

Supplementary Information

Ba-addition Induced Enhanced Surface Reducibility of SrTiO₃: Implication on Catalytic Aspects

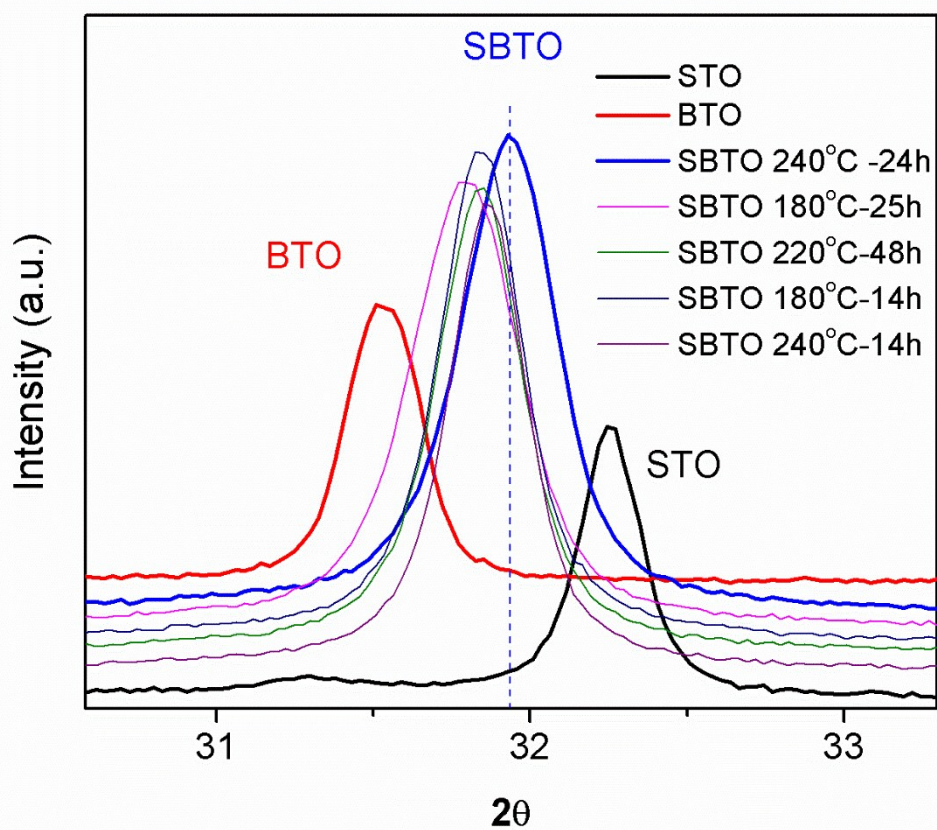


Figure S1. Synthesis of SBTO. XRD patterns of SBTO prepared by varying the temperature in a range of 180-240 °C and time in the range of 14-48 h. The peaks of SBTO prepared at 240 °C for 24 h lies exactly in between the XRD peaks of STO and BTO.

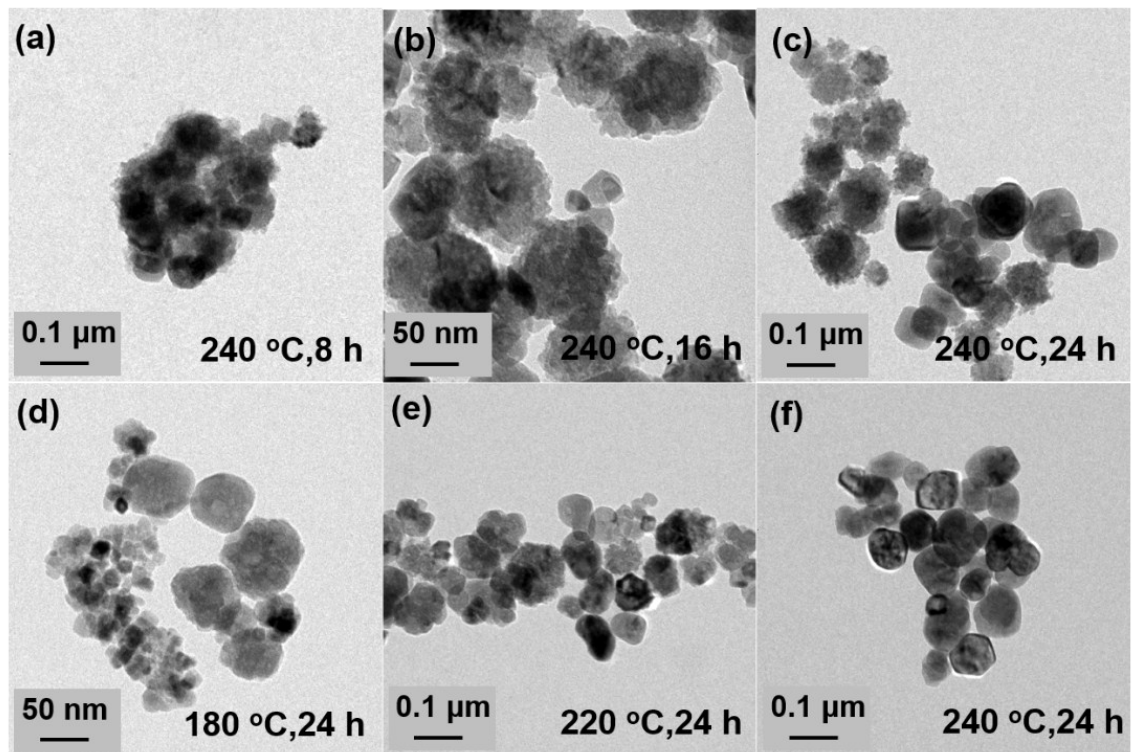
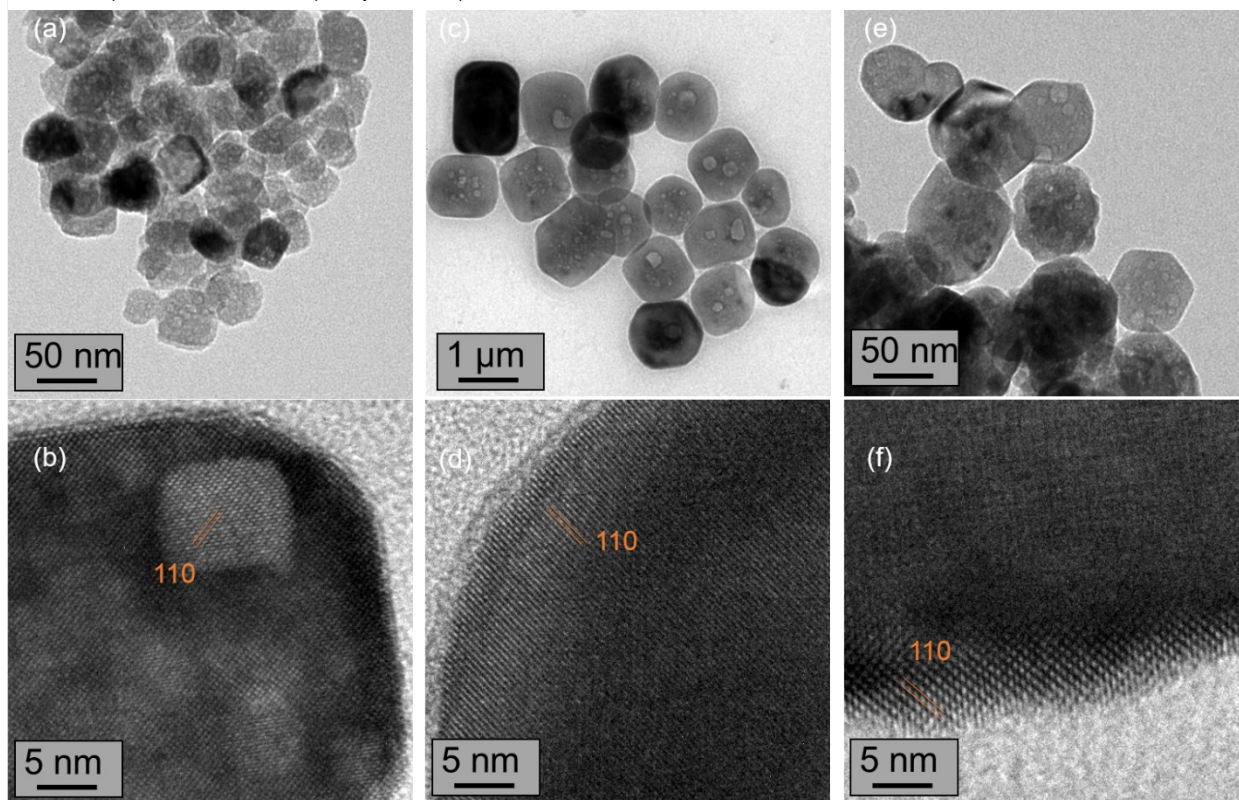


Figure S2. Synthesis of SBTO. The temperature is varied from 180-240 °C (d-f) for a 24 h
Figure S3. After NaBH_4 treatment. TEM bright field images of (a) RSTO, (c) RBTO and (e) RSBTO.
 The HRTEM images showing 110 planes of (b) RSTO, (d) RBTO and (f) RSBTO corresponding to $d=2.76$, 2.82 and 2.79 Å, respectively.



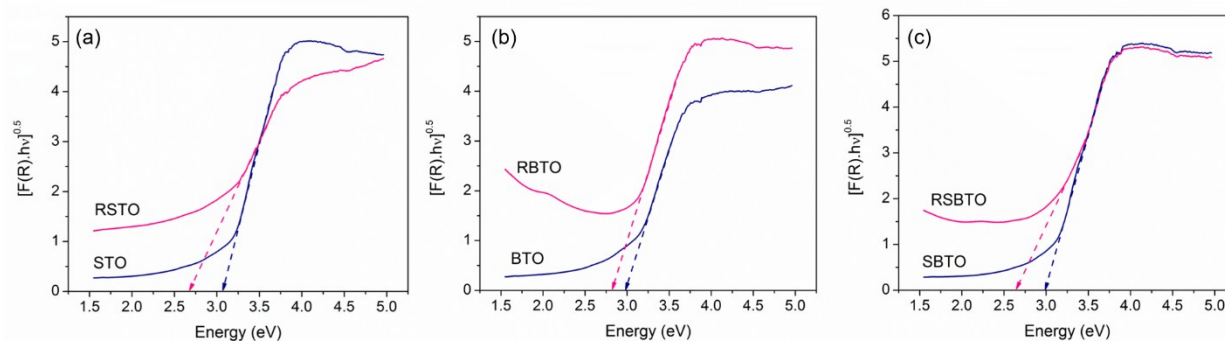


Figure S4. Plot of transformed Kubelka-Munk function vs the energy of the excitation source absorbed. Comparison of (a) STO and RSTO, (b) BTO and RBTO, and (c) SBTO and RSBTO.

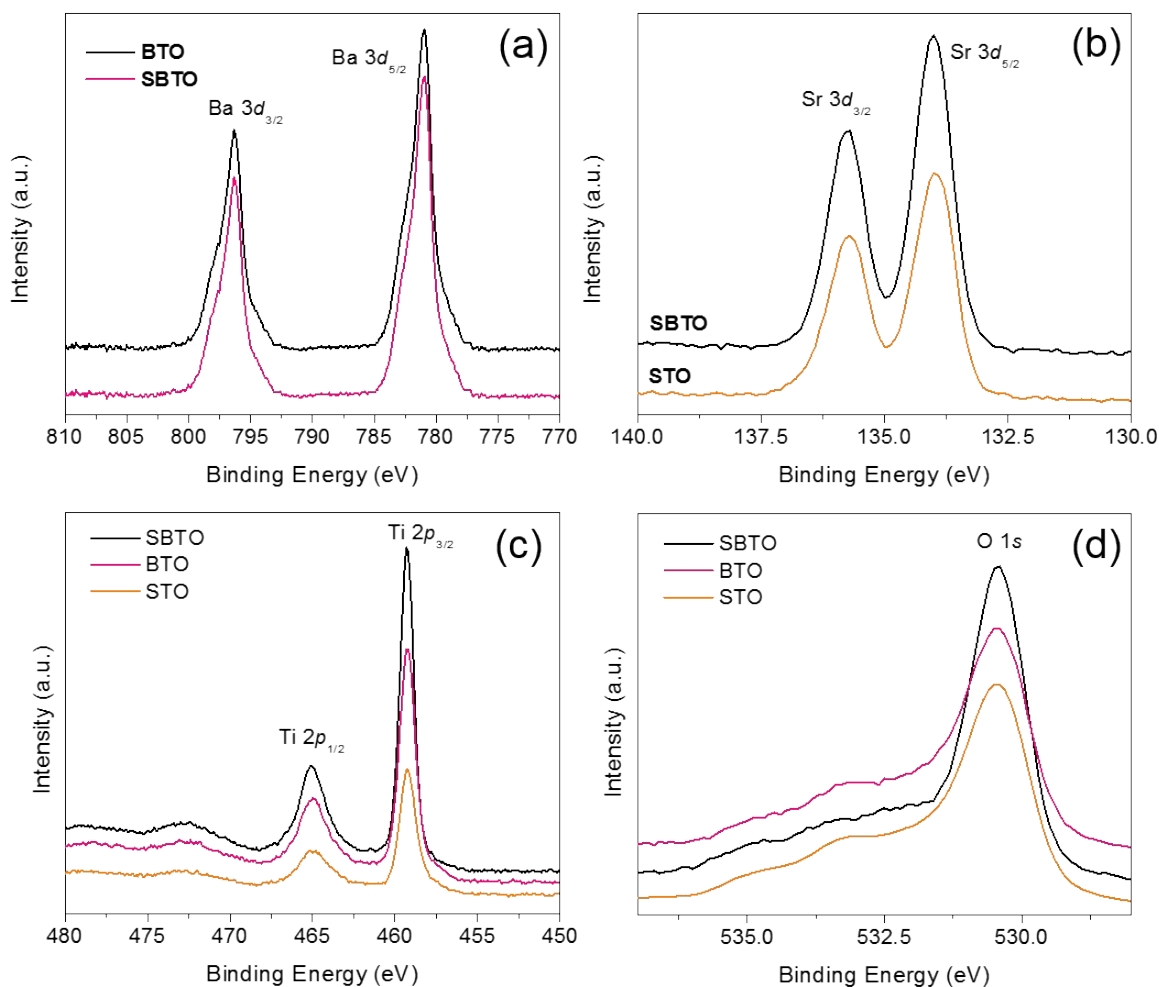


Figure S5. XPS spectra comparing (a) Ba 3d spectra of BTO and SBTO, (b) Sr 3d spectra of STO and SBTO, (c,d) Ti 2p and O 1s spectra of STO, BTO and SBTO.

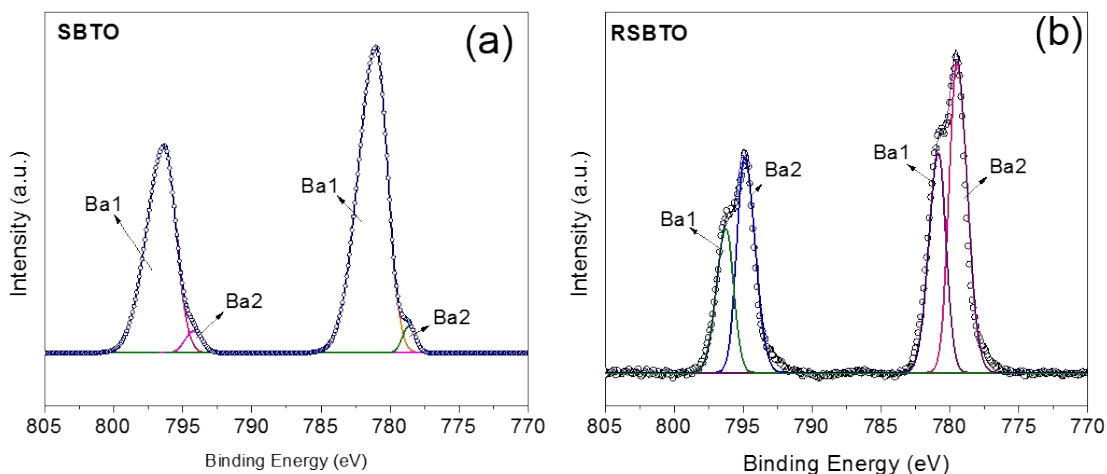


Figure S6. Deconvoluted XPS spectra showing Ba 3d spectra of (a) SBTO indication a small peak at the higher B.E., (b) RSBTO showing two deconvoluted peaks and the peak at the higher B.E. increased in intensity.

Temperature Programmed Reduction

As seen in Figure 4a, the peaks at 300 °C show different behaviours in H₂ consumption over STO, BTO and SBTO. Careful observation of the graphs in Figure 4a at 300 °C reveals that the peak intensity ratio is much higher for SBTO compared to the bare STO/BTO. This is in synchronization to our hypothesis that extra O-vacancy are introduced upon Ba-alloying, prominent from the high intensity of the first peak at 300 °C. In literature reports, we find that the oxygen vacancy formation during reduction is not a sharp peak.¹ The accessible surface and interior vacancy for bare oxides might be same, leading to almost similar peak intensity. It's important to note that the structure almost remains unaffected after reduction, so all the peaks ideally correspond to the oxygen vacancy formation in the structure². We also rule out the spillover of H₂ that is usually observed during temperature-programmed reduction when metal is present on the surface of the support^{3, 4}.

In Figure 4b, it can be seen that RBTO and RSTO show a sharp peak for oxygen consumption at temperature below 200 °C. This suggests that the oxygen vacancies are being filled at lower temperatures. But if we look at the light-off curves of the reduced oxides, it can be noticed that the CO conversion activity for RSTO as well as RBTO is negligible at temperatures below 200 °C. This would mean the irrespective of consuming oxygen, they are not being accessible for CO oxidation reaction. In the case of RSBTO, the initial peak is missing but there is a broad peak with maximum consumption of oxygen. This observation suggests that Ba addition to the STO structure leads to oxygen vacancies that are more accessible for CO oxidation. The inhomogeneity of the solid surface cannot be neglected. The shifts in peaks are best explained by the inhomogeneous distribution of oxygen vacancies on the surface.

S. No.	Sample Name	Specific surface area (m ² g ⁻¹)
1	SrTiO ₃ (STO)	24
2	Reduced SrTiO ₃ (RSTO)	28
3	BaTiO ₃ (RBTO)	19
4	Reduced BaTiO ₃ (RBTO)	22
5	Sr _{0.5} Ba _{0.5} TiO ₃ (SBTO)	25
6	Reduced Sr _{0.5} Ba _{0.5} TiO ₃ (SBTO)	31

Table S1: Specific surface areas of all the catalysts as determined by BET.

References:

1. T.-J. Huang and Y.-C. Kung, *Catalysis Letters*, 2003, **85**, 49-55.
2. A. Q. Boon, F. van Looij and J. W. Geus, *Journal of Molecular Catalysis*, 1992, **75**, 277-291.
3. P. Fornasiero, R. Dimonte, G. R. Rao, J. Kaspar, S. Meriani, A.-. Trovarelli and M. Graziani, *Journal of Catalysis*, 1995, **151**, 168-177.
4. N. Jain, N. Ravishankar and G. Madras, *Journal of Molecular Catalysis*, 2017, **432**, 88-98.