Supporting Information

Room temperature synthesis of upconversion fluorescent nanocrystals

Jie Fang,[a,b] Rajesh S. Pillai,[c] Martin Saunders,[d] Jianli Zou,[b] Dirk Lorenser,[c] David D. Sampson,[c,d] Yanglong Guo,[a] Guanzhong Lu[a] and K. Swaminathan Iyer*[b]

[a] *Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, P. R. China.*

[b] *Centre for Strategic Nano-Fabrication, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA-6009, Australia. E-mail: swaminatha.iyer@uwa.edu.au*

[c] *Optical + Biomedical Engineering Laboratory, School of Electrical, Electronic and Computer Engineering, The University of Western Australia, Crawley, WA-6009, Australia.*

[d] *Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, Crawley, WA-6009, Australia.*

Materials and Methods

All chemicals utilized in the synthesis were purchased from Sigma-Aldrich and were used without further purification. High purity single wall carbon nanotubes (SWCNTs) were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. Graphite was purchased from Bay Carbon Inc. The carbon nanotubes were acid treated using a literature method for producing water soluble SWCNT.[1] Briefly, the SWCNT was functionalized by treating 10 mg in an acid mixture of 10 ml of concentrated HNO_3 and 10 ml of concentrated H_2SO_4 followed by heating to 80°C for 2.5 hours. The SWCNT were purified by multiple washes with water to neutral pH.

Graphene was prepared according to a literature method.[2] Graphite was first oxidised by H_2SO_4 and $KMnO_4$. And the resulting graphite oxide underwent exfoliation to afford graphene oxide. A mixture of hydrazine and ammonia were subsequently used to reduce graphene oxide to water-soluble graphene.

A rotating tube microfluidic platform was used to aid room temperature crystallization.[3] We have previously reported the use of the platform to access nanoparticles under continuous flow. Briefly, the hydrodynamics of film flow over a rotating surface is important in controlling the outcome of the reaction. The distinct flow features associated with rotating surfaces are of importance, as they provide platforms for very effective nucleation and growth of nanoparticles under intense mixing. In essence, the behavior of the thin film on a rapidly rotating surface can be classified into two zones. One corresponds to the injection zone where the reagents hit the rotating tube to form a pool. 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. 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.

In a typical synthesis, 1 mM $LnCl_3$ (5% $ErCl_3$ and 95% $YbCl_3$) was pumped in one feed to the rotating tube processor (RTP) with the other feed being 1 mM of NaH_2PO_4. The rotational speed was fixed at 1700 rpm, and the products were collected at the other end of the tube after about 7 sec. For the synthesis of hybrids (SWCNT-$YbPO_4$:Er or Graphene-$YbPO_4$:Er), a solution of graphene or SWCNT was mixed with $LnCl_3$ to prepare a solution with a concentration of 15 mg/L for graphene or SWCNT and 1 mM for $LnCl_3$ instead of the pure $LnCl_3$ solution.

TEM images and selected area electron diffraction patterns (SAED) were obtained using a JEOL 2100 TEM operated at 120 kV. High-resolution TEM (HRTEM) images, energy filtered TEM (EFTEM) images and energy dispersive X-ray spectroscopy (EDS) were obtained on a JEOL 3000F FEGTEM operated at 300 kV.

Topographical image was obtained using a VEECO Dimension 3100 AFM with Nanoscope IIIa controller in ambient air. Silica wafers were first cleaned in an ultrasonic bath for 30 min, placed in a “piranha” solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 1 h, and then rinsed several times with high purity water. Then the silica wafer was coated with graphene by dip coating in a 0.05 % concentration solution for characterisation.

The upconversion fluorescence spectra were measured using a custom set-up. Excitation was performed using a fibre-coupled CW diode laser (Nortel LC92JG74-20) with a wavelength of 978.8 nm (10217 cm^{-1}) and an output power of 140 mW. The laser light was delivered via a single-mode fibre, collimated using an aspheric lens (New Focus 5715-B-H, f = 10mm) and focused down to a spot diameter of 3.5 µm using a second aspheric lens (New Focus 5713-B-H, f = 6 mm). The fluorescence was collected using a 0.1-NA microscope objective (Leitz Wetzlar). The output of the microscope objective was filtered using a band pass filter (Thorlabs FGS 900) and coupled into the input light guide (Ocean Optics R400-7) of the spectrometer (Ocean Optics USB 4000) using a 35-mm focal length singlet lens.

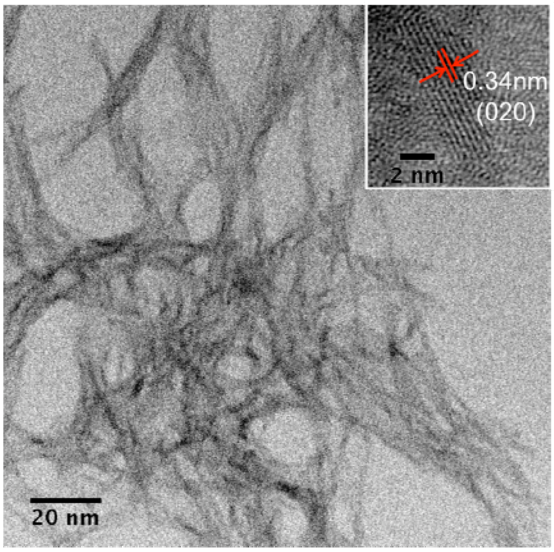

Figure S1. TEM image of SWCNT-$YbPO_4$:Er. Inset, high-resolution TEM image showing typical (020) spacings of tetragonal $YbPO_4$.

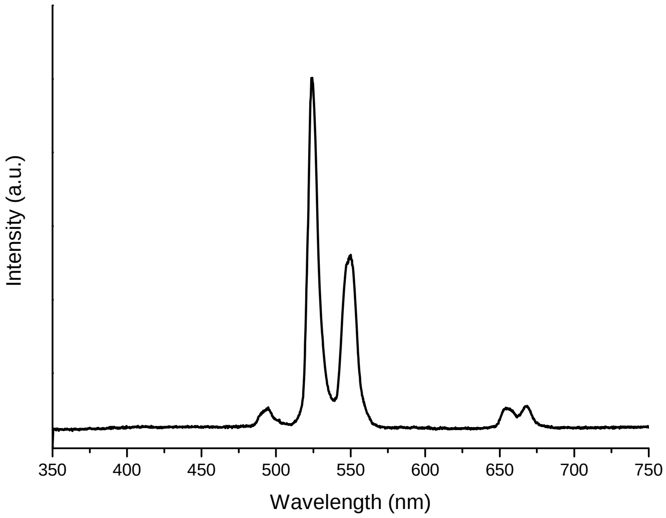

Figure S2. Fluorescence spectrum of SWCNT-$YbPO_4$:Er synthesized at room temperature (excitation wavelength = 980nm).

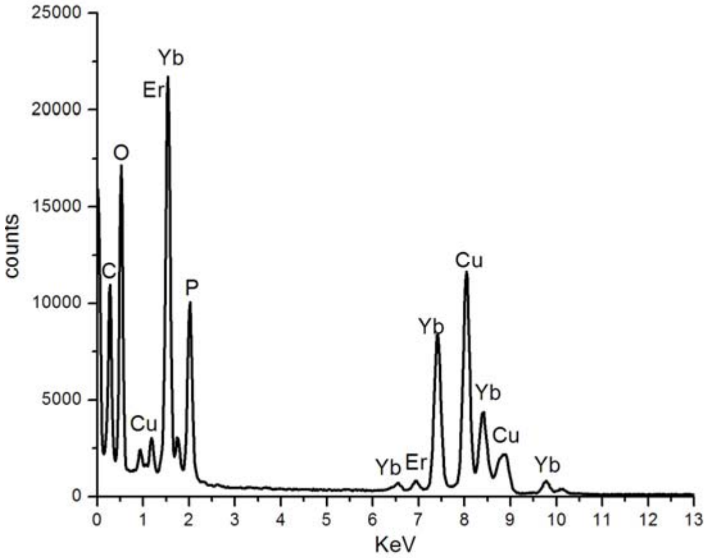

Figure S3. EDS of graphene-$YbPO_4$:Er.

References:

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