

## Supporting Information

### **Bi<sub>2</sub>SiO<sub>5</sub>@g-SiO<sub>2</sub> Upconverting Nanoparticles: A Bismuth-Driven Core-Shell Self-Assembly Mechanism**

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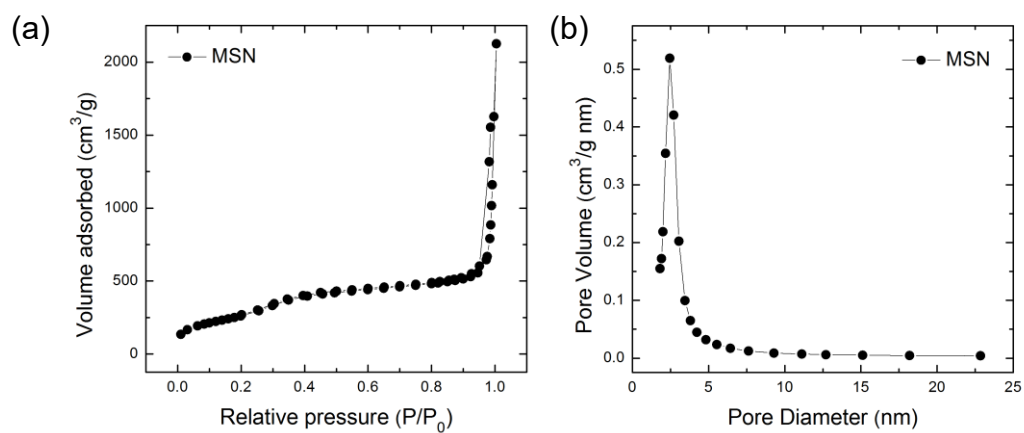
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In order to evaluate how the system could be influenced by the thermal treatments, the bismuth/lanthanides concentration and the nature of the selected lanthanides, three series of samples were prepared as described below:

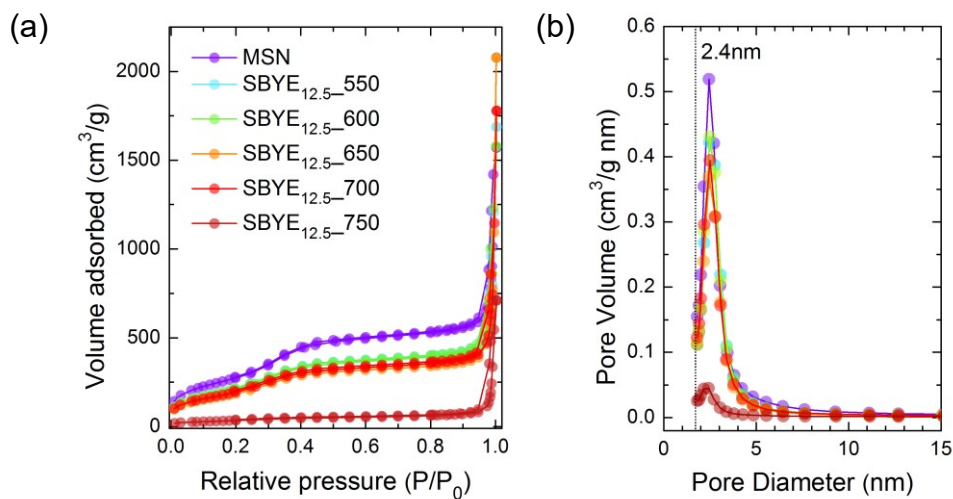
- 1) In the first series, the samples were calcined at different temperature between 550°C and 750°C range, fixing the nominal fraction of the loaded lanthanide-doped Bi oxide into the MSNs pores. A nominal concentration of 14.52 wt% for the Ln-doped Bi<sub>2</sub>O<sub>3</sub> (Ln=Yb,Er) was calculated in order to achieve a pore occupancy of 12.5 vol% by means of the impregnation procedure. The considered Bi:Yb:Er molar ratio was 1:0.1:0.02. The samples are labelled as SBYE<sub>12.5</sub>\_T, where T represents the temperature (°C) of calcination (T=550, 600, 650, 700, 750), and are listed in Table S1.
- 2) For the second series, different degrees of MSN impregnation with Bi and Ln (Ln=Yb,Er) precursor salts were considered up to the complete volume pore occupancy (impregnation at 12.5, 25, 50 and 100 vol%). As in the case of the previous series, Bi:Yb:Er molar ratio was 1:0.1:0.02. The samples were treated fixing the calcination temperature at 750°C and labelled as SBYE<sub>x</sub>\_750, where x=12.5, 25, 50, 100 vol% refers to the pore occupancy. The samples of SBYE<sub>x</sub>\_750 series are listed in Table S1. A sample loaded at 100 vol% (SBYE<sub>100</sub>) was maintained unheated for in situ temperature dependent SR-XRPD measurement.
- 3) In the third series, the samples were doped with ytterbium in combination with one or more other lanthanides, among Ho, Tm, and Er. For this study, the impregnation degree was kept at 100 vol% and the thermal treatment fixed at 750°C. The considered Bi:Ln molar ratio was 1:0.12. The samples are referred as SBYLn series, where Ln= H, T, E represent Ho, Tm and Er, respectively.

**Table S1** Molar ratios and calcination temperature of the synthesized samples belonging to the different Yb, Ln codoped series, labeled as SBYE<sub>12.5</sub>\_T, SBYE<sub>x</sub>\_750 and SBYLn series; nominal pore occupancy refers to the fraction of MSN pore volume impregnated by salt precursors.

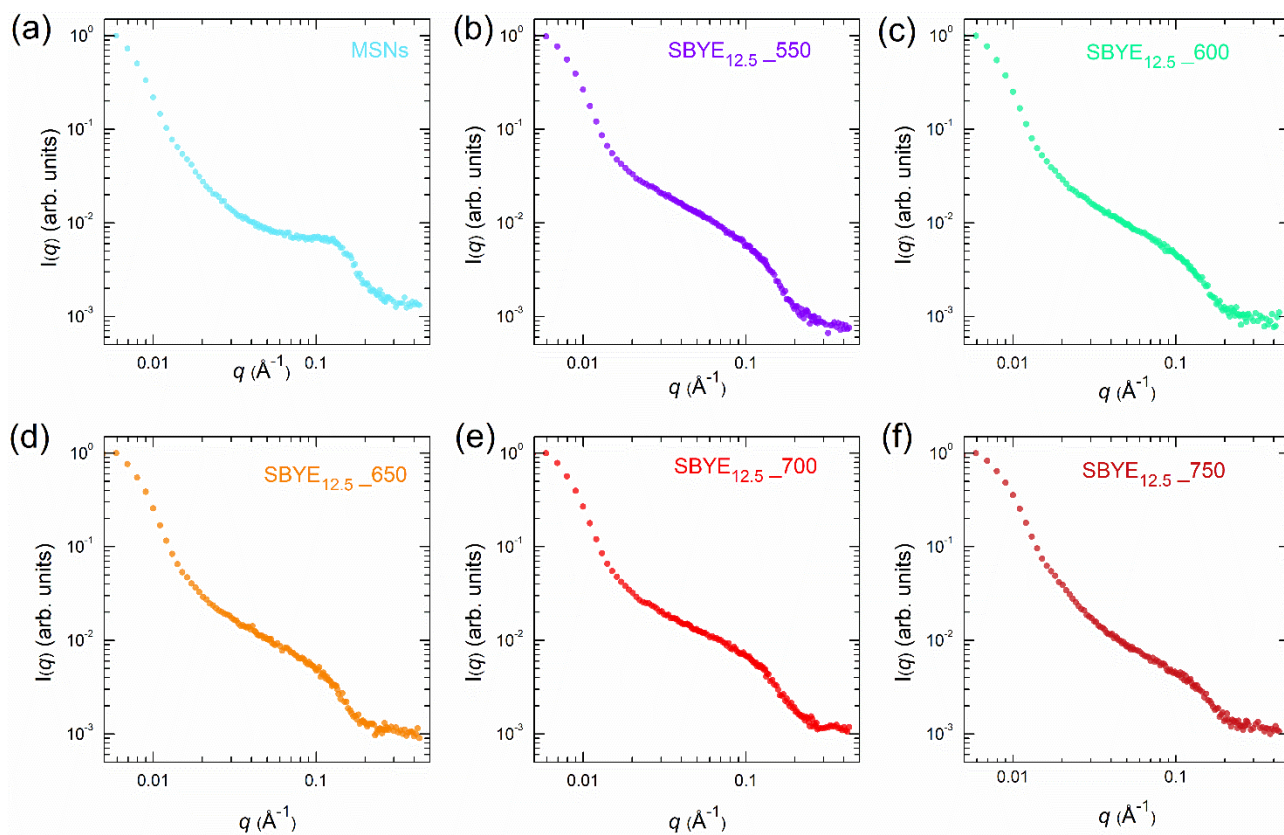
Sample	Ln	Ln-doped Bi <sub>2</sub> O <sub>3</sub> concentration [wt%]	Pore occupancy [vol%]	Si:(Bi+Ln) molar ratio	Temperature [°C]
<b>SBYE<sub>12.5</sub>_T series</b>					
SBYE <sub>12.5</sub> _550					550
SBYE <sub>12.5</sub> _600					600
SBYE <sub>12.5</sub> _650	Er	14.52	12.5	22.85:1	650
SBYE <sub>12.5</sub> _700					700
SBYE <sub>12.5</sub> _750					750
<b>SBYE<sub>x</sub>_750 series</b>					
SBYE <sub>12.5</sub> _750		14.52	12.5	22.85:1	
SBYE <sub>25</sub> _750	Er	25.36	25	11.43:1	750
SBYE <sub>50</sub> _750		40.46	50	5.71:1	
SBYE <sub>100</sub> _750		57.61	100	2.86:1	
<b>SBYLn series</b>					
SBYE	Er				
SBYT	Tm				
SBYH	Ho				
SBYET1	Er+Tm	57.61	100	2.86:1	750
SBYET2	Er+Tm				
SBYHT	Ho+Tm				
SBYEHT	Er+Ho+Tm				



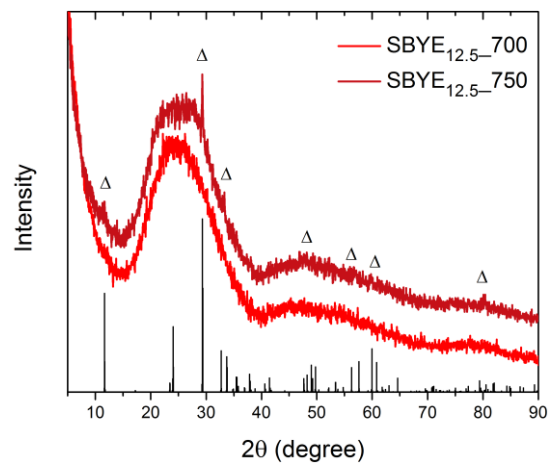
**Figure S1.** N<sub>2</sub> adsorption/desorption isothermal curves (a) and pore size distribution curve (b) of the bare MSNs.



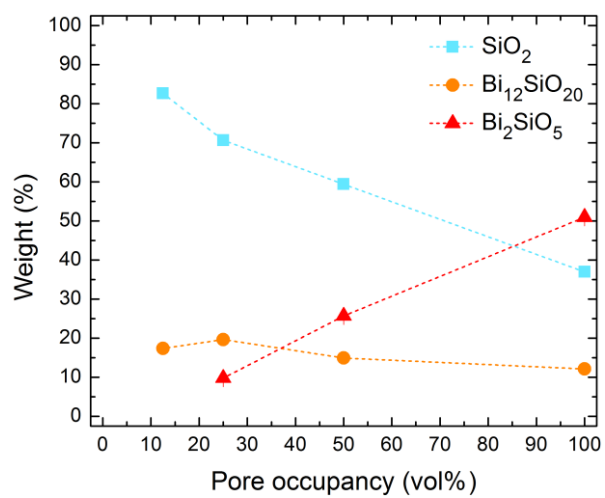
**Figure S2.** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) BJH pore size distribution of the SBYE<sub>12.5</sub>\_T samples.



**Figure S3** SAXS measurements for the series SBYE<sub>12.5</sub>\_T of samples impregnated at the lowest loading content (12.5%) and annealed between 550 and 750°C.



**Figure S4** Comparison between the samples annealed at 700 and 750 °C with the Bi<sub>2</sub>SiO<sub>5</sub> phase patterns (triangles).



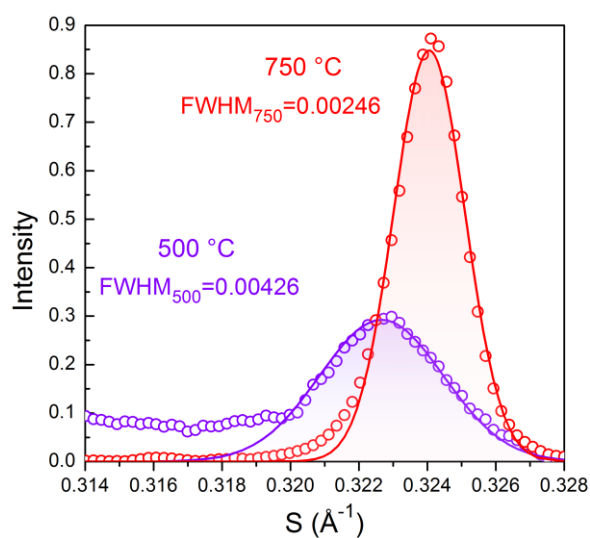
**Figure S5** Weight percentages of the phases from Rietveld refinement *versus* bismuth precursor loading content calculated as percentages of volume occupied by the salt on the total MSN volume accessible.

**Table S2** Comparison of the nominal and experimental (from Rietveld refinement) weight percentages of SiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> of the samples.

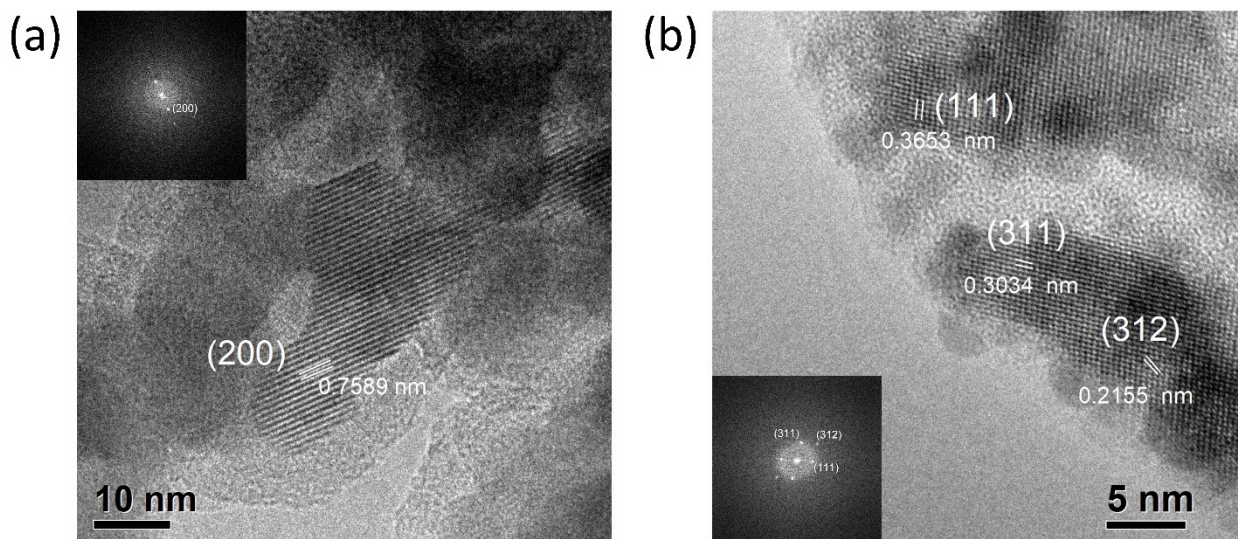
Sample	nominal		experimental	
	SiO <sub>2</sub> (wt%)	Bi <sub>2</sub> O <sub>3</sub> (wt%)	SiO <sub>2</sub> (wt%)	Bi <sub>2</sub> O <sub>3</sub> (wt%)
SBYE <sub>12.5</sub>	85.48	14.52	83.03	16.97
SBYE <sub>25</sub>	74.64	25.36	72.15	27.85
SBYE <sub>50</sub>	59.34	40.46	62.64	37.36
SBYE <sub>100</sub>	42.39	58.61	43.03	56.97

**Table S3** BET specific surface area  $S.A._{BET}$  and total pore volume  $V_p$  of the MSN and SBYE<sub>x</sub> samples.

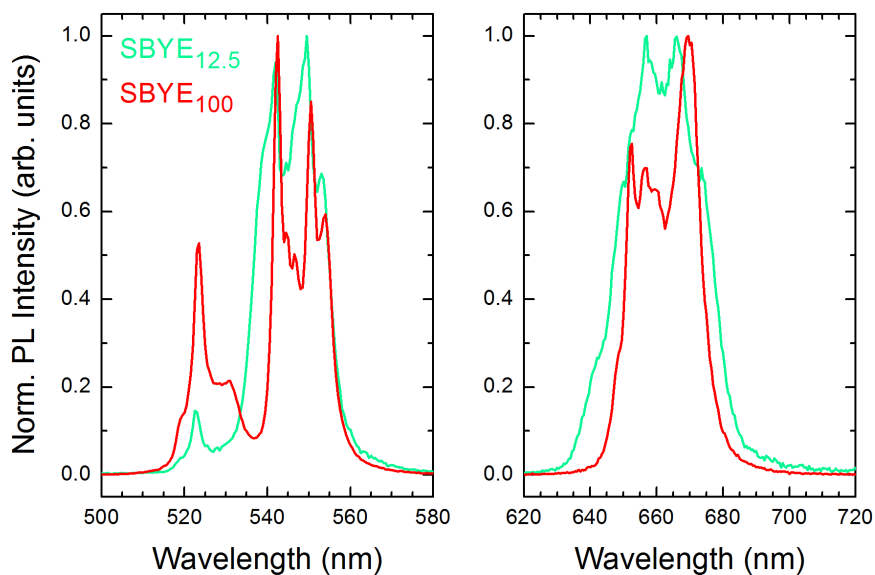
Sample	$S.A._{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_p$ (cm <sup>3</sup> g <sup>-1</sup> )
MSN	1050	1.2
SBYE <sub>12.5</sub>	135	0.26
SBYE <sub>25</sub>	109	0.21
SBYE <sub>50</sub>	18	0.07
SBYE <sub>100</sub>	14	0.06



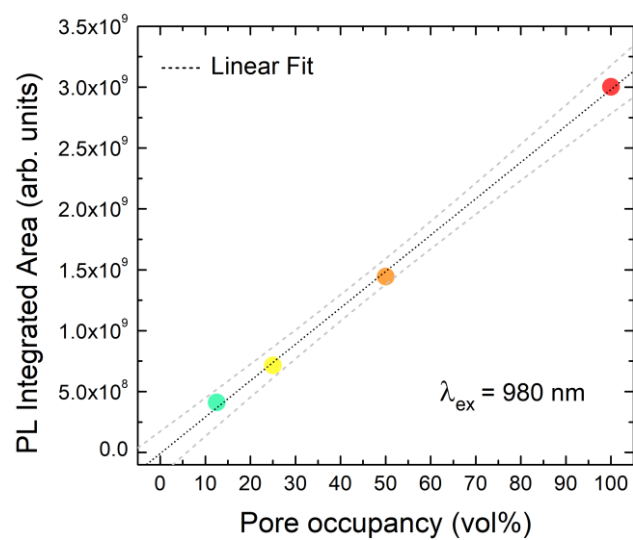
**Figure S6** Magnification of the (311) reflection peak of SR-XRPD patterns ( $\lambda=1.03333 \text{ \AA}$ ) of SBYE<sub>100</sub> sample.



**Figure S7** HR-TEM, FFT and relative plane distances with family plane assignment of the core of different SBYE<sub>100\_750</sub> nanoparticles.



**Figure S8** Comparison of the green and red UCPL emission shapes at the lowest and highest loading (SBYE<sub>12.5\_750</sub> and SBYE<sub>100\_750</sub> respectively).



**Figure S9** UCPL integrated area of the  $\text{Er}^{3+}$  emission (points) and linear fit (dotted line) as a function of the pore occupancy in the MSNs.

**Table S4** CIE Colour Coordinates ( $x,y$ ) for the samples under 980 nm excitation.

Sample	CIE( $x,y$ )
SBYE	(0.31,0.68)
SBYH	(0.65,0.34)
SBYT	(0.25,0.13)
SBYET1	(0.26,0.26)
SBYET2	(0.27,0.43)
SBYTH	(0.39,0.20)
SBYETH	(0.41,0.32)