

Supporting information

F, Ca co-doped TiO₂ Nanocrystals with Enhanced Photocatalytic Activity

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Experimental

1. Catalyst Preparation

Calcium nitrate and titanium powder (99.99%) were slowly added into hydrofluoric acid aqueous solution (1M) and stirred at room temperature for 10 h. The molar ratio of Ca and Ti is 0, 0.005, 0.02, 0.05, 0.1, 0.12, 0.15, 0.2. The obtained liquor was transferred into PTFE container and kept at 473K for 24-48 h. The last obtained precipitate was washed with deionized water until neutral and dried in the oven (85 °C) overnight.

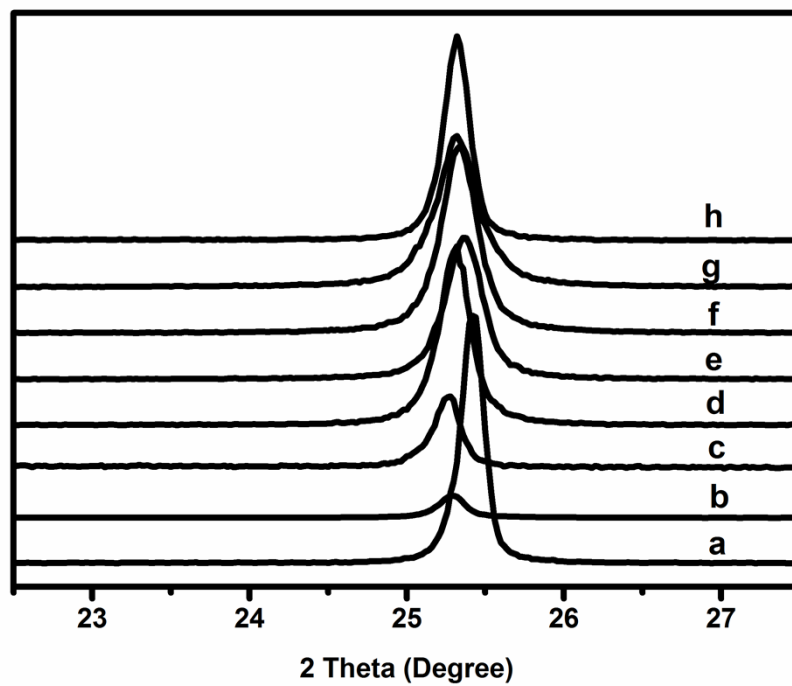
2. Catalyst Characterization

Crystal structure patterns of the doped TiO₂ powder samples were characterized using X-ray diffraction (XRD, D/max-2550 with CuK_α radiation) and transmission electronic micrograph (TEM, JEM-3010, operated at 300 KV). The images of TiO₂ materials nanoparticles were characterized using emission electronic micrograph (SEM, JSM-6700). The content of the elements in the sample was analyzed by EDAX (INSPECT F FEG-SEM). Optical property was characterized using UV-visible diffuse reflectance spectra (Lambda 20). Surface electronic states were analyzed using x-ray photoelectron

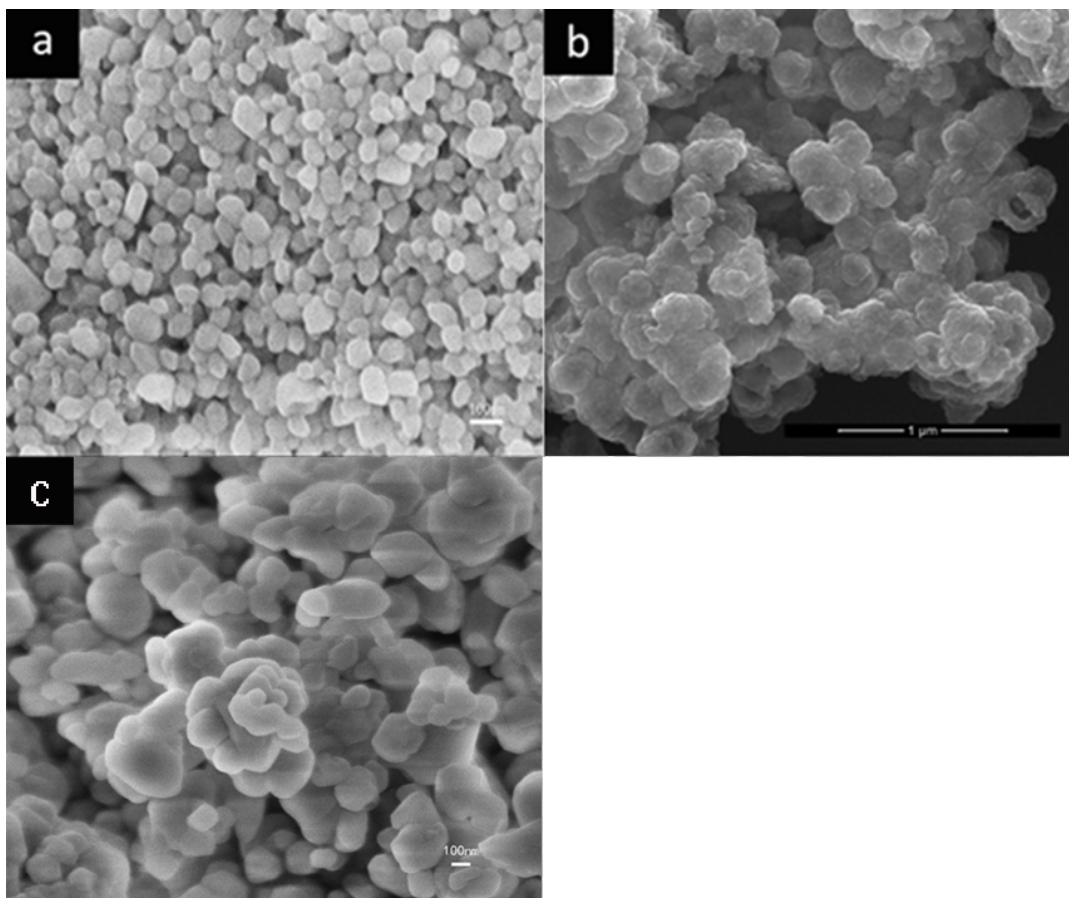
spectroscopy (XPS, ESCALAB250) using contaminant carbon (C1S = 284.6 eV) as referenced binding energy. FT-IR spectra were recorded using a FT-IR spectrometer (IFS 66v/S).

3. *Photocatalytic Activity Test*

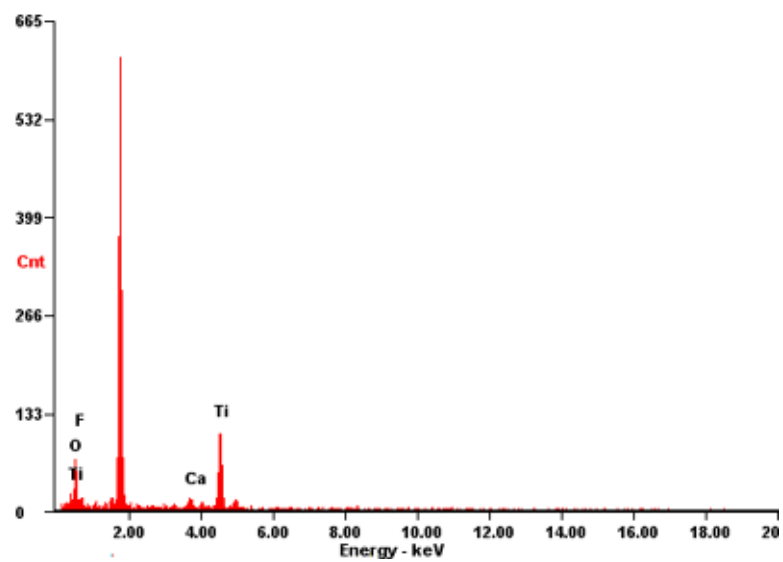
The photocatalytic activities of the photocatalysts were performed at room temperature in a glass reactor fitted with a Xe lamp (300 W). A 420 nm cut-on filter can be used to ensure that only visible light illuminated the photocatalyst. The reaction liquid was prepared by mixing 0.5 g photocatalysts and 100 ml rhodamine B aqueous solution (10 mg/L). Then the suspension was stirred in the dark for 30 min to reach adsorption–adsorption equilibrium before irradiation. Then it was irradiated under visible light or broader-band UV-vis irradiation. 8 ml of suspension was withdrawn from the irradiated solution at preset time intervals and centrifuged to separate the photocatalyst particles, and then the supernatants were analyzed by UV-vis spectrophotometer (UV-2450).



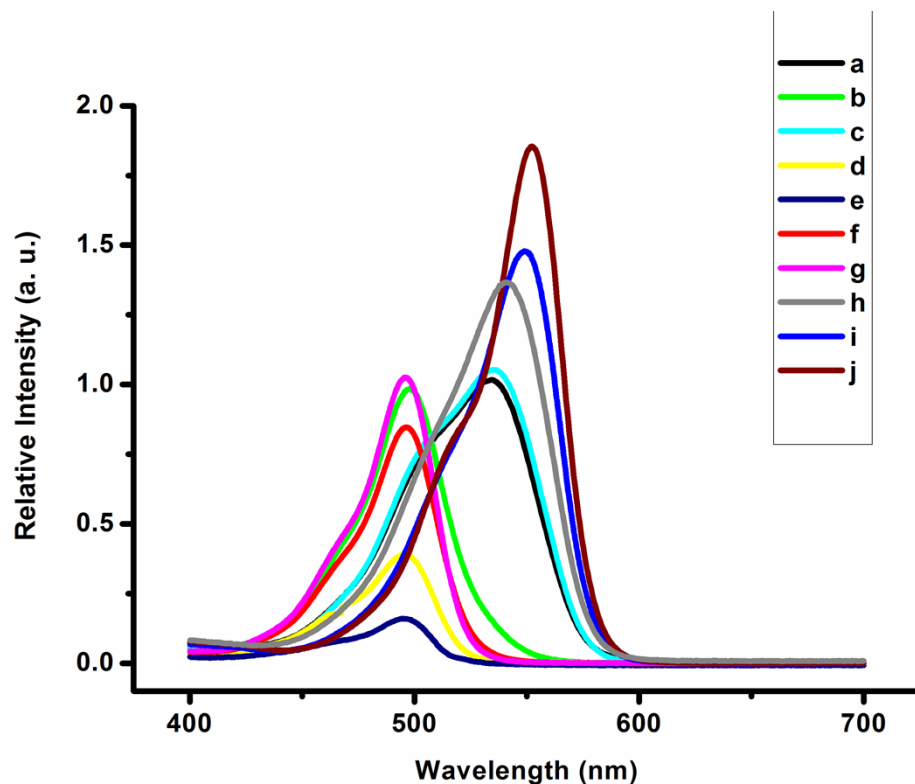
S-Fig. 1 Enlarged view of the A(101) (Fig. 1) diffraction region (22.5-27.5°).



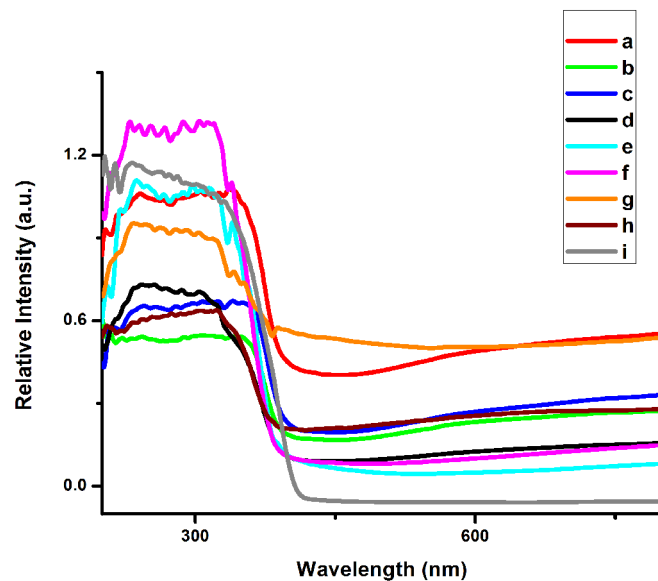
S-Fig. 2 SEM images: (a) F-TiO₂ nanocrystals, (b) 10 atom % Ca doped F-TiO₂ nanocrystals, (c) pure CaF₂.



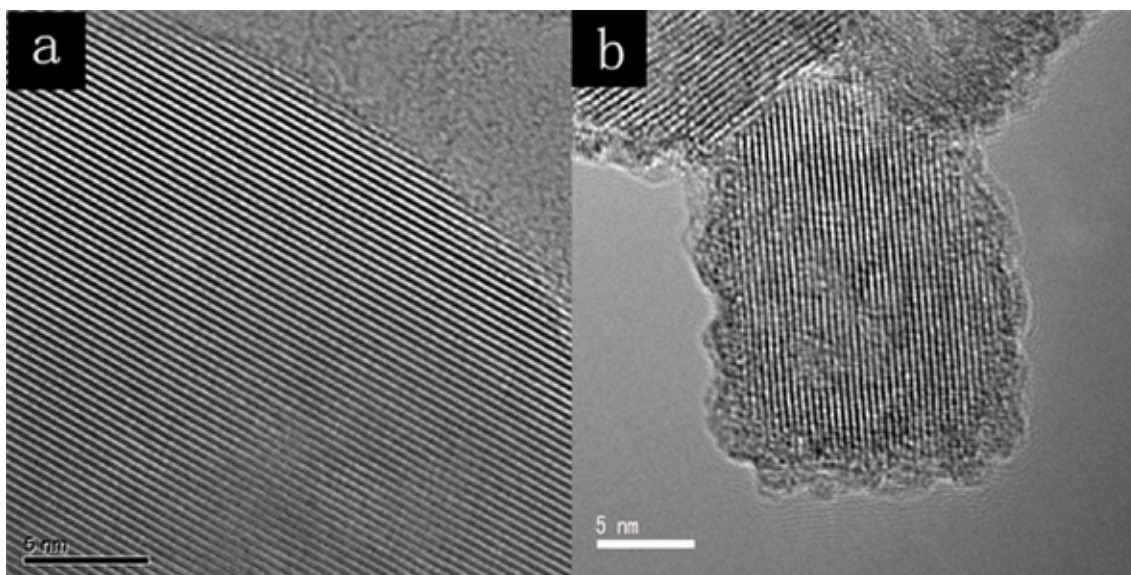
S-Fig. 3 EDX of 10 atom % Ca doped F-TiO₂ nanocrystals.



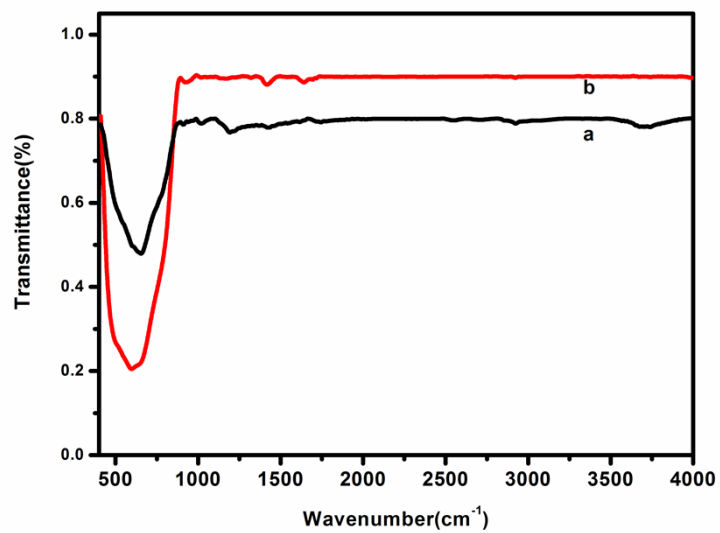
S-Fig. 4 Absorption spectra of a solution of RhB (10 mg/L, 100 ml) at room temperature in the presence of (a) F-TiO₂, (b) 0.5 atom% Ca doped F-TiO₂, (c) 2 atom % Ca doped F-TiO₂, (d) 5 atom % Ca doped F-TiO₂, (e) 10 atom % Ca doped F-TiO₂, (f) 12 atom % Ca doped F-TiO₂, (g) 15 atom % Ca doped F-TiO₂, (h) 20 atom % Ca doped F-TiO₂, (i) P25, (j) without any photocatalyst under visible light for 100 min.



S-Fig. 5 UV-vis absorbance spectra of (a) F-TiO₂, (b) 0.5 atom % Ca doped F-TiO₂, (c) 2 atom % Ca doped F-TiO₂, (d) 5 atom % Ca doped F-TiO₂, (e) 10 atom % Ca doped F-TiO₂, (f) 12 atom % Ca doped F-TiO₂, (g) 15 atom % Ca doped F-TiO₂, (h) 20 atom % Ca doped F-TiO₂, (i) P25.



S-Fig. 6 TEM images: high-resolution TEM: (a) F-TiO₂ nanocrystals, (b) 10 atom % Ca doped F-TiO₂ nanocrystals.



S-Fig. 7 FT-IR spectra of (a) F-TiO₂ nanocrystals, (b) 10 atom % Ca doped F-TiO₂ nanocrystals.

S-Table 1. The calculated lattice parameters of (a) TiO₂, (b) F-TiO₂ nanoparticles, (c) 0.5 atom % Ca doped F-TiO₂, (d) 2 atom % Ca doped F-TiO₂, (e) 5 atom % Ca doped F-TiO₂, (f) 10 atom % Ca doped F-TiO₂, (g) 12 atom % Ca doped F-TiO₂, (h) 15 atom % Ca doped F-TiO₂, (i) 20 atom % Ca doped F- TiO₂.

Sample	a (Å)	b (Å)	c (Å)	cell volume (Å ³)
a	3.785	3.785	9.514	136.30
b	3.783	3.783	9.494	135.85
c	3.791	3.791	9.511	136.72
d	3.791	3.791	9.511	136.69
e	3.792	3.792	9.498	136.57
f	3.792	3.792	9.499	136.56
g	3.790	3.790	9.491	136.33
h	3.792	3.792	9.494	136.5
i	3.790	3.790	9.500	136.44

S-Table 2. The (101) interplanar distance of (a) F-TiO₂ nanoparticles, (b) 0.5 atom % Ca doped F-TiO₂, (c) 2 atom % Ca doped F-TiO₂, (d) 5 atom % Ca doped F-TiO₂, (e) 10 atom % Ca doped F-TiO₂, (f) 12 atom % Ca doped F-TiO₂, (g) 15 atom % Ca doped F-TiO₂, (h) 20 atom % Ca doped F- TiO₂.

Sample	a	b	c	d	e	f	g	h
(101) Interplanar distance ^[a] [nm]	0.1754	0.1806	0.1807	0.1802	0.1800	0.1803	0.1804	0.1803

[a] The (101) interplanar distance was calculated from the diffraction angle.

S-Table 3. Content of the elements in all the samples analyzed by EDX measurement.

sample(Ca/Ti)	O	F	Ti	Ca
2 %	67.73	2.46	29.44	0.37
5 %	66.08	5.40	27.90	0.62
10 %	64.36	9.01	24.91	1.73
12 %	67.46	8.01	22.35	2.18
15 %	65.58	8.81	22.79	2.82
20 %	52.81	9.79	32.95	4.44