

Supporting Information

Instantaneous crystallization of ultrathin one-dimensional fluorescent rhabdophane nanowires at room temperature

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Materials and Methods:

LaCl₃·7H₂O, CeCl₃·7H₂O, TbCl₃·6H₂O and NaH₂PO₄ of reagent grade were purchased from Sigma-Aldrich, and used without further purification. The feed rate in both platforms described below was 60ml/min. Equal concentrations of NaH₂PO₄ and lanthanide chloride (LnCl₃) were fed throughout the whole experiment. In a typical synthesis of LaPO₄:Ce³⁺:Tb³⁺ in either SDP or RTP, a mixed lanthanide chloride solution (0.01M, 0.05M or 0.1M) was fed with the molar ratio of 45%, 40% and 15% for La, Ce and Tb respectively in one feed jet, with a same concentration (0.01M, 0.05M or 0.1M) of NaH₂PO₄ in the other feed jet. 50ml of LnCl₃ and NaH₂PO₄ each was fed into SDP or RTP at the same time with a same feed rate. Products were collected at the other end of tube in RTP or at bottom of SDP. In both platforms, the concentration of reactants and the spinning/rotating speed of the platforms could be changed to investigate the influence to the products. The samples were then purified by multiple centrifugations and washing, and analyzed instantaneously.

Micromixing using SDP and RTP:

The concept of “Process Intensification” offers alternative routes alleviating the obstacles of the relaxed fluid dynamic regime associated with conventional batch processes affording more environmentally benign synthetic approaches that can save on energy consumption,

reduce the generation of waste and the use of toxic substances, and provide a safer working environment, and at the same time it can be more economically beneficial. Herein, we exploit two modules of process intensification Rotating Tube Processing (RTP) and Spinning Disc Processing (SDP) to demonstrate it is possible to decouple the nucleation and growth of the nanowires and fabricate highly crystalline ultrathin lanthanide phosphate nanowires with high aspect ratios under scalable plug flow conditions.

The demand for intensified processing has led to the design and development of a range of reactors that offer operating conditions with rapid heat and mass transfer under continuous flow conditions with residence times reduced to seconds rather than minutes or hours. SDP and RTP offer novel avenues for intensified nanotechnology via exploitation of high centrifugal acceleration to generate thin films providing rapid heat and mass transfers. The key components of SDP include: (i) a 100 mm rotating disc with controllable speed (up to 3000 rpm), and (ii) feed jets located at a radial distance of 5 mm from the center of the disc and that of an RTP include (i) a 6 cm internal diameter tube of 30 cm length with controllable speed (up to 1700 rpm) and (ii) feed jets located at the end of the cylinder pointing towards the periphery of the inner walls of the cylinder. SDP and RTP generate a very thin fluid film (1 to 200 μm) on a rapidly rotating disc surface within which the nanoparticle formation occurs. The hydrodynamics of film flow over a spinning surface is indeed important in controlling the reactions. The distinct flow features associated with the SDP and the RTP is of importance as it provides platforms for very effective nucleation and growth of nanoparticles under intense mixing. In essence, the behavior of the thin film on a rapidly rotating disc can be classified into two zones. One corresponds to the injection zone where the reagents hit the spinning disc to form a pool at the centre of the disc.

The pool is often referred to as the spin-up zone and is related to viscous drag of the liquid film associated with centrifugal forces. Rapid nucleation and instantaneous growth initiation is associated with this zone. The other zone corresponds to the acceleration and synchronized flow zone where the fluid film initially experiences an increase in radial flow velocity and then the liquid is rotating close to the disc velocity. In the case of a RTP, the initial spin up zone is completely eliminated as the film experience a rapid acceleration right from the beginning. In both the cases, the thinness of the film contributes to many influential chemical processing characteristics, one being a very high surface area to volume resulting in rapid crystallization of nanocrystals under supersaturation.

Characterization: Transmission electron microscopy images were obtained using TEM JEOL 3000F operated at 300 kV. The fluorescence spectra were measured on Varian Spectrofluorometer. XRD patterns were obtained on D5000 X-ray Diffraktometer after the samples had been freeze dried for 24 hours.

The Ln ratios in the final products were determined against Omnian program on Axios-mAX sequential wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer. Sample for analysis was first dried at 100°C overnight before ground to $\leq 30\ \mu\text{m}$ in an agate mortar, then mixed 8 g of the sample powder with 2 g of wax and ground together for another 10 min. Then this mixture was free pressed into a 40 mm pellet at 25 t load. The WD-XRF results indicated that Ln ratio in the final products was 45.23%, 40.34% and 14.43% for La, Ce and Tb, respectively.

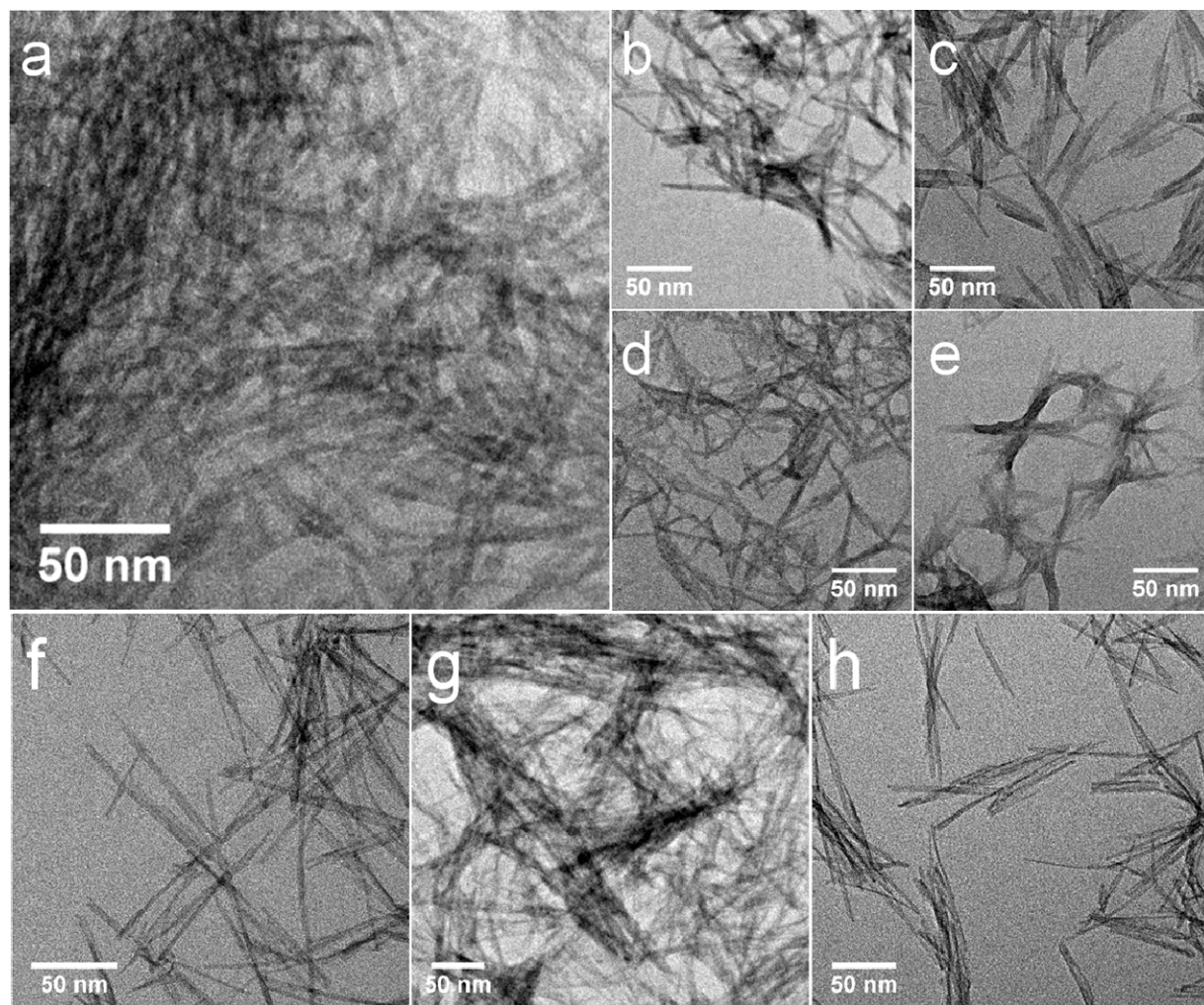


Figure S1. TEM images of $\text{LaPO}_4:\text{Ce}^{3+}:\text{Tb}^{3+}$ prepared by RTP (top) and SDP (bottom) with different concentration or rotating speed. (a) 1700rpm, 0.01M: diameter (d)= $3.1\pm0.2\text{nm}$, (b) 1700rpm, 0.05M: d= $3.3\pm0.5\text{nm}$, (c) 1700rpm, 0.1M: d= $5.6\pm1.2\text{nm}$, (d) 1000rpm, 0.01M: d= $4.0\pm0.9\text{nm}$, (e) 500rpm, 0.01M: d= $8.2\pm3.2\text{nm}$, on RTP and (f) 2500rpm, 0.01M: d= $2.2\pm0.2\text{nm}$, (g) 2500rpm, 0.1M: d= $4.1\pm1.5\text{nm}$, (h) 1500rpm, 0.01M: d= $4.4\pm0.6\text{nm}$ on SDP.

Fluorescence Analysis:

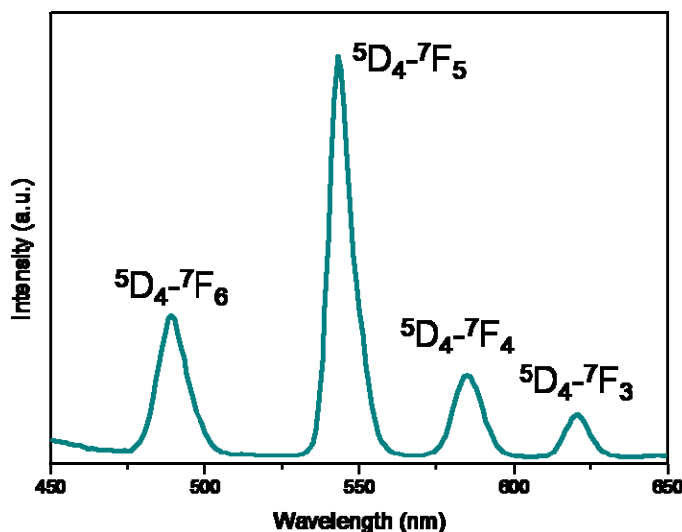


Figure S2 Fluorescence spectrum of LaPO₄:Ce³⁺:Tb³⁺ prepared by RTP at the concentration of 0.01M and rotating speed at 1700 rpm.

The colloidal solution of LaPO₄:Ce³⁺:Tb³⁺ exhibited strong green luminescence at room temperature (Fig SI3). The fluorescence spectrum of LaPO₄:Ce³⁺:Tb³⁺ consisted of four main peaks between 450 and 650 nm due to transitions between the excited ⁵D₄ state and the ⁷F_J (J = 0-6) ground states of terbium upon the UV excitation at 272nm.¹ Owing to the high concentration of Ce³⁺ in the nanocomposite, the excited state of Ce³⁺ is not completely quenched by energy transfer to Tb³⁺ and thus its emission (d-f radiative transition) can be seen as a broad band between 300 and 400 nm in addition to the terbium lines (not shown here).² The cerium emission consists of two transitions from the lowest component of the ²D state to the spin-orbit components of the ground state, ²F_{7/2} and ²F_{5/2}. In contrast to the f electrons of terbium, the d electrons of cerium couple strongly to the lattice phonons resulting in broad overlapping bands and a significant Stokes shift.^{3,4}

References

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