

Supporting Information

Organic salt assisted colloidal synthesis and X-ray luminescence of (Tm, Tb, Eu)-doped LaOBr nanocrystals

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Experimental details

Materials.

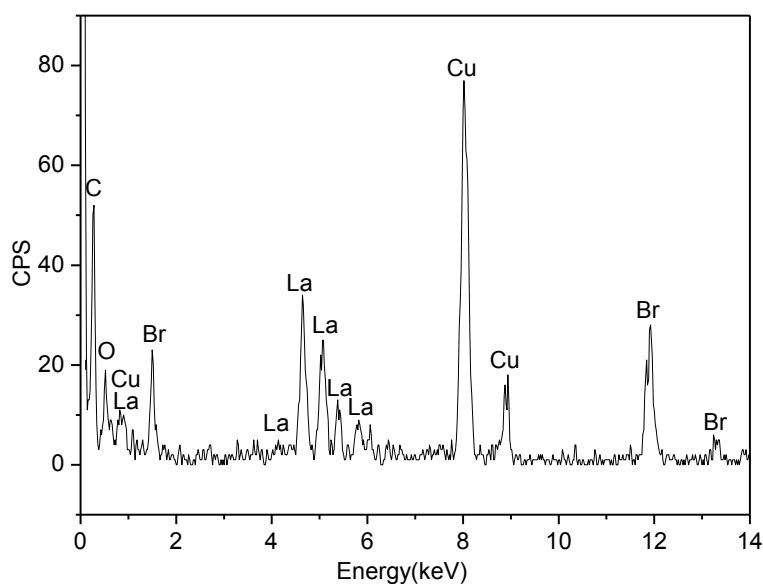
La(CH₃COO)₃·xH₂O (99.99 %), Eu(CH₃COO)₃·xH₂O (99.9 %), Tb(CH₃COO)₃·xH₂O (99.9 %), and Tm(CH₃COO)₃·xH₂O (99.9 %) are synthesized by dissolving the corresponding rare earth oxides in acetic acid solution and dried up by evaporation of water. Ce(CH₃COO)₃·xH₂O (99.9 %) is purchased from Aladdin-reagent. Oleylamine (OM, C18:80~90%, Alfa Aesar), oleic acid (OA, 90%, Alfa Aesar), and 1-Octadecene (ODE, >90%, Alfa Aesar) are used as starting materials without further purification. Tetrabutylammonium bromide (TBAB, 98%, Aladdin-reagent) and tetrabutylammonium chloride (TBAC, 97%, Aladdin-reagent) are the selected organic salts.

Synthesis of colloidal LaOBr nanocrystals.

In a typical synthesis, 1.5 mmol La(CH₃COO)₃ and 1.0 g TBAB are added to mixed solvent composed of 4 mL of oleylamine (OM), 2 mL oleic acid (OA), and 6 mL 1-Octadecene (ODE) at room temperature. The mixture is heated to 110 °C in a vacuum for 30 min to remove water and oxygen, forming a transparent solution. The solution is heated to 300 °C over approximately 8 min under Ar atmosphere and kept for 25 min. After air cooling by taking off the temperature-controlled electromantle, the nanocrystals are precipitated with ethanol and centrifuged for three cycles, and redispersed in cyclohexane for the transmission electron microscopy (TEM) characterizations or dried in a vacuum oven overnight for the X-ray diffraction (XRD) and other measurements. Colloidal LaOCl and CeOBr nanocrystals are synthesized under the same conditions.

Physical Characterization

XRD patterns are recorded with a Bruker D8 diffractometer using Cu K α radiation with 40 mA and 40 kV. Transmission electron microscope (TEM), energy-dispersive X-ray spectroscopy (EDS), and selected the selected area electron diffraction (SAED) are carried out on a JEOL JEM-2010F electron microscope operated at 200 kV. X-ray-excited luminescence (XEL) spectra have been measured at room temperature on a home-made X-ray-excited spectrometer, FluorMain, where a FII-30 movable X-ray tube (Tungsten anticathode target, 80 kV/4 mA) is used as the X-ray source and operated at room temperature. ¹H NMR measurements are performed on a Bruker 400 MHz NMR spectrometer.



Element	Peak	Area	k	Abs	Weight%	Weight%	Atomic%
	Area	Sigma	factor	Corn.		Sigma	
C K	201	30	2.208	1.000	14.61	1.99	50.94
O K	56	22	1.810	1.000	3.33	1.27	8.72
Cu K	709	47	1.366	1.000	31.84	2.02	20.99
Br K	293	33	1.966	1.000	18.94	1.94	9.93
La L	479	45	1.983	1.000	31.28	2.36	9.43
Totals					100.00		

Figure S1 Energy-dispersive X-ray spectroscopy (EDS) of individual LaOBr nanocrystal, corresponding to the TEM image in Figure 1C in the main text. Cu and carbon elements are coming from the holey carbon film coated Cu grid supporting sample during EDS measurement.

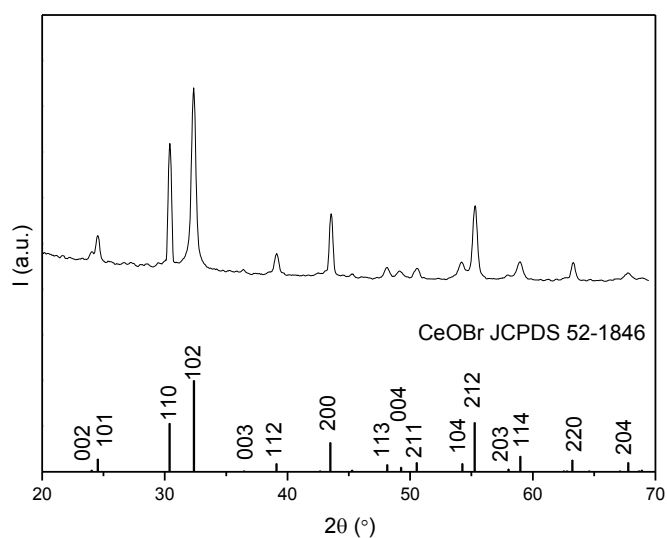


Figure S2 XRD pattern of CeOBr nanocrystals. The standard pattern is of bulk CeOBr (JCPDS 52-1846) for wide angle.

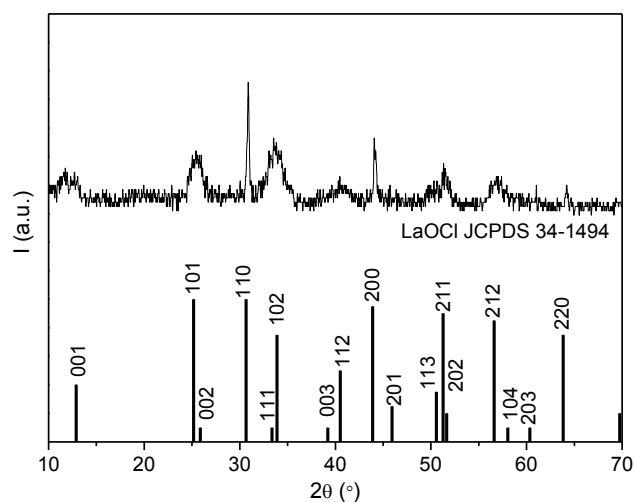


Figure S3 XRD pattern of LaOCl nanocrystals. The standard pattern is of bulk LaOCl (JCPDS 34-1494) for wide angle.

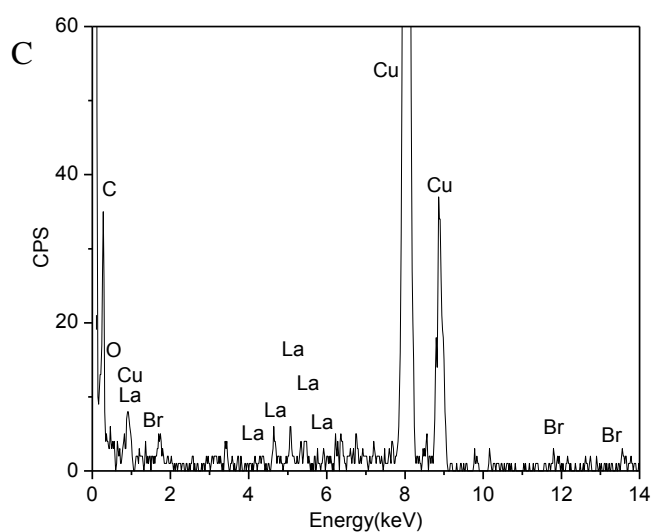
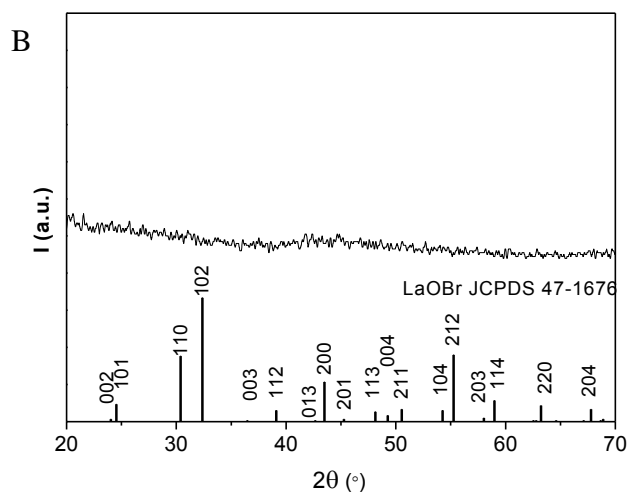
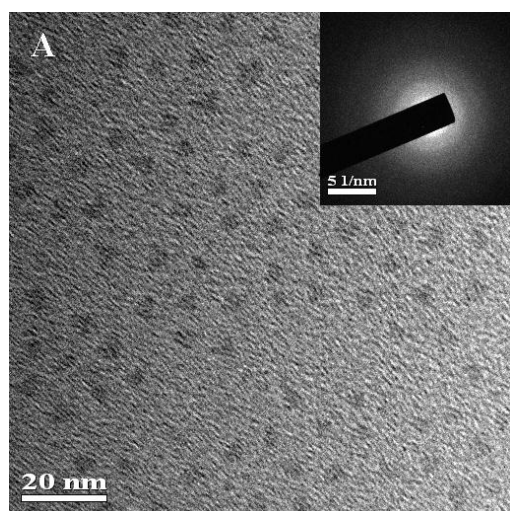


Figure S4 TEM, SAED, XRD pattern, and EDS of the amorphous La-O-Br nanoparticles without ageing at 300 °C. (A) TEM image; (B) XRD pattern, and the standard pattern is of bulk LaOBr (JCPDS 47-1676) for wide angle; (C) EDS of the amorphous La-O-Br nanoparticles.

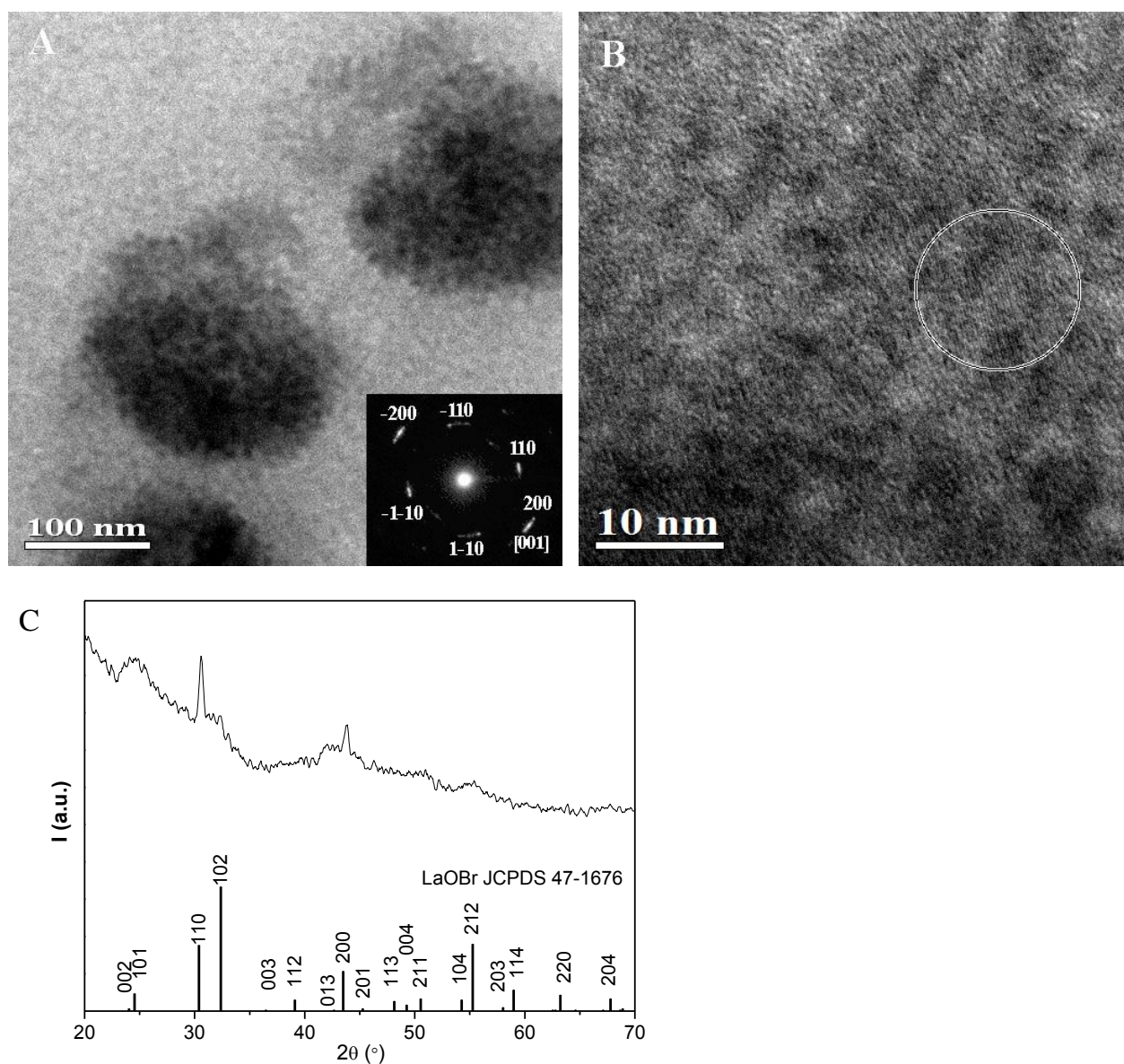


Figure S5 TEM, SAED, HRTEM, and XRD of the assembled nanostructures with ageing at 300 °C for 5 min. (A) TEM image and SAED pattern; (B) HRTEM of the individual nanostructure, the lines in the circle are corresponding to the (110) plane of crystalline LaOBr; (C) XRD pattern, and the standard pattern is of bulk LaOBr (JCPDS 47-1676) for wide angle.

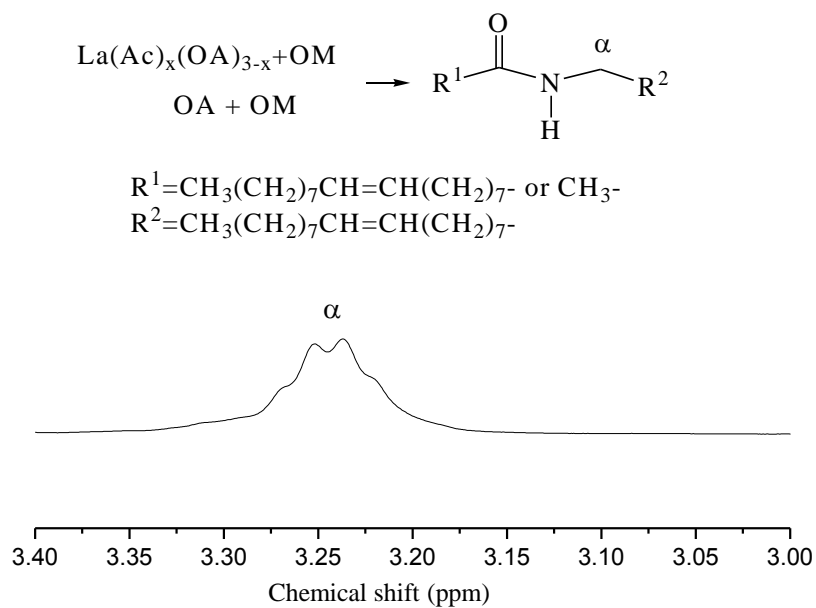


Figure S6 NMR measurement of amides produced in the colloidal system. The protons (α) at 3.25 ppm on amide molecules are used as a probe to confirm the amidation reactions.