Electronic Supplementary Material (ESI) for RSC Advances.

SUPPLEMENTARY INFORMATION

TOWARDS NEAR-INFRARED PHOTOSENSITIZATION OF TUNGSTEN TRIOXIDE NANOSTRUCTURED THIN FILMS BY UPCONVERTING NANOPARTICLES

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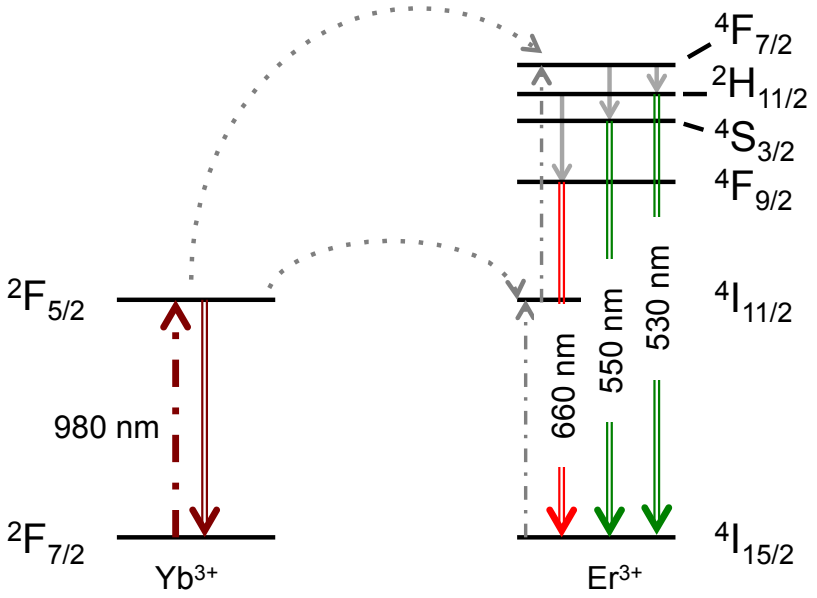

Fig. S1 Partial $NaGdF_4:Er^{3+}$, Yb^{3+} UCNPs energy levels diagram. For the sake of clarity, only the energy levels involved in the upconversion process are shown. Dashed lines are associated with energy absorption, dotted lines are associated with energy transfer, full grey lines are associated with non-radiative processes, and full double lines are associated with radiative processes.

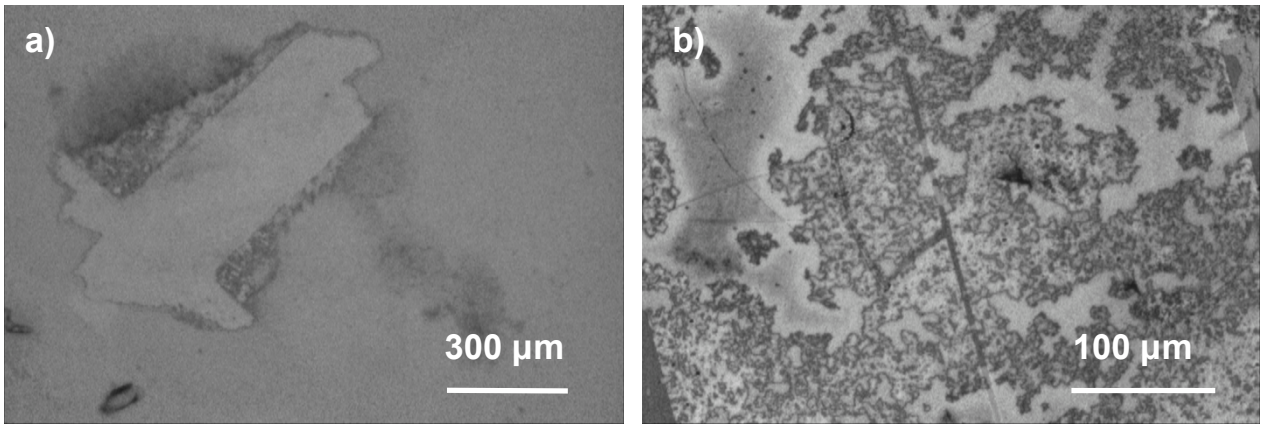

Fig. S2 Optical microscopy images of 16 mol% UCNP/WO_3 films thermally treated at 385 °C deposited on a) glass and b) SiO_2.

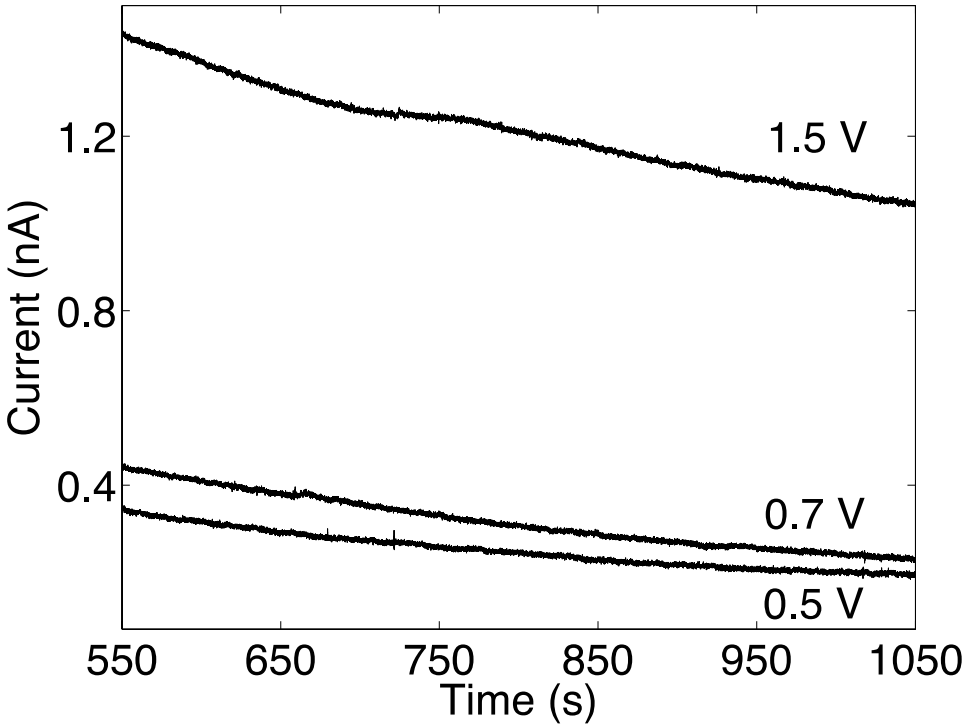

Fig. S3 Current-time measurements under NIR chopped light (λ_{exc} = 980 nm, power density of 1 W/cm^2) for films made of 6 mol% UCNP/WO_3 deposited on patterned ITO (interelectrode distance of 100 μm), thermally treated at 385 °C. Samples were kept under a constant electrical bias for 300 s in ambient light conditions, followed by 300 s in the dark, before chopping the light (60 s in the dark and 30 s under irradiation).

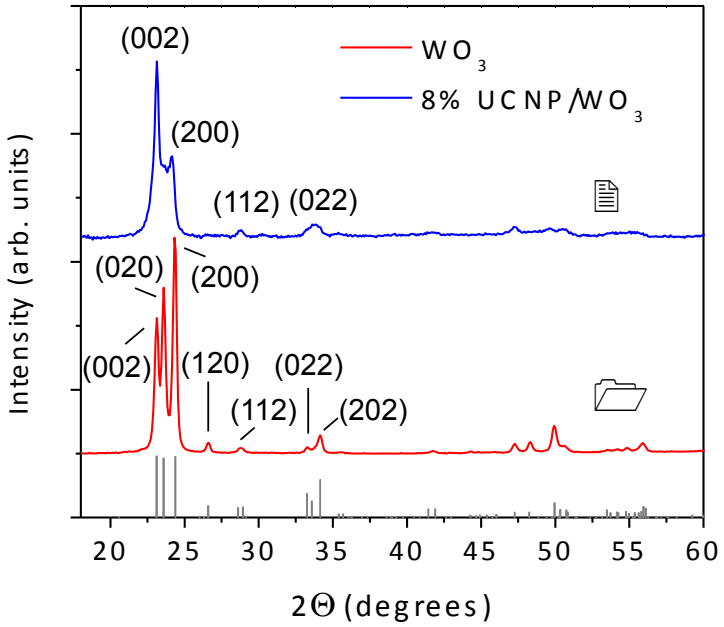

Fig. S4 XRD measurements of WO_3 (pattern 1) and ~ 8 mol% UCNP/WO_3 thin films deposited on glass and thermally treated at 385 °C (pattern 2).

Comments on Fig. S4

XRD measurements were performed to assess the structure of WO_3 and 8 mol% UCNP/WO_3 thin films. The XRD pattern of WO_3 thin films shows three sharp peaks in the 22-25° region, two peaks in the 26-29° region, and two peaks in the 32-35° region (pattern 1): the peaks are indexed to the planes of monoclinic WO_3 (ICDD # 00-043-1035). 8 mol% UCNP/WO_3 thin films annealed at 385 °C show two peaks in the 22-25° region, one centered at 28.8° and another centered at 33.7° (pattern 2). No peaks from UCNPs were observed in the pattern from UCNP/WO_3 thin films, probably because of the excessively low concentration of UCNPs. A slight shift in the position as well as a broadening of the peaks is observed when WO_3 films contain UCNPs.

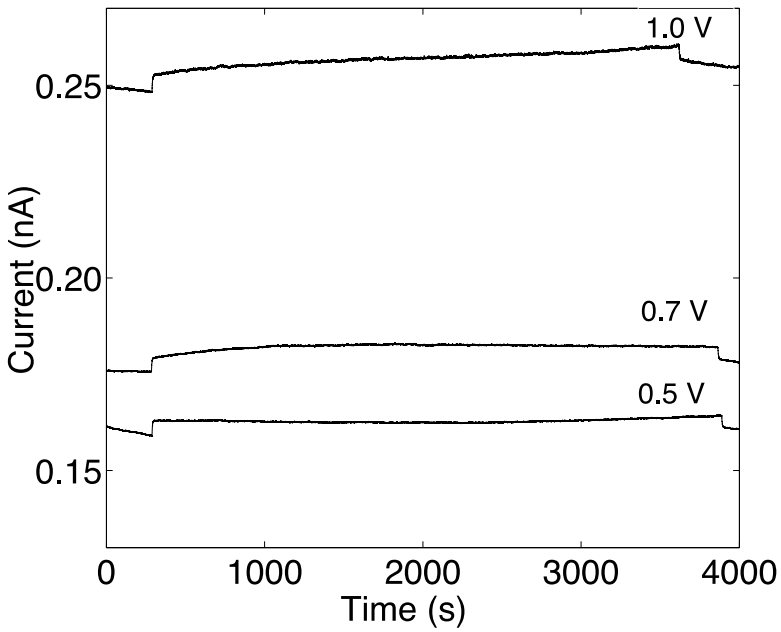

Fig. S5 Prolonged current-time measurements (300 s in the dark, 3000 s under NIR light irradiation at λ_{exc} = 980 nm and power density of 1 W/cm^2, then dark conditions again) for 8 mol% UCNP/WO_3 films deposited on patterned ITO (interelectrode distance of 100 μm), thermally treated at 385 °C. Samples were kept under constant electrical bias for 300 s in ambient light conditions, followed by 3000 s in the dark, before being exposed to the NIR laser. The results show the good stability of the performance of the films under NIR irradiation.

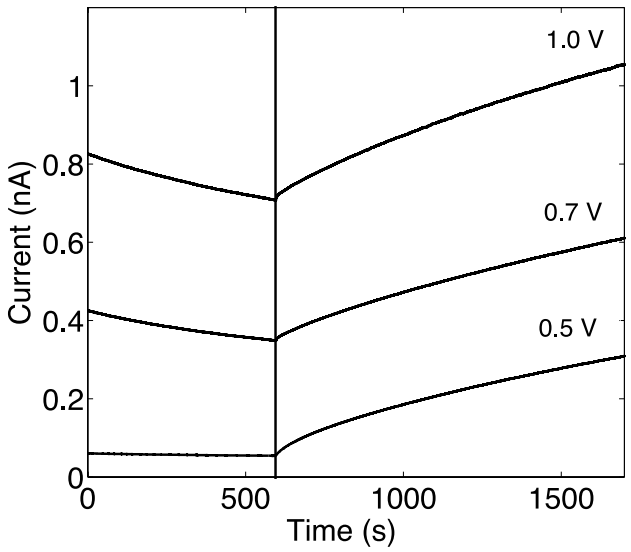

Fig. S6 Current-time measurements under simulated solar light (power density of 1 W/cm^2, irradiation starts at t = 600 s; before irradiation samples were kept under bias in the dark) for 8 mol% UCNP/WO_3 films deposited on patterned ITO (interelectrode distance 100 μm), thermally treated at 385 °C.

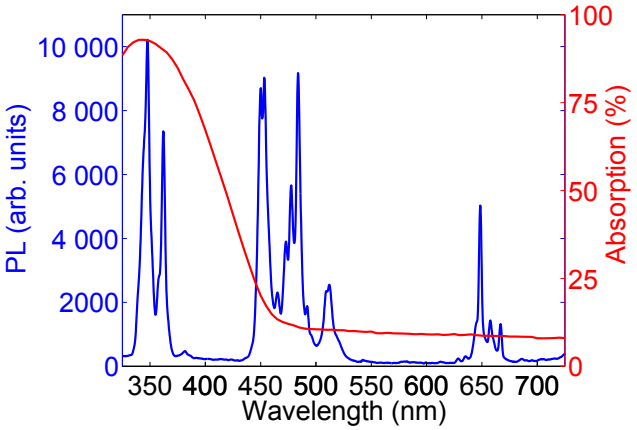

Fig. S7a: Absorption spectrum of ca. 1.2 µm-thick WO_3 films (left y axis) and PL spectrum of $LiYF_4$: Tm^{3+}, Yb^{3+} upconverting nanoparticles on glass (right y axis). When excited at λ_{exc} = 980 nm, the UCNPs have three emission bands in the visible range, partially overlapping with the spectrum of WO_3.

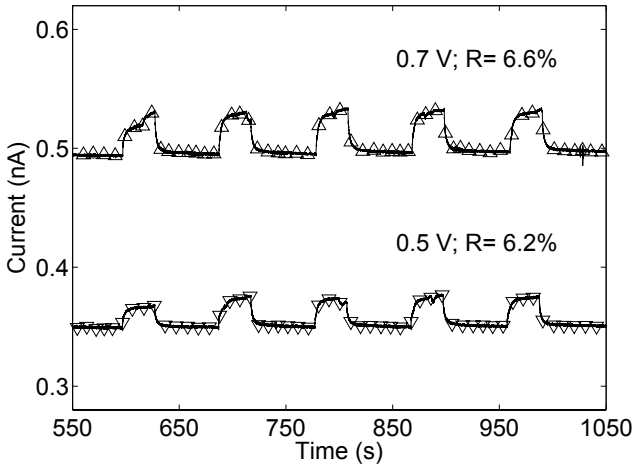

Fig. S7b: Current-time measurements under NIR chopped light (60 s dark and 30 s under irradiation, λ_{exc} = 980 nm, 1 W/cm^2) for 6 mol% $LiYF_4$: Tm^{3+}, Yb^{3+} UCNP/WO_3 films deposited on patterned ITO (interelectrode distance 100 µm), treated at 385 °C.