

Supplementary Information

Solution-processed La-substituted Ba₂Bi₂O₆ photocathodes with enhanced photoelectrochemical activity: a combined experimental and computational study

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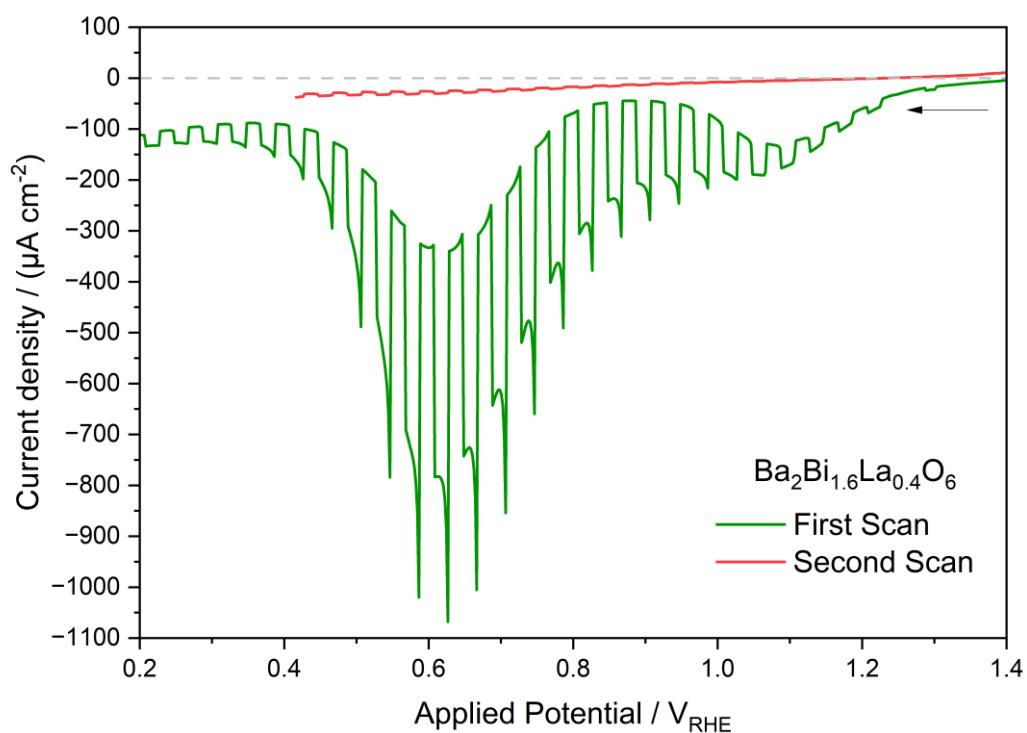


Figure S1: Comparison of first and second current–potential curves for $Ba_2Bi_{1.6}La_{0.4}O_6$ under chopped simulated sunlight ($AM1.5G$, 100 mW cm^{-2}) in $pH\ 12\ 0.1\ M\ Na_2SO_4$. Linear sweep from $+1.4$ to $+0.2\ V_{RHE}$ at 10 mV s^{-1} .

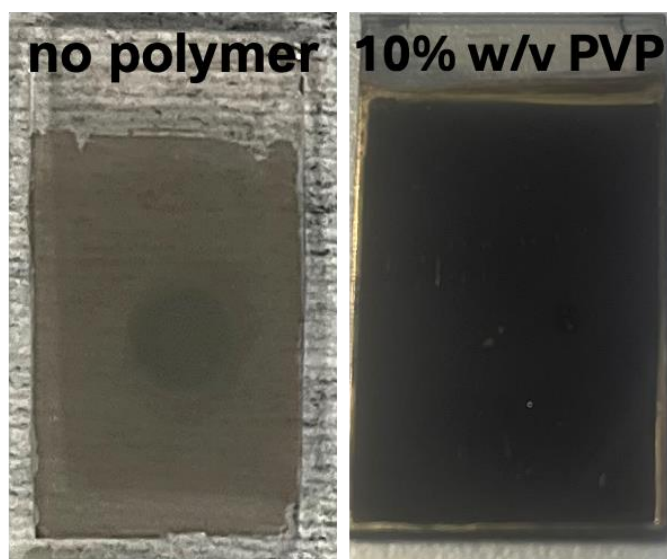


Figure S2: Images of $Ba_2Bi_2O_6$ thin films fabricated (left) polymer free and (right) with $10\% \text{ w/v PVP}$.

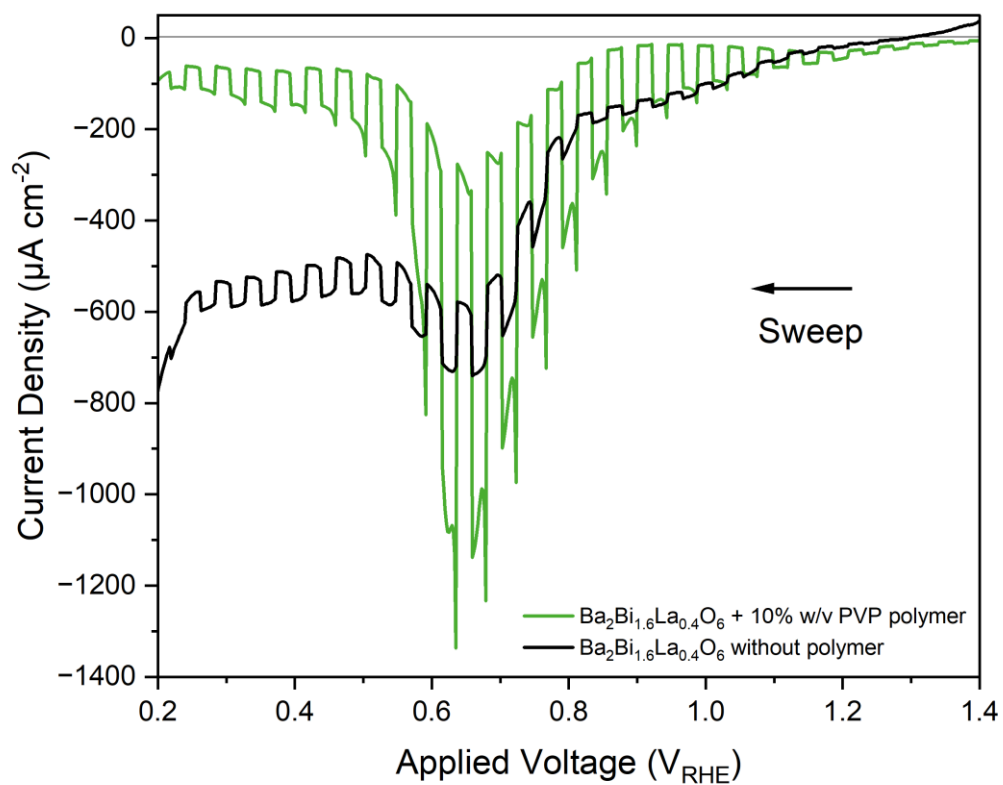


Figure S3: Current–potential curves for $Ba_2Bi_{1.6}La_{0.4}O_6$ films with and without polymer templates under chopped simulated sunlight ($AM1.5G$, 100 mW cm^{-2}) in $pH\ 12\ 0.1\ M\ Na_2SO_4$. Linear sweep from $+1.2$ to $+0.2\ V_{RHE}$ at 10 mV s^{-1} .

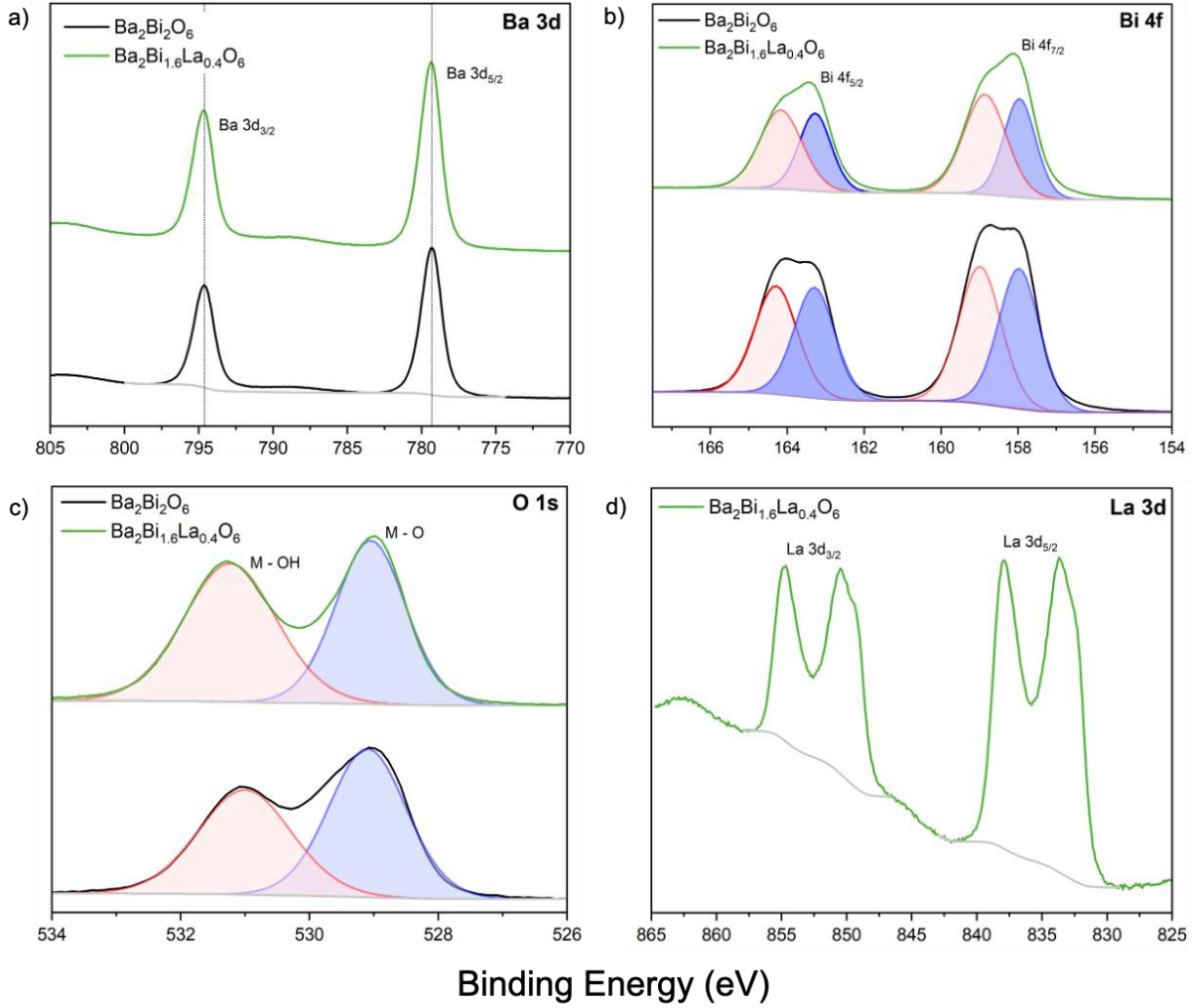


Figure S4: a) Ba 3d , b) Bi 2p , c) O 1s , and d) La 3d X-ray photoemission spectra of $Ba_2Bi_2O_6$ and $Ba_2Bi_{1.6}La_{0.4}O_6$ thin films.

Table S1: XPS surface elemental percentages of Ba, Bi, O and La atoms on $Ba_2Bi_2O_6$ and $Ba_2Bi_{1.6}La_{0.4}O_6$ thin films.

Compound	Ba [at. %]		Bi [at. %]		La [at. %]		O [at. %]	
	XPS	Expected	XPS	Expected	XPS	Expected	XPS	Expected
$Ba_2Bi_2O_6$	21.5	20	6.2	20	-	-	72.3	60
$Ba_2Bi_{1.6}La_{0.4}O_6$	21.0	20	8	14	1.7	6	69.2	60

Table S2: Basis sets for each of the atoms used in computational results.

Atom	Link
Ba	https://www.crystal.unito.it/Basis_Sets/barium.html#Ba_m-S-RSC_Heyd_2005
Bi	https://www.crystal.unito.it/Basis_Sets/bismuth.html#Bi_weihrich_2006
La	https://www.crystal.unito.it/Basis_Sets/lanthanum.html#La_9761111sp-631d_Towler_1996
O *	https://www.crystal.unito.it/Basis_Sets/oxygen.html#O_8-411_towler_1994

O * The oxygen basis set has been improved by adding additional d-shells. Each has a single gaussian function with the following exponents (1.0 and 0.4 bohr⁻²).