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Supporting Information

Defects in black zirconia responsible for solar energy harvesting

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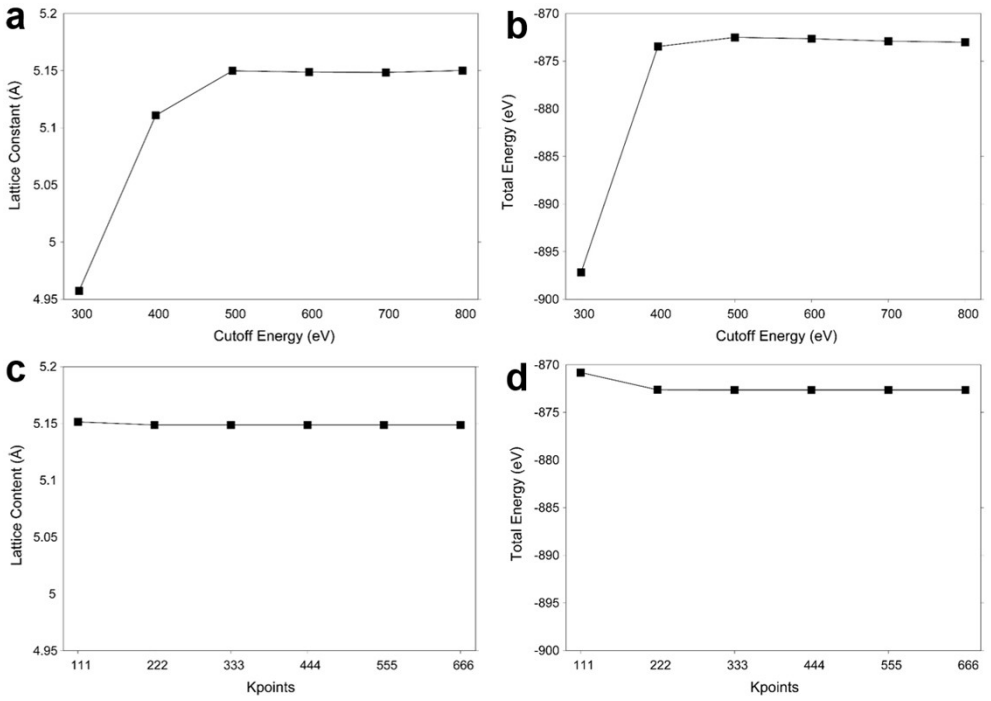

Fig. S1 Initial tests of cutoff energy and K-point mesh for c-ZrO_2 model ($Zr_{32}O_{64}$).

Fig. S2a-c shows the crystal structure of black zirconia (ZrO_2), which has a disordered core and well-regulated shell as reported before[1]. The difference of crystal structure between black and pristine ZrO_2 is observed in Fig. S2. In addition, Fig. 2a and 2b are the high magnifications of the center of Fig. S2d and the core region of Fig. S2b, respectively.

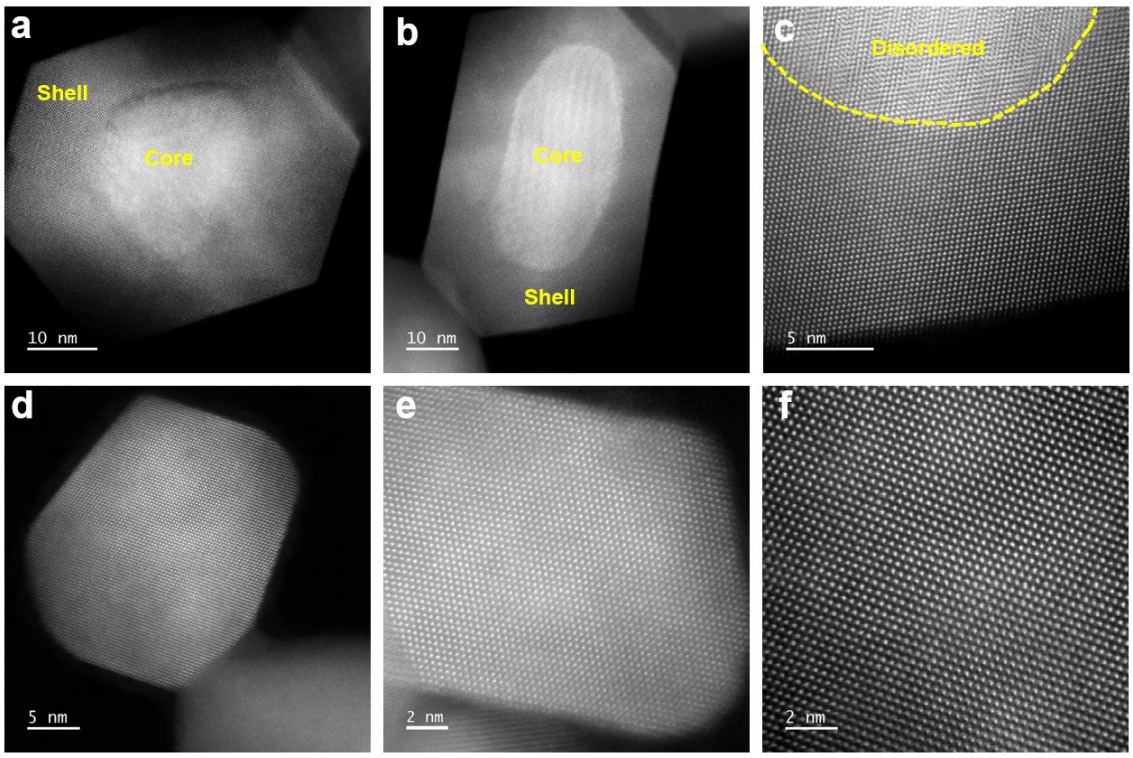

Fig. S2 HAADF-STEM images of (a-c) black and (d-f) pristine ZrO_2.

The calculated band gap of c-ZrO_2 (3.9 eV) is in good agreement with the other reported calculated results[2, 3]. Although it is lower than the experimental value due to the self-interaction error of DFT[4], the DOS results are sufficient to illustrate the electronic properties difference between these defective and defect-free models. Since the color and band gap of ZrO_2 does not change after Y_2O_3 doping (Fig. S3), it can be inferred that the dopant of Y_2O_3 and the resulting oxygen vacancies have no relationship with the darkening of ZrO_2. Thus, to unveil the secret of the darkening of ZrO_2, the Y_2O_3 was not considered in the models and the c-ZrO_2 structure was used to simulate the pristine and black ZrO_2.

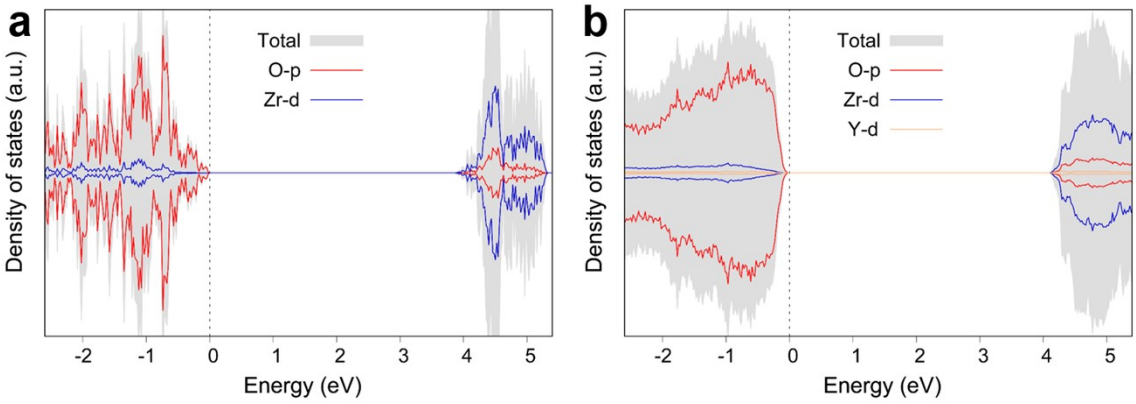

Fig. S3 DOS of (a) the defect-free crystal structure of c-ZrO_2 ($Zr_{32}O_{64}$) and (b) Y_2O_3 stabilized ZrO_2 ($Zr_8Y_4O_{62}$).

To investigate the effect of the point defects distribution in ZrO_2 models on their lattice constant, two groups of I_{Zr} defect model with different concentration was investigated and its lattice constants are shown in Fig. S4 (red square). It can be found that the lattice constants of the models with the same defect concentration differ very little.

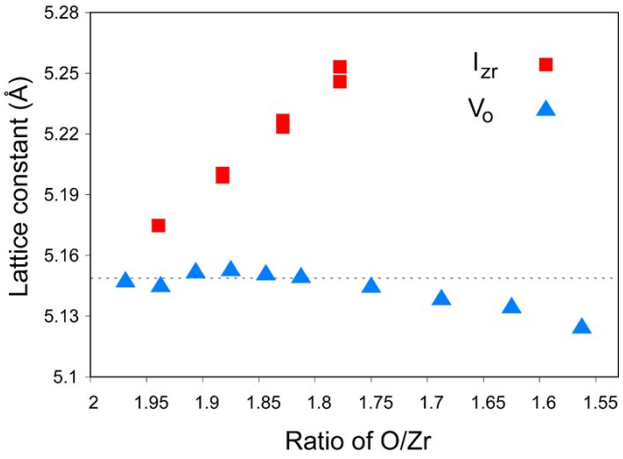

Fig. S4 The lattice constant change of the defective models with different concentrations of I_{Zr} and V_O defect. The models with different distributions of I_{Zr} defects were calculated, and the lattice constant difference induced by defect distribution is negligible compared to the defect concentration.

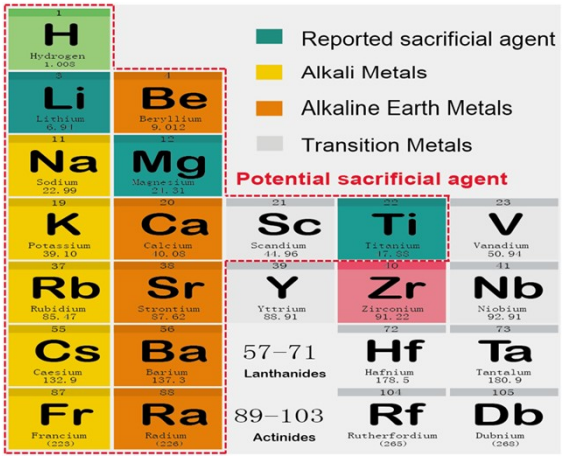

Fig. S5 Potential sacrifice agents for synthesizing black ZrO_2.

Table S1 Calculated Bader charge of prepared models.

Atoms	Defect-free ZrO_2		I_{Zr}-1		V_O-16		V_O-16 & I_{Zr}-1	
	O	Zr	O	Zr	O	Zr	O	Zr
1	7.361241	9.270336	7.370512	9.261482	7.477445	10.56446	7.467343	10.15891
2	7.365571	9.270336	7.339383	9.261482	7.441571	9.964929	7.436387	9.906411
3	7.361675	9.270336	7.339715	9.236227	7.446567	10.52575	7.41839	10.12475
4	7.365699	9.270336	7.377587	9.236227	7.434361	10.0431	7.443392	9.790019
5	7.357281	9.270336	7.339892	9.236227	7.416276	9.30716	7.412109	9.423486
6	7.365699	9.270336	7.377587	9.236227	7.441671	9.72524	7.463237	9.657208
7	7.361993	9.270336	7.379036	9.455619	7.485072	9.770431	7.459132	10.33052
8	7.365889	9.270336	7.387351	9.455625	7.430186	9.66865	7.409264	10.68614
9	7.367861	9.270336	7.410734	9.261477	7.386523	9.561829	7.398658	9.621458
10	7.368421	9.270336	7.387352	9.236222	7.411701	9.880186	7.406547	9.828846
11	7.365022	9.270336	7.374041	9.261477	7.406674	9.973839	7.40149	9.884698
12	7.360004	9.270336	7.411823	9.236222	7.414273	9.984848	7.407429	10.04943
13	7.363837	9.270336	7.376589	9.236222	7.463982	9.751983	7.494509	9.982481
14	7.368231	9.270336	7.411823	9.455619	7.442324	10.20207	7.431226	9.784784
15	7.368792	9.270336	7.406611	9.236222	7.41746	10.19338	7.435899	10.15356
16	7.363837	9.270336	7.377079	9.455619	7.440724	9.857576	7.439886	10.12704
17	7.365138	9.270331	7.396883	9.261477	7.475603	9.932892	7.47305	9.80342
18	7.369289	9.270331	7.387351	9.236222	7.463893	9.435114	7.467217	9.801843
19	7.365201	9.270331	7.364687	9.236222	7.407143	10.1544	7.398853	10.04658
20	7.365635	9.270331	7.40272	9.455619	7.417912	10.38592	7.410178	10.40462
21	7.365329	9.270336	7.364687	9.261477	7.417322	9.760887	7.427529	9.58868
22	7.365889	9.270336	7.40272	9.236222	7.449726	9.489905	7.446502	9.690763
23	7.361368	9.270336	7.394889	9.236222	7.417672	9.665366	7.427479	9.712362
24	7.365826	9.270336	7.364675	9.455619	7.438829	9.560493	7.428275	10.53702
25	7.3639	9.270341	7.382701	9.242856	7.362148	9.834549	7.38273	9.675069
26	7.364958	9.270341	7.351316	9.242856	7.445498	9.753975	7.4542	9.779271
27	7.367924	9.270341	7.35354	9.242856	7.402506	9.528373	7.447412	9.553819

28	7.3639	9.270341	7.38744	9.242856	7.414581	9.705212	7.410098	9.706587
29	7.364027	9.270336	7.35354	9.242856	7.447264	9.994418	7.447382	9.829414
30	7.364895	9.270336	7.386691	9.242856	7.409892	9.859573	7.407542	9.602832
31	7.367797	9.270336	7.392527	9.242856	7.38983	9.751398	7.409167	9.924336
32	7.364091	9.270336	7.387351	9.242856	7.447703	9.529536	7.438187	9.559508
33	7.364768		7.361785	10.64587	7.430527		7.42431	10.58808
34	7.365699		7.395794		7.455454		7.464341	
35	7.365329		7.40163		7.428841		7.418726	
36	7.365699		7.387352		7.440003		7.436171	
37	7.364831		7.395355		7.396863		7.407495	
38	7.361929		7.364198		7.48192		7.504381	
39	7.367628		7.364185		7.382537		7.394395	
40	7.365826		7.40272		7.433483		7.42461	
41	7.363964		7.351806		7.423269		7.42563	
42	7.363964		7.386691		7.397142		7.366038	
43	7.364461		7.382701		7.41479		7.386714	
44	7.364027		7.351559		7.437991		7.449577	
45	7.368051		7.387421		7.445881		7.453142	
46	7.363964		7.387351		7.483926		7.447628	
47	7.362035		7.351794		7.447584		7.459499	
48	7.363964		7.393616		7.418013		7.422703	
49	7.369659		7.361472					
50	7.361305		7.395045					
51	7.365265		7.394889					
52	7.365826		7.364198					
53	7.369659		7.40163					
54	7.365011		7.387352					
55	7.3675		7.366421					
56	7.369723		7.40272					
57	7.360501		7.351806					
58	7.360437		7.386691					
59	7.364207		7.38778					
60	7.363709		7.387351					
61	7.364334		7.382701					
62	7.3639		7.351559					
63	7.362035		7.351971					
64	7.363773		7.393616					

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