Electronic Supplementary Material (ESI) for Energy & Environmental Science

Use of Potential Determining Ions to Control Energetics and Photochemical Charge Transfer of a Nanoscale Water Splitting Photocatalyst

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Supporting Information (8 pages)

Electron microprobe analyses, charge density calculations, photocurrent scans, and hydrogen evolution data.

1. Electron microprobe analysis (Table S1, S2) yielded mass percent of 0.73 (Sr^{2+}) and 1.45 (K^+) in the products, which corresponds to 0.11 Sr ions and 0.21 K ions per $[Ca_2Nb_3O_{10}]^-$ formula unit. This confirms partial exchange of H^+ and TBA+ cations with K^+ and Sr^{2+} respectively.

Table S1 Electron microprobe data for $\mathbf{Sr_{1/2}[Ca_2Nb_3O_{10}]\ x\ Sr(NO_3)_2}$

Data Set	**Weight Percent**					**Adjusted Atomic Percent***				
	Ca	**Sr**	**Nb**	**O**	**Total**	**Ca**	**Sr**	**Nb**	**O**	**Total**
1	13.86	1.21	46.30	25.47	86.84	14.11	0.56	20.35	64.98	100
2	13.14	2.06	43.73	24.07	83.00	14.09	1.01	20.23	64.67	100
3	13.42	1.51	45.82	25.09	85.83	13.88	0.71	20.44	64.97	100
4	13.18	1.61	43.07	23.80	81.66	14.31	0.80	20.17	64.73	100
5	13.85	1.27	46.77	25.67	87.56	14.01	0.59	20.40	65.01	100
Average						14.08	0.73	20.32	64.87	
Atomic Composition						2.01	0.11	2.90	9.27	

*Carbon and hydrogen cannot be accurately quantified due to analytical limitations

Table S2 Electron microprobe data for $\mathbf{K[Ca_2Nb_3O_{10}] \text{ x } KNO_3}$

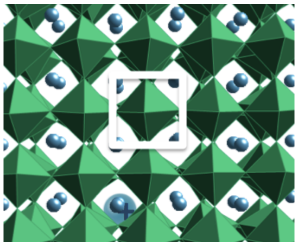
Data Set	Weight Percent					Adjusted Atomic Percent*				
	Ca	K	Nb	O	Total	Ca	K	Nb	O	Total
1	14.07	1.57	46.93	25.82	88.39	13.99	1.60	20.12	64.29	100
2	13.94	1.14	47.04	25.82	87.93	13.93	1.17	20.28	64.63	100
3	13.37	1.58	47.15	25.64	87.74	13.43	1.63	20.43	64.51	100
4	13.38	1.28	45.56	24.96	85.17	13.81	1.35	20.29	64.54	100
5	12.98	1.40	44.94	24.53	83.85	13.62	1.51	20.36	64.51	100
Average						13.75	1.45	20.30	64.50	
Atomic Composition						1.97	0.21	2.90	9.21	

*Carbon and hydrogen cannot be accurately quantified due to analytical limitations

2. Calculation of surface charge density from estimated surface potential

Physical Constants

N_A (Avogadro number)	6.02E+23	mol^{-1}
R (Ideal Gas constant)	8.314	$J\ K^{-1}\ mol^{-1}$
F (Faraday constant)	96485	$sA\ mol^{-1}$
T (absolute Temperature)	298	K
z (Charge)	1	
ε_0 (Permittivity)	8.85E-12	$F\ m^{-1}$
ε (relative Permittivity)	30	
Geometrical footprint of $LiCa_2Nb_3O_{10}$ formula unit on nanosheet (one side, see figure below)	0.149	nm^2
(both sides)	0.298	nm^2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$LiCa_2Nb_3O_{10}$ footprint calculated from structural data from Dion et al. [1]

Grahame Equation from reference [2]

$$\sigma = \sqrt{8RT\varepsilon\varepsilon_0 c^0}\ \sinh\left(\frac{zF\phi_0}{2RT}\right)$$

σ: surface charge density ($C\ m^{-2}$), ϕ_0: surface potential (V), c_0: counterion concentration

($mol\ L^{-1}$); for other constants see table above

Importantly, the unknown Cl^- counterion concentration c^0 in the nanosheet films is estimated as only 10% of the solution value (0.1 M) because the large $(C_2H_5)_4N^+$ ion has limited ability to penetrate the film. Using the solution concentration value of 0.1 M produces surface potentials of ~ 10 mV, a factor of 10 below the experimental values.

PDI induced surface potential / V	Nanosheet film electrolyte conc / mol m^{-3}	Nanosheet film charge density / C m^{-2}	Elemental charge per nm^2 of nanosheet	Elemental charge per nanosheet formula unit	PDIs per formula unit from microprobe analysis
0.04	**1.00E+01**	**6.24E-03**	**3.89E-02**	**1.31E-01**	**K+: 0.21 (=0.21 +)**
0.12	**1.00E+01**	**3.72E-02**	**2.32E-01**	**7.79E-01**	**Sr^{2+}: 0.11 (=0.22 +)**

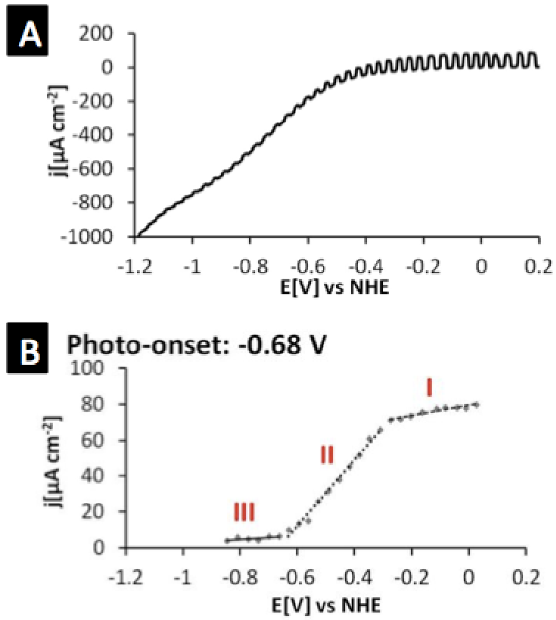

Figure S1. A) Photocurrent scan for pH 3-modified nanosheet film on FTO. Irradiated using chopped light from 300 W Xe arc lamp in 0.1 M TEACl in methanol. B) Absolute photocurrent density versus voltage curve for same photocurrent scan.

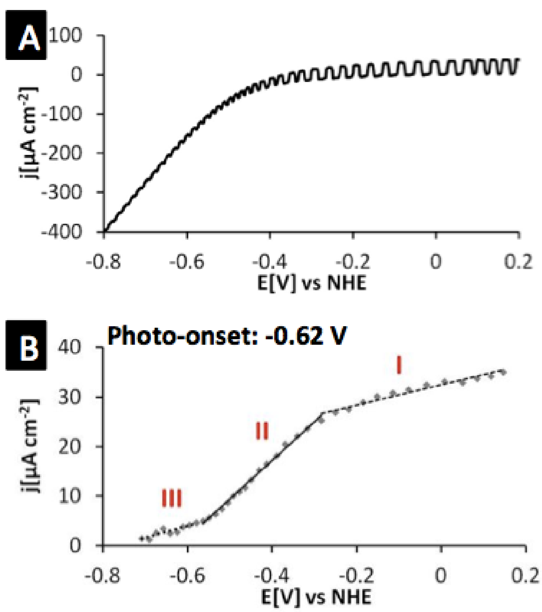

Figure S2. A) Photocurrent scan for pH 1-modified nanosheet film on FTO. Irradiated using chopped light from 300 W Xe arc lamp in 0.1 M TEACl in methanol. B) Absolute photocurrent density versus voltage curve for same photocurrent scan

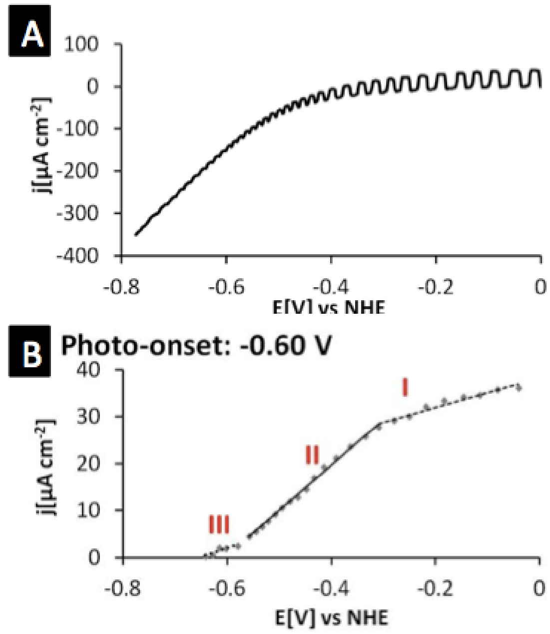

Figure S3. A) Photocurrent scan for Sr^{2+}-modified nanosheet film on FTO. Irradiated using chopped light from 300 W Xe arc lamp in 0.1 M TEACl in methanol. B) Absolute photocurrent density versus voltage curve for same photocurrent scan

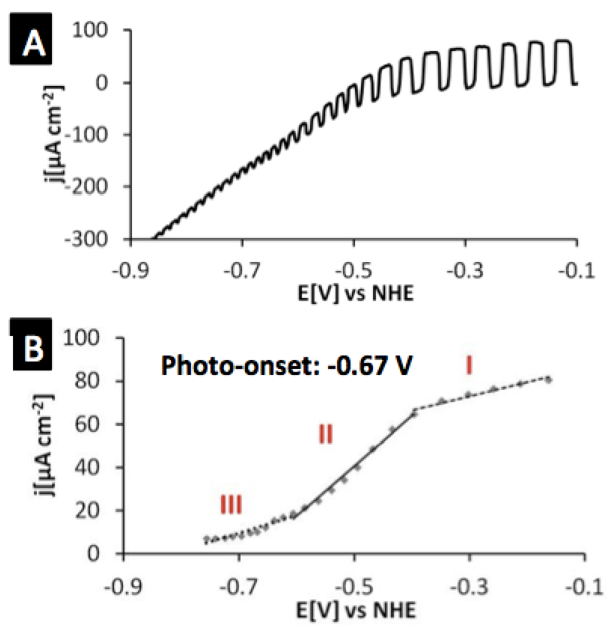

Figure S4. A) Photocurrent scan for K^{+}-modified nanosheet film on FTO. Irradiated using chopped light from 300 W Xe arc lamp in 0.1 M TEACl in methanol. B) Absolute photocurrent density versus voltage curve for same photocurrent scan

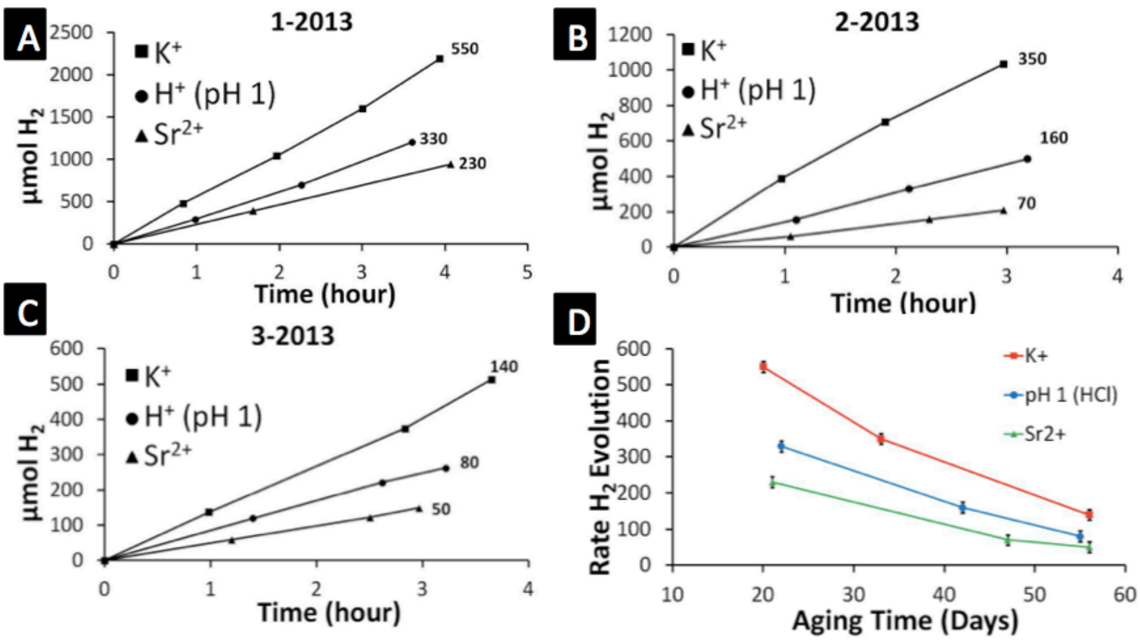

Figure S5. Time-dependent hydrogen evolution of cation-modified $M_xH_{1-x}[Ca_2Nb_3O_{10}]$. Results are for 25 mg of catalyst dispersed in 50 mL 20% aqueous methanol at pH 1 in a 100 mL quartz flask under irradiation with a 300 W Xe arc lamp. Age of stock $TBA_xH_{1-x}[Ca_2Nb_3O_{10}]$ increases from A) to C). D) Dependence of rate of H_2 evolution on aging time of stock $TBA_xH_{1-x}[Ca_2Nb_3O_{10}]$

References

1. M. Dion, M. Ganne and M. Tournoux, *Materials Research Bulletin*, 1981, **16**, 1429-1435.
2. A. J. Bard and L. R. Faulkner, *Electrochemical methods : fundamentals and applications*, John Wiley, New York, 2001.