Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Modulating the electronic structure of lanthanum manganite by Ruthenium doping for enhanced photocatalytic water oxidation

*Anindya Sundar Patra[a], Gaurangi Gogoi[a], Ranjan Kumar Sahu[b], Mohammad Qureshi[a]**

[a]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, India

[b]CSIR-National Metallurgical Laboratory, Jamshedpur-831007, India.

$LaMn_{1-x}Ru_xO_3$	x = 0.0	x = 0.1	x = 0.2	x = 0.3	x = 0.4
Crystal system	Rhombohedral	Rhombohedral + cubic	Rhombohedral + cubic	Rhombohedral + cubic	Rhombohedral + cubic
Space group	R-3c	R-3c + Pm-3m	R-3c + Pm-3m	R-3c + Pm-3m	R-3c + Pm-3m
% of R-3c phase	1	0.992	0.54	0.199	0.014

Lattice parameters (R-3c)

a, Å	5.526	5.527	5.539	5.541	5.542
b, Å	5.526	5.527	5.539	5.541	5.542
c, Å	13.350	13.352	13.356	13.337	13.319
Cell volume, $Å^3$	353.02	353.234	354.936	354.513	354.355

Lattice parameters (Pm-3m)

a = b = c, Å	-	3.808	3.831	3.899	3.904
Cell volume, $Å^3$	-	55.204	56.230	59.263	59.481

Atomic positions (R-3c)
La

x	0.0000	0.0000	0.0000	0.0000	0.0000
y	0.0000	0.0000	0.0000	0.0000	0.0000
z	0.2500	0.2500	0.2500	0.2500	0.2500

Mn/Ru

x	0.0000	0.0000	0.0000	0.0000	0.0000
y	0.0000	0.0000	0.0000	0.0000	0.0000
z	0.0000	0.0000	0.0000	0.0000	0.0000

O

x	0.44186	0.44506	0.44707	0.42585	0.44110
y	0.0000	0.0000	0.0000	0.0000	0.0000
z	0.2500	0.2500	0.2500	0.2500	0.2500

Atomic positions (Pm-3m)
La

x	-	0.5000	0.5000	0.5000	0.5000
y	-	0.5000	0.5000	0.5000	0.5000
z	-	0. 5000	0. 5000	0. 5000	0. 5000

Mn/Ru

x	-	0.0000	0.0000	0.0000	0.0000
y	-	0.0000	0.0000	0.0000	0.0000
z	-	0.0000	0.0000	0.0000	0.0000

O

x	-	0.5000	0.5000	0.5000	0.5000
y	-	0.0000	0.0000	0.0000	0.0000
z	-	0.0000	0.0000	0.0000	0.0000

R_{wp}	31.1	24.4	28.8	25.9	26.6
R_p	42.2	25.3	30.2	25.5	26.4
R_{exp}	17.97	14.55	13.98	11.63	12.47
χ^2	3.0	2.81	4.26	4.96	4.56

Table S1 Structural parameters obtained by Rietveld refinement of the powder X-ray diffraction data of $LaMn_{1-x}Ru_xO_3$ (x = 0.0-0.4) catalysts.

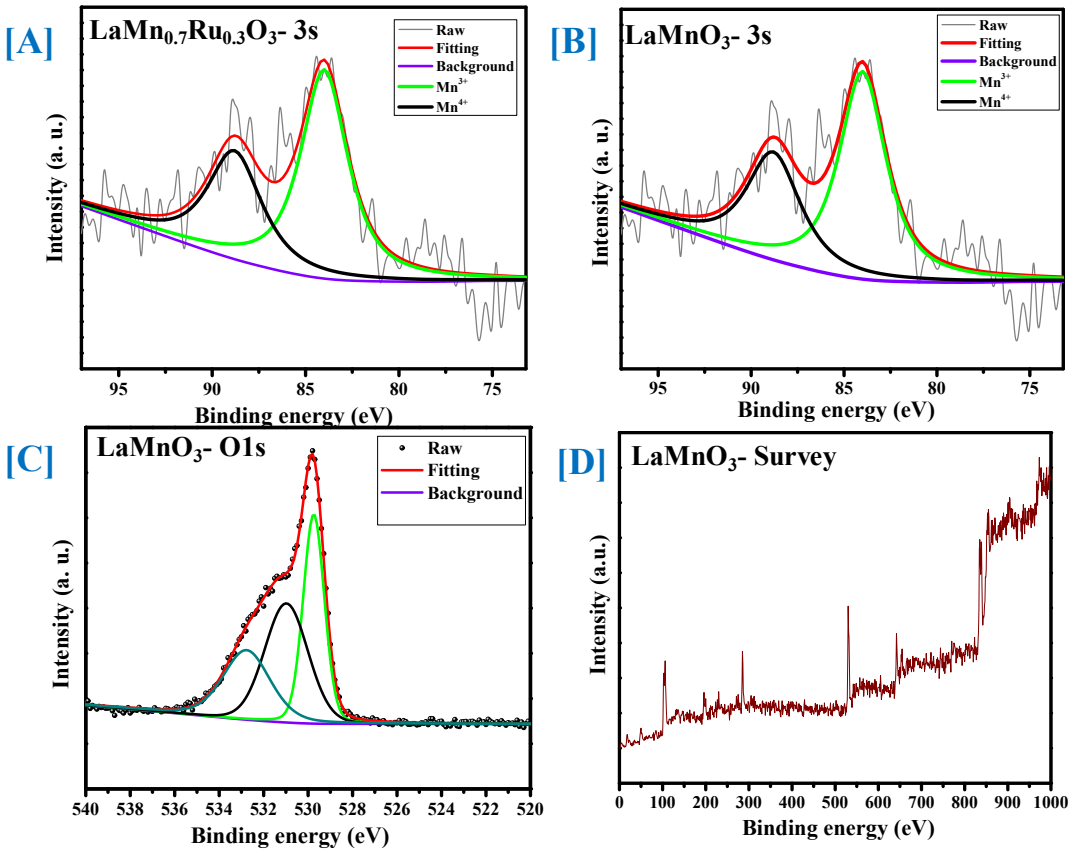

Fig. S1 XPS spectra of $LaMn_{0.7}Ru_{0.3}O_3$ [A] Mn 3s, [B] $LaMnO_3$ Mn 3s, [C] $LaMnO_3$ O 1s core levels and [D] $LaMnO_3$ survey spectrum.

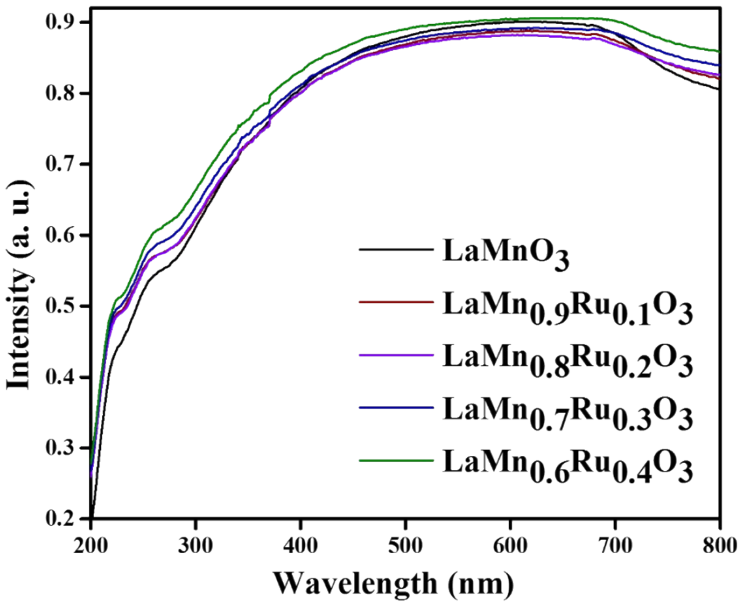

Fig. S2 UV-Visible diffuse reflectance spectra of $LaMn_{1-x}Ru_xO_3$ (x = 0.0-0.4).

Calculation of band position

The VB position of an inorganic semiconductor can be calculated by using the following formulas reported earlier by Xu and Schoonen, [S1]

$$E_{VB} = \left(\chi_M{}^a \chi_X{}^b\right)^{\frac{1}{a+b}} + \frac{1}{2}E_g - E^e \quad \ldots \text{(i)}$$

$$\chi = \frac{1}{2}(IP + EA) \quad \ldots\ldots \text{(ii)}$$

$$E_{CB} = E_{VB} - E_g \quad \ldots\ldots\ldots \text{(iii)}$$

Where, E_{VB} is the valence band maximum (VBM), E_{CB} is conduction band minimum (CBM), E_g is the estimated band gap of the semiconductor evaluated from the Tauc plot, E^e is the energy of free electrons on the hydrogen scale (- 4.5 eV), χ_M and χ_X are the absolute electronegativities of *M* and *X* atoms, respectively, χ is the electronegativity of the individual atoms of the multi-atomic semiconductor, calculated by using equation (ii), [S2] IP is the ionization potential and EA is the electron affinity values of each atom.

Compound	**Valence band maximum(eV)**	**Conduction band minimum (eV)**	**Band gap (eV)**
$LaMnO_3$	**1.501**	**0.111**	**1.39**
$LaMn_{0.9}Ru_{0.1}O_3$	**1.51**	**0.160**	**1.35**
$LaMn_{0.8}Ru_{0.2}O_3$	**1.529**	**0.199**	**1.33**
$LaMn_{0.7}Ru_{0.3}O_3$	**1.528**	**0.258**	**1.27**
$LaMn_{0.6}Ru_{0.4}O_3$	**1.602**	**0.242**	**1.36**

Table S2. Calculated values of valence band, conduction band positions and band gap values of $LaMn_{1-x}Ru_xO_3$ (x = 0.0-0.4).

In LMO, the IP values for La, Mn, O and Ru atoms are 5.57 eV, 7.43 eV, 13.6 eV and 7.36 eV respectively. Again, the EA values for La, Mn, O and Ru atoms are 0.55 eV, -1.0 eV, 1.46 eV and 1.046 eV respectively. From equation (ii), the calculated absolute electronegativity values of La, Mn, O and Ru are 3.06 eV, 3.215 eV, 7.535 eV and 4.203 eV respectively. Hence, the absolute electronegativity values of $LaMnO_3$, $LaMn_{0.9}Ru_{0.1}O_3$, $LaMn_{0.8}Ru_{0.2}O_3$, $LaMn_{0.7}Ru_{0.3}O_3$ and $LaMn_{0.6}Ru_{0.4}O_3$ calculated by the geometric mean of individual electronegativity of the constituent atoms are found to be 5.306 eV, 5.335 eV, 5.364 eV, 5.393 eV and 5.422 eV respectively. The VBM and CBM calculated by using equations (i) and (iii) are shown in Table 2.

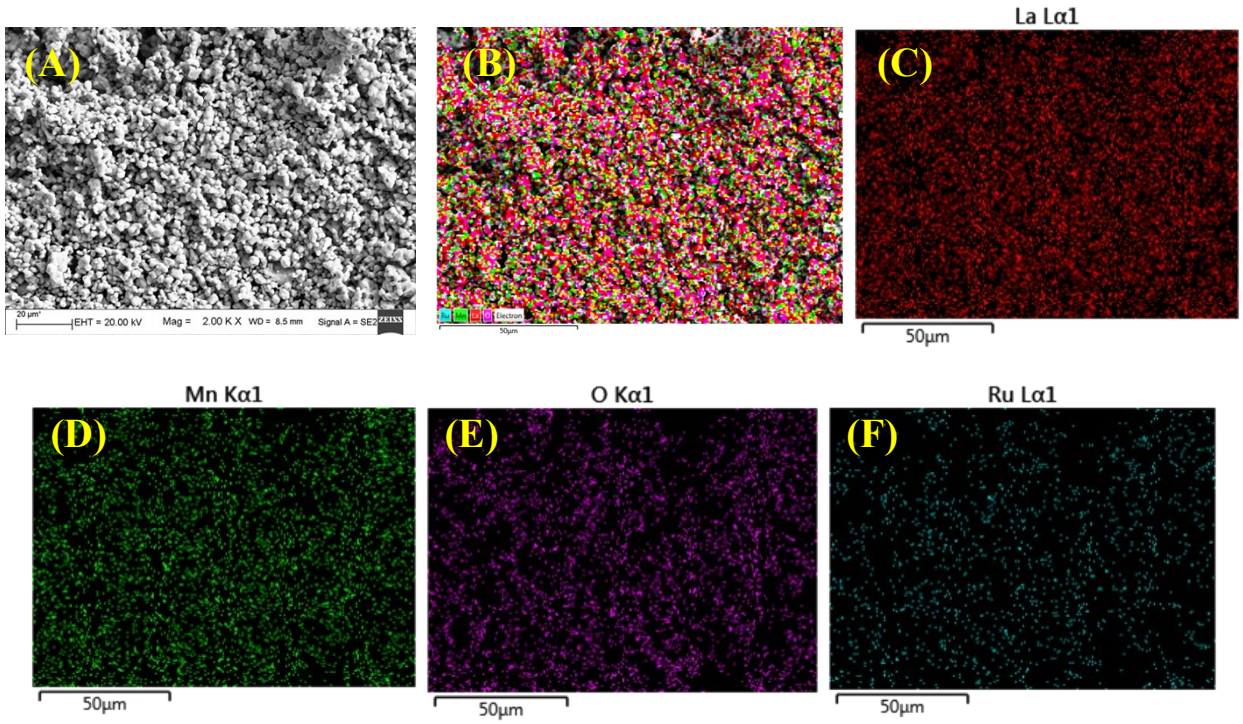

Fig. S3 [A] FESEM image of $LaMn_{0.7}Ru_{0.3}O_3$, [B] EDX mapping of [A], elemental distribution of [C] La, [D] Mn, [E] O and [F] Ru in [B].

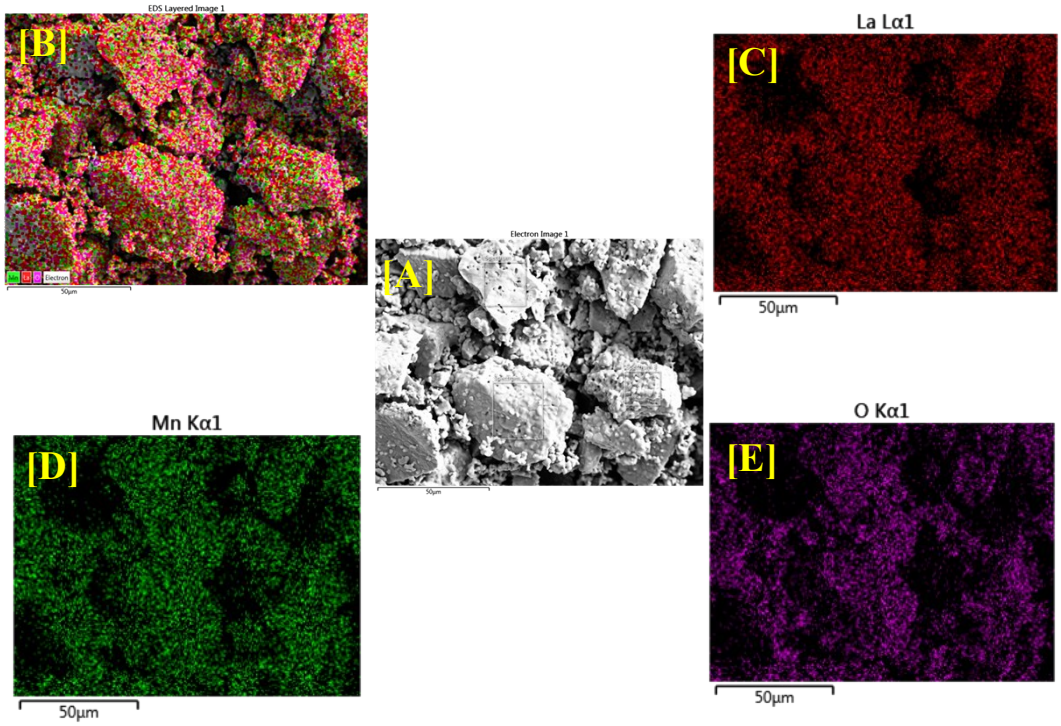

Fig. S4 [A] FESEM image of $LaMnO_3$, [B] EDX mapping of [A], elemental distribution of [C] La, [D] Mn, [E] O in [B].

	Rate of O_2	**Rate of O_2**	**Rate of O_2**	**Rate of O_2**	**Rate of O_2**

	production (μmol/h/g) **$LaMnO_3$**	**production (μmol/h/g)** **$LaMn_{0.9}Ru_{0.1}O_3$**	**production (μmol/h/g)** **$LaMn_{0.8}Ru_{0.2}O_3$**	**production (μmol/h/g)** **$LaMn_{0.7}Ru_{0.3}O_3$**	**production (μmol/h/g)** **$LaMn_{0.6}Ru_{0.4}O_3$**
	598	3250	3682	4730	1140
	727	2804	3970	4410	928
	554	2951	3750	4564	860
Average	626.33	3001.67	3800.67	4568	976
Standard deviation	73.41	185.57	122.91	130.67	119.24
Standard error	42.39	107.14	70.96	75.44	68.84

Table S3 Standard deviation and the error chart of the oxygen production of $LaMn_{1-x}Ru_xO_3$ (x = 0.0-0.4)

References:

(S1) Y. Xu and M. A. A. Schoonen, *Am. Mineral.*, 2000, **85**, 543–556.

(S2) A. H. Nethercot, *Phys. Rev. Lett.*, 1974, **33**, 1088–1091.