Nanoscale

COMMUNICATION

Electronic Supplementary Information

One-Step Synthesis and Luminescence Properties of Tetragonal Double Tungstates Nanocrystals

Z. J. Wang, Y. L. Zhang, J. P. Zhong,* H. H. Yao, J. Wang, M. M. Wu and A. Meijerink

Experimental

Chemicals

The synthesis was conducted with commercially available reagents. Absolute ethanol (A.R.), toluene (A.R.), oleic acid (A.R.), oleylamine (80%-90%), 1-octadecene (> 90%), RE ion (Y, La-Lu) (III) acetate (99.9%)/acetylacetonate (99.9%), hexacarbonyl tungsten (97%), sodium oleate (A.R.) and sodium hydroxide (A.R.) were used without further purification.

Synthesis

In a three-necked flask, oleic acid (10 mL), oleylamine (10 mL) and 1-octadecene (20 mL) were added while stirring and heating at 120 °C for 0.5 h. After cooling down to 50-60 °C, the RE ion (III) acetate (1 mmol), hexacarbonyl tungsten (2 mmol) and sodium hydroxide (1.5 mmol) were added to the solution. The reaction temperature was raised to 300 °C and kept for 2 h while refluxing under a protective nitrogen atmosphere. When the solution was cooled down, the product was washed with ethanol and toluene for three times via centrifugation, then dried at 80 °C overnight. The final NCs can be re-dispersed into apolar solvents. For the RE ion (III) acetylacetonate synthesis method, the ingredients are RE ion (III) acetylacetonate (1 mmol), hexacarbonyl tungsten (2 mmol) and sodium oleate (1 mmol), keeping other reaction parameters the same.

Characterizations

The XRD patterns were collected using a D8 ADVANCE (Bruker Co., Germany) X-ray diffractometer (Cu Kα radiation, λ=1.5406 Å). Samples dropped on amorphous carbon-coated copper grids were imaged on a JEM-2010HR TEM (200 kV) with an energy-dispersive X-ray spectrometer. The thickness of the NCs was measured on a Dimension Fast Scan AFM (Bruker Co., Germany) in tapping mode on the substrate of mica. FT-IR spectra were measured in a Vertex 70 (Bruker Co., Germany) infrared spectrometer with the KBr pellet technique. The photoluminescence spectra and lifetime measurements were measured on an Edinburgh Instruments FLS 920 spectrometer. Low temperature 4K was realized by liquid helium, where the high resolution spectra were measured under the same parameters for MCs and NCs. For the upconversion emission spectrum of the Yb^{3+}, Er^{3+} co-doped sample a diode laser was used for excitation.

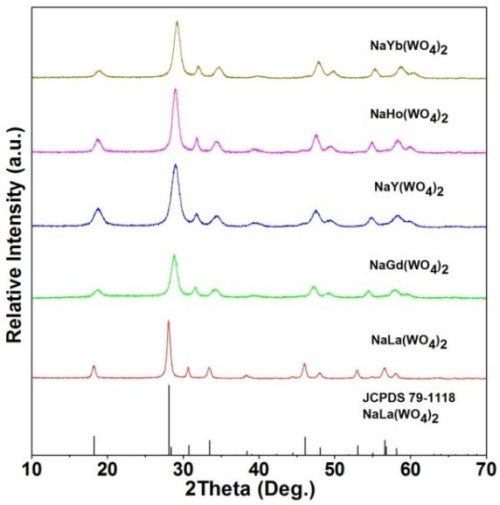

Fig. S1 XRD patterns of $NaRE(WO_4)_2$ NCs.

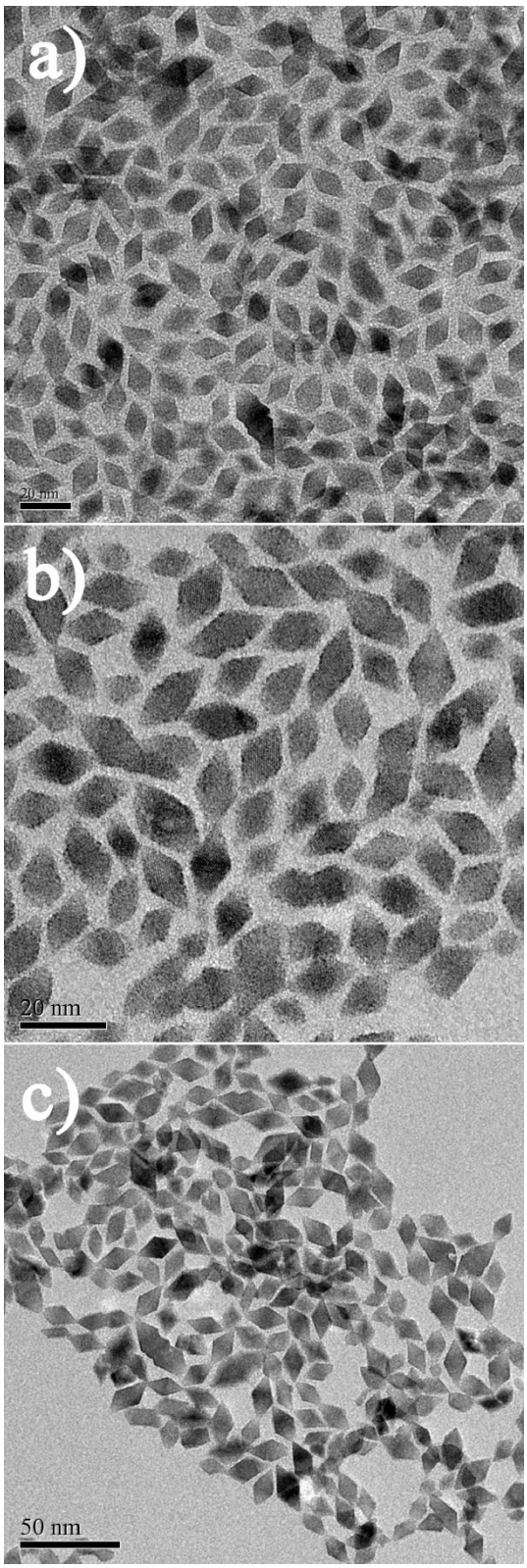

Fig. S2 TEM images of $NaRE(WO_4)_2$ NCs: a) RE = Gd; b) RE = Y and c) RE = Yb.

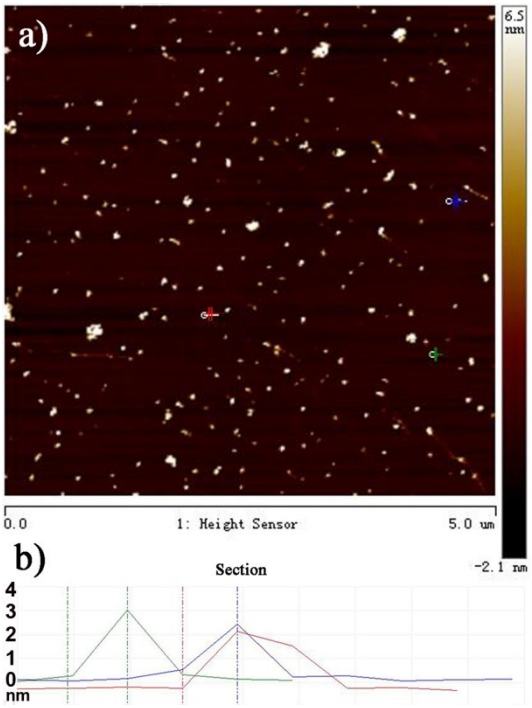

Fig. S3 a) AFM image and b) height profiles of $NaLa_{0.9}Eu_{0.1}(WO_4)_2$ NCs with post-sintering at 300 °C for 2 h.

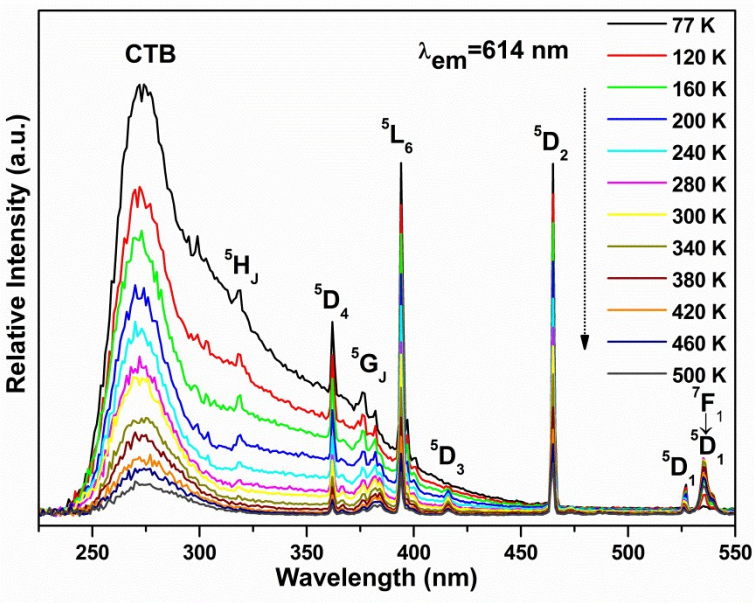

Fig. S4 Temperature dependent excitation spectra of $NaLa_{0.9}Eu_{0.1}(WO_4)_2$ NCs with monitoring the emission at 614 nm. Excitation lines are labelled by the final state for excitation from the $^7F_0$ ground state, except for the lines around 535 nm corresponding to transitions from the thermally populated $^7F_1$ state.

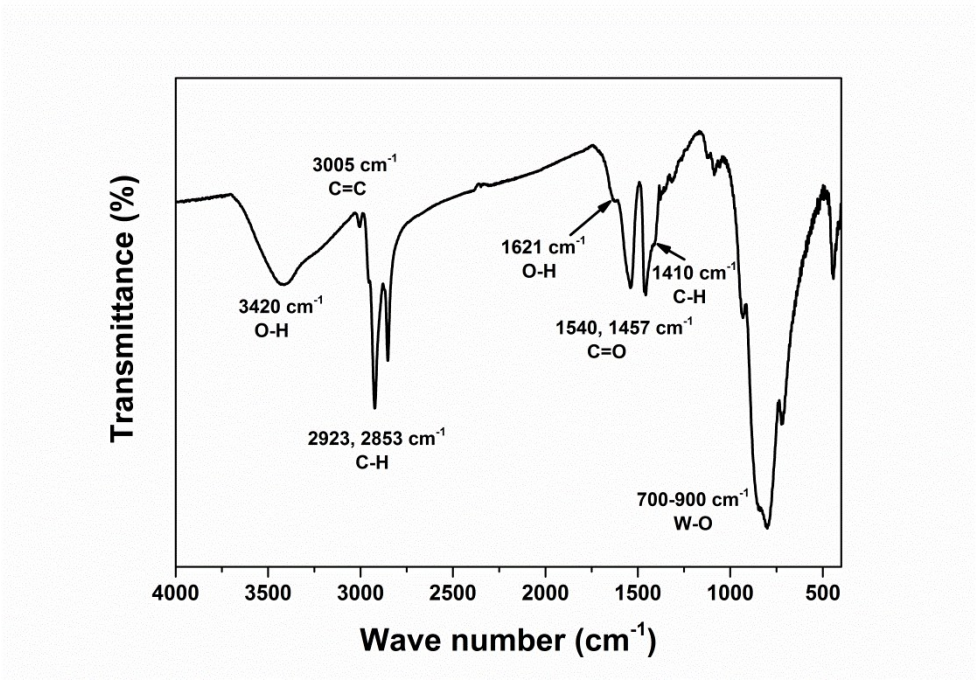

Fig. S5 Fourier transform infrared (FT-IR) spectrum of $NaLa_{0.9}Eu_{0.1}(WO_4)_2$ NCs.

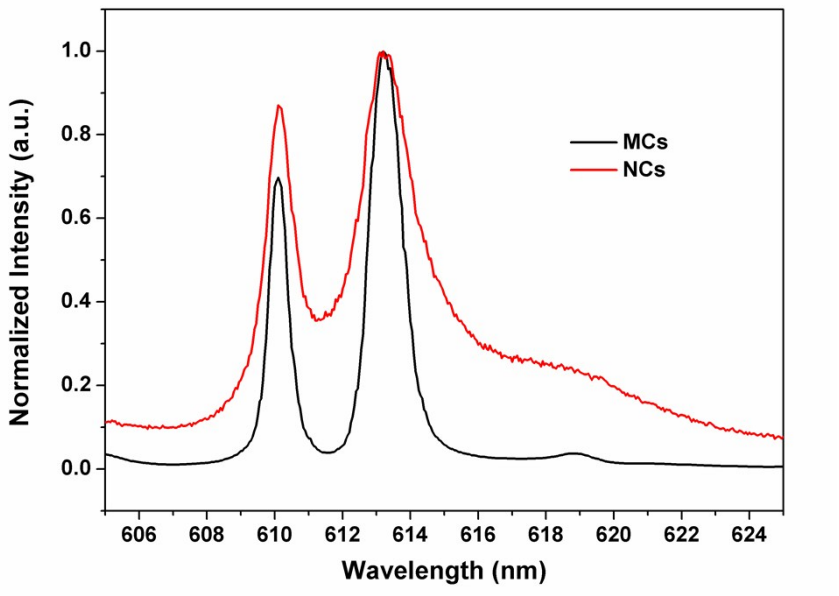

Fig. S6 The high resolution emission spectra (λ_{ex} = 394 nm) of $NaLa_{0.9}Eu_{0.1}(WO_4)_2$ NCs and MCs recorded at low temperature 4 K.

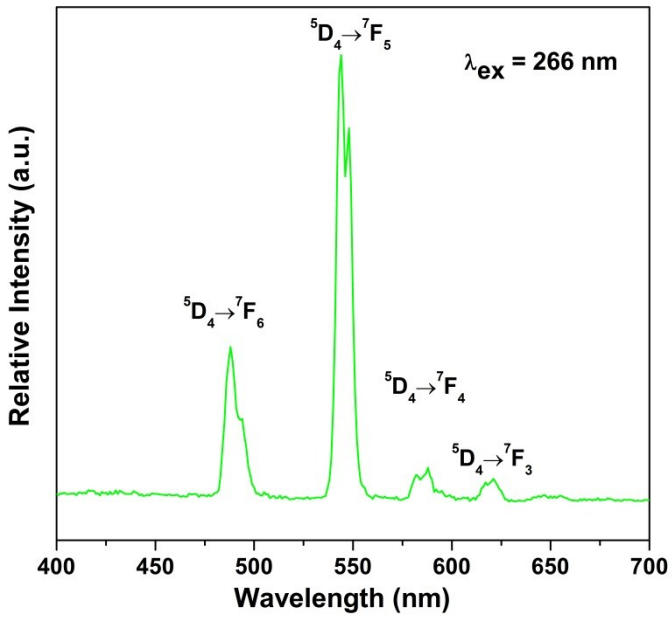

Fig. S7 The emission spectrum (λ_{ex} = 266 nm) of $NaLa_{0.9}Tb_{0.1}(WO_4)_2$ NCs.

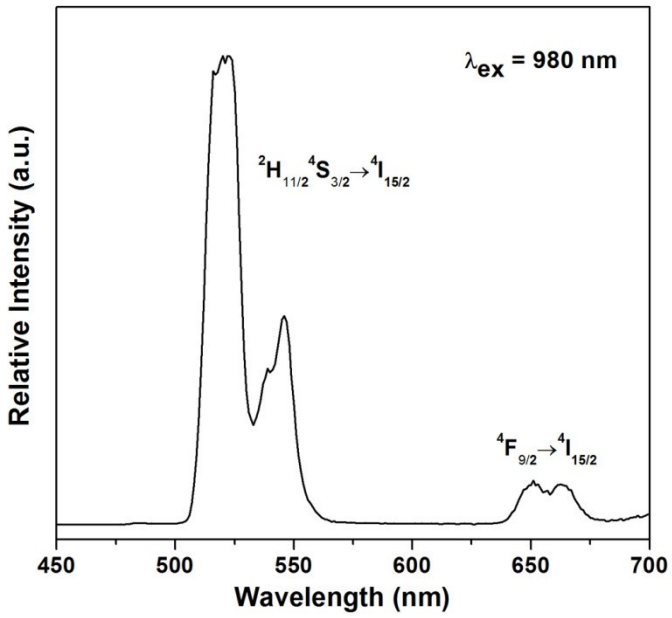

Fig. S8 The emission spectrum (λ_{ex} = 980 nm laser) of $NaLa_{0.8}Er_{0.02}Yb_{0.18}(WO_4)_2$ NCs.