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Electronic Supplementary Information

Template-free molten salt synthesis of pure and Sr-doped LaCrO3 1D nanorods with enhanced electrical transport properties

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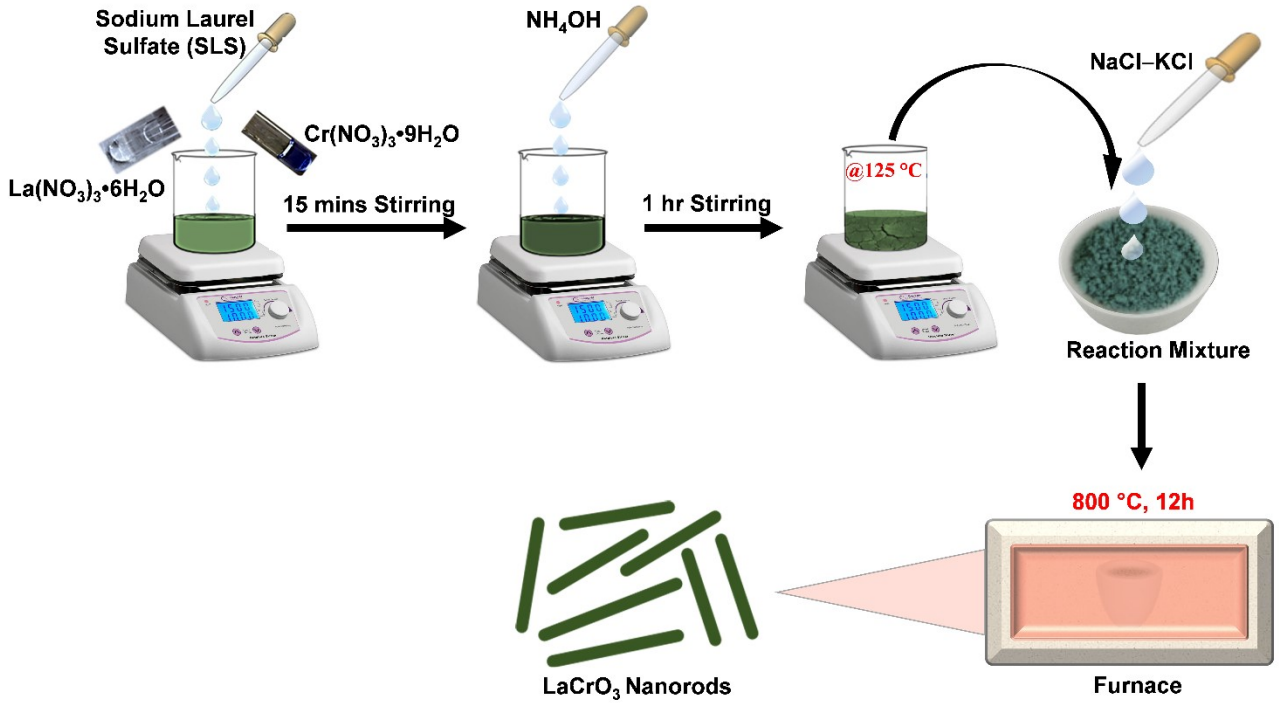
Materials and Method:

Chemicals

Lanthanum (III) Nitrate Hexahydrate $La(NO_3)_3 \cdot 6H_2O$, Chromium (III) Nitrate Nonahydrate $Cr(NO_3)_3 \cdot 9H_2O$, Strontium (II) Nitrate Anhydrous $Sr(NO_3)_2$, Ammonium Hydroxide (NH_4OH, 30%), Ethanol (99.9%), *iso*-propyl alcohol (IPA) (HPLC grade) and Sodium Laurel Sulphate were purchased from Loba Chemie Pvt. Ltd. India. Sodium Chloride (NaCl), Potassium Chlorides (KCl), Sodium Sulphate (Na_2SO_4) and Potassium Sulphate (K_2SO_4) were purchased from Spectrochem Pvt. Ltd. India, and used without further purification. Ultrapure Milli-Q water (18.2 MΩ·cm) was used for all the experiments.

Molten salt synthesis of pure $LaCrO_3$ (LCO) nanorods using KCl:NaCl (1:1):

In the typical synthesis procedure, $La(NO_3)_3 \cdot 6H_2O$ (433.0 mg, 1 mmol), and $Cr(NO_3)_3 \cdot 9H_2O$ (400.0 mg, 1 mmol) salts were dissolved in 10 mL of Milli-Q water. In another beaker sodium laurel sulphate (SLS, 288.0 mg, 1 mmol) was dissolved in 2 mL of Milli-Q water and added dropwise to the above aq. the metal salt solution while stirring. After 15 minutes of constant stirring, 1 mL of ammonium hydroxide (NH_4OH, 30%) was added dropwise to the reaction mixture while the mixture was stirred for another hour. The solution was then heated at 125 °C and held at this temperature till all the solvent was evaporated and solid (green-coloured) powder was obtained. The powder was then ground in a mortar pestle and transferred to a quartz crucible. A saturated aq. NaCl and KCl solutions (1 mL of each) were added to the crucible and mixed thoroughly. The crucible was then placed in a muffle furnace for 12 hours at 800 °C with a ramp rate of 5 °C per minute, followed by natural cooling. After the completion of the reaction product was washed with the Milli-Q water several times followed by ethanol to remove excess NaCl and KCl salts. The LCO nanorods were obtained as green-coloured powder which was used for further characterization.



Scheme S1: Schematic representation of the synthetic procedure of $LaCrO_3$ nanorods.

Molten Salt Synthesis of Sr-doped $LaCrO_3$ (LSCO-10 and LSCO-20) nanorods using KCl:NaCl (1:1):

In the typical synthesis procedure of Sr-doped nanorods (LSCO-10), $La(NO_3)_3 \cdot 6H_2O$ (390.0 mg, 0.9 mmol), $Sr(NO_3)_2$ (21.1 mg, 0.1 mmol) and $Cr(NO_3)_3 \cdot 9H_2O$ (400.0 mg, 1 mmol) salts were dissolved in 10 mL of Milli-Q water. In another beaker sodium laurel sulphate (SLS, 288.0 mg, 1 mmol) was dissolved in 2 mL of Milli-Q water. The SLS solution was then added to the precursor's mixture dropwise with constant stirring. After 15 minutes of constant stirring, 1 mL of NH_3 solution (30%) was added dropwise to the reaction mixture while being stirred constantly for another 1 hour. The solution was then heated at 125 °C and held at this temperature till all the solvent was evaporated and solid (green-coloured) powder was obtained. The powder was then ground in a mortar pestle and transferred to a quartz crucible. A saturated aq. NaCl and KCl solutions (1 mL of each) were added to the crucible and mixed thoroughly. The crucible was then placed in a muffle furnace for 12 hours at 800 °C with a ramp rate of 5 °C per minute, followed by natural cooling. After the completion of the reaction product was washed with the milli-Q water several times followed by ethanol to remove excess NaCl and KCl salts.

Similarly, for LSCO-20 sample preparation $La(NO_3)_3 \cdot 6H_2O$ (346.0 mg, 0.8 mmol), $Sr(NO_3)_2$ (42.2 mg, 0.2 mmol) and $Cr(NO_3)_3 \cdot 9H_2O$ (400.0 mg, 1 mmol) salts were dissolved in 10 mL of Milli-Q water and further procedure followed as for 10% doped sample. The LSCO-10 and LSCO-20 nanorods were obtained as brown-coloured powder which were used for further characterization.

Molten Salt Synthesis of Pure $LaCrO_3$ (LCO) nanorods using K_2SO_4:Na_2SO_4 (1:1):

In this synthesis procedure, $(La(NO_3)_3 \cdot 6H_2O$ (433.0 mg, 1 mmol) $Cr(NO_3)_3 \cdot 9H_2O$ (400.0 mg, 1 mmol) salts were dissolved in 10 mL of Milli-Q water. In another beaker sodium laurel sulphate (SLS, 288.0 mg, 1 mmol) was dissolved in 2 mL of Milli-Q water. The SLS solution was added to the precursor's mixture dropwise with constant stirring. After 15 minutes of constant stirring, 1 mL of NH_3 solution (30%) was added dropwise to the reaction mixture while being stirred constantly for another hour. The solution was then heated at 125 °C and held at this temperature till all the solvent was evaporated and solid (green-coloured) powder was obtained. The powder was then ground in a mortar pestle and transferred to a quartz crucible. A saturated aq. K_2SO_4 and Na_2SO_4 solutions (1 mL of each) were added to the crucible and mixed thoroughly. The crucible was then placed in a muffle furnace for 12 hours at 800 °C with a ramp rate of 5 °C per minute, followed by natural cooling. After the completion of the reaction product was washed with the milli-Q water several times followed by ethanol to remove excess K_2SO_4 and Na_2SO_4 salts. The obtained sample was used for further characterization.

Synthesis of Pure $LaCrO_3$ (LCO) nanorods in the absence of molten salts:

In this synthesis procedure, $(La(NO_3)_3 \cdot 6H_2O$ (433.0 mg, 1 mmol) and $Cr(NO_3)_3 \cdot 9H_2O$ (400.0 mg, 1 mmol) salts were dissolved in 10 mL of Milli-Q water. In another beaker sodium laurel sulphate (SLS, 288.0 mg, 1 mmol) was dissolved in 2 mL of Milli-Q water. The SLS solution was then added to the precursor's mixture dropwise with constant stirring. After 15 minutes of constant stirring, 1 mL of NH_3 solution (30%) was added dropwise to the reaction mixture while being stirred constantly for another hour. The solution was then heated at 125 °C and held at this temperature till all the solvent was evaporated and solid (green-coloured) powder was obtained. The powder was then ground in a mortar pestle and transferred to a quartz crucible. The crucible was then placed in a muffle furnace for 12 hours at 800 °C with a ramp rate of 5 °C per minute, followed by natural cooling. After the completion of the reaction product was washed with the Milli-Q water several times followed by ethanol to remove impurities. The obtained sample was used for further characterization.

Instruments details

The phase purity and structural information of synthesized materials were confirmed via powder X-ray diffractogram (PXRD) pattern with the Rigaku SmartLab SE instrument using a wavelength of 1.54 Å (Cu-anode). The morphology of the materials was studied using scanning electron microscopy (SEM) of Zeiss Sigma 500 with lens mode (at 3 keV). Further, morphological and structural investigations were performed by using an electron microscope (TEM) in the Thermo Scientific Themis 300 G3 instrument. X-ray photoelectron spectroscopy (XPS) was performed utilising a PHI Versa Probe II scanning XPS microprobe to confirm the chemical and electronic states of the synthesised materials under air conditioning. The XPS was calibrated using C1s with binding energies of 284.6 eV. Further, to get the structural information, Raman spectra of pure and Sr-doped $LaCrO_3$ samples were recorded at room temperature in the spectral range of 100 – 700 cm^{-1} using a green laser (λ = 532 nm) in WITec ALPHA300 R – Confocal Raman Imaging Microscope. The UV-Vis study of the synthesized materials has been done at room temperature using the Shimadzu UV-NIR spectrophotometer in the wavelength range of 200–800 nm. The electrical characterizations (*I–V* measurement) were performed using a probe station connected to a semiconductor characterization system (Proxima Keysight B1500A) at room temperature. The temperature dependence of the *I–V* curve for these nanorods was measured with the Polaris B1500 semiconductor characterization system.

Device fabrication and electrical characteristics measurements:

In a typical procedure of fabricating the 2-probe device for LCO, LSCO-10 and LSCO-20 nanorod samples. Firstly, the nanorod sample was dispersed in *iso*propyl alcohol (IPA) (HPLC grade) and sonicated for 1 min. The suspension was spin-coated at 3000 rpm for 1 min on a pre-patterned highly p-doped Si/SiO_2 wafer. SEM was used to mark and map the individual nanorods. Nanorods of length 1–2 μm with a 50–580 nm diameter, were selected for the fabrication process. E-beam resist EL9 and PMMA 950K 2% were spin-coated on the substrate with nanorods before e-beam exposure. Source/drain electrodes were patterned by electron beam lithography (Raith 150 two). For development, the substrate was dipped into a 1 : 3 MIBK/IPA mixture for 25 sec and then immediately immersed into IPA for 5 sec. Metal contacts of Cr/Au (5 nm/100 nm) were deposited by sputtering (an Orion sputter) followed by Ar bias cleaning to ensure that the remaining PMMA on the contact pattern is removed, where, Cr was used because of its excellent adhesion property, which makes the lift-off process easier. For the final step, *i.e.*, the lift-off process, the metal-deposited substrate was kept in acetone for 6 h and then washed with acetone, IPA and then dried under an N_2 gun. The two probe devices were measured with a probe station connected to a semiconductor characterization system (Proxima Keysight B1500A) at room temperature under ambient conditions. The temperature dependence of the *I–V* curve for these nanorods was measured with the Polaris B1500 semiconductor characterization system, by ignoring the contact resistance.

Figures:

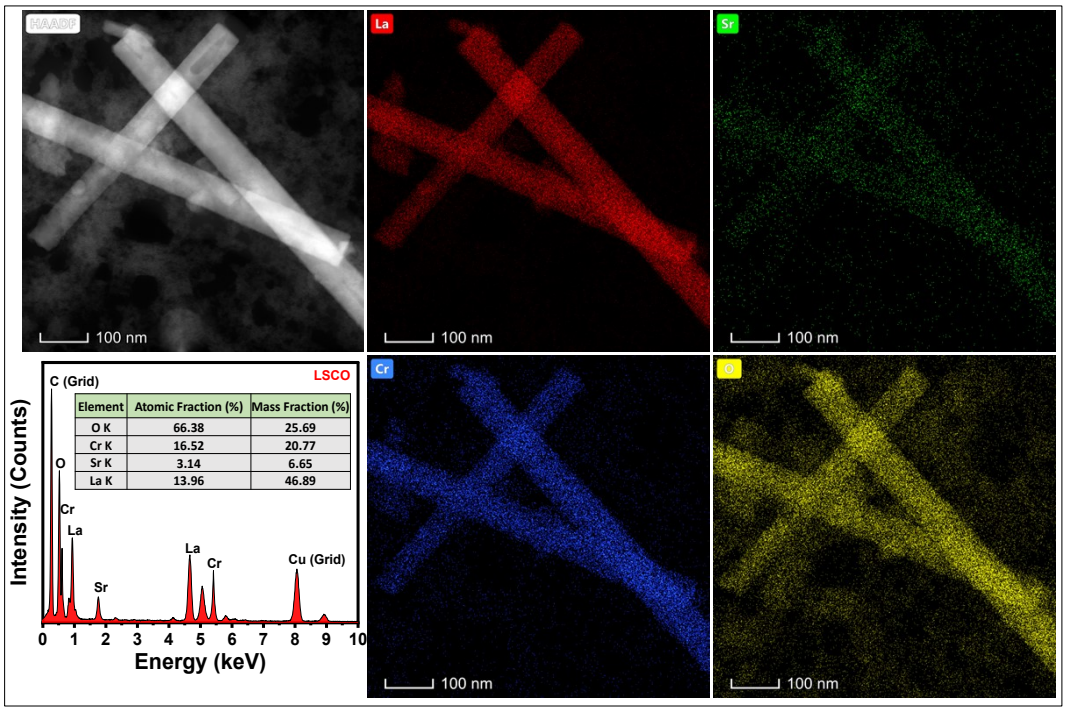


Figure S1: The TEM-EDX elemental mapping images of LSCO-20 nanorods showing the uniform distribution of the elements in the nanorod matrix.

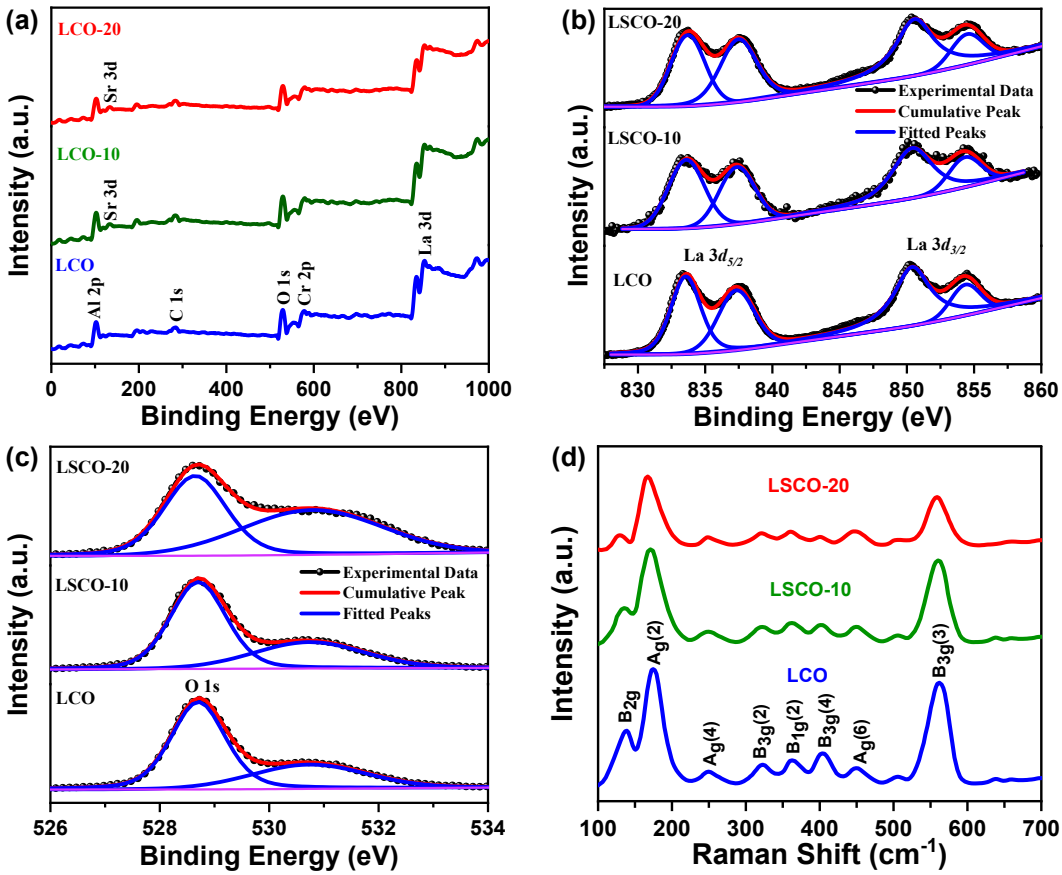


Figure S2: (a) Full scan XPS spectra, (b) HR-XPS spectra of La 3d, (c) HR-XPS spectra of O 1s of pure and Sr-doped $LaCrO_3$ nanorods. and (d) Raman spectra of pure and Sr-doped $LaCrO_3$ nanorods.

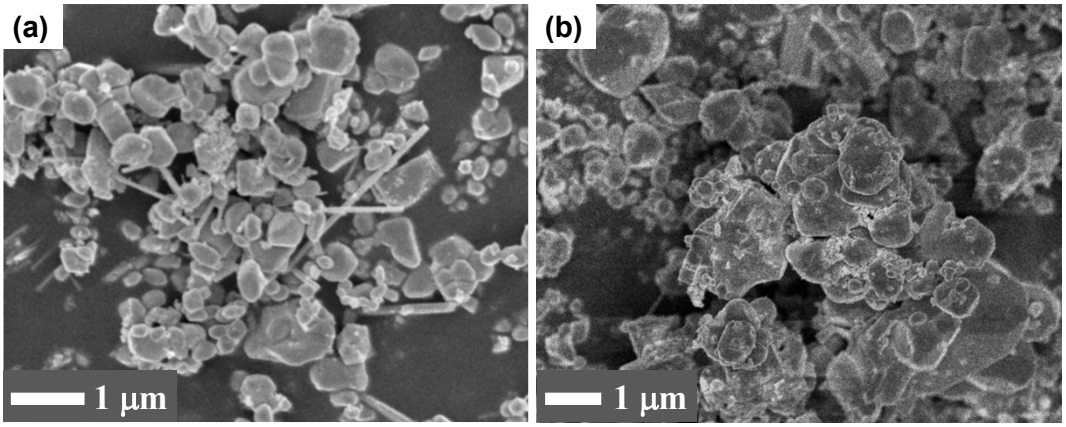
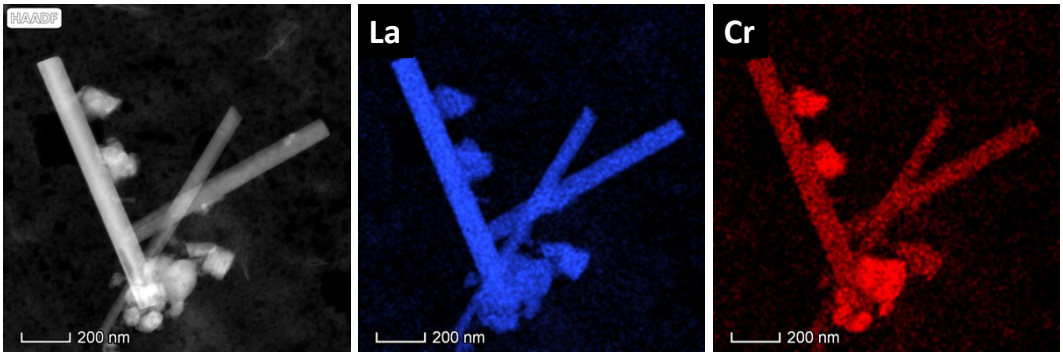


Figure S3: The SEM image of the LSCO-30 sample demonstrating the formation of a few LSCO nanorods, (b) The SEM image of the LSCO-50 sample demonstrating the formation of irregular particles only.



Element	Atomic Fraction (%)	Mass Fraction (%)
O K	63.74	23.65
Cr K	17.98	21.69
Sr K	3.57	7.26
La K	14.71	47.40

Figure S4: The TEM-EDX elemental mapping images of the LSCO-30 sample display a uniform distribution of Sr^{2+} in LSCO material.

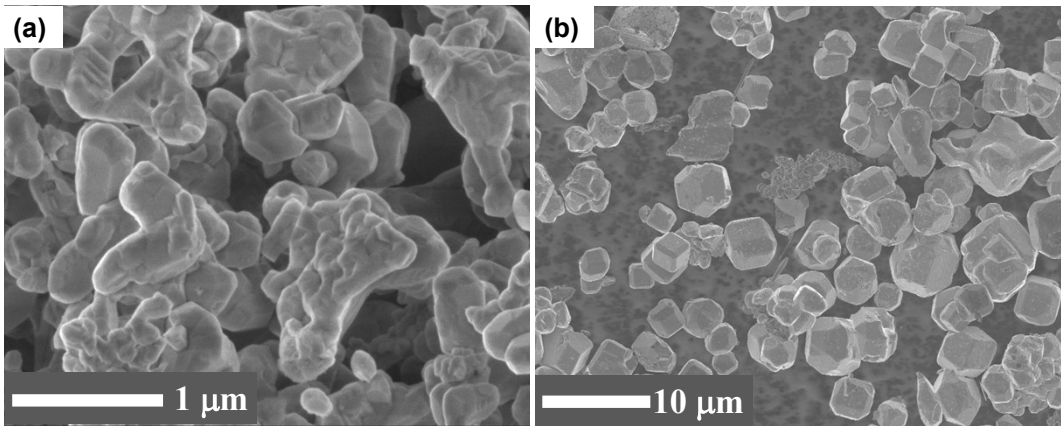


Figure S5: SEM images of (a) as-synthesised $LaCrO_3$ sample in the absence of molten salt and (b) $LaCrO_3$ sample using Na_2SO_4 & K_2SO_4 (1:1) mixture as molten salt.

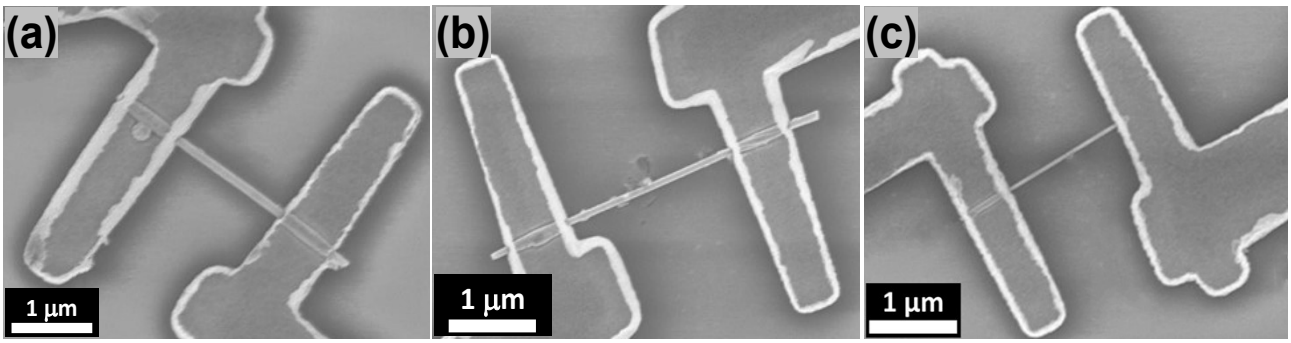


Figure S6: SEM images of two probe devices of; (a) LCO nanorods, (b) LSCO-10 nanorods and (c) LSCO-20 nanorods.

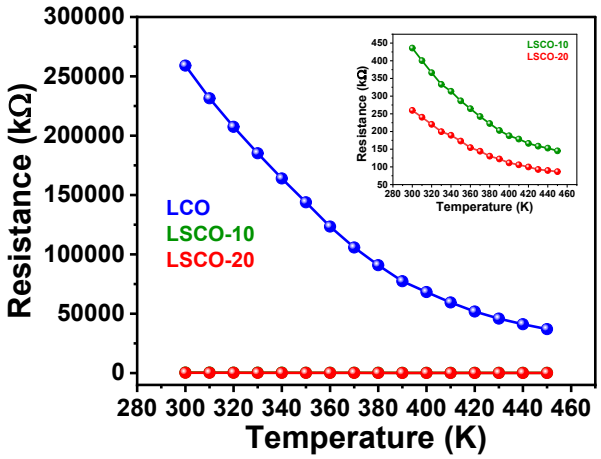


Figure S7: Plot of resistance vs temperature of pure and Sr-doped LCO nanorods showing semiconducting behaviour.

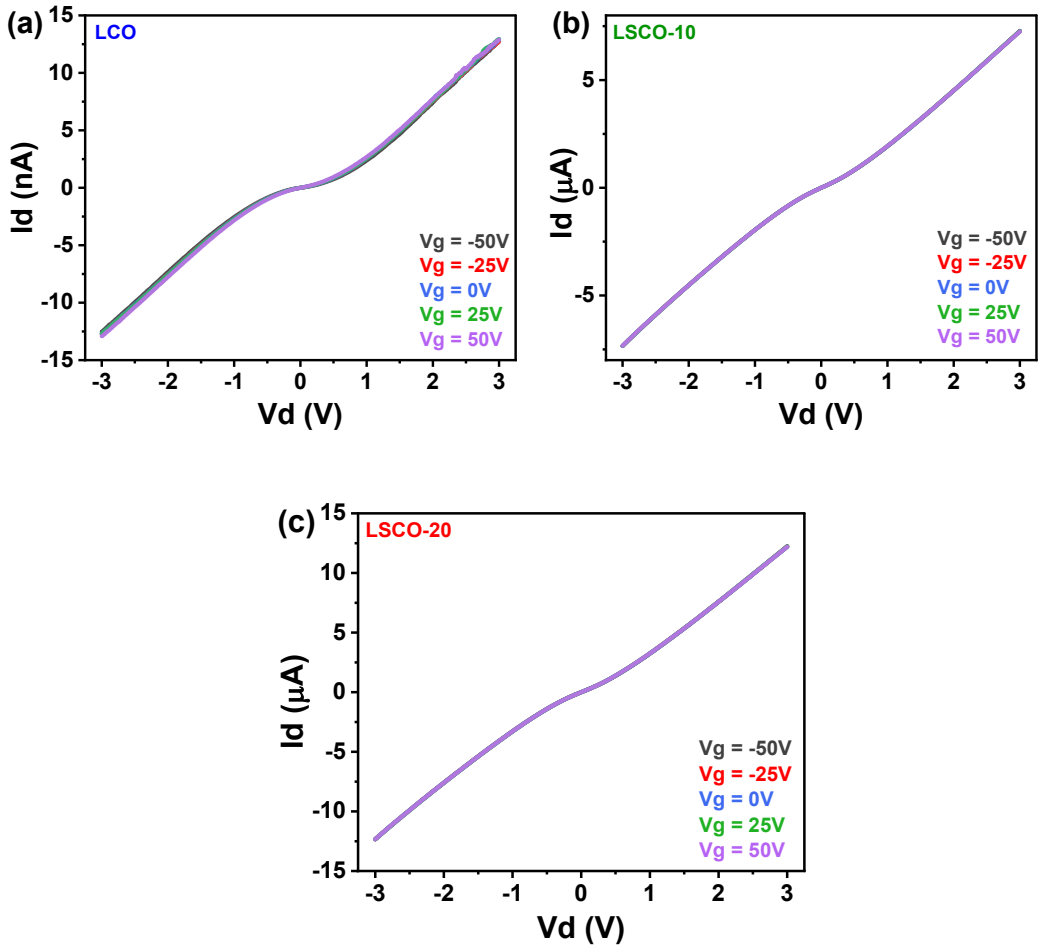


Figure S8: Room temperature I-V characteristics at different gate voltages ranging from -50 V to 50 V; (a) pure LCO, (b) LSCO-10, (c) LSCO-20 nanorod.

Tables:

Table S1: ICP-AES analysis data of pure and Sr-doped LCO nanorod samples.

Sample	Elemental Concentration (ppb)		
	La	Sr	Cr
LCO	32.89	-	36.90
LSCO-10	24.27	2.29	28.03
LSCO-20	36.70	5.59	46.73

Table S2: Conductivity comparison of LCO and LSCO nanorods synthesized via MSS method with existing materials.

Materials	Morphology	T (K)	Conductivity ($S \cdot cm^{-1}$)	Measurement Technique	Ref
$LaCrO_3$	Irregular shape	300	1.7×10^{-5}	No information	1
$LaCrO_3$	Irregular shape	450	0.013	No information	2
$La_{.9}Ca_{.1}CrO_3$	Irregular shape	300	2.98	No information	2
$La_{.7}Ca_{.3}CrO_3$	Irregular shape	300	5.44	No information	2
$La_{.7}Sr_{.3}CrO_3$	Irregular shape	300	0.73	No information	3
$La_{.88}Sr_{.12}CrO_3$	Thin film	300	3.6	Four-probe, VDP Method	4
$La_{.75}Sr_{.25}CrO_3$	Thin film	300	15	Four-probe, VDP Method	4
$LaCrO_3$	Nanorods	300	0.027	Two-probe method	**This Work**
LSCO-10	Nanorods	300	12.64	Two-probe method	
LSCO-20	Nanorods	300	22.70	Two-probe method	

References

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