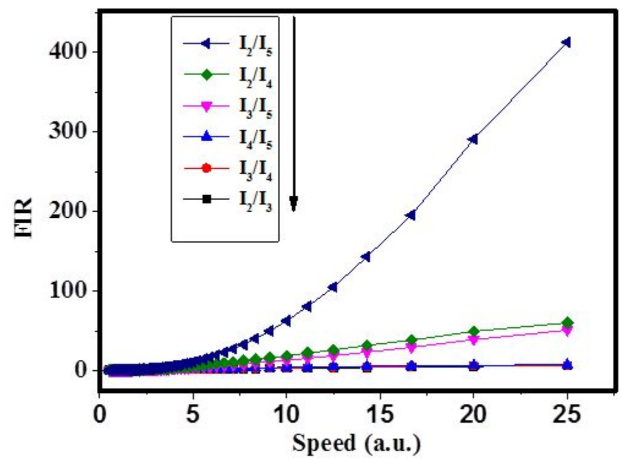

Figure S1. Higher-order FIRs (e.g. I_2/I_4, I_3/I_5 and I_2/I_5) versus moving speed; for comparison, the plots for lower-order FIRs (i.e. I_2/I_3, I_3/I_4 and I_4/I_5) are also provided.

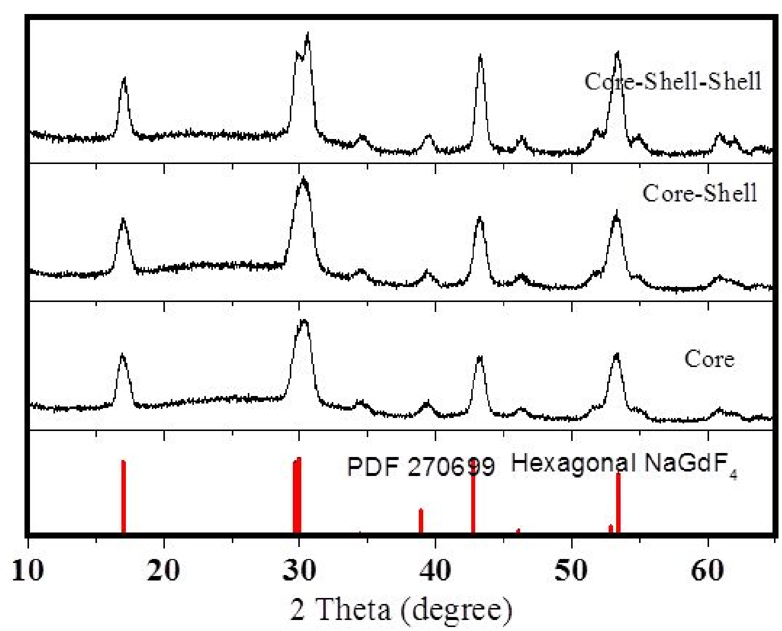

Figure S2. XRD patterns of the synthesized $NaGdF_4$ core, $NaGdF_4@NaYF_4$ and $NaGdF_4@NaYF_4@NaGdF_4$ NCs. Bars represent standard diffraction data for hexagonal $NaGdF_4$ (PDF 270699)

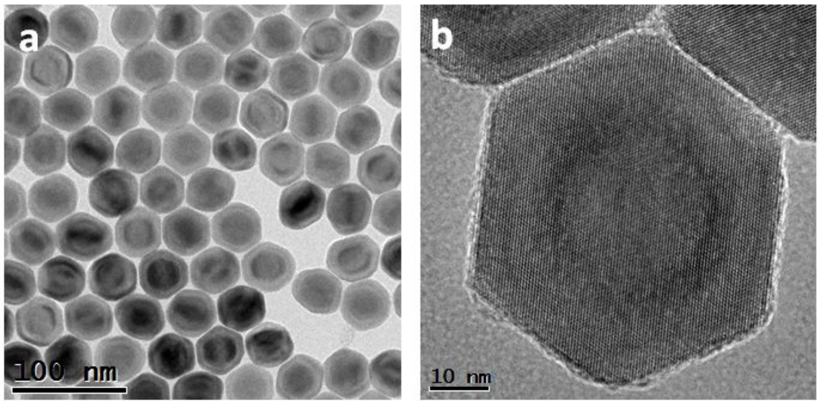

Figure S3. TEM and HRTEM images of the Tm/Yb: $NaGdF_4$@$NaYF_4$@Er/Yb: $NaGdF_4$ UCNCs

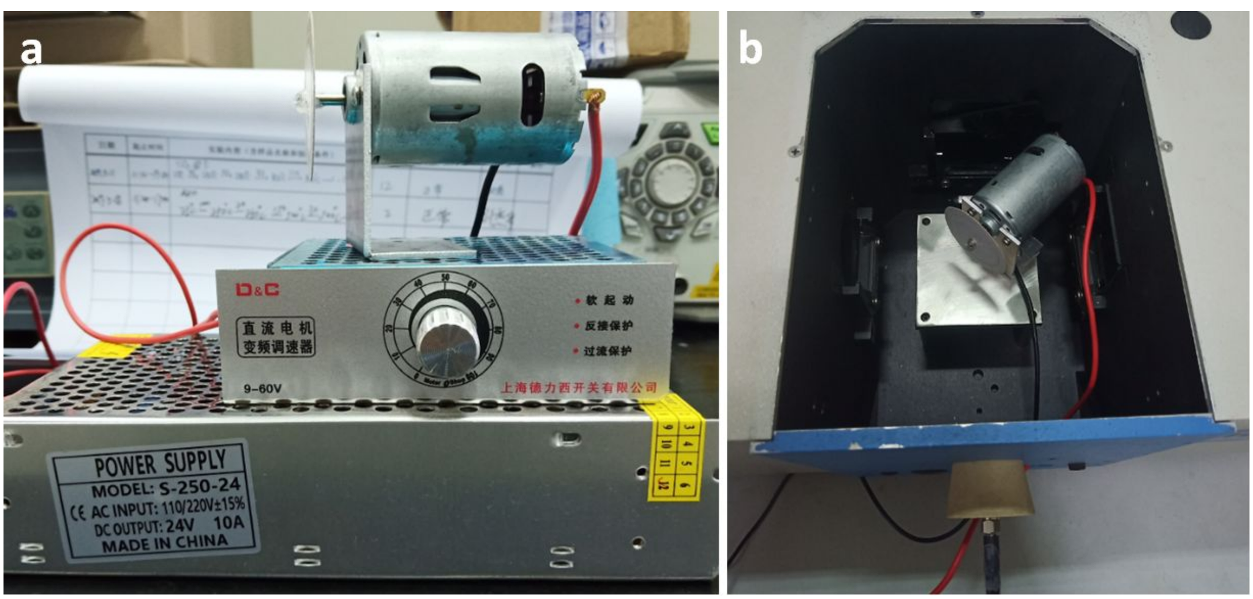

Figure S4. (a) The photograph showing the construct of the home-made speed controlled turnplate (specifically from top to bottom, the motor, the function generator and the voltage source, respectively). (b) The photograph presenting the turnplate equipped in the sample chamber of a JY spectrofluorimeter.

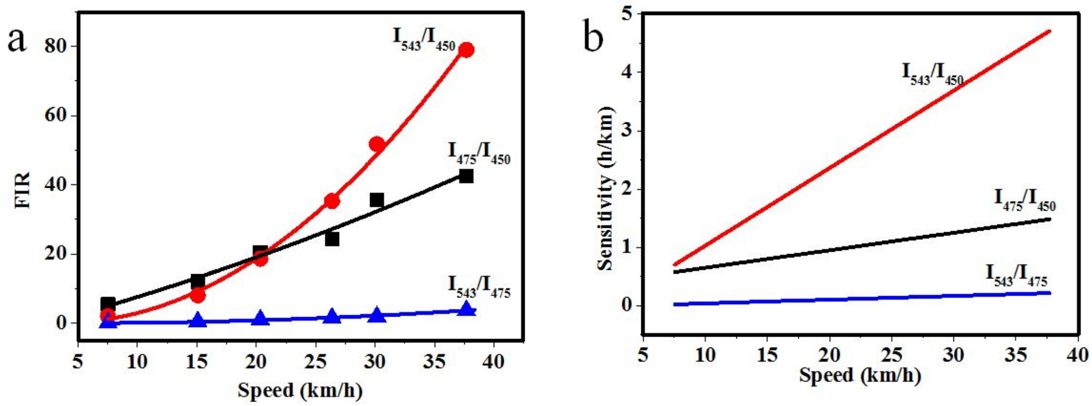

Figure S5. (a) Plots of FIRs (I_{543}/I_{450}, I_{475}/I_{450} and I_{543}/I_{475}) versus speed fitted with quadratic polynomials. (b) Calculated speed sensitivities when using I_{543}/I_{450}, I_{475}/I_{450} and I_{543}/I_{475} as sensing index, respectively.

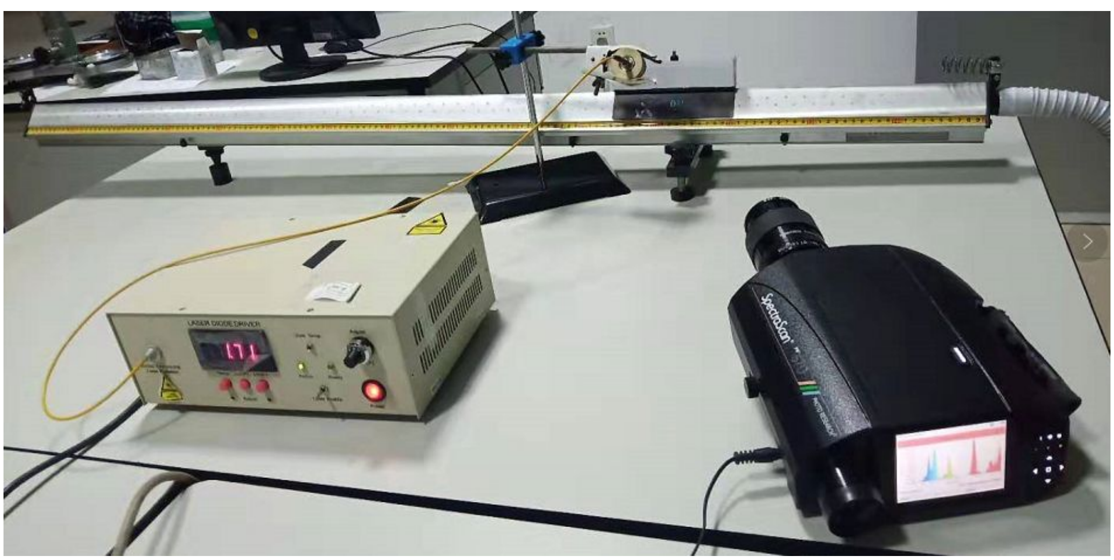

Figure S6. The photo of the trolley on the air cushion track for simulating the practical scene of velocimetry.

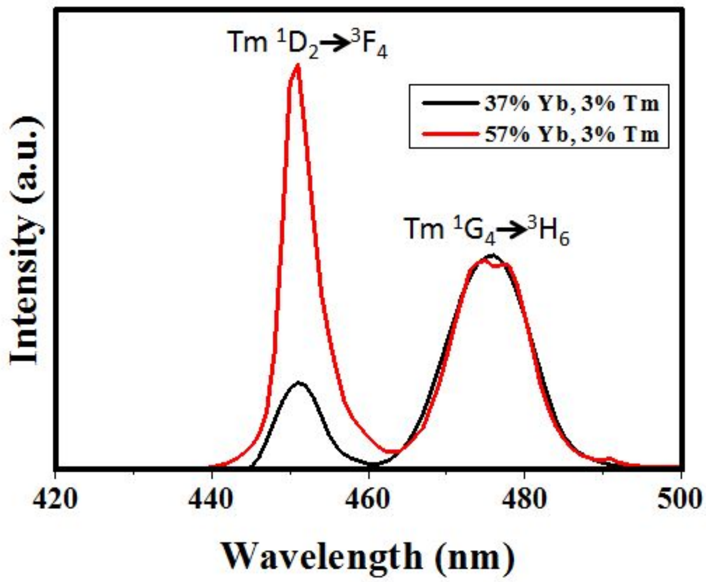

Figure S7. Comparison of the upconversion spectra for the 3% Tm, 37% Yb co-doped $NaGdF_4$ nanocrystals and 3% Tm, 57% Yb co-doped ones.

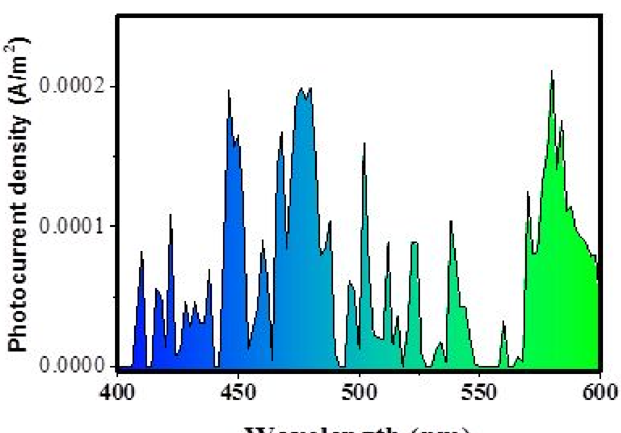

Figure S8. The background noise signal of the CCD grating spectrograph, from which the mean intensity of noise ΔI is calculated to be 0.00009 A/m^2.