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Supporting Information

B-site modified photoferroic Cr^{3+}-doped barium titanate nanoparticles: microwave-assisted hydrothermal synthesis, photocatalytic and electrochemical properties

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Misconception of band gap narrowing

The defect chemistry has long been established as a practical way of extending the absorption cross-section of a material through doping. In principle, the atoms of the dopant create localized defect states, which often introduce intermediate electronic levels within the forbidden gap of the host lattice. These localized states can also be referred to as the charge transfer centers of the dopant atom. Depending on the electronic states of the dopant atom, the conduction band (CB) or the valence band (VB) can be populated with electrons or holes respectively by thermal or optical excitation [1]. At all times, for moderate doping, the band gap remains a generic property of the host lattice. The dopants however may introduce substantial absorption peak below the band gap [2] broadened into bands due to the strong electron-phonon coupling in perovskites. This is illustrated in **Fig. S1** illustrating the fundamental absorption, the presence of a broad absorption band partially overlapping with the fundamental absorption as a possible result of the Frank-Condon principle. The sum of both absorptions representing the net observable absorption signature of the doped

material is also depicted. The experimental configuration for almost all absorption experiments is based on transmission experiments where absorbance is calculated from the loss of optical transmittance. For strong optical absorption, the detectors will operate near or within the noise level thus imposing an upper limit for the detectable absorbance (indicated by a dotted horizontal line). The observable absorption edge has now red-shifted with respect to the fundamental absorption and it is thus a common misinterpretation that the bandgap itself has shrinked. The value of the band gap corresponds to the Fourier-component of the crystal potential (textbook knowledge) and any modification of the corresponding fundamental absorption requires extremely high doping levels that eventually alter the host lattice.

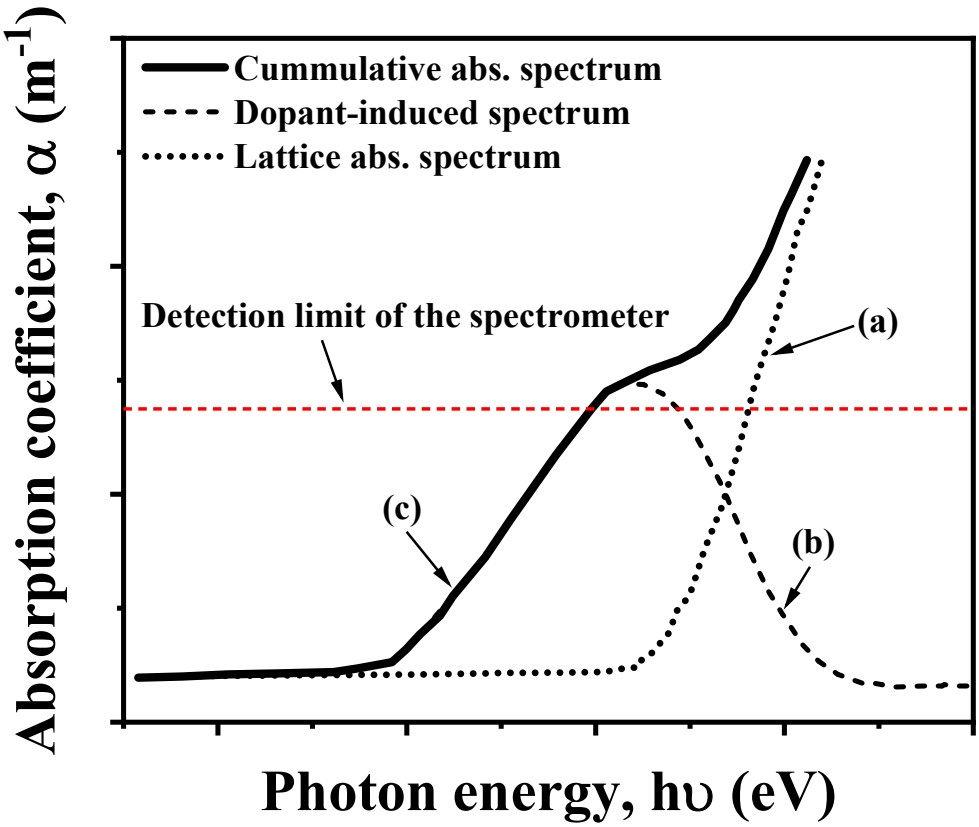

Fig. S1: The optical absorption spectra indicating (a) the absorption edge of the host lattice (b) the extra absorption introduced by the dopant, and (c) the cumulative spectrum obtained from the spectrometer.

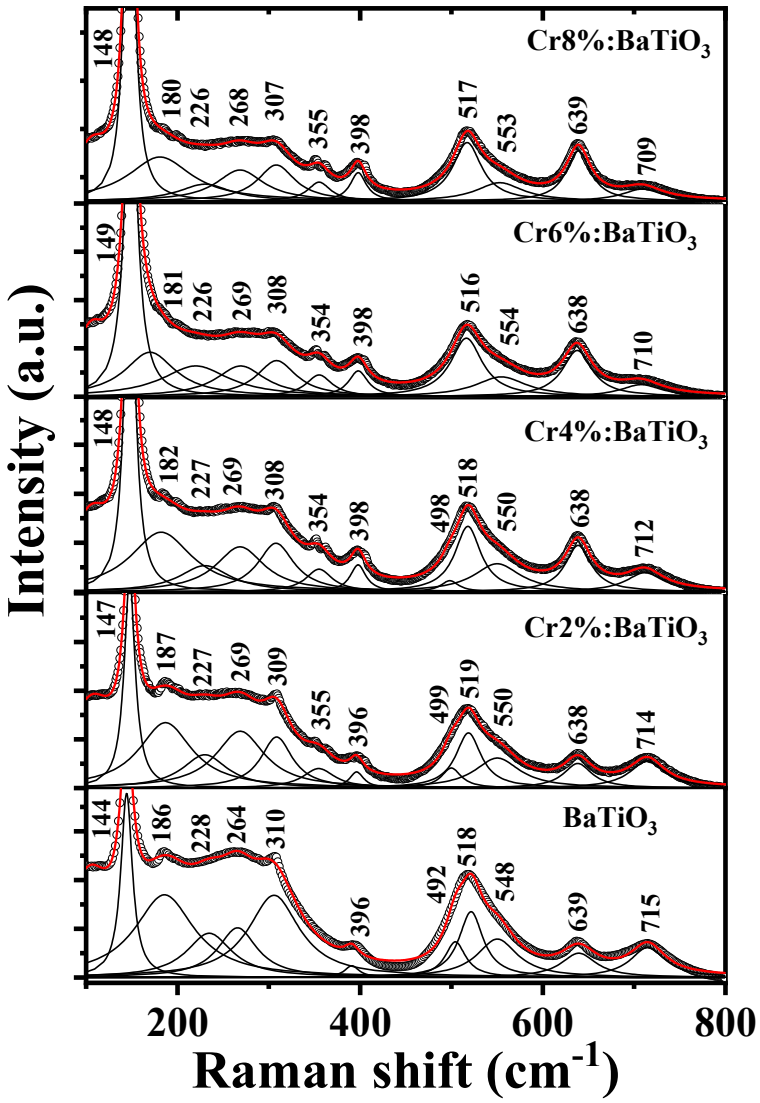

Fig. S2: A Lorentzian peak fit of the Raman spectra for the samples with different Cr compositions.

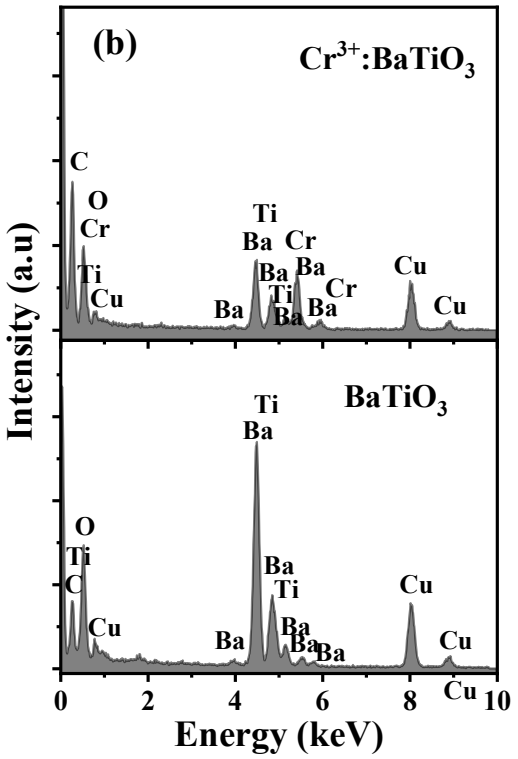

Fig. S3: The EDX spectra of the undoped and 4 mol.% Cr^{3+}-doped $BaTiO_3$ sample.

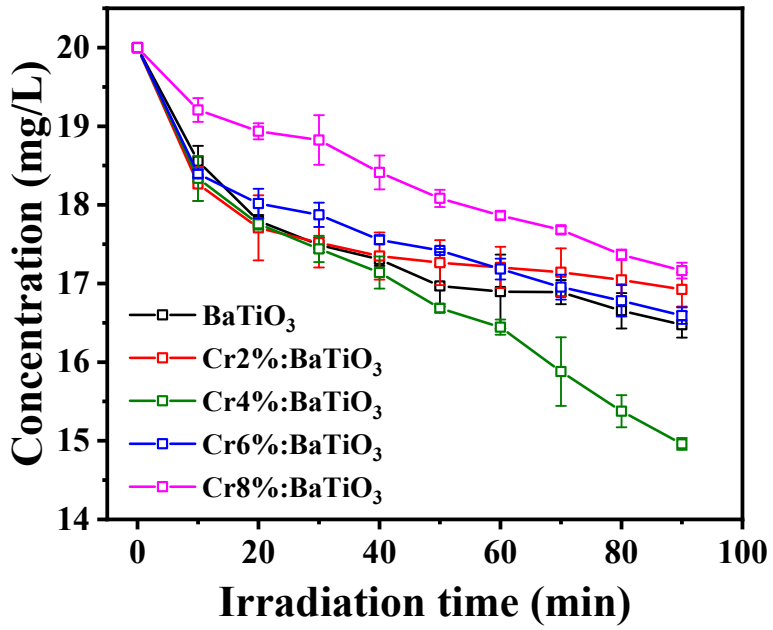

Fig. S4: The adsorption capacity of undoped and doped photoferroic samples after 90 min in the dark.

Table S1: Comparison of degradation efficiency for different photocatalysts.

Photocatalyst	Additive amount (mg)	Organic dye used	Degradation concentration (mg L^{-1})	Degradation rate (%)	Irradiation time (min)	Light source
This study	50	Methyl orange	20	~87	90	Simulated sunlight*
Cr^{3+}-TiO_2	60	XRG	100	~76/71	60/420	UV/Visible [3]
N-$BaTiO_3$	300	RhB	10	~48	240	Visible [4]
$BaTiO_3$	600	Humic acid	10	~99	120	UV [5]
TiO_2/$BaTiO_3$	-	Methylene blue	10	~72	180	UV [6]
$BaTiO_3$	500	Crystal violet	10	~99	2880	UV [7]
Fe_2O_3/$BaTiO_3$	150	RhB	10	~95	120	Simulated sunlight [8]
Hermin/ $BaTiO_3$	300	4-Chloro-phenol	-	~92	150	Visible [9]
$BaTiO_3$	50	Methyl blue	5	~50	50	Simulated sunlight [10]

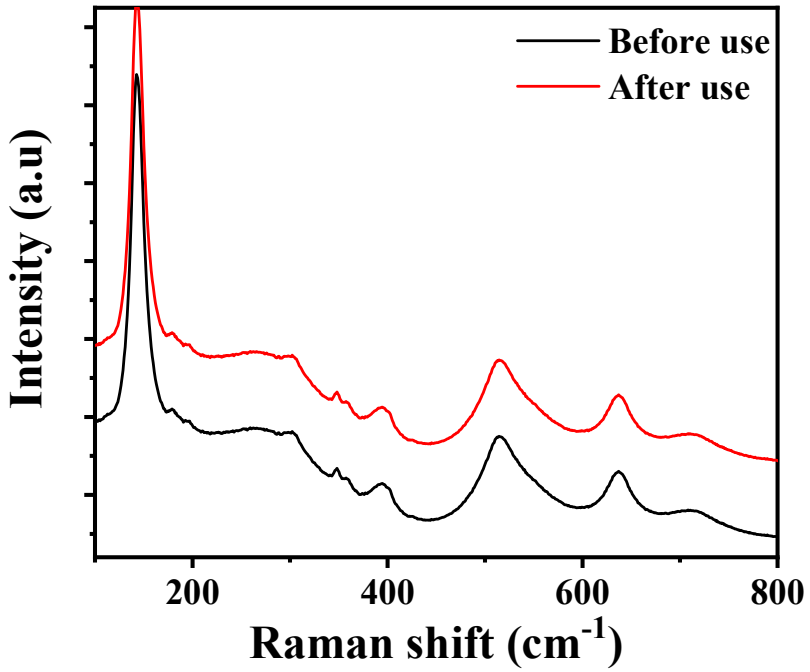

Fig. S5: The Raman spectra of 4 mol.% Cr^{3+}-doped $BaTiO_3$ sample before (black) and after (red) recycling.

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