Electronic Supplementary Material (ESI) for RSC Advances

High-throughput 3-Dimentional Time-resolved Spectroscopy: Simultaneous Characterization of Luminescence Properties in Spectral and Temporal Domains

Supplementary information

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Fig. S1 illustrates the principle and simplified layout of a purpose-built microscopy system. Briefly, it incorporates three basic functions: wide-field microscopy imaging, laser scanning confocal microscopy imaging, and time-resolved spectral measurement. Wide-field imaging is used to find locations of interests when preparing lanthanide samples on a microscopy slide; scanning confocal imaging is then used to zoom in to detect nanoparticles.

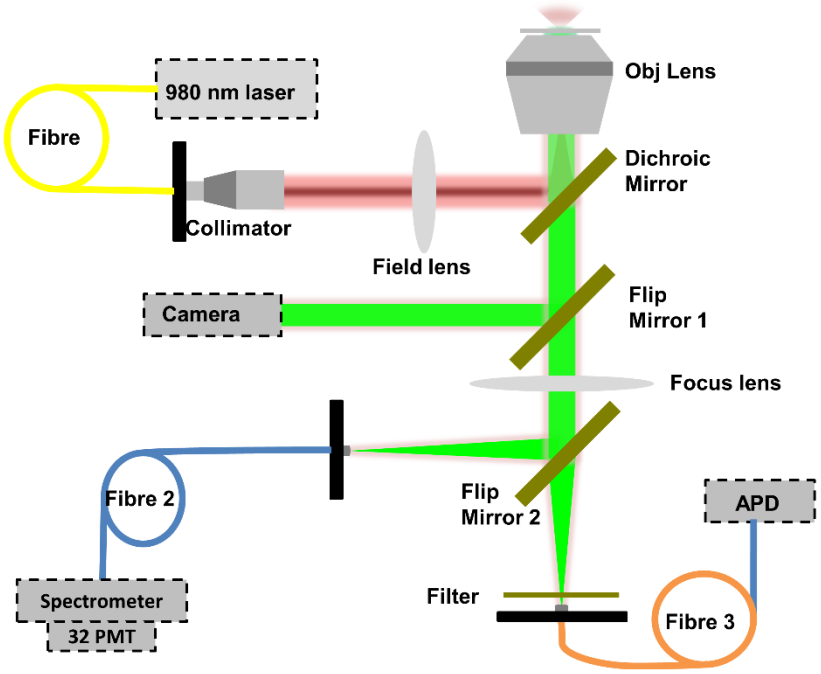


Figure S1. The schematic optical layout for slide-based microscopy imaging system capable of time-resolved spectrum measurement: it has been developed from a x-y-z 3-D stage based scanning microscope via epi-fluorescence configuration, incorporating both wide-field illumination and confocal illumination through a switching lens.

The illumination from a fibre-coupled single-mode diode laser (350 mW, 975 nm, LEO Photonics Co., Ltd) was collimated by a commercial collimator (F240FC-780, NA=0.5, Thorlabs) and focused onto the microscopy slide by an objective lens (60×, 0.75 NA, Edmund Optics) via a dichroic mirror (FF01-842/SP-25, Semrock). The fluorescent image was collected and projected onto a colour CCD camera (2.11 MP, Ds-Vi1, Nikon) reflected by the flip mirror 1 after passing through the dichroic mirror for alignment. Here, the viewing field was enlarged by inserting a field lens in excitation beam to construct a telescope structure with the help of objective lens. Then the flip mirror 1 would be moved out of the optical path, and the optical signal was launched on to an avalanched photodiode (APD) (SPCM-AQRH-14-FC, PerkinElmer Optoelectronics) via 50-μm core diameter optical fibre for confocal imaging of upconversion nanoparticles without flip mirror 2, or to an larger core fibre (600-μm core diameter) and then to a grating-based spectrometer (1200 lines/mm, MicroHR automated, Horiba) for spectrum analysis with flip mirror 2 in optical path. Instead of using a CCD camera (e.g., as a spectroscopy setup), or a single element detector (e.g., as a monochrometer setup), we used a high-gain 32-channel photomultiplier tube (PMT) linear array (H11460, Hamamatsu) was utilised to capture the luminescence decay curves from each wavelength band simultaneously. The spectral resolution was 3 nm, and the temporal resolution was 1 μs (limited by the 1-MHz pre-amplifier bandwidth of PMTs). The photo-electron gain of the PMT array was set to 10^6 V/A. To support real-time data acquisition and analysis in high speed, two 16-channel analog-to-digital data acquisition (DAQ) cards (1.25 MHz bandwidth per channel; PXI e-6358, National Instruments) were connected to a personal computer (i5-core; 4 GB memory; Windows 7 operating system).

The programming work has focused on the synchronisation between the laser excitation pulse sequence, spectroscope grating-mirror scanning, and the data acquisition and accumulation from the 32-channel PMT array. The program was implemented in LabVIEW (version 2010, National Instruments) by controlling two output channels (to control the laser and grating mirror) and all 32 input channels (connected to 32 channels of the PMT array) of the two DAQ cards. The DAQ cards were also software controlled

using customised LabVIEW code. To generate a sequence of pulsed laser illumination, a software-based analog function generator was programmed. Both the duty cycle and the repetition rate of the laser diode were controlled according to the experiment requirements. For the results shown in this work, the pulse width was 78 µs and repetition rate was 500 Hz. The arrangement between the grating and the 32-channel PMT array allow approximately 100 nm to be collected simultaneously; each channel capturing emission decays for 3.125 nm spectral bands. The grating mirror position was stepped to collect sequential 100 nm bands to give the broad 300–800 nm spectrum at high resolution as shown in Figure 1 and Figure S3.

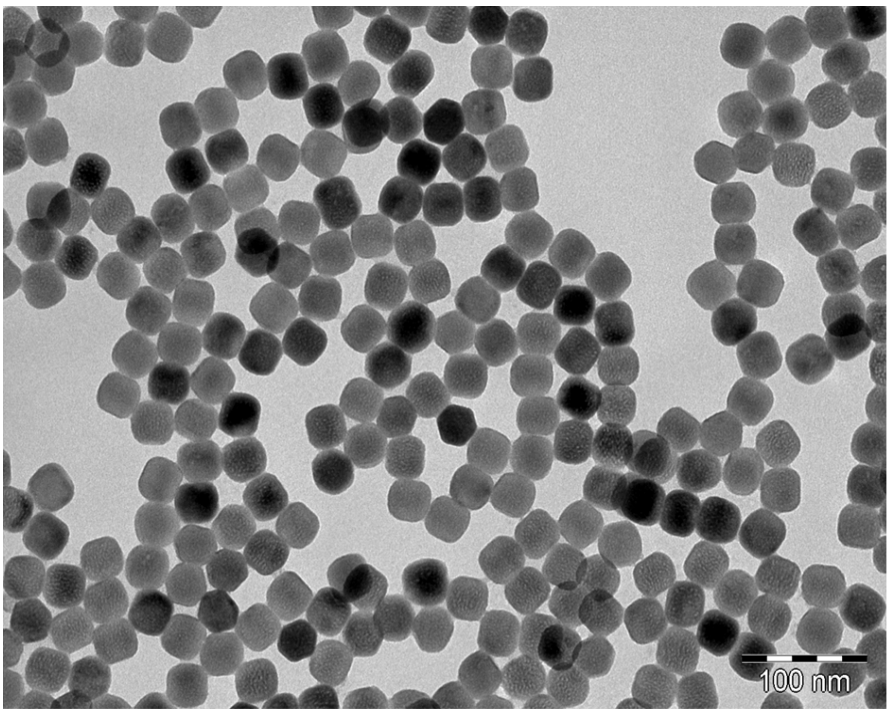
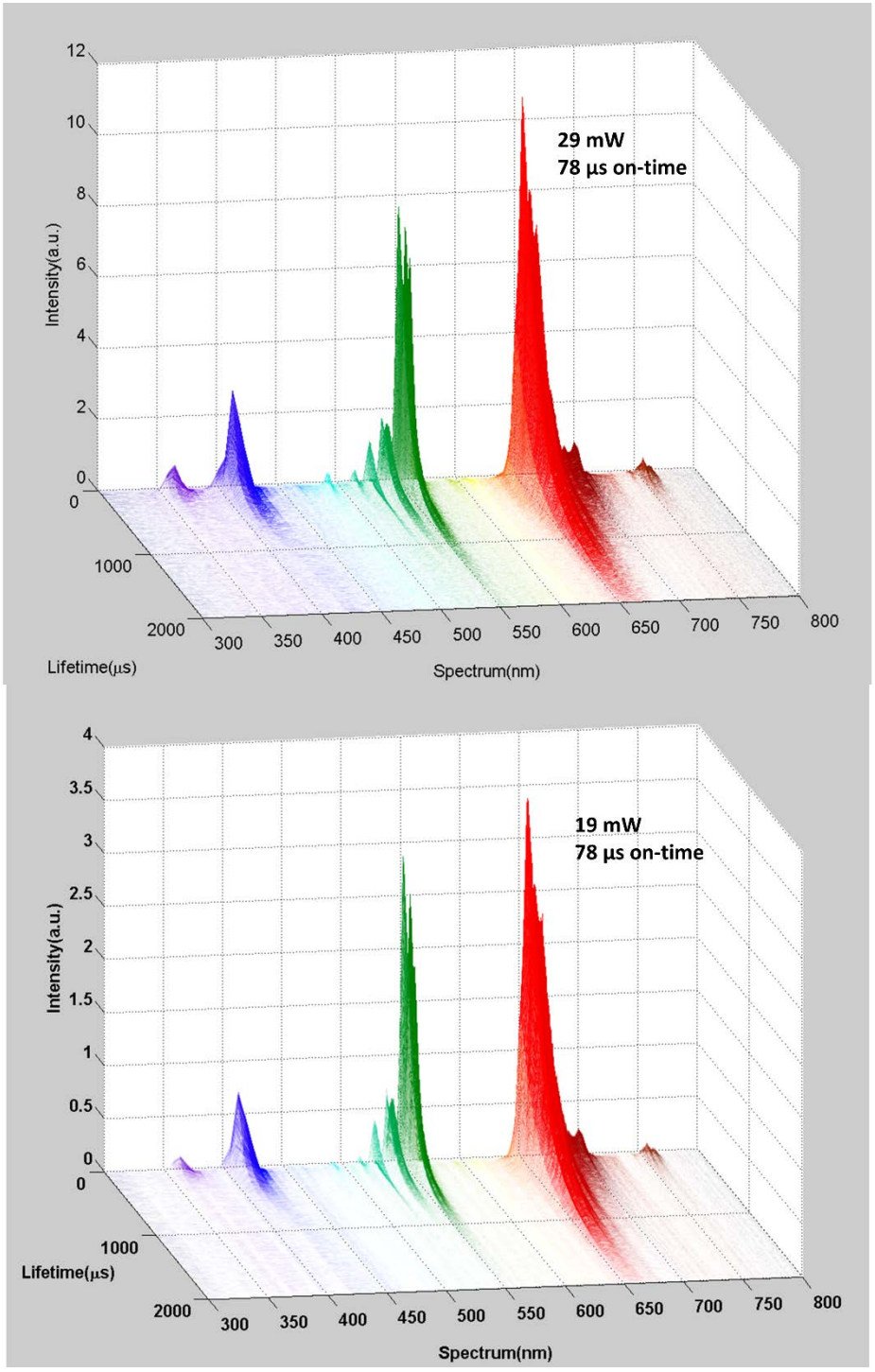


Figure S2. TEM image of hexagonal NaYF4: Yb(20%),Er(2%) nanocrystals

The hexagonal phase $NaYF_4$:$Yb_{20\%}$,$Er_{2\%}$ upconversion nanocrystals with average size of 40 nm were produced using a modified user-friendly synthesis method via the solvothermal route.



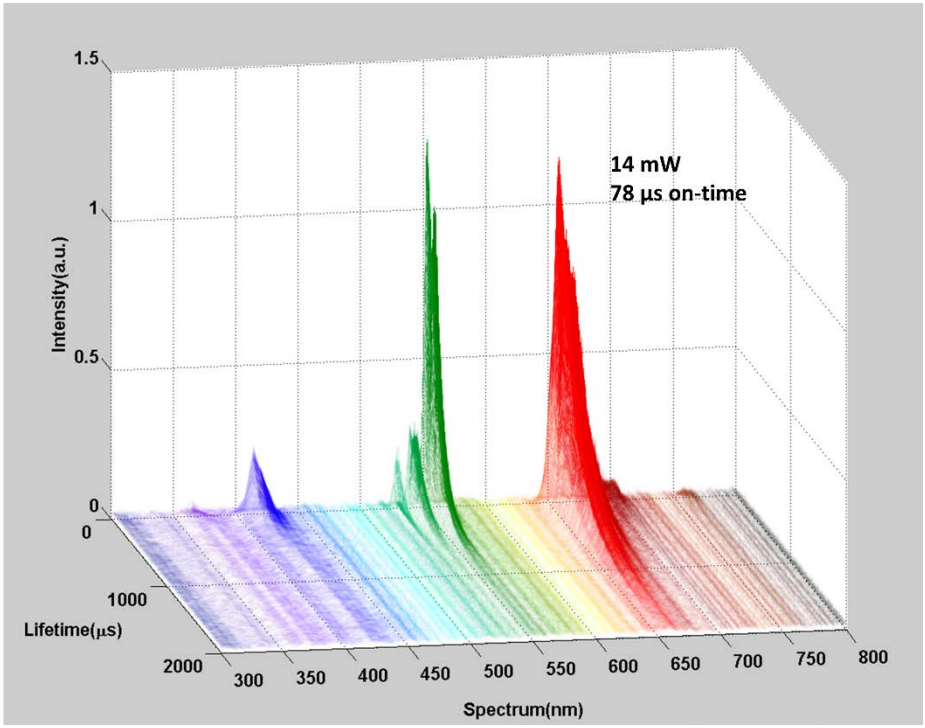


Figure S3. The 3-D time-resolved spectra of NaYF4: Yb(20%),Er(2%) upconversion nanocrystals at three different levels of excitation powers (29 mW, 19 mW, and 14 mW)

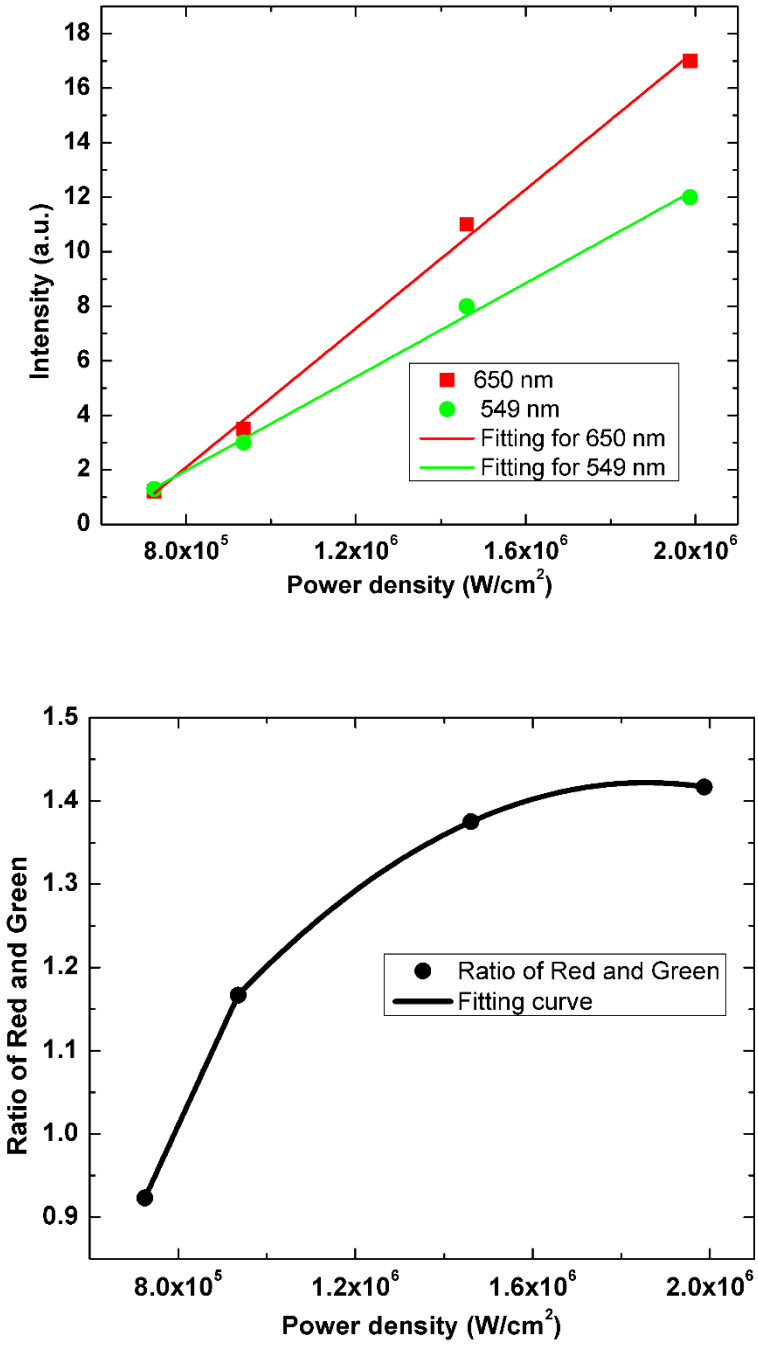


Figure.S4 Power dependence of ratio-metric luminescence intensity of Er-doped upconversion nanocrystals
The left one shows the power dependence of green and red emission, individually; the right one shows the ratio of red and green emission.

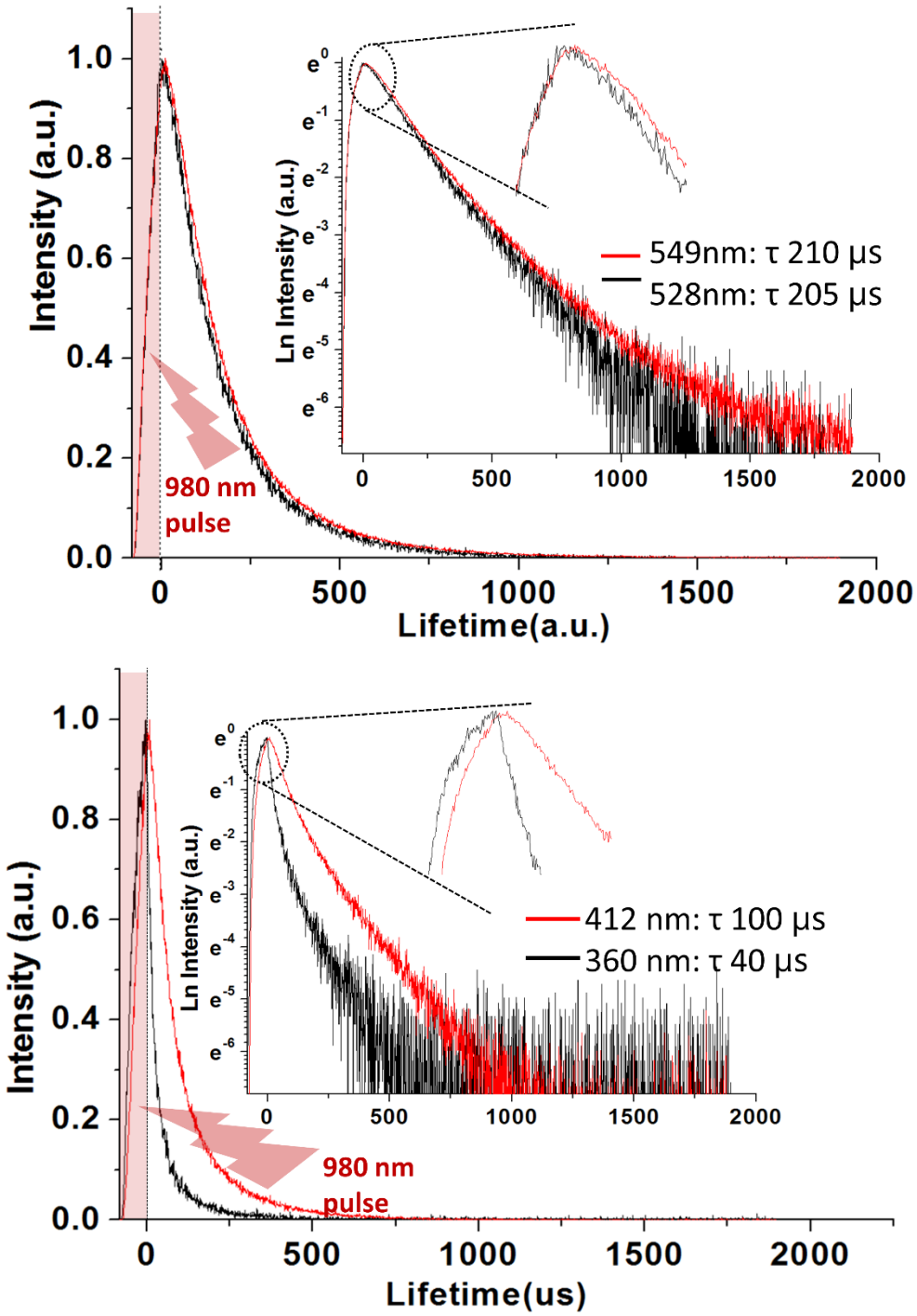


Figure.S5 the typically lifetime curves (at Linear and Log scales) of 360 nm, 412 nm, 528 nm and 549 nm emissions
The top figure makes a comparison of lifetimes for 528 nm and 549 nm emission wavelengths: The red clearly decays slower than the green; some difference in intensity peak positions. The bottom one compares the lifetimes of 412 nm and 360 nm: there are obvious differences on the decay time and intensity peak position.