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Direct Evidence on the Efficient Hole-Collecting Process of CoOx Cocatalyst for Photocatalytic Reaction: A Surface Photovoltage Study

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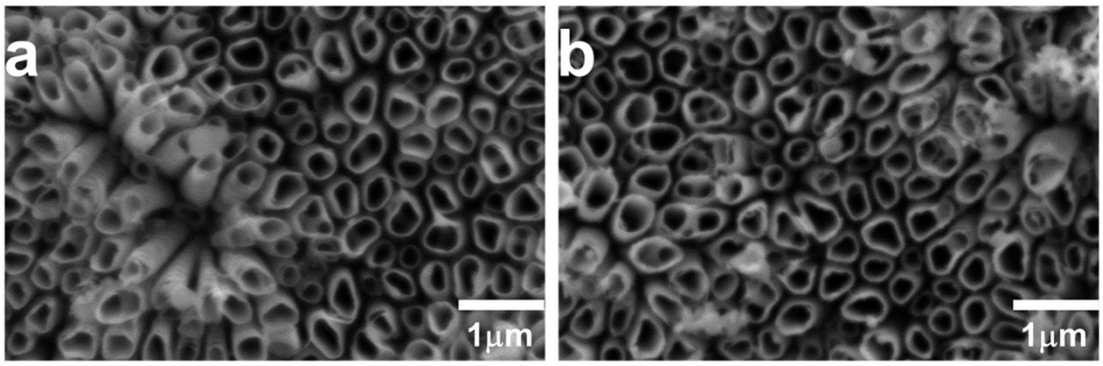

Figure S1. FESEM images of TNAs (a) and CoO_x-TNAs (b).

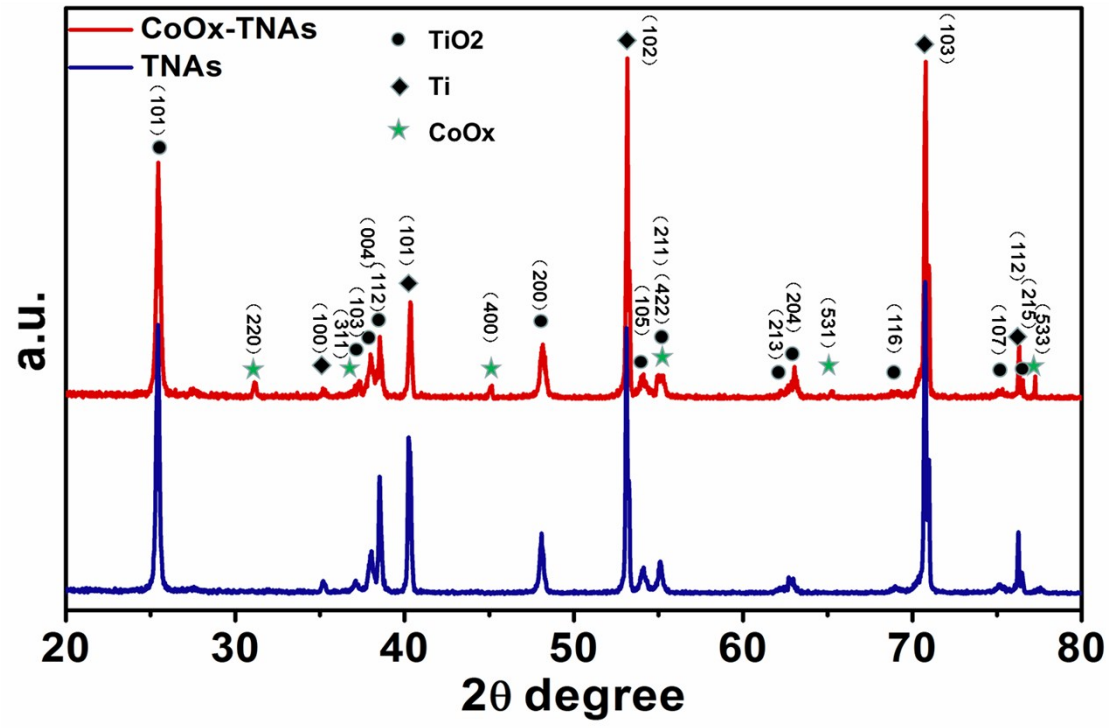

Figure S2. XRD patterns of TNAs and CoO_x-TNAs.

The XRD pattern of pure TNAs can be indexed to the anatase phase of TiO_2 (JCPDS NO. 21-1272) and the substrate Ti (JCPDS No. 44-1294).[1] In contrast, the CoOx-TNAs samples exhibit the diffraction peaks of Co_3O_4 (JCPDS NO. 80-1545).[2]

Reference:

1. B. Huang, W. Yang, Y. Wen, B. Shan and R. Chen, ACS Appl. Mater. Interfaces, 2015, 7, 422-431.
2. Y. F. Wang, M. C. Hsieh, J. F. Lee and C. M. Yang, Appl. Catal. B-Environ., 2013, 142, 626-632.

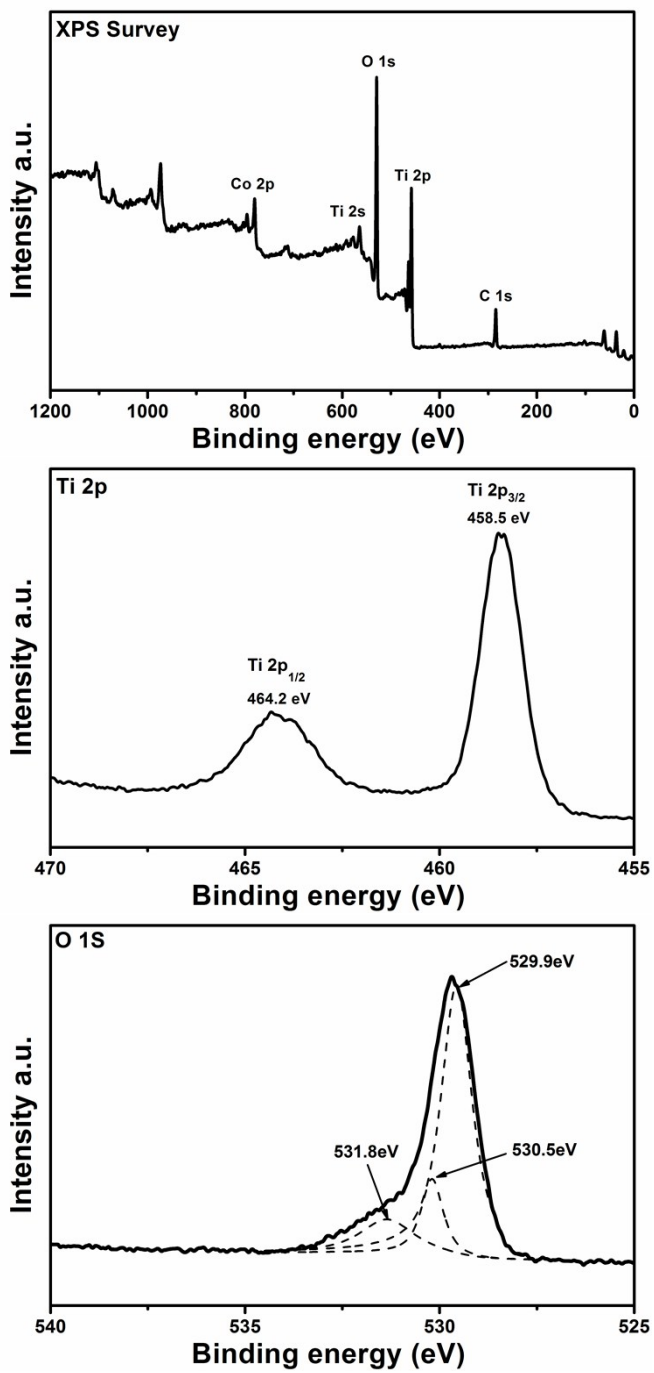

Figure S3. CoO_x-TNAs XPS spectra survey, Ti 2p spectra and O 1s spectra.

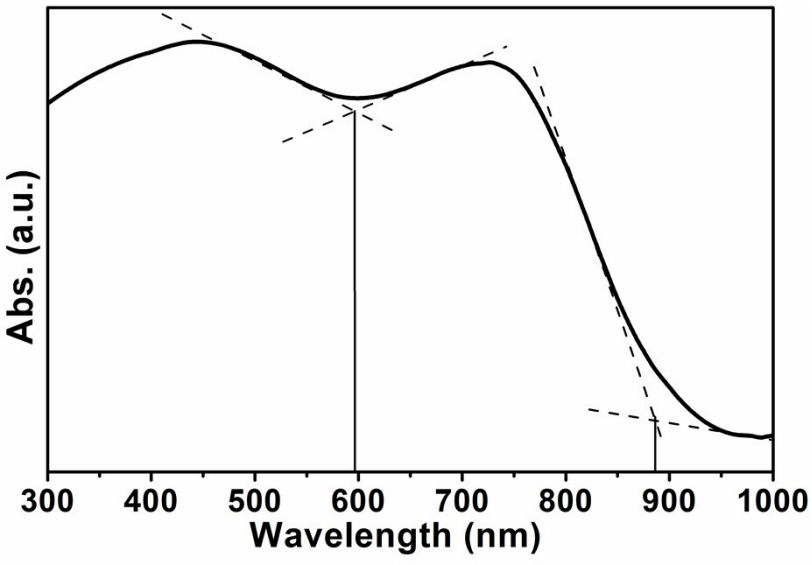

Figure S4. UV-Vis absorption spectra of CoO_x powder.

E_{g1}=1240/599=2.07 eV
E_{g2}=1240/880=1.40 eV

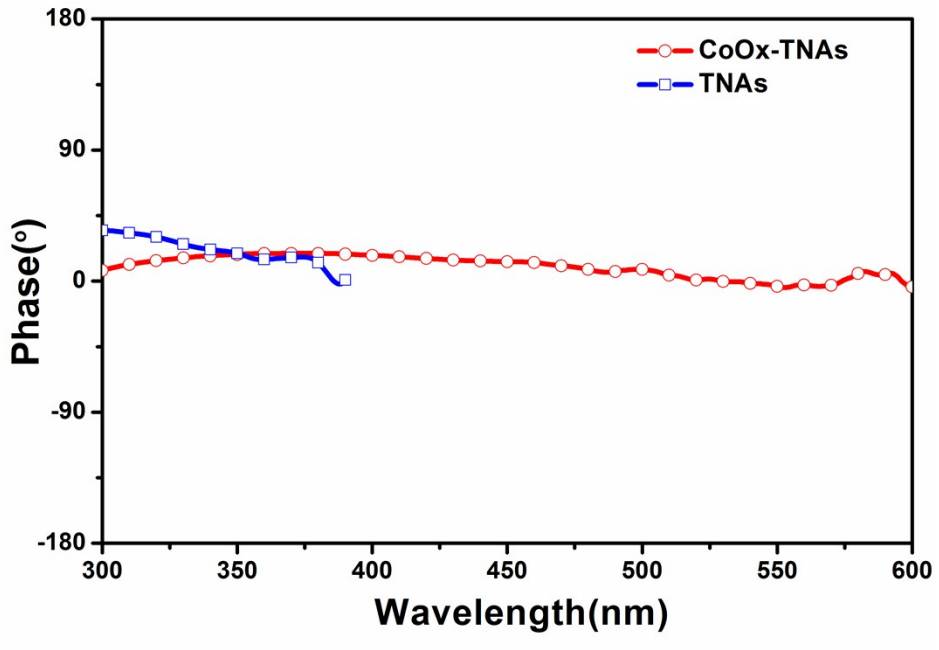

Figure S5. SPV phase spectra of TNAs and CoO_x-TNAs samples.

Butler-Ginley calculation of flat-band potentials
1st Ionization Energy:
Oxygen 13.61806 eV, Cobalt 7.8810 eV, Ti 6.82812 eV

David R. Lide (ed), *CRC Handbook of Chemistry and Physics, 90th Edition*. CRC Press. Boca Raton,Florida, 2010; Section 10, Ionization energies of atoms and atomic ions

Neutral Atoms to +7 Ions

Z	Element	I	II	III	IV	V	VI	VII	VIII
1	H	13.598443							
2	He	24.587387	54.417760						
3	Li	5.391719	75.6400	122.45429					
4	Be	9.32270	18.21114	153.89661	217.71865				
5	B	8.29802	25.1548	37.93064	259.37521	340.22580			
6	C	11.26030	24.3833	47.8878	64.4939	392.087	489.99334		
7	N	14.5341	29.6013	47.44924	77.4735	97.8902	552.0718	667.046	
8	O	13.61805	35.1211	54.9355	77.41353	113.8990	138.1197	739.29	871.4101
9	F	17.4228	34.9708	62.7084	87.1398	114.2428	157.1651	185.186	953.9112
10	Ne	21.56454	40.96296	63.45	97.12	126.21	157.93	207.2759	239.0989
11	Na	5.139076	47.2864	71.6200	98.91	138.40	172.18	208.50	264.25
12	Mg	7.646235	15.03527	80.1437	109.2655	141.27	186.76	225.02	265.96
13	Al	5.985768	18.82855	28.44765	119.992	153.825	190.49	241.76	284.66
14	Si	8.15168	16.34584	33.49302	45.14181	166.767	205.27	246.5	303.54
15	P	10.48669	19.7695	30.2027	51.4439	65.0251	220.421	263.57	309.60
16	S	10.36001	23.33788	34.79	47.222	72.5945	88.0530	280.948	328.75
17	Cl	12.96763	23.8136	39.61	53.4652	67.8	97.03	114.1958	348.28
18	Ar	15.759610	27.62966	40.74	59.81	75.02	91.009	124.323	143.460
19	K	4.3406633	31.63	45.806	60.91	82.66	99.4	117.56	154.88
20	Ca	6.11316	11.87172	50.9131	67.27	84.50	108.78	127.2	147.24
21	Sc	6.56149	12.79977	24.75666	73.4894	91.65	110.68	138.0	158.1
22	Ti	6.82812	13.5755	27.4917	43.2672	99.30	119.53	140.8	170.4
23	V	6.74619	14.618	29.311	46.709	65.2817	128.13	150.6	173.4
24	Cr	6.76651	16.4857	30.96	49.16	69.46	90.6349	160.18	184.7
25	Mn	7.43402	15.6400	33.668	51.2	72.4	95.6	119.203	194.5
26	Fe	7.9024	16.1877	30.652	54.8	75.0	99.1	124.98	151.06
27	Co	7.88101	17.084	33.50	51.3	79.5	102.0	128.9	157.8

Electron Affinity:

Oxygen 1.461 eV，Cobalt 0.662 eV，Titanium 0.079 eV

David R. Lide (ed), CRC Handbook of Chemistry and Physics, 90th Edition. CRC Press. Boca Raton,Florida, 2010; Section 10, Electron affinities

TABLE 1. Atomic Electron Affinities

Atomic number	Atom	Electron affinity in eV	Uncertainty in eV	Method	Ref.
1	H	0.754195	0.000019	LPT	89
		0.75420812	—	calc	205
	D	0.754593	0.000074	LPT	89
	D	0.75465624	—	calc	205
	T	0.75480540	—	calc	205
2	He	not stable	—	calc	1
3	Li	0.618049	0.000020	LPT	185
4	Be	not stable	—	calc	1
5	B	0.279723	0.000025	LPES	191
6	C	1.262119	0.000020	LPT	28
7	N	not stable	—	DA	1
8	O	1.4611096	0.0000007	LPT	4
9	F	3.4011895	0.0000025	LPT	227
10	Ne	not stable	—	calc	1
11	Na	0.547926	0.000025	LPT	1
12	Mg	not stable	—	e-scat	1
13	Al	0.43283	0.00005	LPES	208
14	Si	1.3895220	0.0000024	LPES	227
15	P	0.7465	0.0003	LPT	1
16	S	2.077103	0.000001	LPT	1
17	Cl	3.612724	0.000027	LPT	52
18	Ar	not stable	—	calc	1
19	K	0.50147	0.00010	LPT	1
20	Ca	0.02455	0.00010	LPT	44
21	Sc	0.188	0.020	LPES	1
22	Ti	0.079	0.014	LPES	1
23	V	0.525	0.012	LPES	1
24	Cr	0.666	0.012	LPES	1
25	Mn	not stable	—	calc	1

Atomic number	Atom	Electron affinity in eV	Uncertainty in eV	Method	Ref.
26	Fe	0.151	0.003	LPES	27
27	Co	0.662	0.003	LPES	27

Mulliken Electronegativity for TiO_2 and Co_3O_4

O = (1.461+13.618)/2=7.5395
Co = (0.662+7.881)/2=4.2715
Ti = (0.085+6.828)/2=3.4535

Mulliken Electronegativity for

Co_3O_4 = (7.5395^4*4.2715^3)^(1/7) = 5.9099
TiO_2 = (3.4535*7.5395^2)^(1/3) = 5.8118

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

Co_3O_4: O^{2-} to Co^{2+} 2.07eV; O^{2-} to Co^{3+} 1.4 eV
Co_3O_4=5.91 -4.44+1.6/2=2.27 V for EG 1.4 eV
Co_3O_4=5.91-4.44+2.07/2 = 2.5 V for EG 2.07eV
CB=0.43 eV, VB=2.5 eV, at PZC

TiO_2: 3.2eV
TiO_2 = 5.82-4.44+3.2/2= 3.0 eV
CB=-0.2 eV, VB=3 eV, at PZC

Pzc of Co_3O_4 = 7.3, Elecrrochimica Acta, Vol. 40. No. 16, Pp. 2683 -2686, 1995
Pzc of TiO_2 = 6.2, Thin Solid Films Volume 476, Issue 1, 1 April 2005, Pages 157–161

At pH 7,
TiO_2: (7-6.2)*0.059 = 0.05 V CB = -0.23+0.05=-0.18 V, VB = 3+0.05=3.05 V;
Co_3O_4: (7-7.3)*0.059 = -0.02 V CB = 0.41 V, VB = 2.5 V