

Supporting Online Material

for

Tuning Phase Stability of Complex Oxide Nanocrystals via
Conjugation

Ho-Hung Kuo¹, Lei Chen², Yanzhou Ji², Heng-Jui Liu¹, Long-Qing Chen², Ying-Hao Chu^{1,3}*

¹Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu
30010, Taiwan

²Department of Materials Science and Engineering, Pennsylvania State University, University
Park, Pennsylvania, 16802, USA

³Institute of Physics, Academia Sinica, Taipei 105, Taiwan

To whom correspondence should be addressed. *Email: yhc@nctu.edu.tw

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Additional results and discussion

Fig. S1, S2, S3, S4

References

BFO-NCs were synthesized using pulsed laser ablation (PLA) of BFO target in Ethylene Glycol diluted by 50 % distilled water (EG+H₂O =1:1). These NCs were investigated and identified using transmission electron microscopy (TEM), energy dispersive spectrometry (EDS), X-ray diffractometry (XRD), Raman spectrometry (Raman), X-ray absorption (XAS), and electron energy loss spectrometry (EELS), as shown in Fig. S1 and S2, respectively.

As seen in Fig. S1A, low-magnification TEM shows the BFO-NCs in spherical shape. The spectra including Bi, Fe, O were acquired overall from these NCs. The elemental ratio (atomic percent) was semi-quantitatively measured as Bi:Fe:O = 1:1:3. Fig. S1B shows the XRD, Raman, and XAS spectra of BFO-NCs, respectively. XRD diffraction peaks can be identified referred to X-ray database (JCPDS No.72-2035, $a = 3.96 \text{ \AA}$), suggesting that these NCs have a rhombohedrally distorted perovskite structure belonging to the space group of $R3c$. No secondary phase was detected. From Raman spectra, several phonon peaks were identified and classified to be A_1 and E -type modes with the reference to a rhomb-centered BFO thin film reported by Hermet *et al.*^{S1} and Porporati *et al.*^{S2}

The epitaxial BFO thin film results in sharp Raman peaks due to its high uniformity and symmetry. However, the random distribution of BFO-NCs results in the broad peaks and some overlaps of E and A_1 peaks, which are $E@135 \text{ cm}^{-1}$, $E@153 \text{ cm}^{-1}$, $E@262 \text{ cm}^{-1}$ or $A_1@262 \text{ cm}^{-1}$, and $A_1@316 \text{ cm}^{-1}$. As quoted from statement by Hermet *et al.*^{S1}, Bi atoms only participate in low-frequency modes up to 167 cm^{-1} while oxygen motion strongly dominates in modes above 262 cm^{-1} . Fe atoms are mainly involved in modes between 152 and 261 cm^{-1} but also contribute to some higher-frequency modes. In addition, Porporati *et al.*^{S2} reported that parallel-polarized Raman intensity of the A_1 and E modes locate at around 176 and 136 cm^{-1} , respectively; and the cross-polarized intensity locate at around 263 and 136 cm^{-1} , respectively. Meanwhile, the Fe valence state to BFO is critical since the reduction of Fe^{3+} species to Fe^{2+} will lead to low insulation resistance, which limit the BFO potential to the device application. Therefore, XAS and EELS were used to measure the valence state of Fe- $L_{2,3}$ edges in BFO-NCs.

The XAS spectra, as shown in Fig. S1B, exhibits doublet peaks of L_3 (~708.7 eV) and L_2 (722.3 eV). It is consistent with the one measured from the BFO thin film reported by Ryu *et al.*^{S3}. It can be concluded that XAS data provides us the information that the Fe of these BFO-NCs is trivalent (Fe^{3+}), as well as the chemical environment (is located in oxygen octahedral site). Furthermore, the EELS result, as shown in Fig. S2, are in good agreement with XAS result.

EELS was used to examine the Fe valence state of an individual BFO-NC. The Fe- $L_{2,3}$ edges from a number of phyllosilicates containing various Fe^{3+} - Fe^{2+} ratios were collected by Grävie *et al.*^[S4] in Fig. S2A, which are daphnite, cronstedtite, nontronite. Fig. S2b shows the Fe- $L_{2,3}$ edges of BFO-NC in 40 nm and standard Fe- $L_{2,3}$ edges of Fe_2O_3 from EELS database of Gatan company. As seen in Fig. S2a, Fe- L_3 edge for the bivalent Fe minerals are at ca. 707.8 eV, and the trivalent Fe has L_3 edge at 1.7 eV higher, at ca. 709.5 eV. Fe- L_2 edge for bivalent and trivalent Fe locates at 720.4 eV and 722.6 eV, respectively. Fe in daphnite is bivalent but may present a small amount of Fe^{3+} . Cronstedtite contains both Fe^{3+} and Fe^{2+} features, which is visible from the double-peaked L_3 edge being separated by 1.7 eV. Nontronite gives Fe- $L_{2,3}$ edge shape that indicating the majority of the Fe is Fe^{3+} . From these three reference compounds illustrate that Fe valence state are recognizable by changes in the multiplet structures on the L_3 edges and energy loss peaks of $L_{2,3}$. Based on the criteria, we can state our Fe valence state in BFO-NC is trivalent (Fe^{3+}) since its L_3 edge locates at 709.5 eV and L_2 locates at 722.75 eV, as seen the red profile in Fig. S2B, and no extra peak indicating the bivalent Fe were detected. It is very matched to the Fe- $L_{2,3}$ edges of Fe_2O_3 with trivalent Fe from EELS database of Gatan company, as seen the black profile at below.

The coherent interfacial structure between tetragonal BFO (T-BFO) and LAO discussed in Fig. 3 is shown in Fig. S3. Since the BFO-NC was very sensitive to the electron beam of TEM, leading to the image shifting and difficulty of image focusing, the interfacial image is not revealed in good-quality as well as the images of individual BFO-NC and LAO-NC. Therefore,

we included this one here in order not to destroy the systematic discussion over TEM structure in Fig. 3.

Figure S4 shows the lattice image of rhombohedral BFO (R-BFO, $a = 3.96 \text{ \AA}$) on LAO with size over than critical limit. Unfortunately, owing to the shape effect and large size, only very tiny area of R-BFO lattice image was acquired. On the other hand, the LAO-NC, indicated by the EDS, is too thick to reveal its lattice image by electron beam.

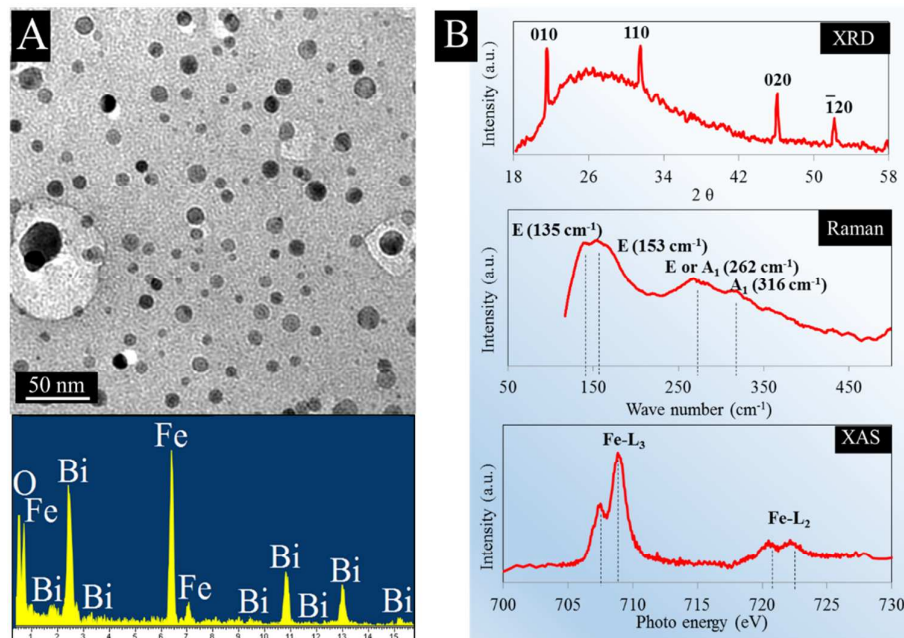


Fig. S1. (A) TEM image and corresponding EDS, (B) structural determinations using XRD, Raman, and XAS of BFO-NCs by PLA in $\text{H}_2\text{O}+\text{EG}$.

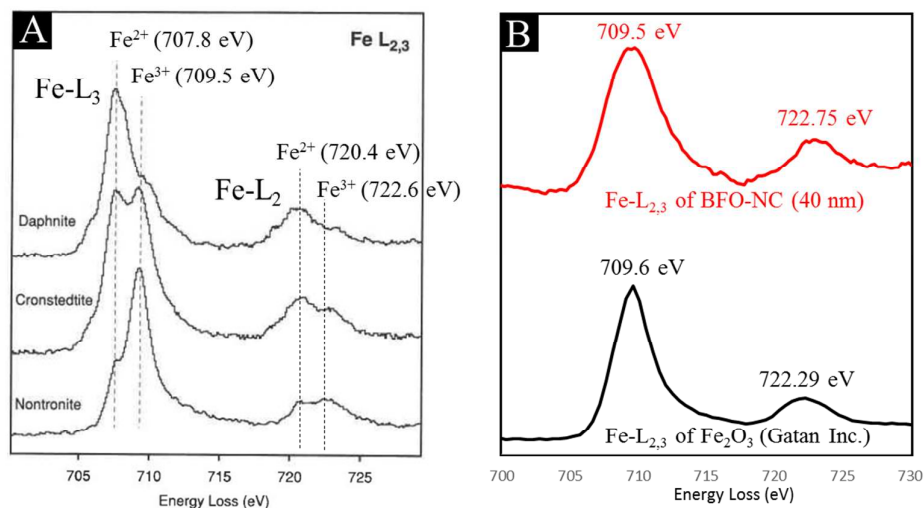


Fig. S2. (A) Fe-L_{2,3} edges from three phyllosilicates, which are daphnite (dominantly Fe^{2+} with a

few percent Fe^{3+}), cronstedtite (Fe^{2+} and Fe^{3+}), and nontronite (dominantly Fe^{3+})^[S1]. (B) $\text{Fe-L}_{2,3}$ edges from BFO-NC (40 nm) and bulk Fe_2O_3 of Gatan Inc. EELS database.

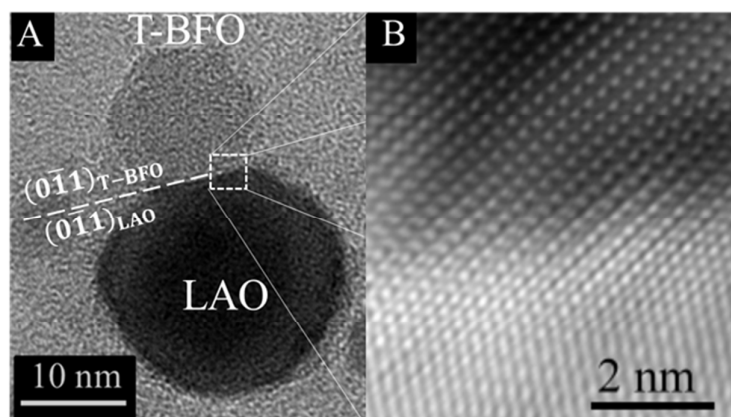


Fig. S3. (A) Low-mag image of T-BFO/LAO heteroconjugation, and (B) the lattice image of their interface.

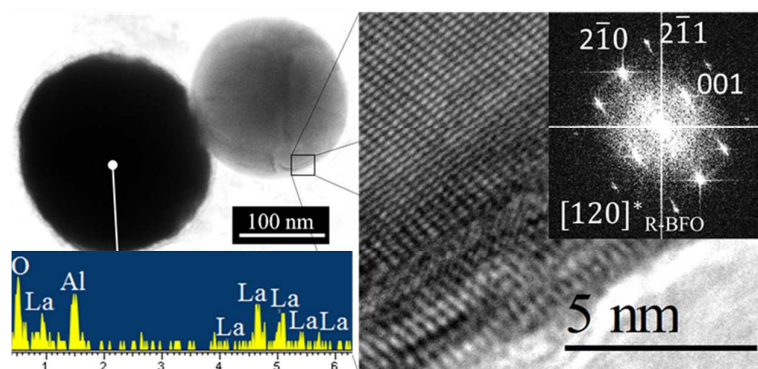


Fig. S4. Lattice image and corresponding FFT pattern of rhombohedral BFO with size over than critical limit, and the EDS shows the LAO-NC on the left.

References

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