Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

In-situ Growth of Porous TiO_2 with Controllable Oxygen Vacancies at Atomic Scale for Highly Efficient Photocatalytic Water Splitting

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Table S1 Lattice information and grain size of as-prepared TiO_2 from XRD Rietveld refinement

samples	a=b (Å)	c (Å)	Grain size (nm)
Ti-5-O-0.1	3.803 (1)	9.611 (8)	18.1
Ti-1-O-0.1	3.805 (7)	9.614 (5)	17.9
Ti-0.1-O-0.1	3.810 (0)	9.613 (5)	18.0
Ti-0.1-O-1	3.826 (8)	9.648 (2)	18.4
Ti-0.1-O-5	3.836 (2)	9.677 (3)	18.0

The XRD Rietveld refinement implied the lattice constant of porous TiO_2 decreased from 3.836 and 9.677 Å to 3.803 and 9.611 Å with the ratio of Ti and O precursors' pulse time increase. This change trend of TiO_2 lattice originated from the lack of O atom and introduction of oxygen vacancies. The lattice relaxation due to the lack of O atom would strength the Ti-O bond, thus lead to the shrinkage of TiO_2 lattice. Meanwhile, the grain size of all as-prepared TiO_2 materials had negligible difference, indicating the same phase change under deposition and calcining process.

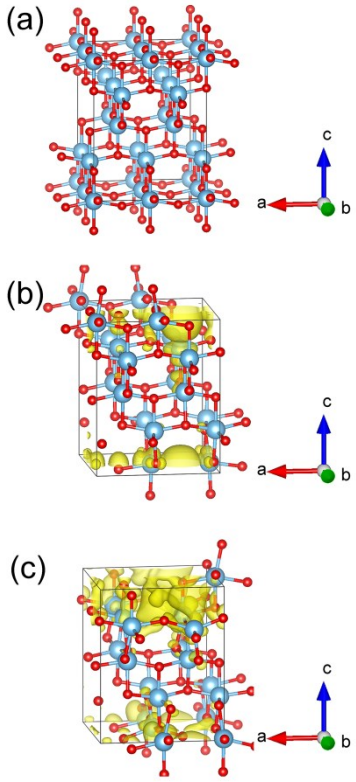

Figure S1 The partial charge density at conduction band edge of (a) perfect anatase TiO_2 crystal, (b) TiO_2 crystal with an oxygen vacancy and (c) TiO_2 crystal with two oxygen vacancies. The red and cyan spheres represent O and Ti atoms, respectively.

Figure S1 revealed that the electrons at conduction band edge accelerated at vicinity of oxygen vacancies. The introduced oxygen vacancies would promote the electrons-holes separation and transfer.

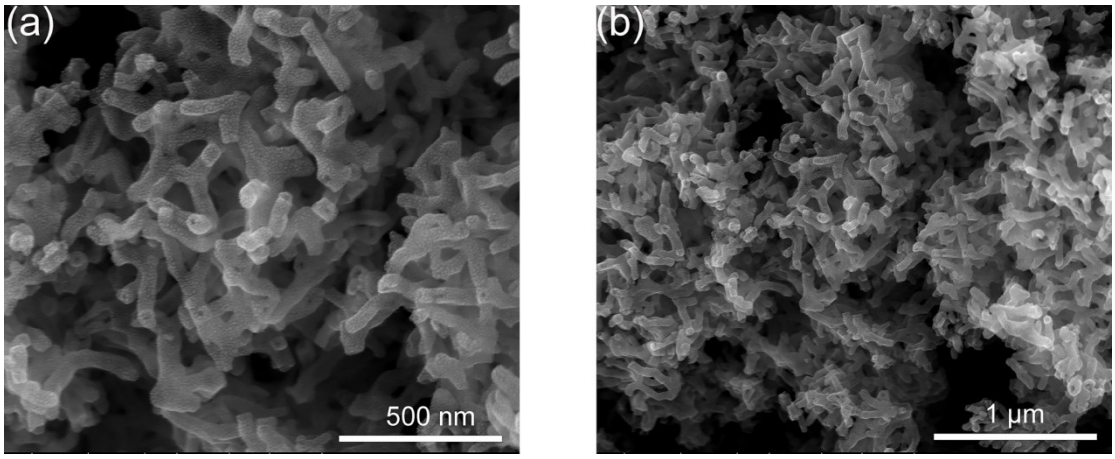

Figure S2 the SEM images of Ti-5-O-0.1

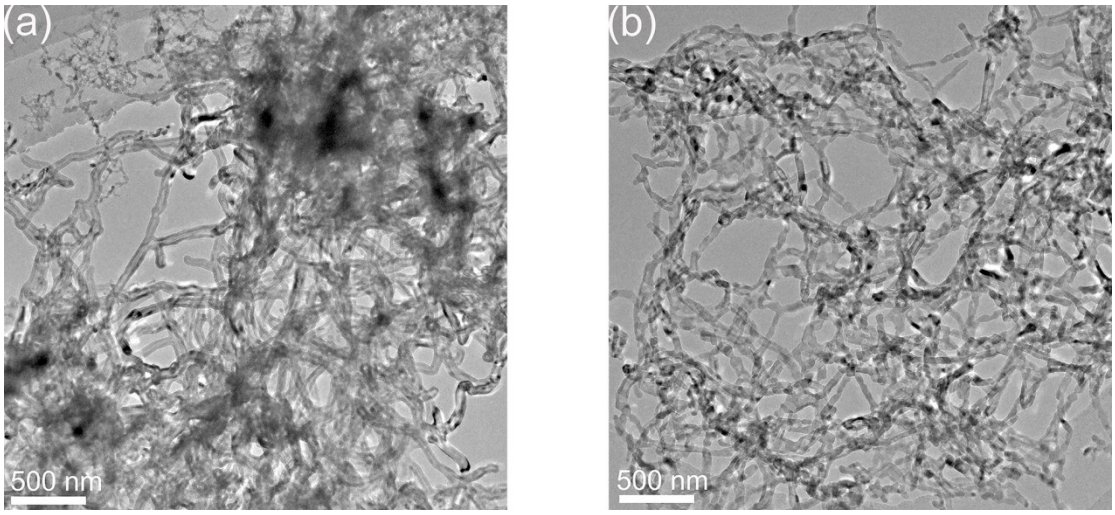

Figure S3 the low- magnification TEM images of Ti-5- O-0.1 (a) and Ti-0.1-O-5 (b)

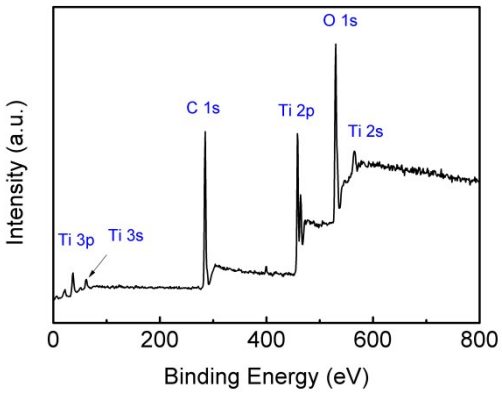

Figure S4 the XPS survey of Ti-5-O-0.1 sample

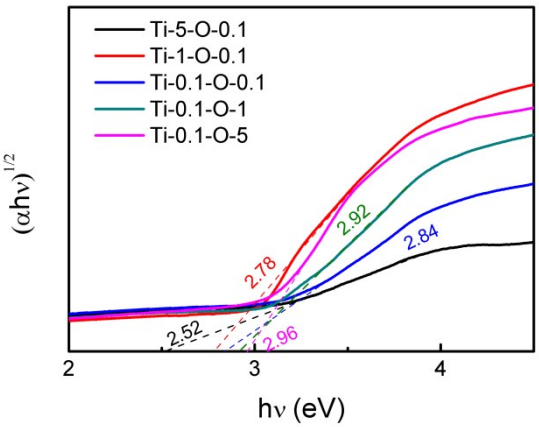

Figure S5 The tauc plots of five as-prepared porous TiO_2 from the UV-Vis diffuse reflectance spectra.

The band gap Eg estimated from the optical measurement showed a blue shift trend with the increase of oxygen vacancies. Based on theoretical calculation, the introduction of oxygen vacancy would bring in new defect level and shift the defect level to valence band, resulting in the narrowed TiO_2 band gap.

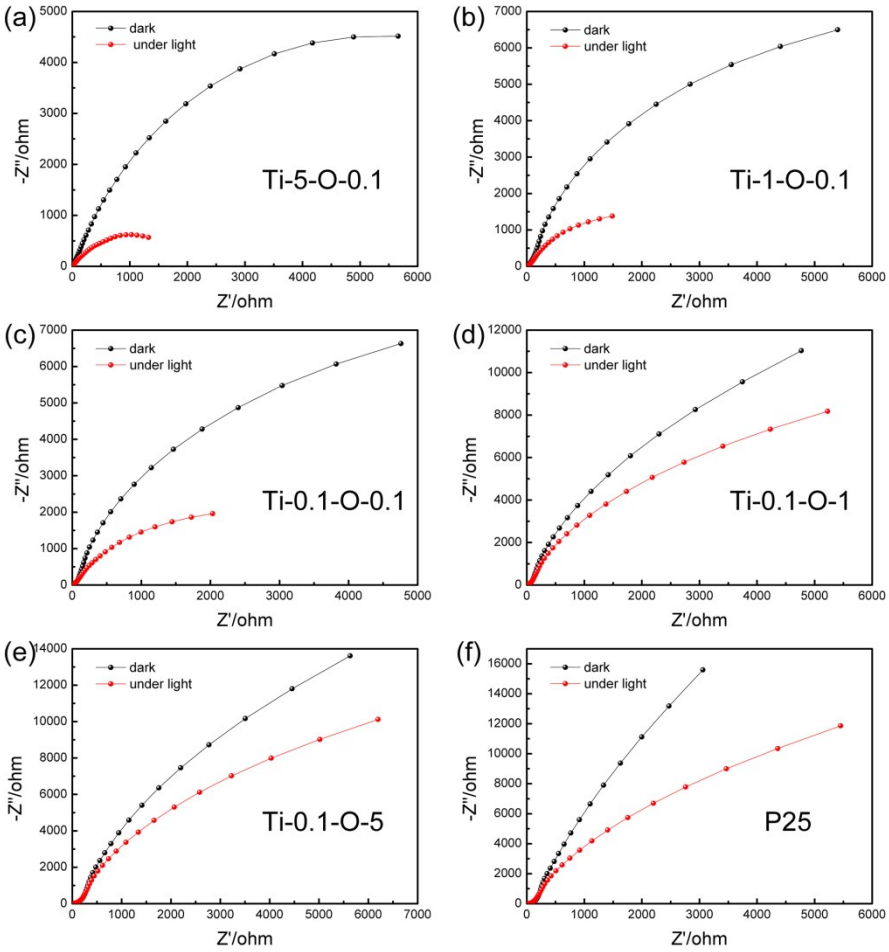

Figure S6 EIS curves under light on/off of five porous TiO_2 materials and commercial P25

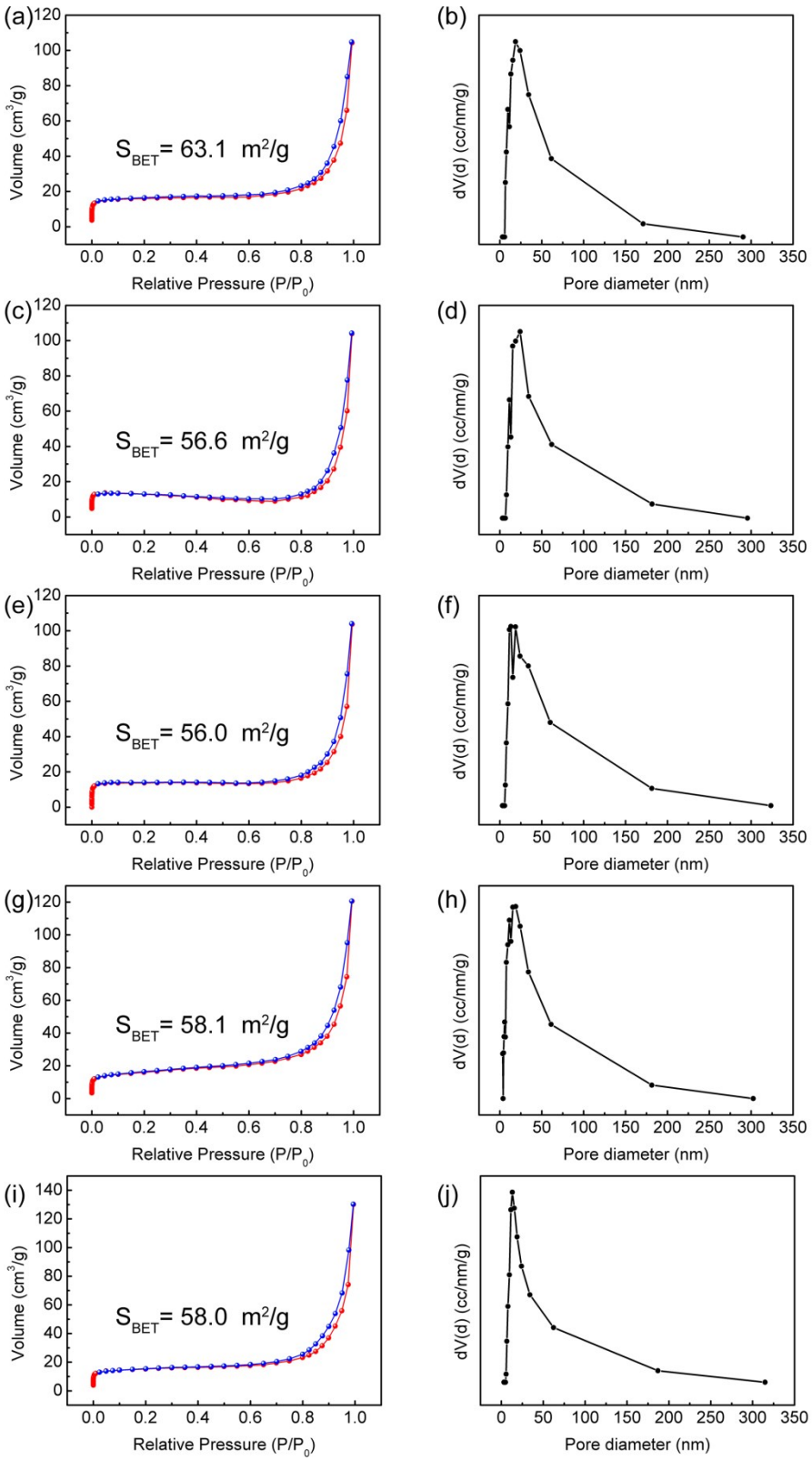

Figure S7 the N_2 absorption/desorption isotherm curves and relevant BJH pore size distribution of Ti-5-O-0.1 (a-b), Ti-1-O-0.1(c-d), Ti-0.1-O-0.1(e-f), Ti-0.1-O-1(g-h) and Ti-0.1-O-5(i-j), respectively.

The pore size distribution curves showed that all samples possessed almost similar pore structure with the main pore at 18-22 nm.

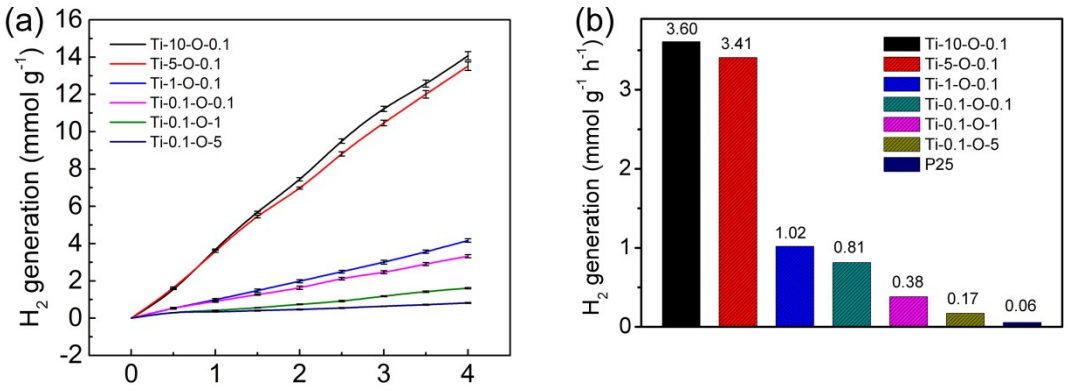

Figure S8 The photocatalytic H_2 generation rate diagram of six porous TiO_2 and commercial P25

We prepared six different porous TiO_2 materials with varying precursors' pulse time. From photocatalytic H_2 generation measurement, there was minor difference between Ti-10-O-0.1 and Ti-5-O-0.1 compared with other four TiO_2 materials. This indicated that further increase of Ti precursor's pulse time had limited influence on concentration of oxygen vacancies and photocatalytic property. Based on that, we chose the Ti-5-O-0.1 sample as the Vo abundant TiO_2 in whole experiments.