Supporting Information:

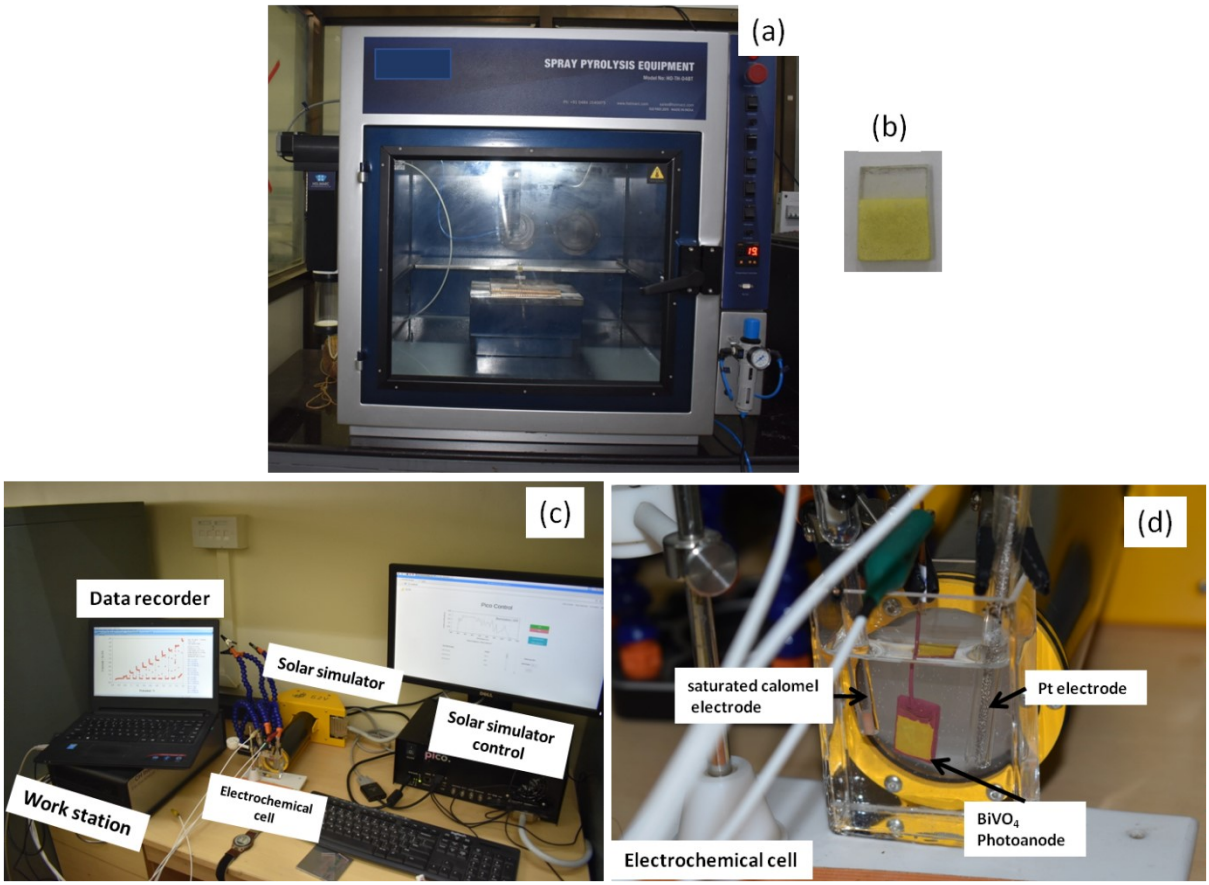

Figure S1: (a-b) Spray coating system and pictures of coated FTO substrates, respectively (c) Photoelectrochemical performance testing system (d) Electrochemical cell used for different $BiVO_4$ photoanode testing.

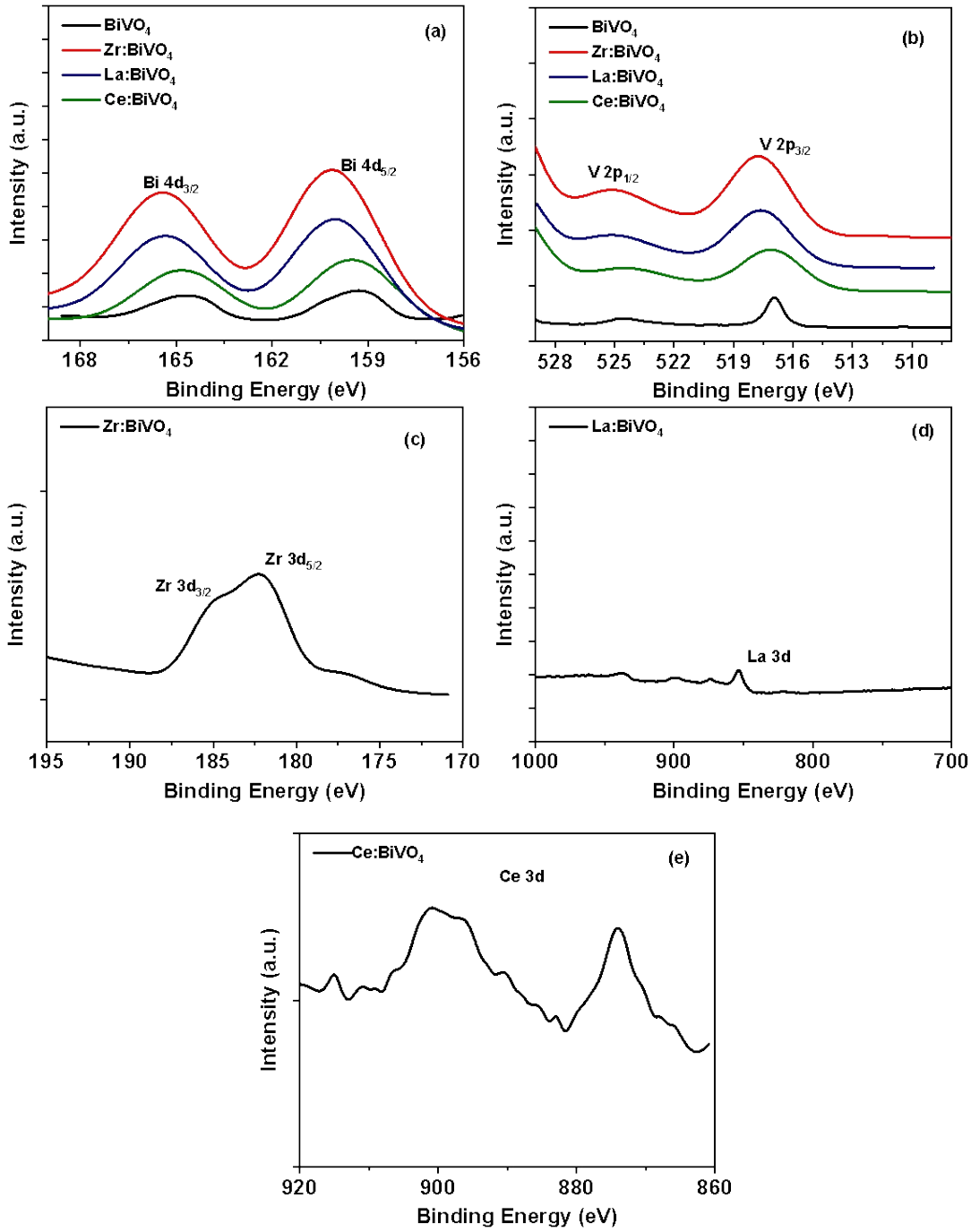

Figure S2: XPS data of different undoped/doped $BiVO_4$ samples. As seen from peak positions, the oxidation states of Bi (4d3/2: 164.05 eV and 4d5/2: 160.03 eV), V (2p3/2: 517.19 eV, 2p1/2: 524.8 eV), Zr (3d3/2-3d5/2: 181.9-185.05 eV), La (3d: ~851 eV) and Ce (3d: 875-901 eV) are confirmed 3+, 5+, 3+, 3+ and 3+, respectively. The 3d peak positions

(binding energies) in Figure S2 c,d and e confirm that the oxidation states for Zr, La and Ce are 3+, 3+ and 3+, respectively substituting Bi3+ sites in the doped samples.

Charge separation and transfer efficiencies calculations

Influence of carbon nano materials in $BiVO_4$ photoanode on light absorption, charge separation and transfer efficiencies was examined using following equations:

$$J_{water} = J_{max} \times \eta_{inj} \times \eta_{sep} \quad (1)$$

$$J_{sulfite} = J_{max} \times \eta_{sep} \quad (2)$$

Where $J_{max} = J_{theoretical} \times \eta_{abs}$ (3)

Herein, J_{water}, $J_{sulfite}$ are PCD for water and sulfite oxidation, respectively, η_{inj}, η_{sep} are charge transfer from film surface to electrolyte and bulk charge separation efficiencies, respectively, $J_{theoretical}$ is maximum photocurrent density achievable assuming 100% IPCE for photons with energy ≥ E_g, η_{abs} is the absorption efficiency and obtained by integrating the product of the incident light spectral irradiance and the LHE. The LHE of each photoanode was calculated using following equation:

$$\text{LHE (\%)} = (1-10^{-A})*100 \quad (4)$$

For sulfite oxidation in equation 2, surface recombination is negligible due to extremely fast sulfite oxidation kinetics, therefore $\eta_{inj} = \sim 1$.

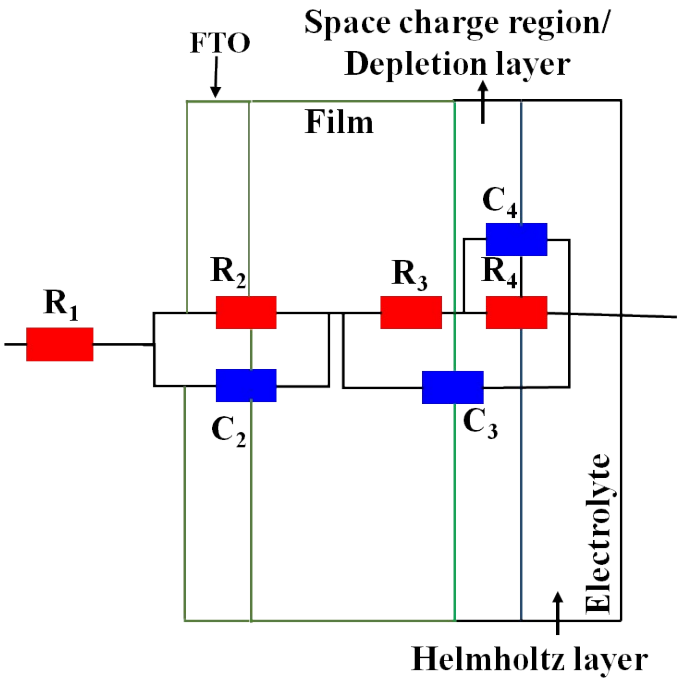

Figure S3 Equivalent circuit used for fitting Nyquist plot and deriving corresponding resistance and capacitance. The equivalent circuit parameters are represented as: R1 is the resistance corresponding to contacts, R2 and C2 are the resistance and capacitance between film and FTO interface, the R3 and C3 are resistance and charge accumulation in bulk and it represent intrinsic properties of bulk photo active film, R4 and C4 are resistance and charge accumulation at film/electrolyte interface and it represent surface characteristic of photo active film.

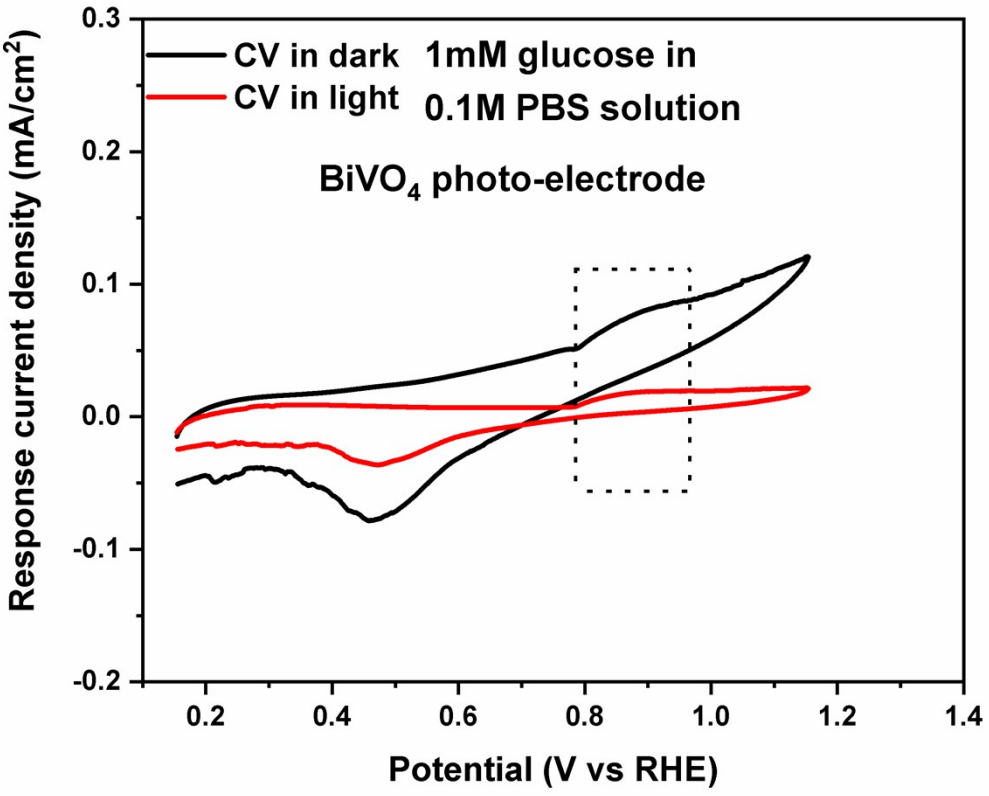

Figure S4 The bare $BiVO_4$ photoanode showed weak peak corresponding to the oxidation of glucose.

Details of the DFT simulation and results:

The optimized lattice parameters and volume of pristine phase are in good agreement (< 3%) with the experimental results. The substitution of La and Ce slightly (< 1 %) increases volume of the pristine phase; while that of Ce in BiVO4 decreases the volume by 4.5 %.

The GGA-PBE calculated band gap of all the phases are listed in column 2 of Supporting Table S5. It can be seen that the calculated band gap of pristine BiVO4 is 2.187 eV which is lower than that obtained experimentally (2.54 eV). It is well known fact that GGA-PBE exchange correlation underestimates the band gap of system, especially for the systems with highly correlated *d* and *f* electrons. To improve the calculated band gap, we performed

DFT+U as well as hybrid functional calculations. In the DFT+U calculations, the 'U_{eff} (U-J)' parameter was taken to be 2.7 eV which was suggested by T. Kim et al. [7]. However, it can be seen that this improves the band gap of the BiVO4 phase, but still lower by 10 %. Therefore, we calculated the U_{eff} of *d*-electrons of V atom in BiVO4 phase using the method suggested by Cococcioni et al. [8]. It has been found that the Ueff on the d-electrons of V atoms should be 6.37 eV. It can be seen that the band gap of the system is hugely improved by introducing U_{eff}=6.37 eV. The band gap of BiVO4 phase, calculated using HSE06 functional, is in very good agreement (within 1%) with the experimental band gap. It can be seen from Supporting Table S5 that the substitution of La and Ce in BiVO4 phase increases the band gap; while that of Zr decreases the band gap.

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Table S1 Cell parameters evaluated from theoretical simulation and Rietveld refinement for pristine $BiVO_4$, La:$BiVO_4$, Zr:$BiVO_4$, Ce:$BiVO_4$ samples.(Experimental results are given in the braces.)

Photoanode	Lattice parameter, a (Å)	Lattice parameter, b (Å)	Lattice parameter, c (Å)	Angle (Degree)	Volume, (Å ^{3})	Average Peak position of (-121)/(121)
$BiVO_4$	5.172 {5.186}	5.164 {5.110}	11.765 {11.690}	89.928 {89.927}	314.18 {309.790}	28.90
La:$BiVO_4$	5.192 {5.185}	5.172 {5.107}	11.831 {11.680}	90.088 {89.998}	317.70 {309.284}	29.00
Zr:$BiVO_4$	5.101 {5.183}	5.098 {5.106}	11.553 {11.675}	89.994 {89.990}	300.44 {308.971}	29.07
Ce:$BiVO_4$	5.198 {5.185}	5.172 {5.109}	11.822 {11.684}	90.032 {89.997}	318.00 {309.511}	28.96

Table S2 Band gap estimated from a Tauc plot depicting (F(R)hυ)2 versus hυ by the application of Kubelka-Munk's function.

Photoanode	Calculated Band Gap

	from Tauc Plot (eV)
$BiVO_4$	2.54
La:$BiVO_4$	2.55
Zr:$BiVO_4$	2.43
Ce:$BiVO_4$	2.57

Table S3 The flat band potential and number of bulk charge carriers in pristine and doped BiVO4 photoanodes as calculated from the Mott−Schottky (M−S) analysis.

Electrodes	**Flat Band Potential (V)**	**Charge Carrier Concentration, N_D (cm^{-3})**
$BiVO_4$	0.43	4.97354E+18
Zr:$BiVO_4$	0.29	1.02397E+19
La:$BiVO_4$	0.34	8.28924E+18
Ce:$BiVO_4$	0.39	6.69516E+18

Table S4 Different resistance involved in the PEC process of photoanode, obtained using a simulated circuit model.

Electrodes	**charge transfer resistance**	**bulk resistance**
$BiVO_4$	3209	920
Zr:$BiVO_4$	2010	759
La:$BiVO_4$	2409	940

Ce:$BiVO_4$	2691	1059

Table S5. GGA+U (Ueff =6.37 eV) calculated band gap of pristine and La, Ce and Zr doped phase. Experimental band gaps are also listed.

Phase	Band gap (eV)	
	DFT calculated	Experimental
BiVO4	2.585	2.540
La:BiVO4	2.686	2.500
Ce:BiVO4	2.683	2.510
Zr:BiVO4	2.446	2.430