Supporting information

Photoelectrochemical-driven nitrogen reduction to ammonia by V_o-SnO_2/TiO_2 composite electrode

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Table. S1 Resistance and CPE values of the corresponding models for the sample of TiO_2 SnO_2/TiO_2 and V_o-SnO_2/TiO_2 nanorod arrays at different solvothermal times.

Catalysts	Rs(Ω)	*CPE*1		R_1(Ω)	*CPE*2		R_{ct}(Ω)
		Q_1(F)	n_1(F)		Q_2(F)	n_2(μF)	
TiO_2	31.32	$1.03*10^{-5}$	0.84	130.08	$1.36*10^{-4}$	0.68	5370
SnO_2-8/TiO_2	30.26	$3.41*10^{-4}$	0.80	35.52	$2.61*10^{-4}$	0.80	4130
SnO_2-16/TiO_2	31.61	$1.55*10^{-4}$	0.85	93.11	$1.94*10^{-4}$	0.68	3171
SnO_2-24/TiO_2	31.11	$2.85*10^{-4}$	0.84	88.78	$2.72*10^{-4}$	0.73	3683
V_o-SnO_2-8/TiO_2	30.7	$2.51*10^{-4}$	0.70	2753	$3.15*10^{-5}$	0.83	2631
V_o-SnO_2-16/TiO_2	29.36	$4.51*10^{-4}$	0.73	3927	$3.81*10^{-5}$	0.68	1321
V_o-SnO_2-24/TiO_2	33.44	$1.41*10^{-3}$	0.39	3362	$3.32*10^{-3}$	1.00	1872

Table. S2 Comparison of the catalytic performance of V_o-SnO_2-16/TiO_2 with other PEC and PC nitrogen fixing catalysts

Photoelectro-catalysts	Light Source	Electrolyte	NH_3 Yield （$\mu g \cdot cm^{-2} h^{-1}$）	Faraday efficiency	References
V_o-SnO_2-16/TiO_2	300 W Xe lamp, 100 mW cm^{-2}	N_2-saturated 0.1 M Na_2SO_4	19.41	59.6	This work
Bi_2S_3/MoS_2	300 W Xe lamp,	N_2-saturated 0.1 M Na_2SO_4	18.5	33.2	[1]
SnO_2/MoS_2	100 mW cm^{-2}	N_2-saturated 0.1 M Na_2SO_4	19.6	40.3	[2]
BiOI-O_v	100 mW cm^{-2}	N_2-saturated H_2O	2.38	/	[3]
Ag/black Si	300 W Xe lamp, 100 mW cm^{-2}	N_2-saturated 0.1 M Na_2SO_4	48.79	40.6	[4]
Au/black Si	300 W Xe lamp,	N_2-saturated 150 p.p.m Na_2SO_4	1.33		[5]
TiO_2/Au/a-TiO_2	300 W Xe lamp 100 mW cm^{-2}	N_2-saturated H_2O	0.228	/	[6]
O_v-TiO_2	400 W Hg lamp	N_2-saturated H_2O	0.189		[7]

RT: room temperature; AP: atmospheric pressure

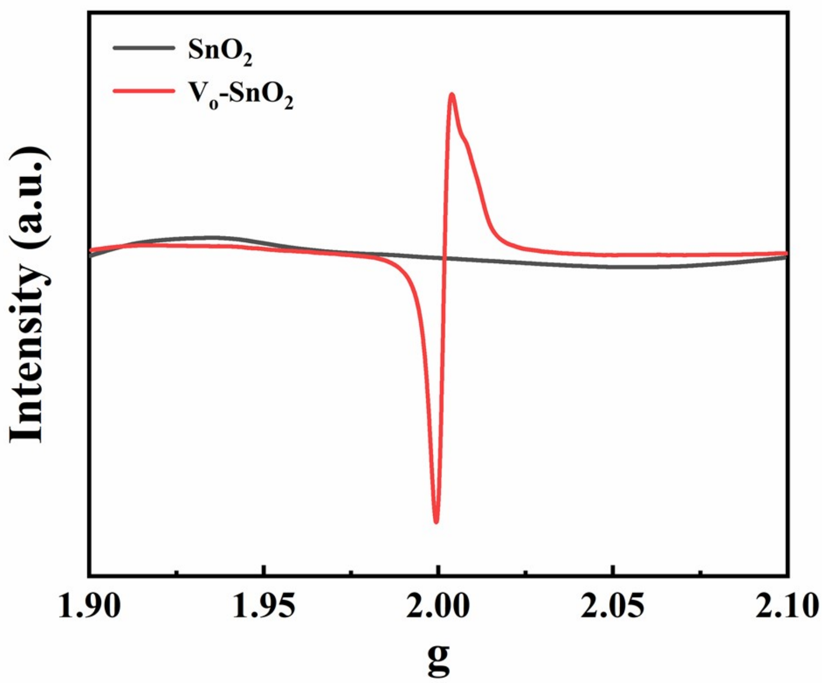

Fig. S1 EPR spectrum of SnO_2 quantum dot before and after high temperature annealing at low temperature of 90 K.

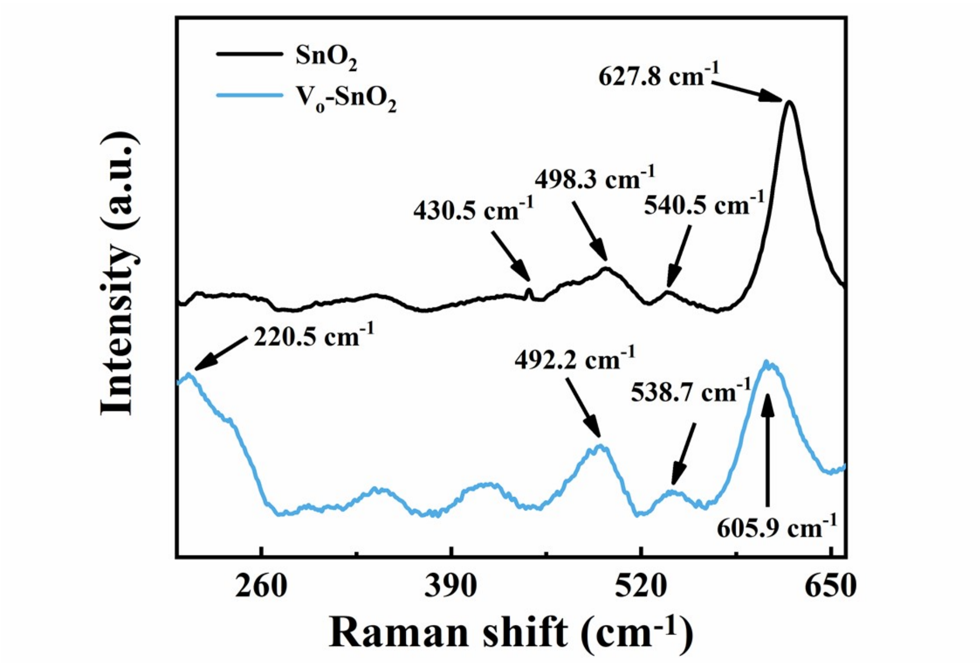

Fig. S2 Raman spectra of SnO_2 and V_o-SnO_2.

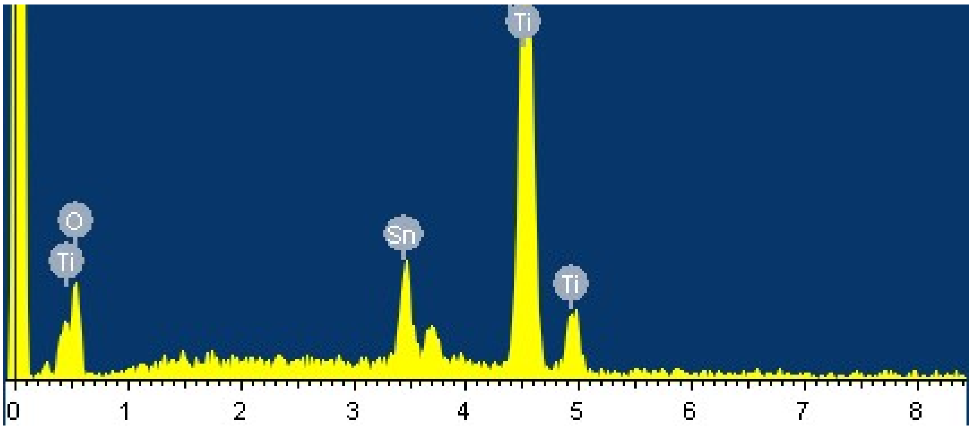

Fig. S3 EDX spectrum of V_o-SnO_2-16/TiO_2.

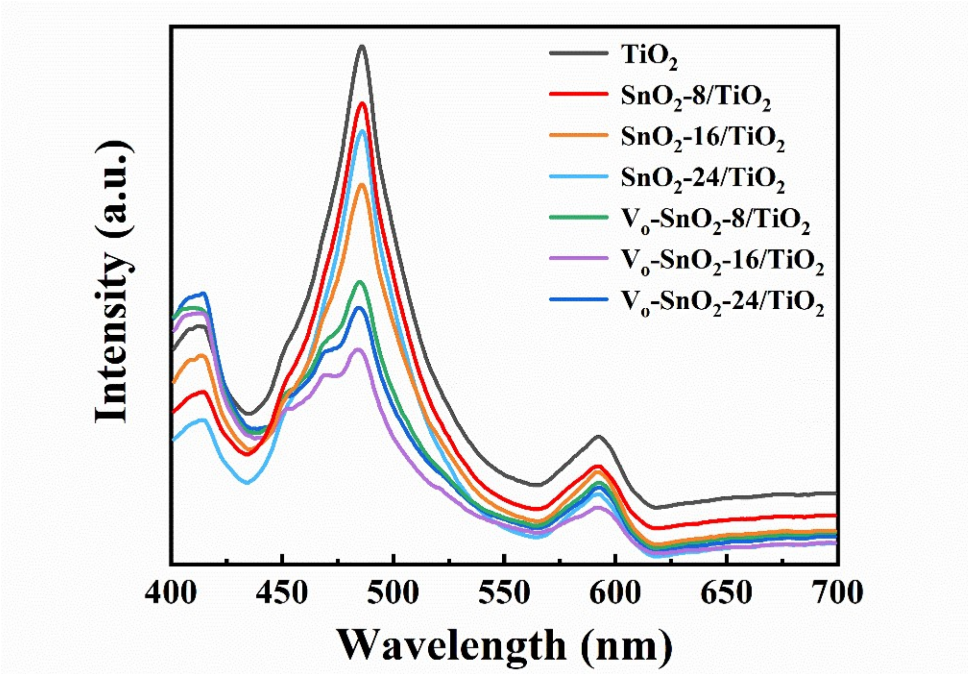

Fig. S4 Room-temperature steady-state PL spectrum of TiO_2, SnO_2/TiO_2 and V_o-SnO_2/TiO_2.

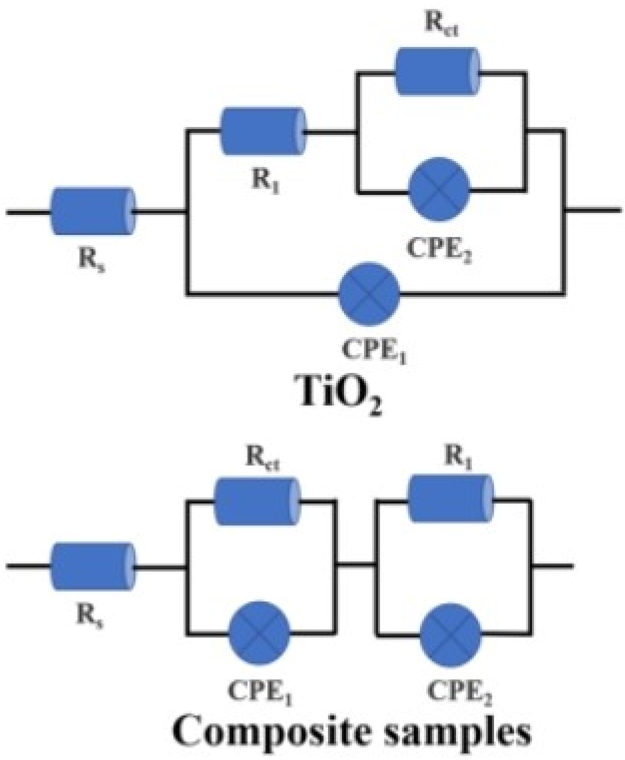

Fig. S5 Analog circuit diagram of TiO_2 and composite samples.

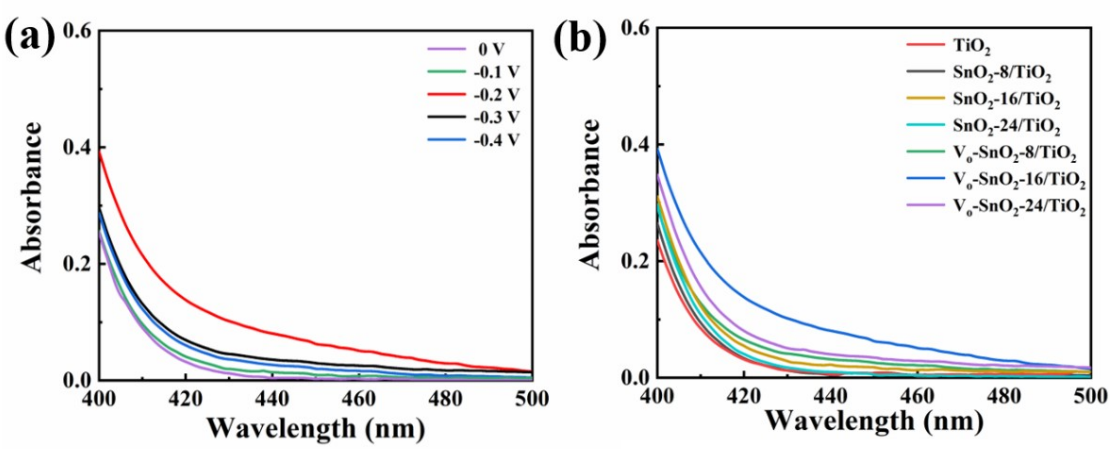

Fig. S6 Ultraviolet-visible absorption spectra of (a) V_o-SnO_2-16/TiO_2 at different potentials and (b) TiO_2, SnO_2/TiO_2 and V_o-SnO_2/TiO_2 at -0.2 V determined by Nessler's reagent.

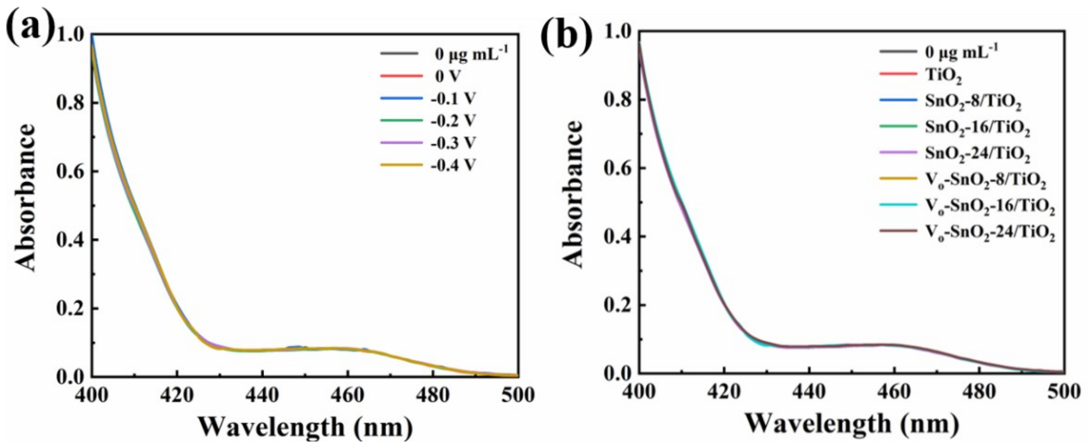

Fig. S7 Ultraviolet-visible absorption spectra of (a) V_o-SnO_2-16/TiO_2 at different potentials and (b) TiO_2, SnO_2/TiO_2 and V_o-SnO_2/TiO_2 at -0.2 V determined by Watt-Chrisp method.

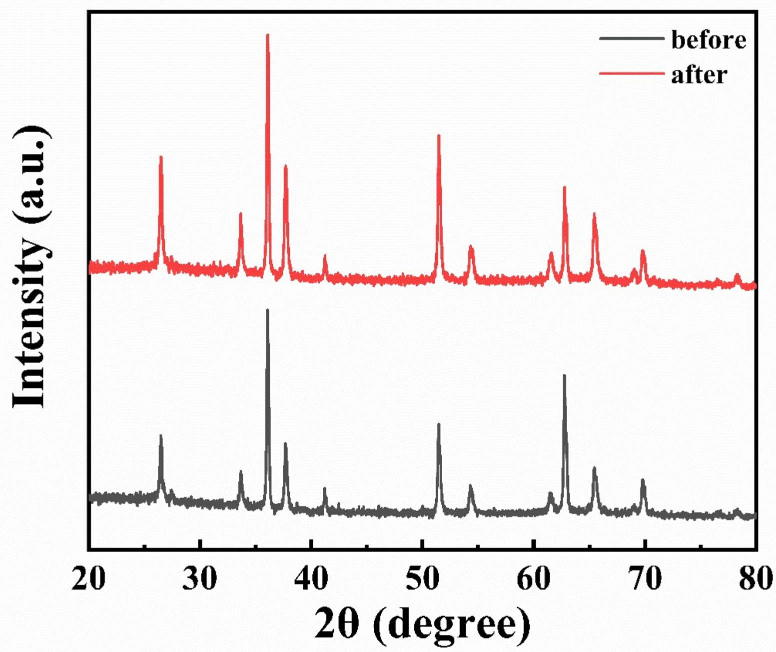

Fig.S8 XRD pattern of V_o-SnO_2/TiO_2 before and after 5 nitrogen fixation cycles.

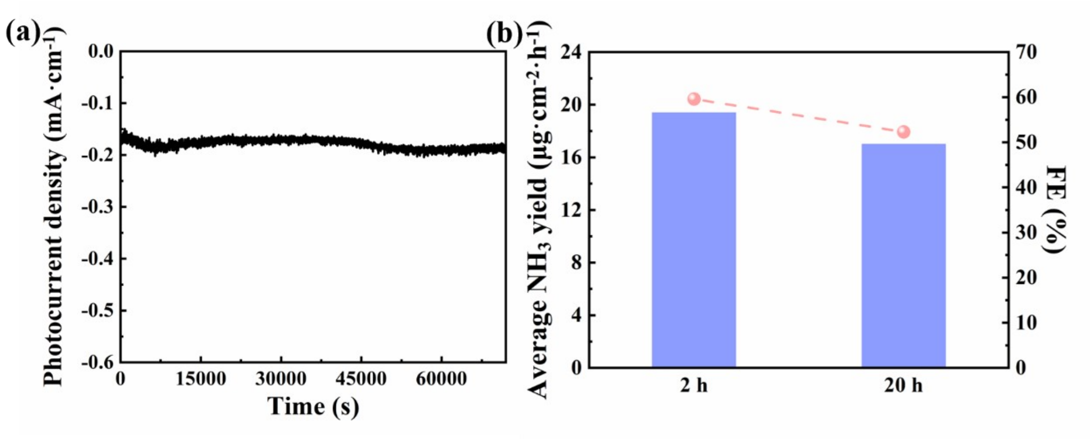

Fig. S9 (a) Chronoamperometry curve of V_o-SnO_2-16/TiO_2 electrolysis for 20 h at -0.2 V potential; (b) Ammonia yield and Faraday efficiency of electrolysis for 2 h and 20 h.

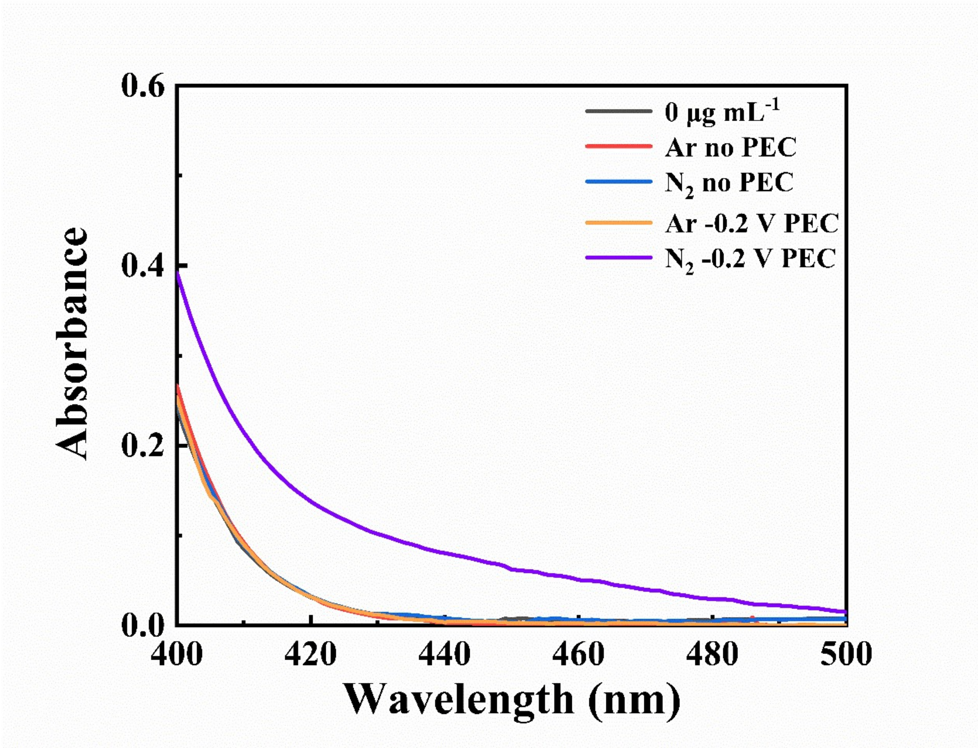

Fig. S10 Ultraviolet -visible absorption spectra of V_o-SnO_2-16/TiO_2 before and after electrolysis under different atmospheres.

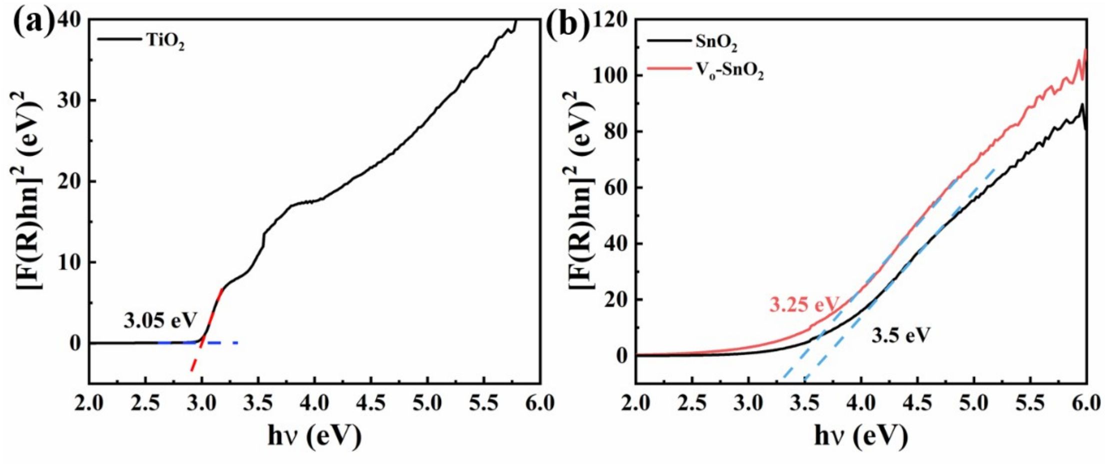

Fig. S11 The band gap of (a) TiO_2 nanorods and (b) SnO_2 and V_o-SnO_2 quantum dots.

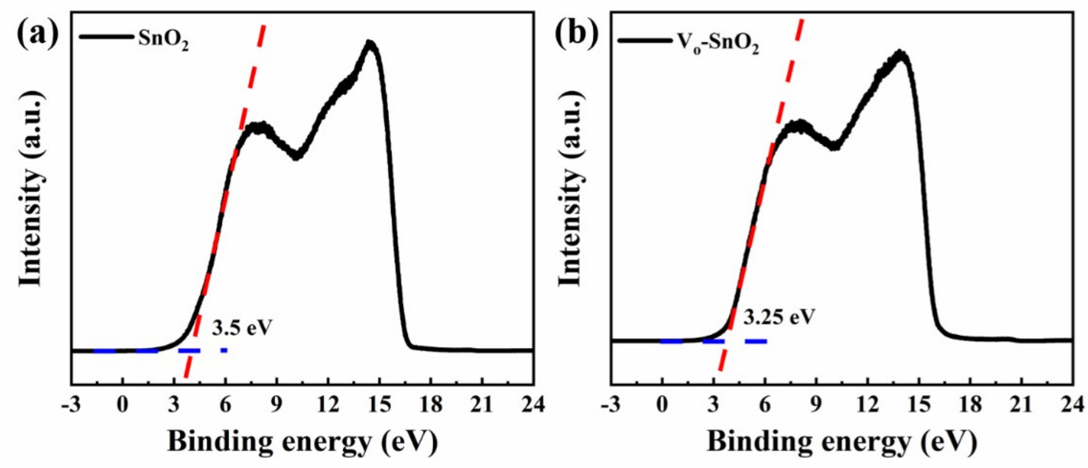

Fig. S12 UPS spectrum of (a) SnO_2 quantum dots, (b) V_o-SnO_2 quantum dots.

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