Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Limiting factors for photochemical charge separation in $BiVO_4/Co_3O_4$, a highly active photocatalyst for water oxidation in sunlight

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Electronic Supplementary Information

The synthesis of $BiVO_4$ involved a solid-solution reaction and 673 K calcination as described previously.[18] The crystal structures of both uncalcined and calcined $BiVO_4$ were verified by powder X-ray diffraction (Figure S1). The XRD patterns agreed well with standard card 00-014-0688 (space group: I2/a, a = 5.195, b = 11.701, c = 5.092, β = 90.38), showing the monoclinic scheelite structure of obtained $BiVO_4$. The monoclinic form is found to be more active under visible light than the tetragonal one. [4, 5, 8] High activity was noted for $BiVO_4$ nanoplates terminated by 001 facets.[6]

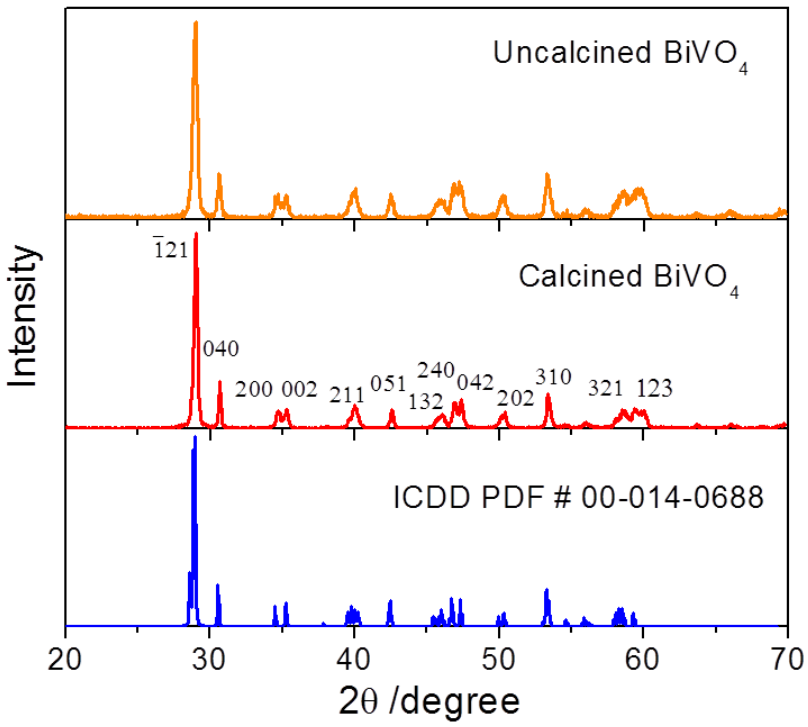


Figure S1. XRD of $BiVO_4$ before and after calcining

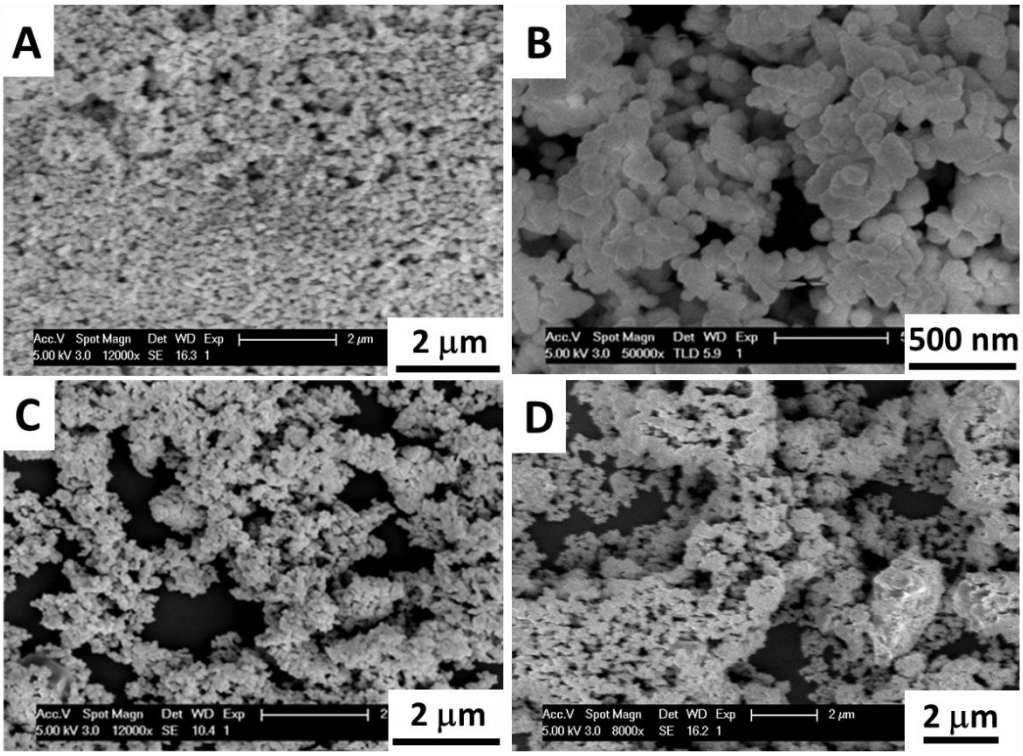


Figure S2. SEM images of $BiVO_4$ (A) before and (B) after calcination, (C) Chem-Co_3O_4-$BiVO_4$ and (D) Phys-Co_3O_4-$BiVO_4$

Butler-Ginley calculation of flat-band potentials

1st Ionization Energy:

Oxygen 13.61806 eV, Cobalt 7.8810 eV, Bismuth 7.2856 eV, Vanadium 6.7462eV

David R. Lide (ed), *CRC Handbook of Chemistry and Physics, 84th Edition*. CRC Press. Boca Raton, Florida, 2003; Section 10, Atomic, Molecular, and Optical Physics; Ionization Potentials of Atoms and Atomic Ions

Electron Affinity:

Oxygen 1.4611134(9) eV

Chaibi, W. and Pelaez, R.J. and Blondel, C. and Drag, C. and Delsart, C., *Eur. Phys. J.* D58, 29 (2010)

Bismuth 0.942362(13) eV

Rene C. Bilodeau and Harold K. Haugen, Phys. Rev. A, 2001, 64, 024501

10.1103/PhysRevA.64.024501

Cobalt 0.6633(6) eV

Scheer, M.; Brodie, C.A.; Bilodeau, R.C.; Haugen, H. K. Phys. Rev. A, 2001, 58,205162

Vanadium 0.526(12) eV

Feigerle, C.S., Corderman, R.R., Bobashev, S.V. and Lineberger, W.C. (1981). Binding energies and structure of transition metal negative ions. J. Chem. Phys. 74, 1580 doi:10.1063/1.441289.

Mulliken Electronegativity for $BiVO_4$:

O = (13.61806+1.4611)/2=7.53958

Co=(0.6634+7.8810)/2=4.2722

Bi=(0.9424+7.2856)/2=4.114

V=(0.5261+6.7462)/2=3.63615

Mulliken Electronegativity for

Co_3O_4 = (7.54^4*4.27^3)^(1/7) = 5.9093

$BiVO_4$ = (4.114*3.63615*7.53958^4)^(1/6) = 6.0355

$E_{VB}=X-4.44+E_G/2$

Co_3O_4: O^{2-} to Co^{2+} 2.2eV O^{2-} to Co^{3+} 1.6 eV

Co_3O_4=5.91-4.44+1.6/2=5.91-4.44+0.8=2.27 V for BG 1.6eV, +1.03 = 2.5 eV for BG 2.07eV

CB=0.43 eV VB=2.5 eV, at PZC

$BiVO_4$: 2.45eV (I) 2.6 eV (D)

$BiVO_4$ = 6.04-4.44+2.45/2= 2.83 V

CB=0.38 eV VB=2.83 eV, at PZC

Pzc of $BiVO_4$ = 3, *Chem. Mater.* **2008,** *20,* 6346–6351,

Pzc of Co_3O_4 = 7, Elecrrochimica Acta, Vol. 40. No. 16, Pp. 2683-2686, 1995

At pH 7,

$BiVO_4$: (3-7)*0.06 = -0.24 V CB = 0.38-0.24=0.14 V, VB = 2.83-0.24=2.59 V

Co_3O_4: (7.3-7)*0.06 = - 0.02 V CB = 0.41 V, VB = 2.48 V

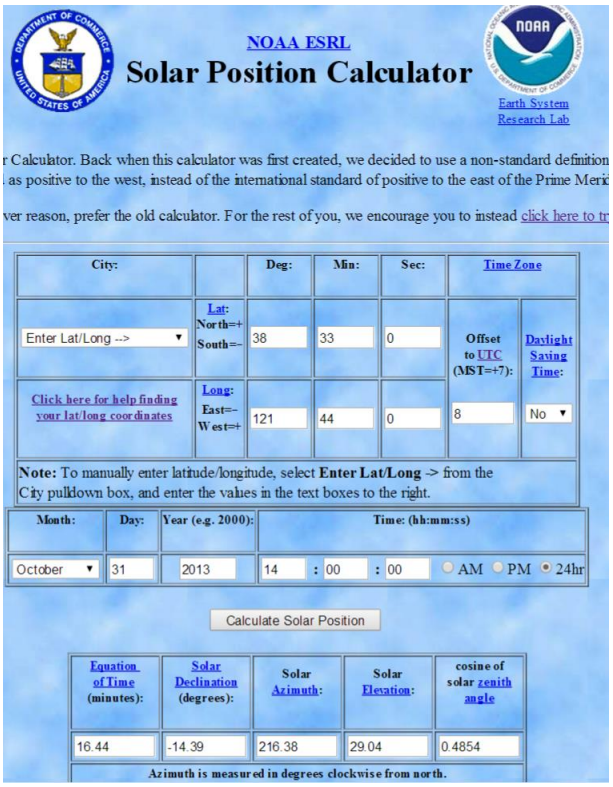
Table S1. Comparison of oxygen evolution catalysts

Catalyst	Sacrificial agent	O_2 evolution rate (umol/h/g)	Reference
Pt(0.5wt%)-WO_3	4mM $NaIO_3$	300	*J. Phys. Chem. B* ***2005,*** *109, 16052-16061*
WO_3	10mM $AgNO_3$	504	*J. Phys. Chem. B* ***2005,*** *109, 16052-16061*
Pt(0.5wt%)-$BiVO_4$	4mM $NaIO_3$	88	*J. Phys. Chem. B* ***2005,*** *109, 16052-16061*
$BiVO_4$	10 mM $AgNO_3$	960	*J. Phys. Chem. B* ***2005,*** *109, 16052-16061*
$BiVO_4$ (nanoplate)	0.05M $AgNO_3$	5500	*Chem. Commun*., **2010**, 46, 1893–1895
TaON	0.01M $AgNO_3$	3300	*Chem. Commun*., **2002**, 1698–1699
$BiVO_4$	0.05M $AgNO_3$	421	*J. Am. Chem. Soc*. **1999**, 121, 11459-11467
$BiVO_4$	0.05M $AgNO_3$	220	*Chem. Mater*. ***2001,*** *13, 4624-4628*
$PbBi_2Nb_2O_9$-1wt% Pt	0.05M $AgNO_3$	520	*J. Am. Chem. Soc*. **2004**, 126, 8912-8913
$TiO_{2-x}N_x$-1wt% Pt	0.05M $AgNO_3$	221	*J. Am. Chem. Soc*. **2004**, 126, 8912-8913

N doped TiO_2-Pt	$AgNO_3$	21	*J. Am. Chem. Soc*. **2004**, *126* (29), 8912–8913
$PbTiO_3$- Pt	$AgNO_3$	523	*J. Solid State Chem.* **2006**, *179* (4), 1214–1218
$Sm_2Ti_2S_2O_5$- Pt	$AgNO_3$	55	*J. Am. Chem. Soc*. **2002**, *124* (45), 13547–13553
$PbBi_4Ti_4O_{15}$- Pt	$AgNO_3$	1443	*J. Solid State Chem.* **2006**, *179* (4), 1214–1218
$K_{0.5}La_{0.25}Bi_{0.25}Ca_{0.75}Pb_{0.75}Nb_3O_{10}$ - Pt	$AgNO_3$	560	*J. Solid State Chem.* **2006**, *179* (4), 1214–1218
$AgVO_4$	$AgNO_3$	57	*Phys. Chem. Chem. Phys.* **2003**, *5* (14), 3061–3065
Bi_2MoO_6	$AgNO_3$	110	*J. Phys. Chem. B* **2006**, *110* (36), 17790–17797
Cr:$PbMoO_4$	$AgNO_3$	143	*J. Chem. Soc. Jpn*. **2007**, *80* (5), 885–893
Ta_3N_5-Pt	$AgNO_3$	500	*Chem. Lett*. **2002**, (7), 736–737
$Y_2Ta_2O_5N_2$	$AgNO_3$	467	*Chem. Commun*. **2004**, (19), 2192–2193
$BiVO_4$-Co_3O_4	0.02M $NaIO_4$	11000	N/A

Brief calculation of sun light intensity

The location of Davis, CA is 38°33′ N, 121°44′ W and the experiment was conducted between 11 am to 5 pm on Oct. 31, 2014. The cosine of solar zenith angle is calculated to be 0.4854 by Solar Position Calculator (shown below), provided by U.S. Department of Commerce, National Oceanic & Atmospheric Administration (NOAA), Earth System Research Laboratory (ESRL) from website http://www.esrl.noaa.gov/gmd/grad/solcalc/sollinks.html.



NOAA ESRL

Solar Position Calculator

Earth System Research Lab

r Calculator. Back when this calculator was first created, we decided to use a non-standard definition
as positive to the west, instead of the international standard of positive to the east of the Prime Meri

ver reason, prefer the old calculator. For the rest of you, we encourage you to instead click here to tr

City:		Deg:	Min:	Sec:	Time Zone	
Enter Lat/Long -->	Lat: North=+ South=-	38	33	0	Offset to UTC (MST=+7):	Daylight Saving Time:
Click here for help finding your lat/long coordinates	Long: East=- West=+	121	44	0	8	No

Note: To manually enter latitude/longitude, select **Enter Lat/Long ->** from the City pulldown box, and enter the values in the text boxes to the right.

Month:	Day:	Year (e.g. 2000):	Time: (hh:mm:ss)
October	31	2013	14 : 00 : 00 AM PM 24hr

Calculate Solar Position

Equation of Time (minutes):	Solar Declination (degrees):	Solar Azimuth:	Solar Elevation:	cosine of solar zenith angle
16.44	-14.39	216.38	29.04	0.4854

Azimuth is measured in degrees clockwise from north.

AM = 1/cos(z) = 1/0.4854 = 2.06

Based on the equation of direct solar irradiation,

$$I_D = 1.353 \cdot 0.7^{(AM^{0.678})}$$

The direct solar irradiation intensity is calculated to be 0.76 kW/m^2 = 760 mW/cm^2

Meinel, A. B. and Meinel, M. P., *Applied Solar Energy*. Addison Wesley Publishing Co.; 1976.