

Supplementary Material

Facile synthesis of aqueous-dispersed luminescent nanosheets from non-layered lanthanum hexaboride

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I. Field Emission Scanning Electron Microscopy (FESEM) image of pristine LaB₆

The FESEM of the bulk LaB₆ powder sample displayed in Fig. S1 indicates the presence of particles of size ranging from a few hundred nanometers to a few micrometers in the pristine sample.

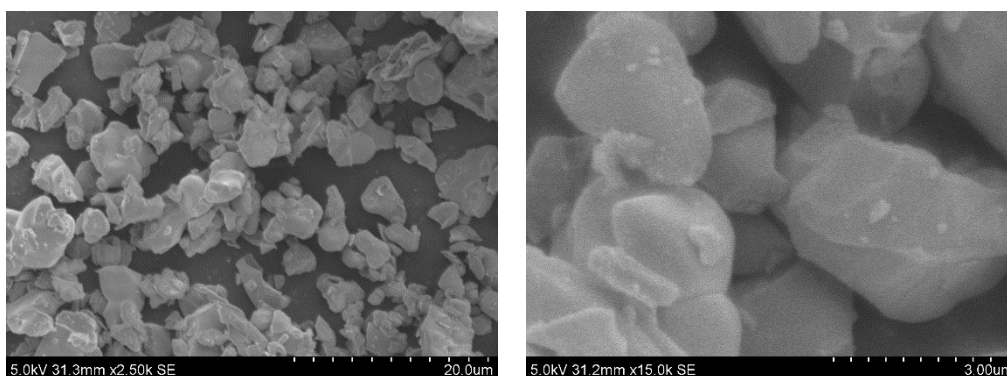


Fig S1: (a) & (b) FESEM images of bulk LaB₆ powder.

II. X-ray Diffraction Analysis (XRD) of bulk LaB₆ in powder form

The X-ray diffraction analysis of LaB₆ powder was carried out using X-ray diffractometer-Rigaku Miniflex 300. The XRD pattern (Fig. S2) comprises 13 significant peaks for the following 2θ (deg) values at 21.45, 30.47, 37.51, 43.57, 49.03, 54.05, 63.29, 67.61, 71.81, 75.79, 79.91, 83.87 and 87.83; which are respectively indexed as (100), (110), (111), (200), (210), (211), (220), (300), (310), (311), (222), (320), (321) crystal planes. The XRD pattern confirms the crystalline nature and purity of LaB₆ powder and the 2θ values corresponding to

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the peaks was found to be in good agreement with the typical (ICDD data -Card No: 01-083-9724) values.

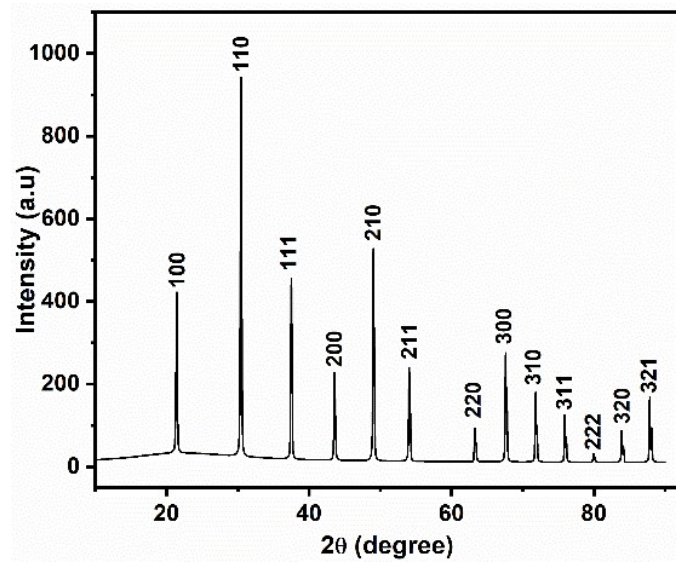


Fig S2: X-ray diffraction (XRD) pattern of pristine LaB₆ powder sample.

III. Photoluminescence spectra of bulk LaB₆ powder

The photoluminescence (PL) spectra of the bulk LaB₆ powder sample were collected at different excitation wavelengths from 250 to 650 nm (as illustrated in Fig. S3) at an interval of 50 nm. The figure shows that the photoluminescence of the bulk LaB₆ powder is extremely weak compared to the background noise.

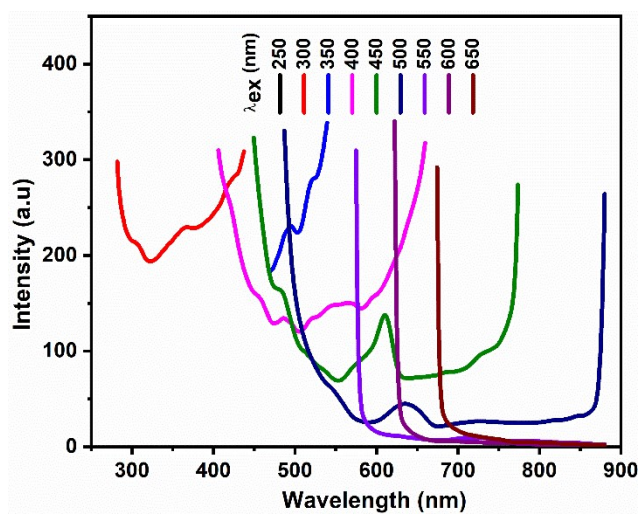


Fig S3: Photoluminescence (PL) spectra of the pristine LaB₆ powder sample collected at different excitation wavelengths from 250 to 650 nm at an interval of 50 nm.

IV) HR-TEM Image of LaB₆ nanosheets

The HR-TEM Image of LaB₆ nanosheet along with highlighted lattice in the inset is shown in Fig: S4 (a). The d-spacing in the nanosheets was measured with image J software and was found to be $\sim 2.6 \text{ \AA}$. This value is closer to the d-spacings of (111) planes than that for other planes of bulk LaB₆. This deviation in the d-spacings of nanosheets from that of the corresponding bulk material may be due to the functional groups attached in the material in the nanoform. Fig: S4 (b) displays the HR-TEM image of a LaB₆ nanosheet with, the edge of the sheet giving a clear picture about the number of layers and the highlighted image in the inset shows the presence of 9 layers in the nanosheet and the nanosheet thickness was measured to be 3.1 nm. This was found to be in agreement with the AFM height profile of the nanosheets showing a thickness of $\sim 2 \text{ nm}$ for the nanosheets.

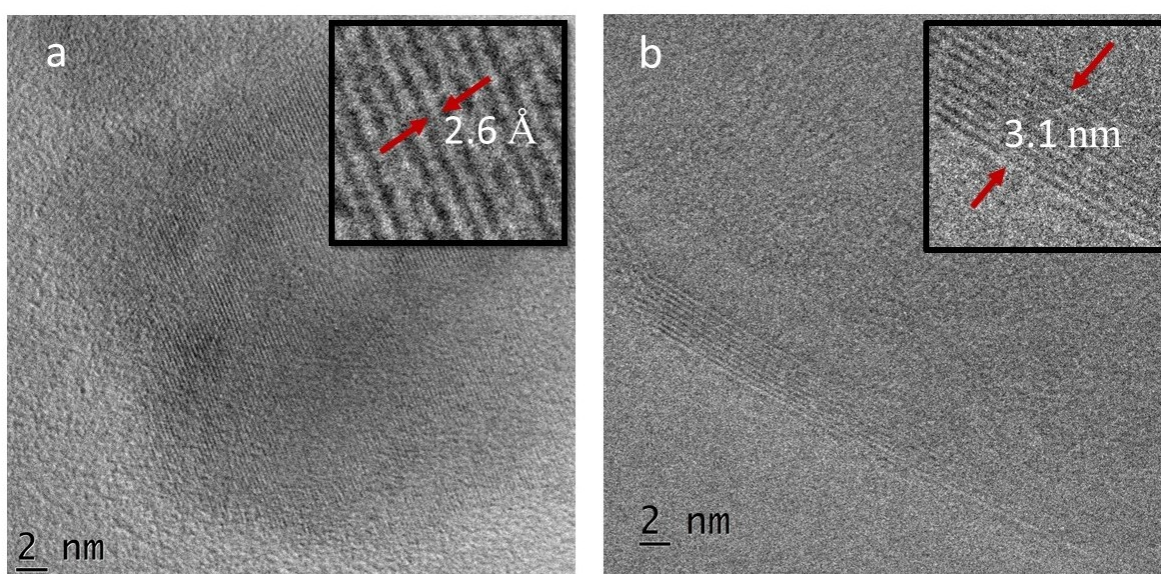


Fig S4: (a) HR-TEM image of LaB₆ nanosheet with highlighted lattice in the inset. (b) HR-TEM image of a LaB₆ nanosheet with the edge of the sheet giving a clear picture about the number of layers and the highlighted image in the inset shows the presence of 9 layers in the nanosheet.

V. Indexing of SAED Pattern

The d spacings were calculated from the SAED pattern using image J software. The d spacings were matched against standard ICDD data (Card No: 01-083-9724). Some of the d-

spacings were found to be matching with d-spacings obtained from the ICDD data of bulk LaB_6 and are marked in the figure S5. Some other d-spacings were found not to be matching with d-spacings obtained from the XRD data bulk LaB_6 . This may be due to two reasons (i) in the SAED pattern, since the zone axis is not aligned in the plane, some out of plane reflections can be present and (ii) as we have discussed in the article, the nanosheets are chemically modified (containing $-\text{OH}$ functional groups) and therefore, may not have perfect LaB_6 crystalline structure.

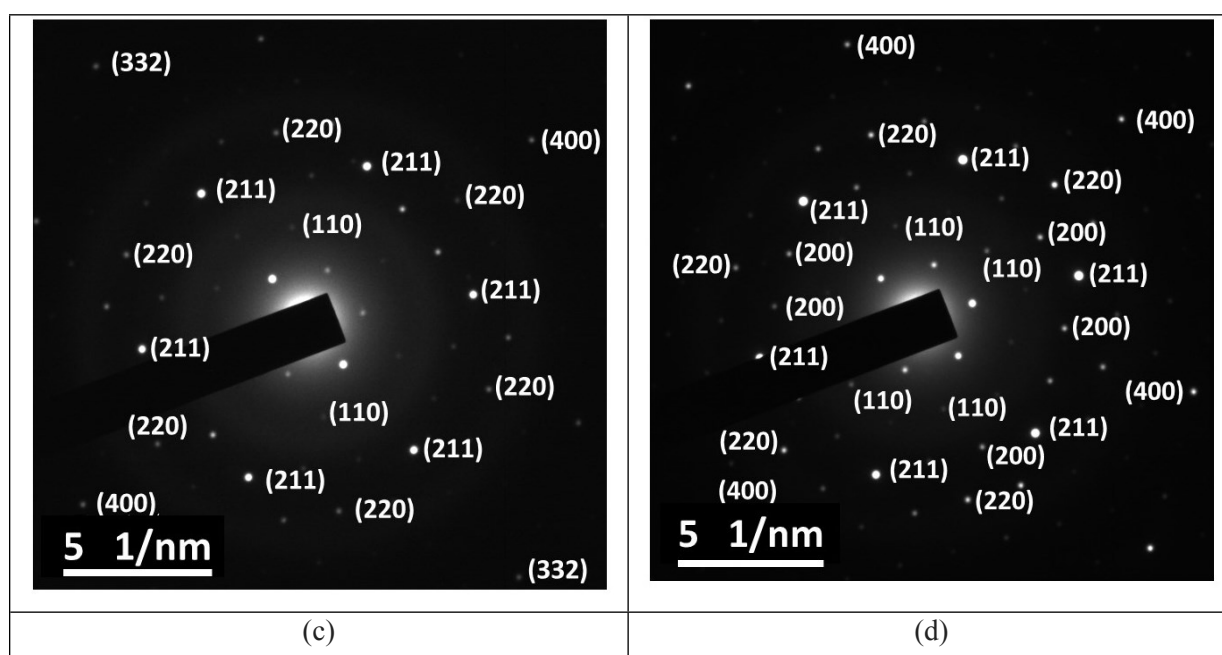


Fig. S5: Indexed SAED pattern of LaB_6 nanosheets

VI. X-ray Diffraction Analysis (XRD) of LaB_6 nanosheet powder

The X-ray diffraction pattern of the powder obtained by the lyophilisation of the nanosheet dispersion was collected and is given in figure S6. The spectrum indicates a completely amorphous nature of the nanosheet powder and this may be the result of the disruption of the long-range order caused by the hydroxy functionalisation of the nanosheets.

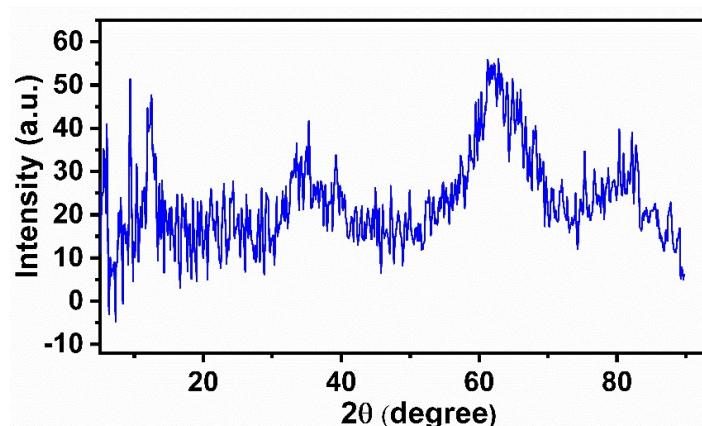


Fig. S6: XRD pattern of LaB₆ nanosheet powder sample

VII. Energy-level scheme of LaB₆ nanosheets

The fig. S7 below is the complete spectrum of photoluminescence emission of LaB₆ nanosheets dispersion. The emission peak corresponding to the sample around 408 nm. The additional peaks in the lower wavelength and higher wavelength region are harmonics of the excitation signal.

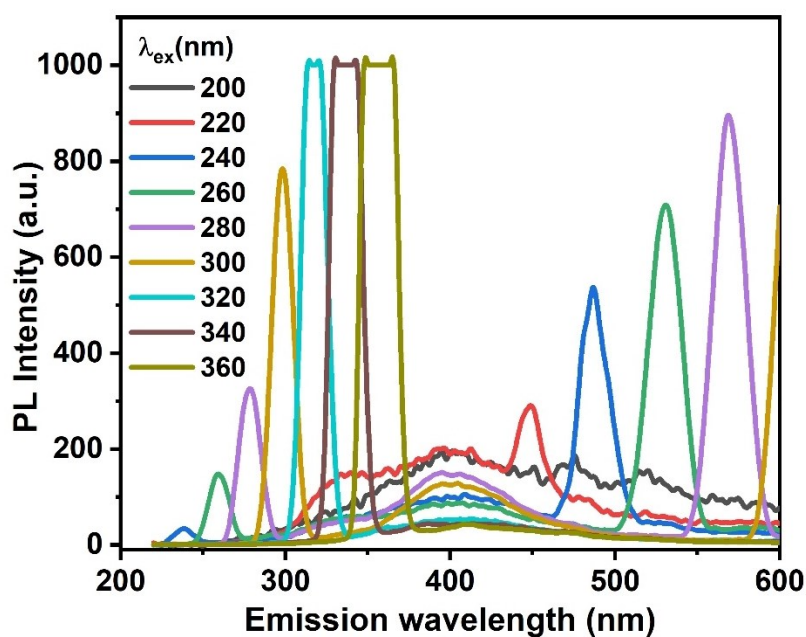


Fig. S7 PL emission spectra of the aqueous dispersion of LaB₆ nanosheets collected at different excitation wavelengths. The excitation wavelengths were increased from 220 to 360 nm (with a step of 20 nm)

VIII. Energy-level scheme of LaB₆ nanosheets

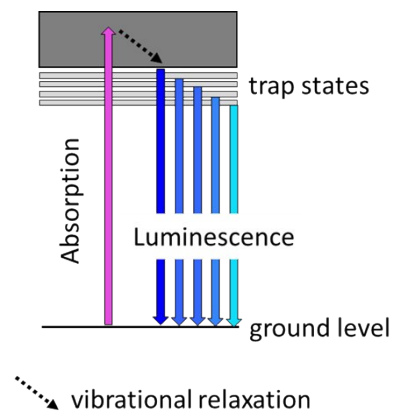


Fig. S8: The proposed energy level diagram of the nanosheets.

IX. More TEM Images of LaB₆ nanosheets

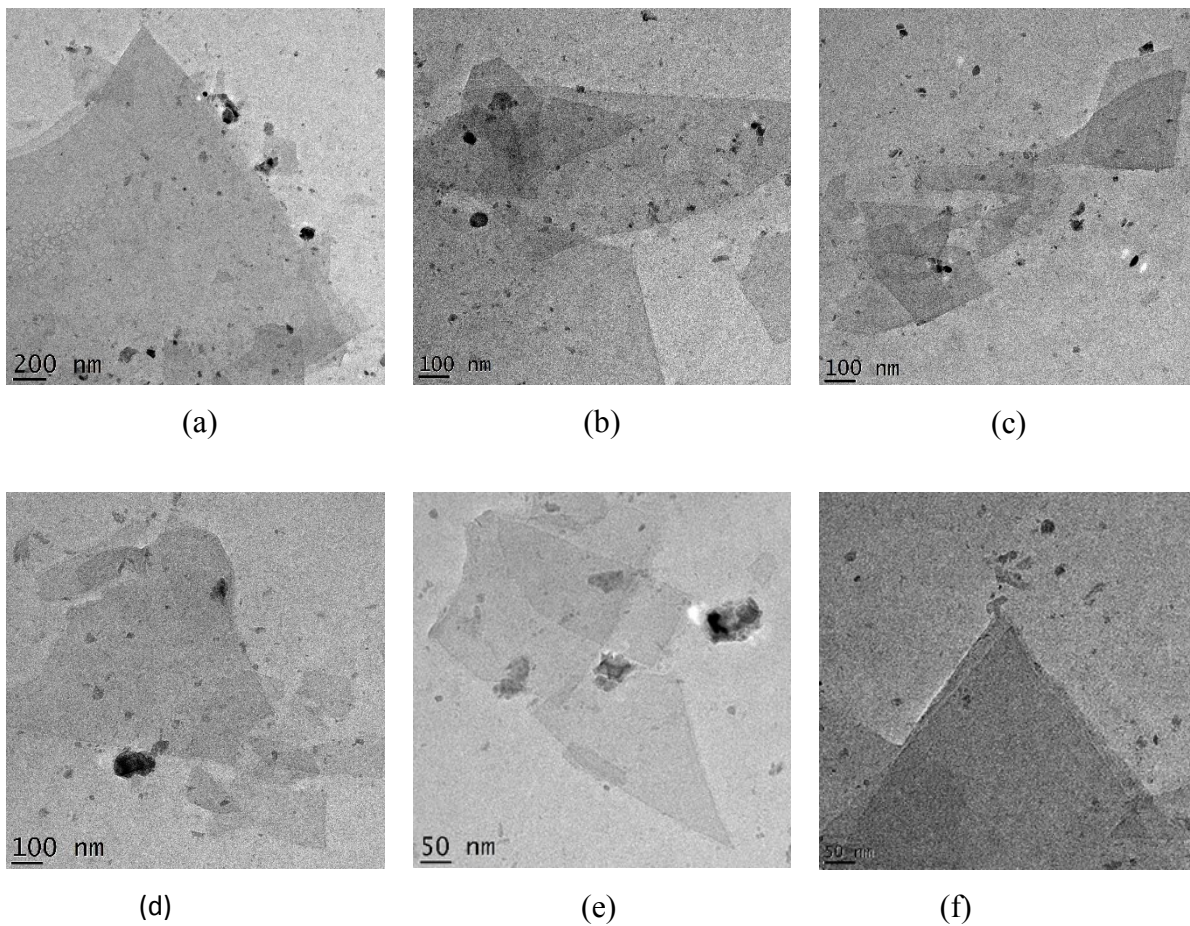


Fig. S9: TEM images of the nanosheets obtained by depositing the dialyzed dispersion on the TEM grid.