HfO_2 nanodots incorporated in TiO_2 and its hydrogenation for High Performance Dye Sensitized Solar Cells

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Electronic Supporting Information (ESI)

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Table S1 Different doping in TiO_2

S. No.	Dopant (doping %)	Band gap (eV)	Solar cell parameters				Ref
			Jsc	Voc	η	FF	
1.	Zr (5) Zr (10)	3.27 3.34	4.5 3.2	0.7 0.72			[1]
2.	Fe_2O_3 (10)	2.51	16.88	0.77	7.27	56	[2]
3.	Nb (0.7) Nb (2.7) Nb (3.5)	3.16 3.12 3.06	14.4 17.7 18	0.76 0.74 0.68	8.0 9.0 8.2	73 69 67	[3]
4.	Zr (4)	2.7	NA	NA	NA	NA	[4]
5.	Nb (2)*	NA	20.4	1.036	16.3	77	[5]
6.	Zr (1)	NA	16.5	.715	8.1	69	[6]
7.	Fe (10)	2.8	NA	NA	NA	NA	[7]
8.	Sr (0.06 M)#	3.08	NA	NA	0.69	NA	[8]
9.	S (0.22)	2.98	NA	NA	NA	NA	[9]
10.	Ce (10)	2.69	NA	NA	NA	NA	[10]
11.	Ce (0.03)	1.678	NA	NA	NA	NA	[11]
12.	Ce (3.5) Nd (1) Pr (3) Sm (2) Gd (2) Eu (2) La (3)	2.70 3.10 3.10 3.15 3.10 3.05 3.15	NA	NA	NA	NA	[12]
13	SiO_2	2.88	NA	NA	NA	NA	[13]
14	Ag	2.7	NA	NA	NA	NA	[14]
15	V_2O_5	2.78	NA	NA	NA	NA	[15]
16	CuO	1.44	NA	NA	NA	NA	[16]

*Perovskite solar cell; # Photoelectrochemical cell

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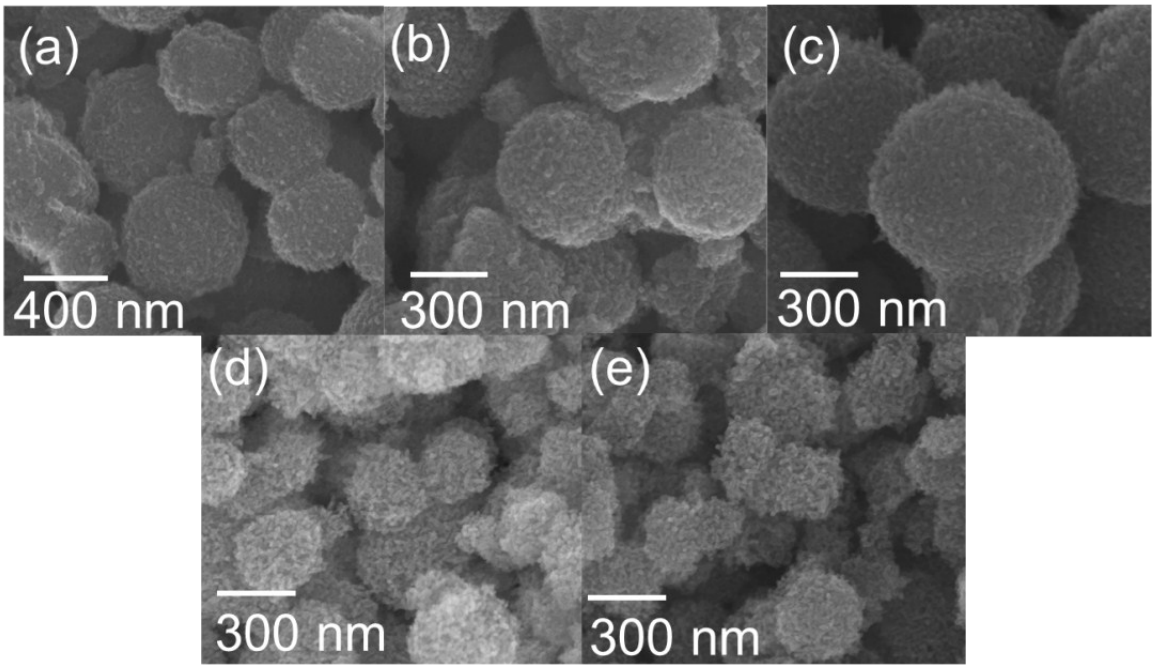

Figure S1 FESEM images of (a) TiO_2 (b) 1% doped HfO_2/TiO_2 (c) 1% doped H-HfO_2/TiO_2 (d) 5% doped HfO_2/TiO_2 and (e) 10% doped HfO_2/TiO_2.

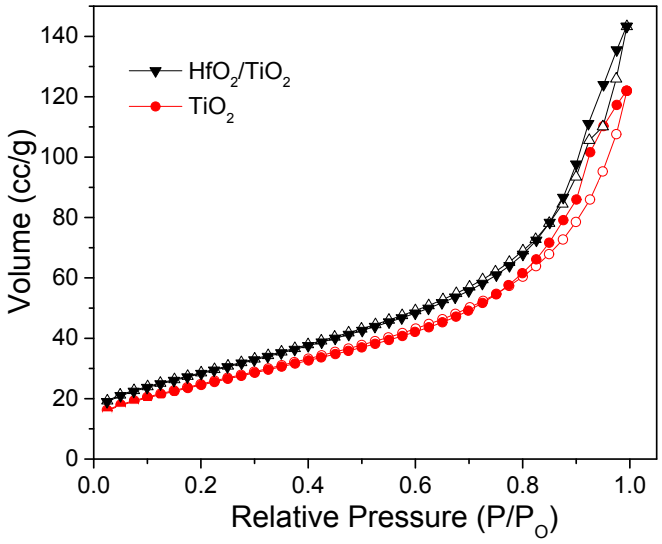

Figure S2 Nitrogen adsorption-desorption isotherms of HfO_2/TiO_2 and TiO_2. The isotherm can be classified as type IV with a hysteresis loop. The surface area of HfO_2/TiO_2 is (103.656 m^2/g) more as compared to TiO_2 (91.08 m^2/g).

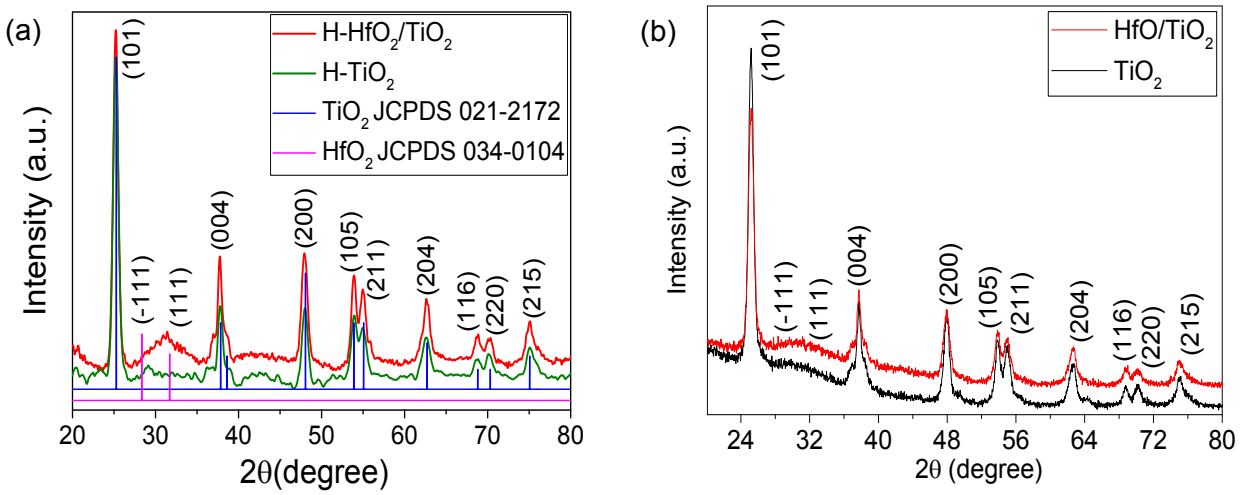

Figure S3 XRD patterns of (a) hydrogenated HfO_2/TiO_2 and TiO_2 and (b) HfO_2/TiO_2 and TiO_2 without hydrogenation.

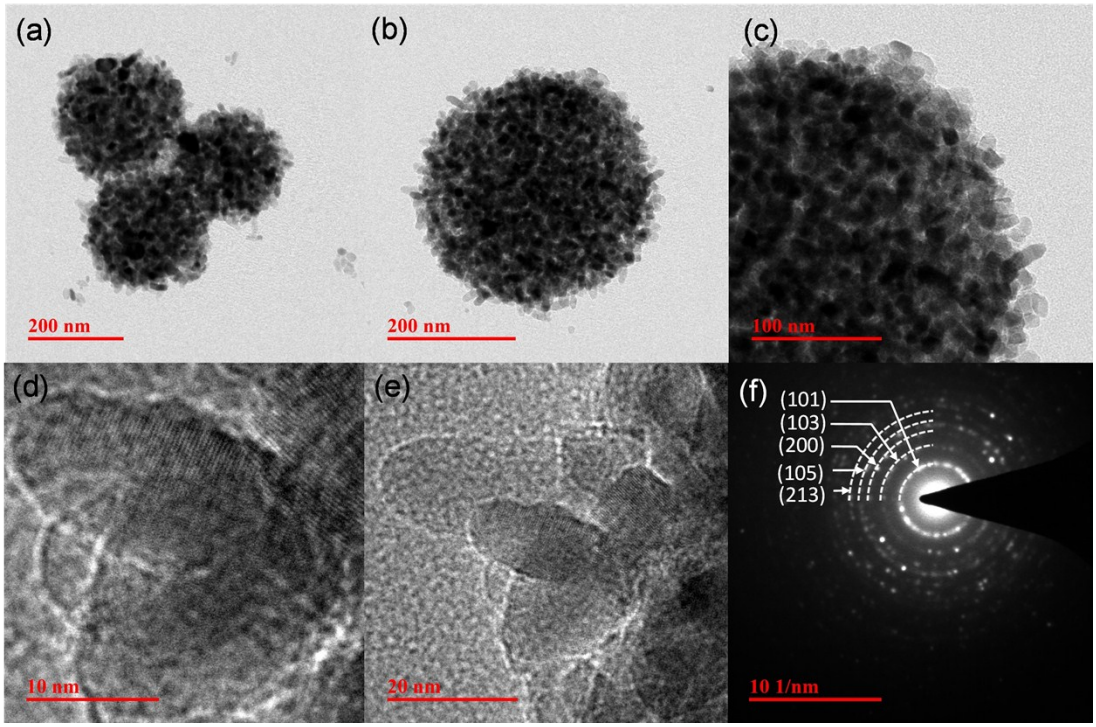

Figure S4: Low and high magnification TEM images (d-e) high resolution TEM and (f) ED pattern of H-TiO_2. It is similar to H-HfO_2/TiO_2 in comparison.

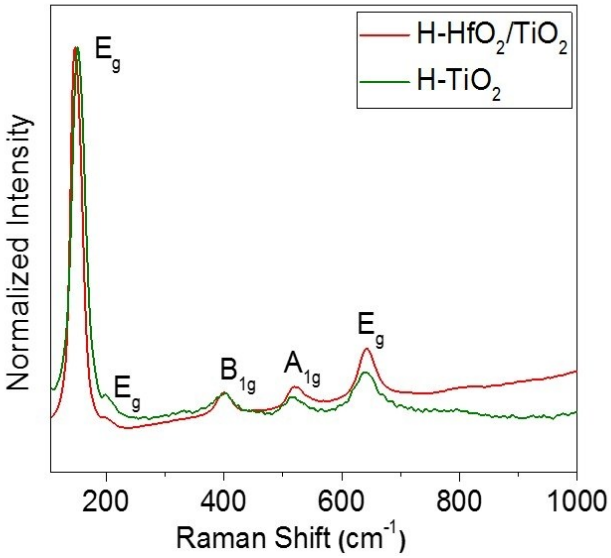

Figure S5 Raman spectra of H-HfO_2/TiO_2 and H-TiO_2.

The Raman spectra of H-HfO_2/TiO_2 and H-TiO_2 correspond to TiO_2 anatase phase with observed peaks at 144,197, 399, 518 and 641 cm^{-1}. These peaks correspond to E_g modes at (144, 192 and 641 cm^{-1}) and B_{1g} and A_{1g} modes at 399 and 518 cm^{-1} respectively.[1] The highly intense peak of E_g arising at 146 cm^{-1} in the lower wavenumber indicates long range ordering in the nanocrystal.[2,3] The shift in the stretching mode of E_g peak from 146 to 151 cm^{-1}, is attributed to the induced defects and possible disorientation in the lattice structure upon HfO_2 doping in H-TiO_2. The E_g, A_{1g} and B_g peaks are due to the symmetric stretching, symmetric bending and antisymmetric bending vibrations of O-Ti-O.[4]

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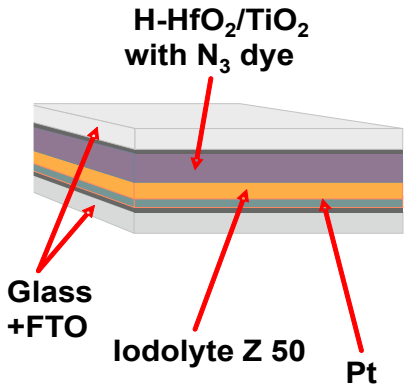

Figure S6 A schematic showing sandwich model of the fabricated DSSC device.

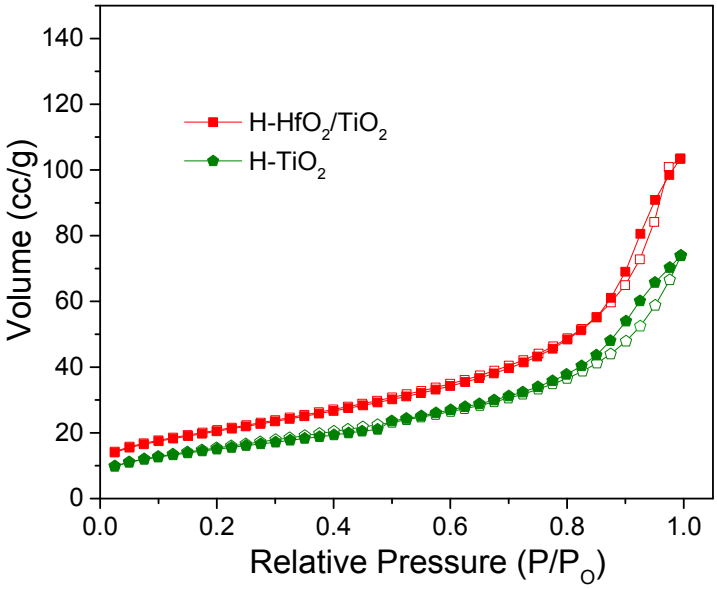

Figure S7 Nitrogen adsorption-desorption isotherms of H-HfO_2/TiO_2 and H-TiO_2. The isotherm can be classified as type-IV with a hysteresis loop. The surface area of H-HfO_2/TiO_2 is (74.21m^2/g) more as compared to H-TiO_2 (56.186 m^2/g).

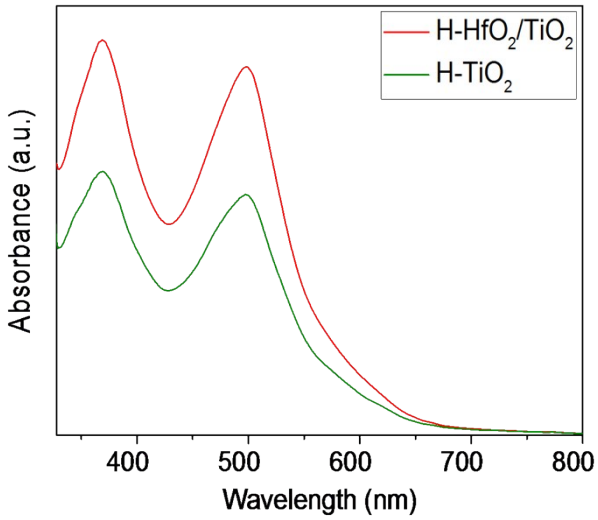

Figure S8 Absorbance spectra of the dye deloaded from H-HfO_2/TiO_2 and H-TiO_2 photoanode.

Calculation for dye loading capacity

Concentration of dye absorbed

1. H-HfO_2/TiO_2 = 10.1×10^{-9} mol cm^{-2}
2. H-TiO_2 = 6.55×10^{-9} mol cm^{-2}

Molar extinction coefficient (ε) for N3 dye at 500 nm is 1.45×10^{4} cm^{-1}.

From Beer Lambert's law, A = εlc where l and c are the length of the cuvette (1 cm) and concentration of the dye respectively.

For H-HfO_2/TiO_2, A = 0.147 (found from the graph)

Thus, concentration of dye absorbed = 1.01×10^{-5} M or 10.1×10^{-9} mol cm^{-2}

For H-TiO_2, A = 0.095 (found from the graph)

Thus, concentration of dye absorbed = 6.55×10^{-6}M or 6.55×10^{-9} mol cm^{-2}

Table S2 EIS performance results of the DSSC based on H-HfO_2-TiO_2 and H-TiO_2.[a]

Photoanode for DSSC	R_s (Ω)	R_1 (Ω)	C_1 (μF)	f_{max} (Hz)	$\tau_n=(R_1*C_1)$ (ms)	η_c (%)
H-HfO_2/TiO_2	19.63	14.35	9.898	19.54	0.142	42.23
H-TiO_2	17.5	13.3	4.247	29.10	0.056	43.18

[a] R_s is series resistance, R_1 is charge transfer resistance, C_1 is chemical capacitance, τ_n is electron lifetime, and η_c is charge collection efficiency.