Supporting information

Effect of Catalytically Silent Cerium Hydroxide in Cobalt - Cerium Mixed Double Hydroxide for Enhanced Water Oxidation Kinetics in $BiVO_4$ Photoanode

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Similar optical absorption behaviour was observed on $BiVO_4$ and $BiVO_4$-CoCe$(OH)_x$ films as shown in Figure S1a. An absorption edge around 510 nm was observed for both films, which corresponds with the typical band gap of $BiVO_4$. Optical curves and band gaps estimated from Tauc analysis (Figure S1b) for bare, and modified BiVO4 photoanodes, shows that co-catalyst modification does not influence the absorption edge of BiVO4 as well as band gaps.

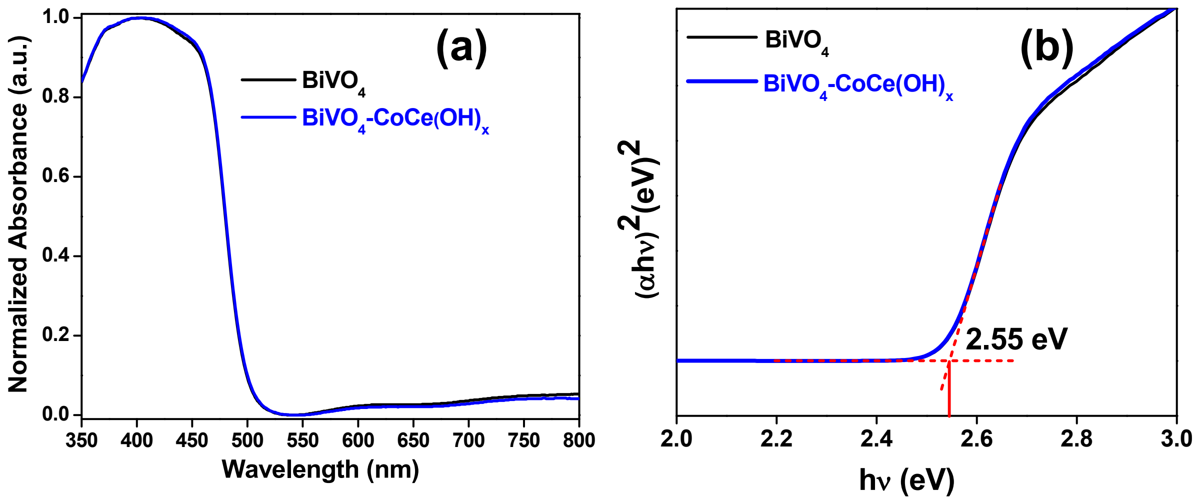

Figure S1. *(a) UV-visible absorption spectra and the corresponding (b) Tauc's plots of $BiVO_4$ and $BiVO_4$-CoCe$(OH)_x$.*

In order to confirm the presence of $Co(OH)_x$ and $Ce(OH)_x$ in the composite photoanode, inverse fast Fourier transform (IFFT) was calculated from the HRTEM obtained for the composite. A d-spacing of 0.34 nm corresponds to (220) plane of $Co(OH)_x$ as shown in Figure S2. Also, a d-spacing of 0.33 nm corresponds to (012) plane of $Ce(OH)_x$ in the composite as shown in Figure S3.

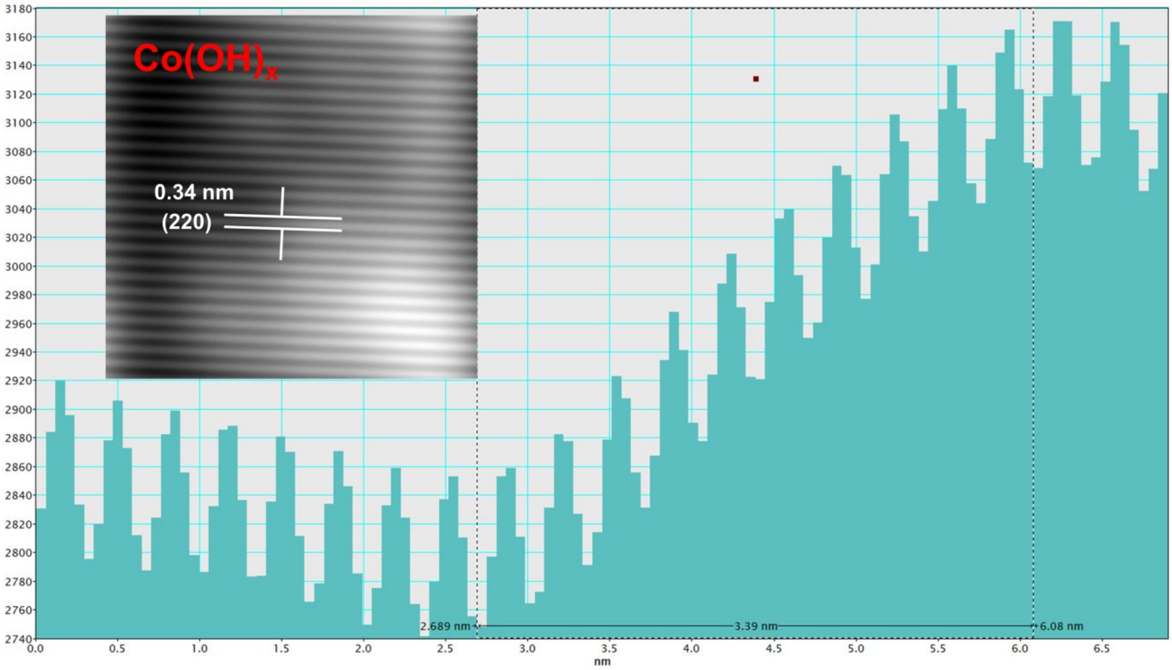

Figure S2. *IFFT of $Co(OH)_x$ extracted from the HRTEM of $BiVO_4$-$CoCe(OH)_x$.*

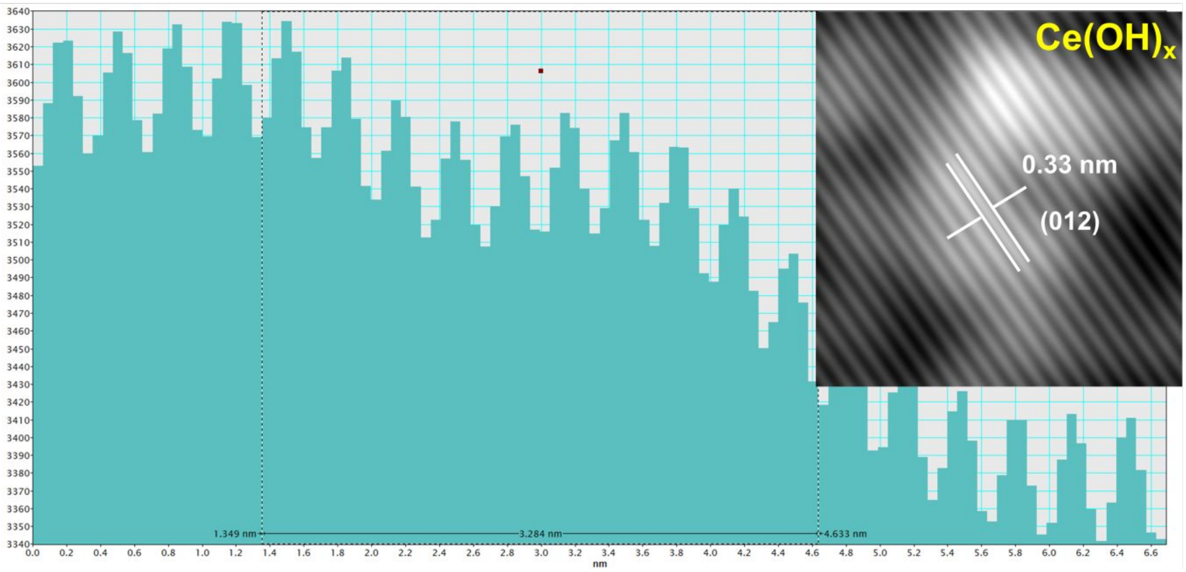

Figure S3. *IFFT of $Ce(OH)_x$ extracted from the HRTEM of $BiVO_4$-$CoCe(OH)_x$.*

In order to confirm the effect of concentration on surface catalytic properties of co-catalyst, different ratios of cobalt to cerium was deposited over $BiVO_4$ photoanode. It is found that $Co_{0.75}Ce_{0.25}(OH)_x$ has the optimized co-catalytic effect over $BiVO_4$ surface where the photocurrent density reaches up to 3.74 mA/cm^2 at 1.23V vs. RHE. As cerium is catalytically silent, excess amount of cerium in mixed metal hydroxide may leads to blockage of active sites.

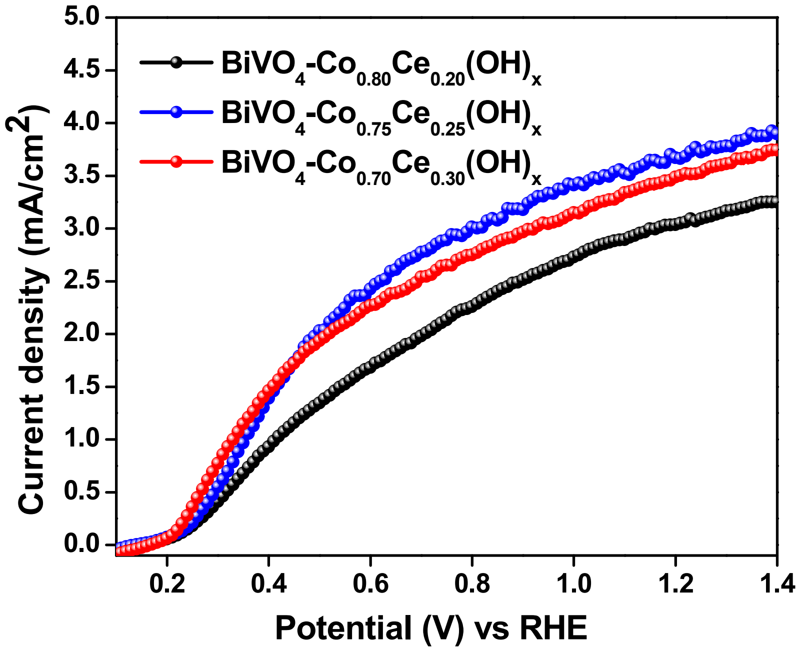

Figure S4. *J-V curves of $BiVO_4$-CoCe$(OH)_x$ photoanodes with different ratios of cobalt to cerium.*

The reproducibility of the photoanode is an important parameter for its wide applicability. The photocurrent density of 5 random films modified with co-catalyst were checked and found to be similar in all cases.

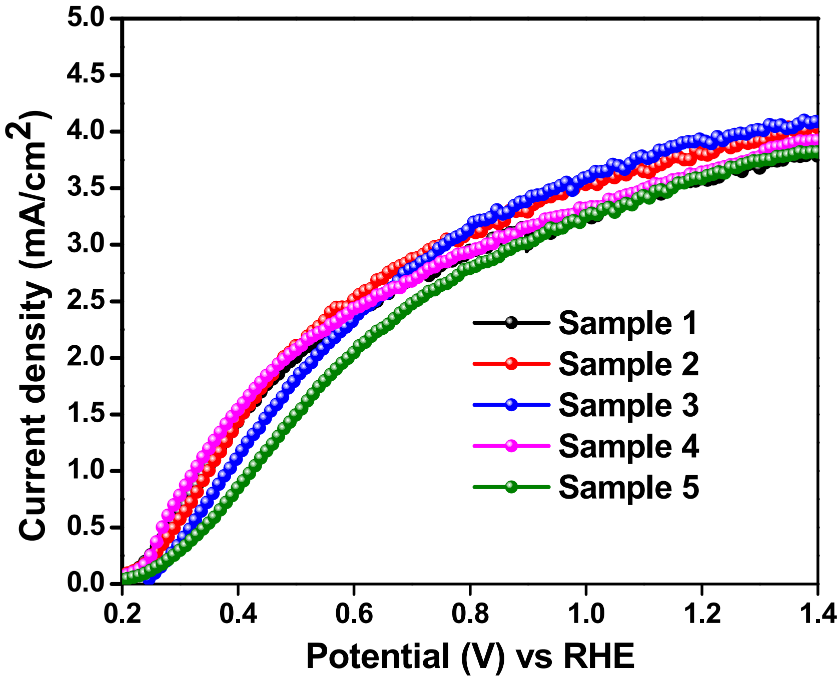

Figure S5. *J-V curves of $BiVO_4$-$Co_{0.75}Ce_{0.25}(OH)_x$ photoanode with 5 different films.*

In order to confirm the behaviour of $Ce(OH)_x$ over $BiVO_4$ photoanode, 4 different films fabricated in different course of time were measured for photoelectrochemical water oxidation activity. The results for all the photoanodes is found to be in similar trend confirms catalytically silent behaviour of cerium.

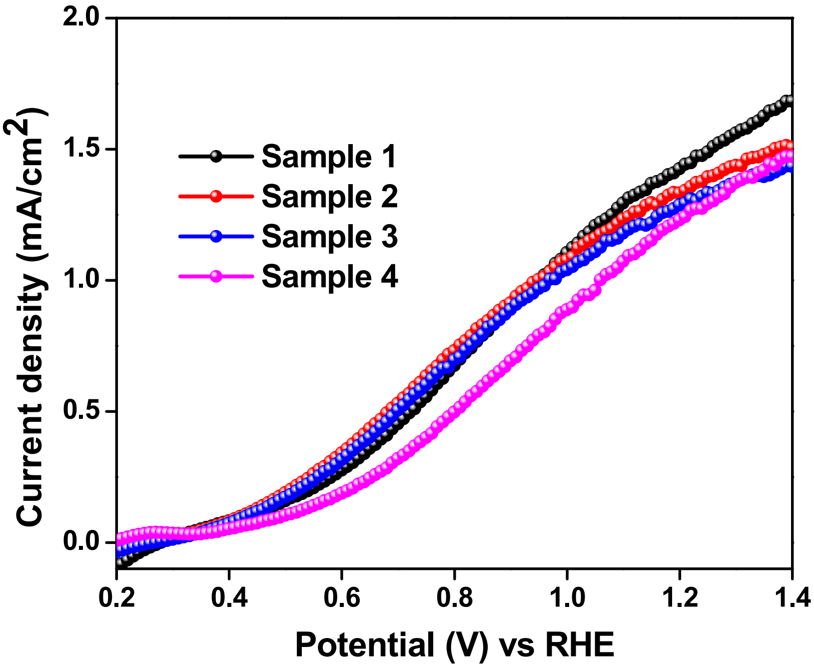

Figure S6. *J-V curves of $BiVO_4$-$Ce(OH)_x$ photoanode with 4 different films.*

Linear sweep voltammogram (LSV) of $CoCe(OH)_x$, $Co(OH)_x$, and $Ce(OH)_x$ were measured in in dark condition to confirm the role of $Ce(OH)_x$ in the $CoCe(OH)_x$ composite. Although $Ce(OH)_x$ itself has a low catalytic activity, it helps in improving the electrocatalytic activity of $Co(OH)_x$.

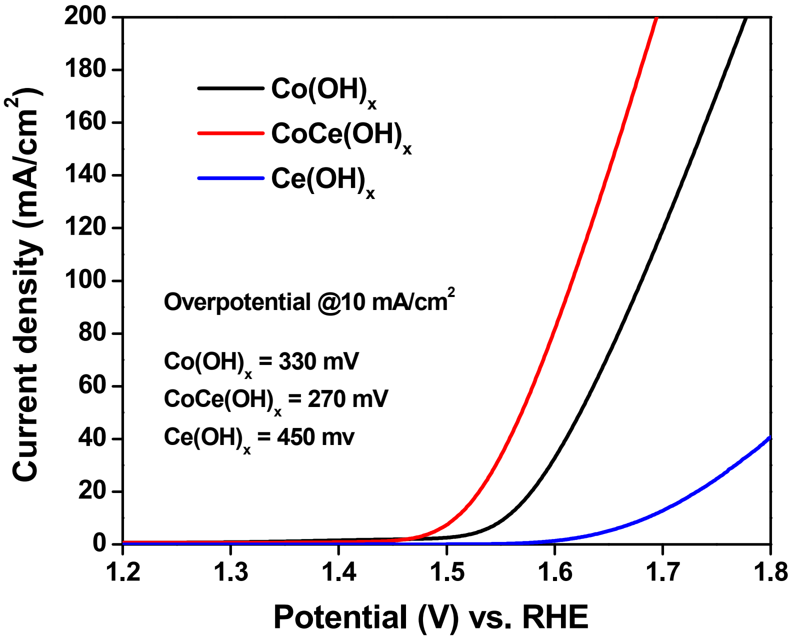

Figure S7. Linear sweep voltammogram (LSV) of $CoCe(OH)_x$, $Co(OH)_x$, and $Ce(OH)_x$ in dark condition.

To demonstrate the versatility of the modified photoanode in the extended pH range, photocurrent were measured at pH 6.5. Modified photoanode shows a photocurrent density of 3.5 mA/cm^2 at 1.23V vs. RHE as compared to 1.2 mA/cm^2 for bare $BiVO_4$. Comparable photocurrent in different pH concludes the versatility of co-catalyst which can be applicable to different photoanodes.

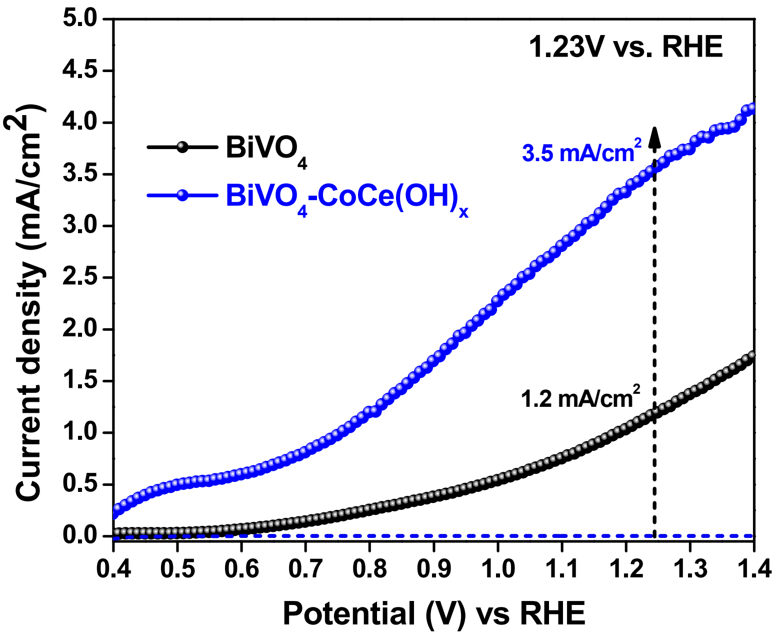

Figure S8. *J-V curves of $BiVO_4$ and $BiVO_4$-CoCe(OH)$_x$ photoanodes in 0.5 M Na_2SO_4 electrolyte (pH = 6.5).*

As an efficient hole scavenger, sulphite can be oxidized on photoanode with favourable kinetics, and thus, the interfacial hole-transfer kinetics on photoanode is normally negligible. The $BiVO_4$-$CoCe(OH)_x$ film exhibits higher photocurrent for sulphite oxidation than the bare $BiVO_4$ film, but their onset potential is pretty close as expected.

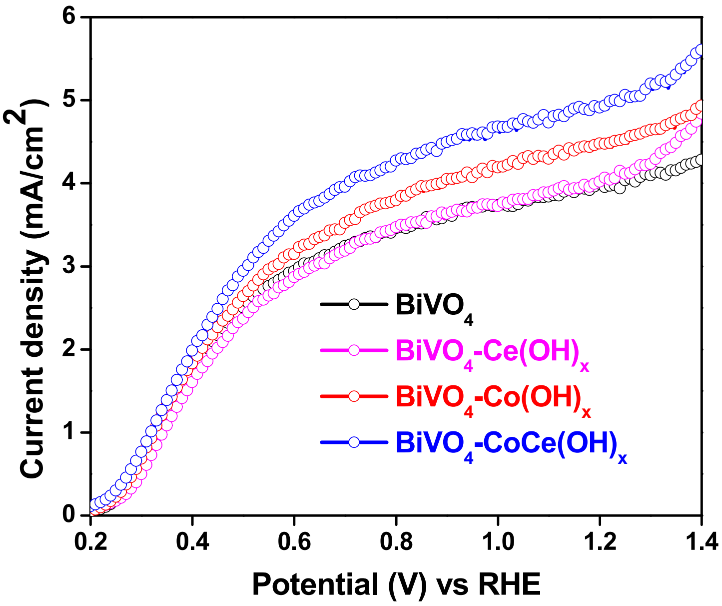

Figure S9. *J-V curves of the photoanodes with addition of hole scavenger Na_2SO_3 in potassium borate electrolyte.*

Table S1. Summary of the water oxidation properties of high performing OER catalysts for $BiVO_4$ based photoanodes.

System	Synthesis method	Current density (@1.23V vs. RHE)	References
$BiVO_4$-$CoCe(OH)_x$	**Electrodeopsition + Hydrothermal**	**3.74 mA/cm^2**	**This Work**
$BiVO_4$-CoAl-LDH	Hydrothermal	2.0 mA/cm^2	*J. Mater. Chem. A*, **2015**, *3*, 17977-17982
$BiVO_4$-Co-Pi	Spray pyrolysis	1.7 mA/cm^2	*J. Phys. Chem. C* **2012**, *116*, 9398-9404
$BiVO_4$-NiCoLDH	Electrodeposition	3.4 mA/cm^2	*Applied Catalysis B: Environmental*, **2020**, *263*, 118280
$BiVO_4$-$NiCoO_2$	Electrodeposition	3.6 mA/cm^2	*Adv. Mater. Interfaces*, **2017**, *4*, 1700540
$BiVO_4$-$[Co_2(bim)_4]$	Electrodeposition	3.1 mA/cm^2	*ChemSusChem*, **2018**, *11*, 2710-2716
$BiVO_4$-NiOOH - FeOOH	Electrodeposition	4.2 mA/cm^2	*Science*, **2014**, *45*, 990-994
$BiVO_4$-CoO_x-NiO	Drop-casting	3.5 mA/cm^2	*J. Am. Chem. Soc.* **2015**, *137*, 5053-5060
$BiVO_4$-CoFe-H	Electrodeposition	2.48 mA/cm^2	*Adv. Funct. Mater.*, **2017**, *27*, 1603904.
$BiVO_4$-NiB	Electrodeposition	3.47 mA/cm^2	*Nanoscale*, **2017**, *9*, 16133-16137
$BiVO_4$-Co_3O_4	Electrodeposition	2.71 mA/cm^2	*J. Am. Chem. Soc.*, **2015**, *137*, 8356-8359
$BiVO_4$-$Co(CO_3)_xOH_y$	Electrodeposition	5.00 mA/cm^2	*J. Mater. Chem. A*, **2020**, *8,* 2563-2570
$BiVO_4$-$Co(OH)_2$	Electrodeposition	4.52 mA/cm^2	*Electrochim. Acta*, **2020**, *330*, 135183
$BiVO_4$-CoLaLDH	Electrodeposition	2.09 mA/cm^2	*ACS Energy Lett.* 2017, *2*, 1062–1069