Supporting information

Critical assessment of exsolution process in Cu-doped $SrTiO_3$ by a combined spectroscopic approach.

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ICP-OES characterization

Table S1: ICP results

Sample	Cu ICP counts	Nominal absolute Cu content (% m/m)	Measured Cu content (%m/m)
Blank	0.07305	n.a.	0.1
5Cu-STO	0.94823	1.76	1.5
STO	0.07064	0	0.1

XRD characterization

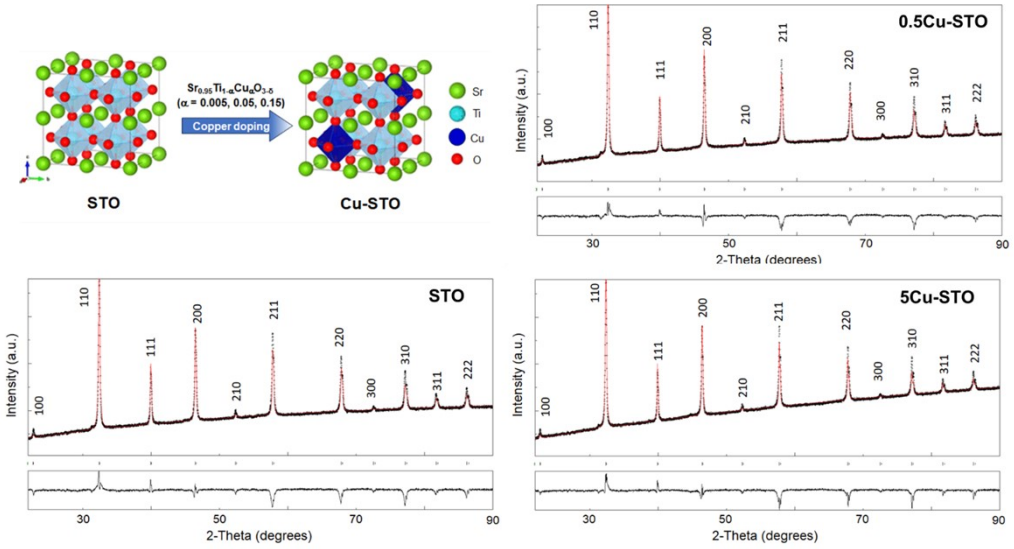

Figure S1: XRD patterns and corresponding fitting of STO, 0.5Cu-STO, 5Cu-STO.

XAS characterization

Table S2: Coordination number and bond length for 0.5Cu-STO and 5Cu-STO as prepared, after reduction and after reoxidation, fitted from EXAFS data.

Sample	Cu-O (Cu_2O)				Cu-O (CuO)			
	Bond length [Å]	**Coordination Nr.**	**ΔE [eV]**	**σ^2**	**Bond length [Å]**	**Coordination Nr.**	**ΔE [eV]**	**σ^2**
0.5Cu-STO	1.59(0)	4.00(0)	2.5	0.12735	1.98(0)	2.17(1)	2.5	0.0004
0.5Cu-STO_r	1.60(1)	4.00(0)	2.5	0.08985	1.99(0)	1.61(5)	2.5	0.0003
0.5Cu-STO_ox	1.57(1)	3.66(34)	2.5	0.07891	1.99(0)	1.48(9)	2.5	0.0001
5Cu-STO	1.95(1)	3.14(15)	2.5	0.00229	2.25(2)	2.07(13)	2.5	0.004
5Cu-STO_r	1.95(1)	2.43(30)	2.5	0.00208	2.24(5)	1.23(05)	2.5	0.003
5Cu-STO_ox	1.94(1)	2.99(24)	2.5	0.00120	2.21(3)	1.86(91)	2.5	0.003

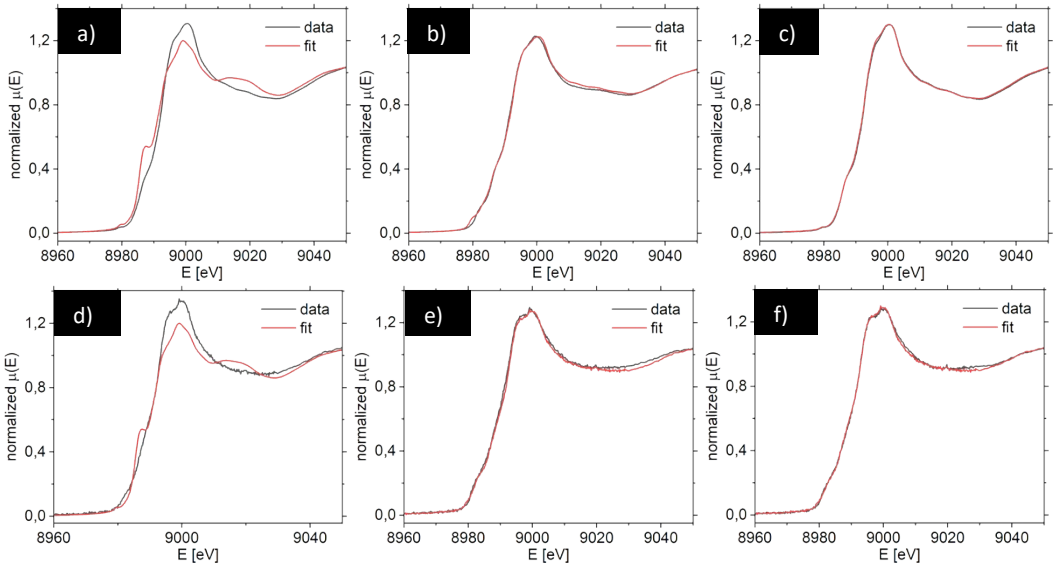

Figure S2: XANES spectra and fitting of a) 5Cu-STO, b) 5Cu-STO_r, c) 5Cu-STO_ox, d) 0.5Cu-STO, e) 0.5Cu-STO_r, f) 0.5Cu-STO_ox,

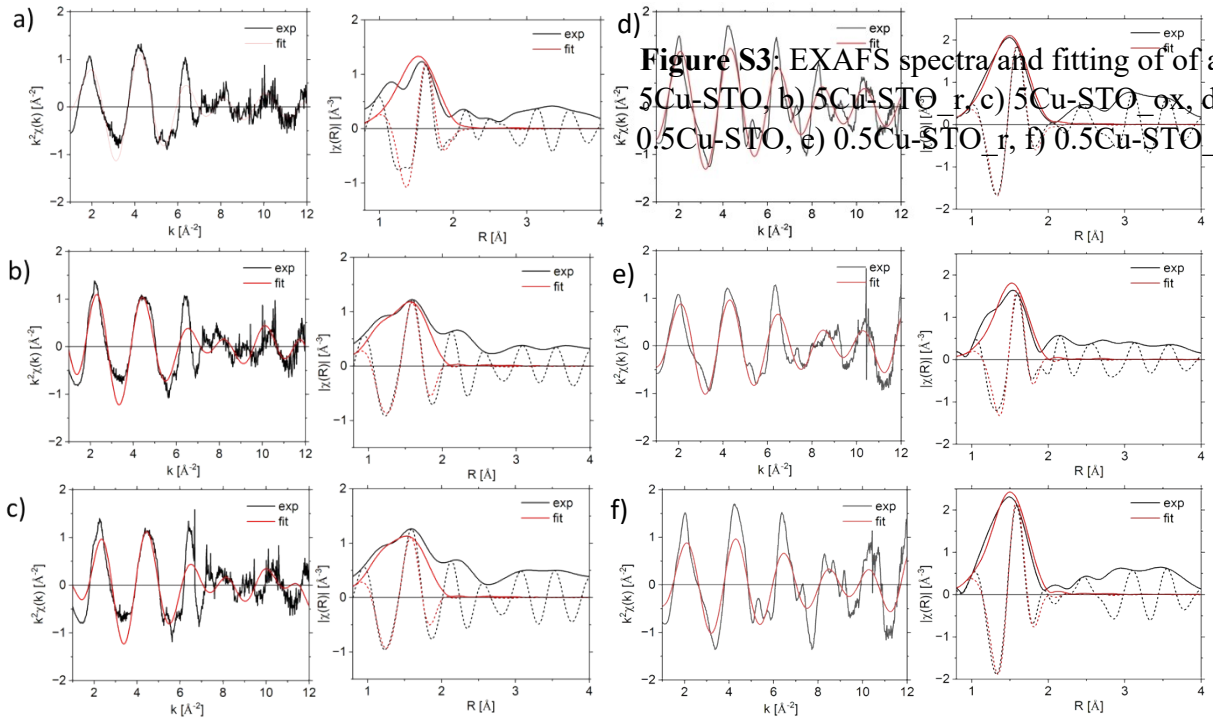

Figure S3: EXAFS spectra and fitting of of a) 5Cu-STO, b) 5Cu-STO_r, c) 5Cu-STO_ox, d) 0.5Cu-STO, e) 0.5Cu-STO_r, f) 0.5Cu-STO_ox.

XPS characterization

The Sr 3*d* levels were fitted keeping constant the branching ratio (0.66±0.1), spin-orbit splitting (1.75 eV, Sr $3d_{3/2}$ at 132.7 eV) and gamma (0.28 eV), while the peak's intensity and FWHM were free parameters.

Sr 3*d*								
	STO	STO_r	5Cu-STO 1st comp	5Cu-STO 2nd comp	5Cu-STO_r 1st comp	5Cu-STO_r 2nd comp	5Cu-STO_ox 1st comp	5Cu-STO_ox 2nd comp
Position	132.7	132.7	132.7	131.1	132.7	131.1	132.7	131.1
gamma	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
FWHM	1.3	1.8	1.36	1.36	1.36	1.63	1.36	1.36
Branching ratio	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72
Energy splitting	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75

The Ti 2*p* level was fitted using one doublet, keeping constant the branching ratio, spin-orbit spliting (5.7 eV) and gamma (for the $2p_{3/2}$ 0.25 eV and $2p_{1/2}$ 0.52 eV), while the intensity and FWHM were free fitting parameters.

Ti 2*p*								
	STO	STO_r	5Cu-STO 1st comp	5Cu-STO 2nd comp	5Cu-STO_r 1st comp	5Cu-STO_r 2nd comp	5Cu-STO_ox 1st comp	5Cu-STO_ox 2nd comp
Position	453.8	453.8	453.8	456.9	453.8	456.9	453.8	456.9
gamma	0.25 -0.52	0.25 - 0.52	0.25 - 0.52	0.25 - 0.52	0.25 - 0.52	0.25 - 0.52	0.25 - 0.52	0.25 - 0.52
FWHM	1.3	1.6	1.45	1.65	1.45	1.65	1.45	1.65
Branching ratio	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51
Energy splitting	5.67	5.67	5.67	5.67	5.67	5.67	5.67	5.67

The Cu $2p_{3/2}$ of the 5Cu-STO and 5Cu-STO_ox samples were fitted using two main components, one located at 933.3 eV (gamma 0.61 eV, FWHM of 1.8 eV), the other at 934.9 eV (gamma 0.61 eV and FWHM of 2.3 eV). A further component at 944.0 (5Cu-STO) or at 943.8 eV (5Cu-STO_ox) was used to reproduce the satellite peaks. The Cu $2p_{3/2}$ of the reduced 5Cu-STO_r was fitted using one single component at 932.2 eV (gamma 0,61 eV and FWHM of 2.3 eV).

Cu $2p_{3/2}$							
	5Cu-STO 1st comp	5Cu-STO 2nd comp	5Cu-STO 3rd comp	5Cu-STO_ox 1st comp	5Cu-STO_ox 2nd comp	5Cu-STO_r 3rd comp	5Cu-STO_r
Position	933.3	934.9	944.0	933.3	934.9	943.8	932.2
gamma	0.61	0.61	0.61	0.61	0.61	0.61	0.61
FWHM	1.8	2.3	4.2	1.65	1.45	4.2	2.3

Table S3: Atomic ratios of the metal elements in STO and 5Cu-STO samples pristine and after reduction/re-oxidation process.

	STO	STO_r	5Cu-STO	5Cu-STO_r	5Cu-STO_ox
Sr/Ti	0.9 ± 0.1	1.0± 0.1	0.9± 0.1	1.4± 0.1	1.3± 0.1

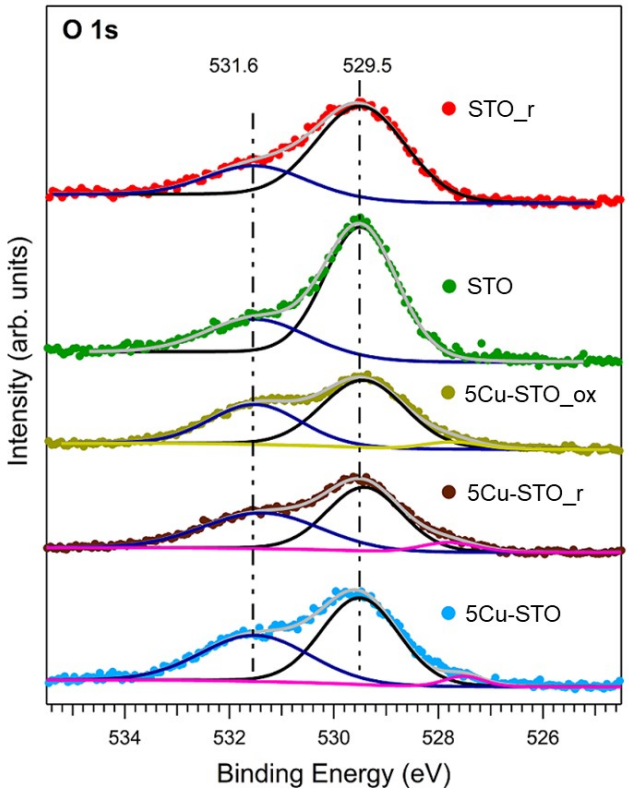

Figure S4: XPS core levels spectra of O1s for bare STO and Cu-STO samples.

TEM analysis

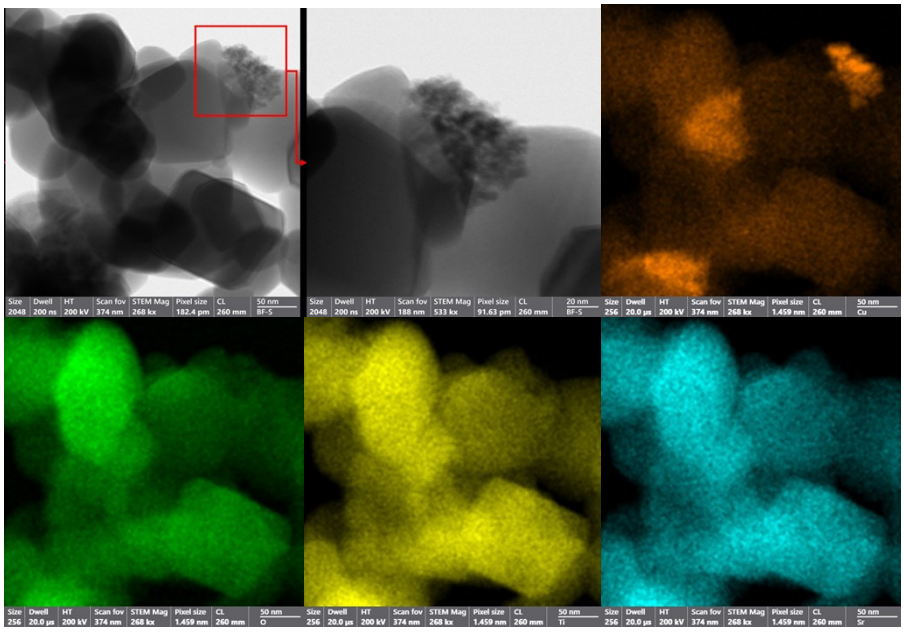

Figure S5: HR-TEM analysis of 0.5Cu-STO after reduction

UV-DRS characterization

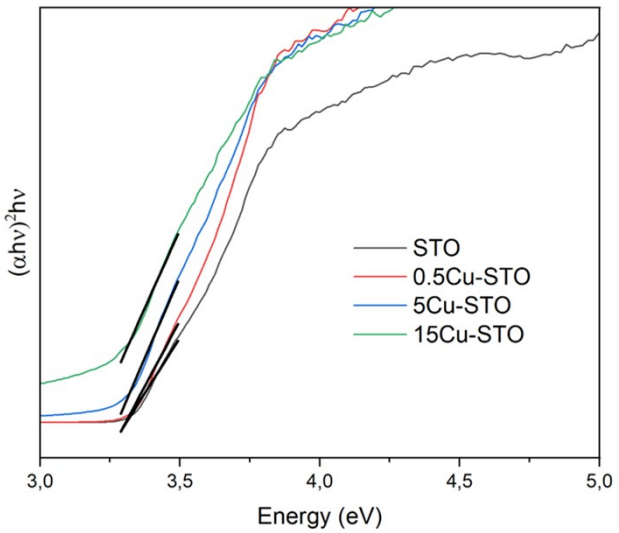

Figure S6: Tauc Plot for STO, 0.5Cu-STO, 5Cu-STO, 15Cu-STO

Table S4: Band gap energy calculated from Tauc plot.

Sample	STO	0.5Cu-STO	5Cu-STO	15Cu-STO
Band Gap (eV)	3.31	3.30	3.27	3.19

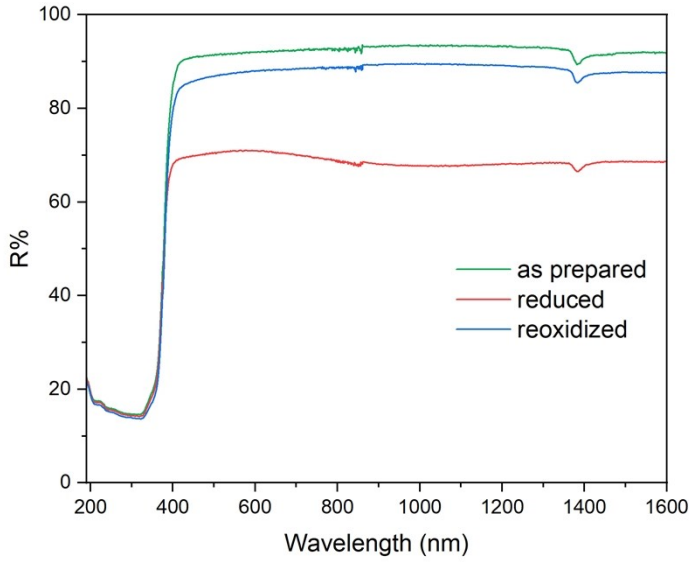

Figure S7: UV-DRS spectra of undoped STO presented in %R on the full measured range.