

Supplementary Information

Cerium-doped iron oxide nanorod arrays for photoelectrochemical water splitting

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Table S1. H₂ Production of Ce-doped Materials

Materials	H ₂ Production Of Materials	Ce-doped Materials	H ₂ Production of Ce-doped Materials	Bias	Electrolyte	ref
Fe ₂ O ₃ nanorods	3.96μmol h ⁻¹ cm ⁻²	Ce-Fe ₂ O ₃ nanorods	122μmol h ⁻¹ cm ⁻²	1.6V vs. RHE	1MKOH	This work
ZnO nanowire	125ppm	CeO ₂ /Ce-ZnO nanowire	225ppm	1.0 V vs. RHE	0.1 MKOH with 0.1 M glycerol	[1]
BaTiO ₃ nanoassemblies	13μmol h ⁻¹ cm ⁻²	Ce-BaTiO ₃ nanoassemblies	23μmol h ⁻¹ cm ⁻²	0.7 V vs. Pt	1 mM NaOH	[2]
TiO ₂ nanotube	125ml h ⁻¹ cm ⁻²	Ce/Ce ₂ O/CeO ₂ /TiO ₂ nanotube	223μmol h ⁻¹ cm ⁻²	0.7 V vs. open circuit potential	0.1M Na ₂ SO ₄ with 10vol % Ethylene glycol	[3]

Table S2. ICP and ICP-MS of Fe₂O₃ (FT) and Ce-doped Fe₂O₃ (1CFT, 5CFT, 10CFT).

Sample	Fe(ppb)	Ti(ppb)	atomic ratio(%)	Ce(ppb)	atomic ratio(%)
FT	5695	22.186	0.390%	0.0007	0.000012%
1CFT	4443	26.925	0.606%	0.368	0.0083%
5CFT	4521	40.967	0.906%	0.162	0.0036%
10CFT	4124	22.054	0.535%	0.115	0.0028%

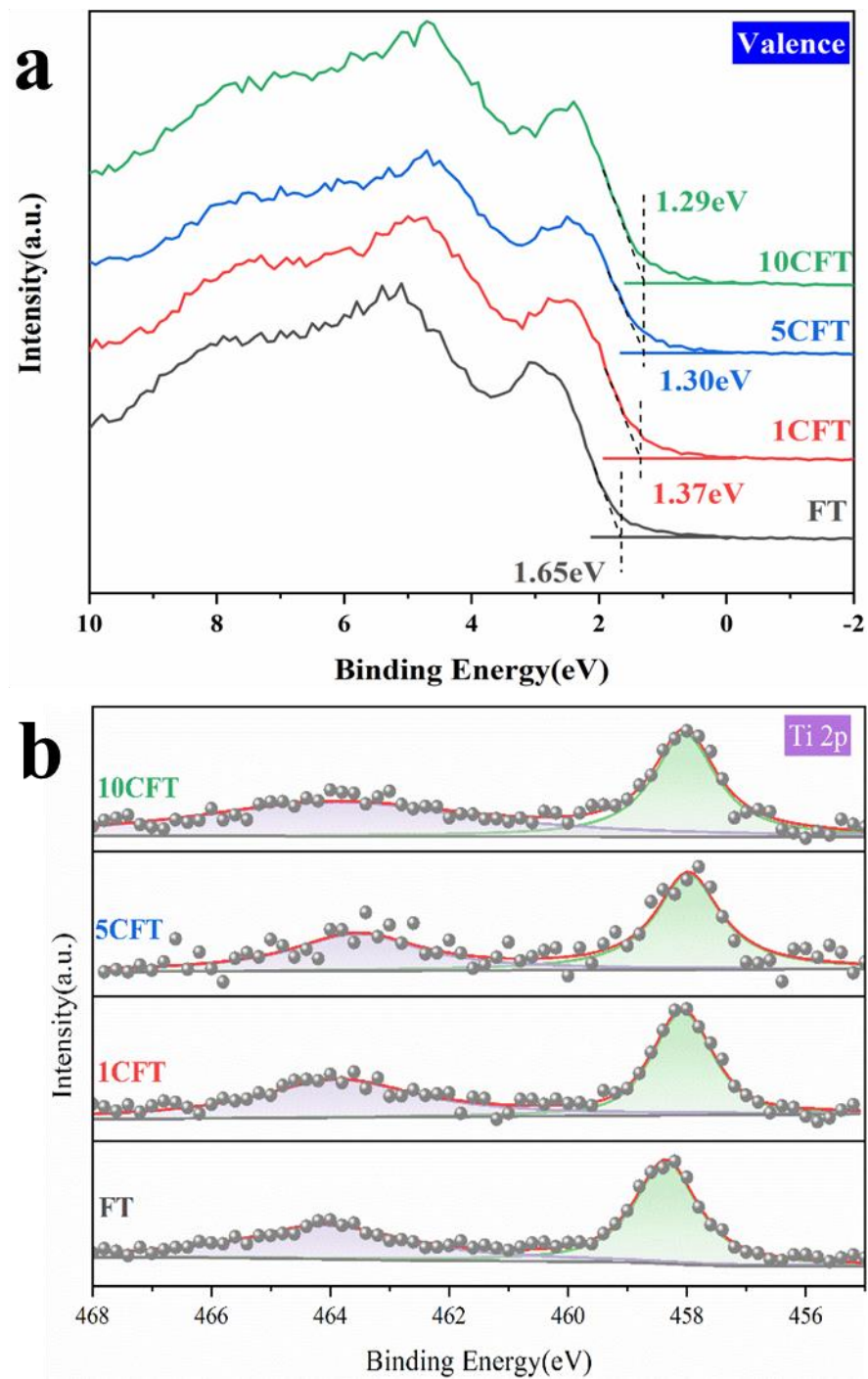


Figure S1. XPS Valence of Fe_2O_3 (FT) and Ce-doped Fe_2O_3 (1CFT, 5CFT, 10CFT).(a); Ti 2p (b)

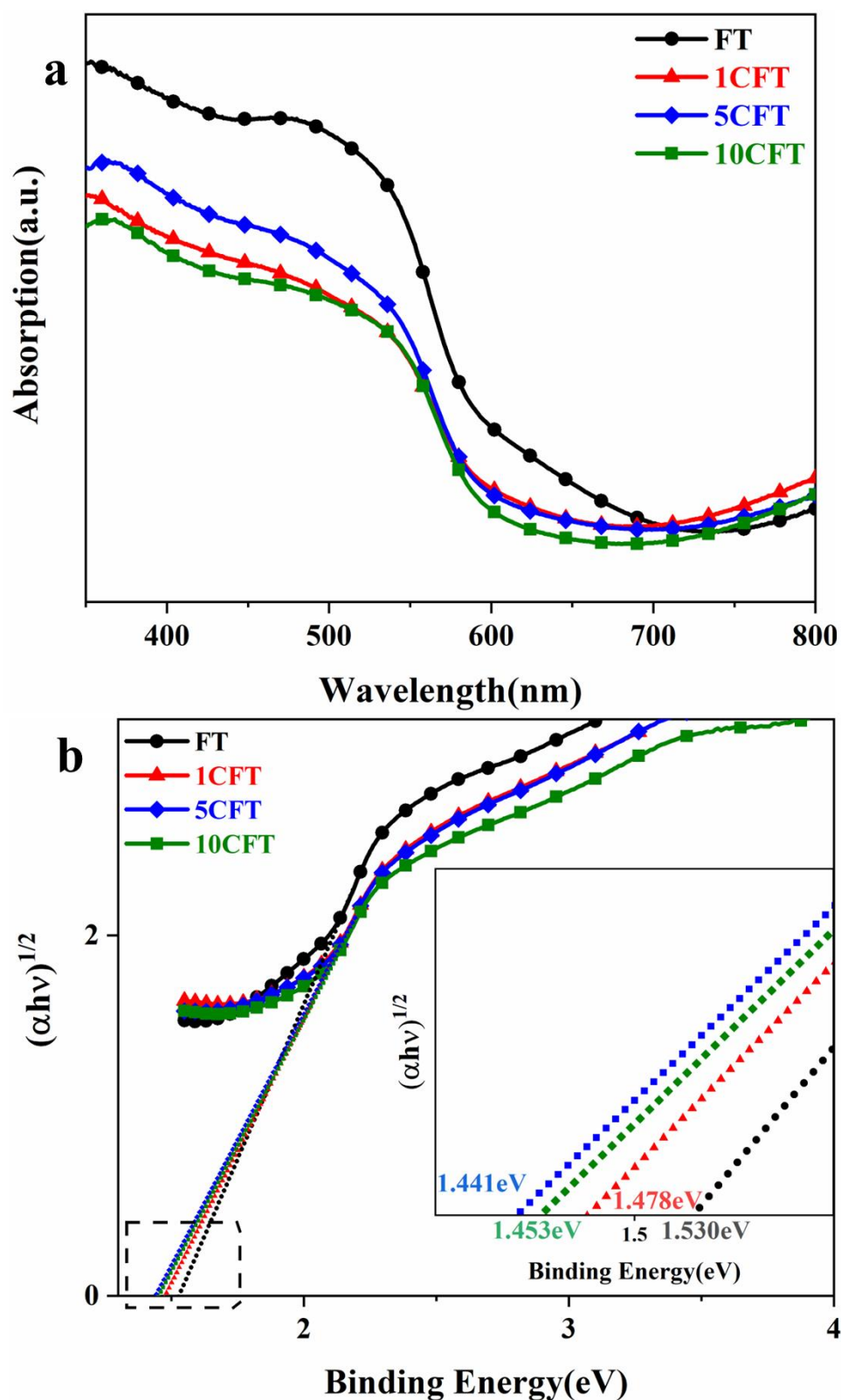


Figure S2. UV-vis absorption profile of Fe₂O₃ (FT) and Ce-doped Fe₂O₃ (1CFT, 5CFT, 10CFT). (a) and optical bandgaps, inset is the refined spectrum of 0.4eV-1.7eV(b)

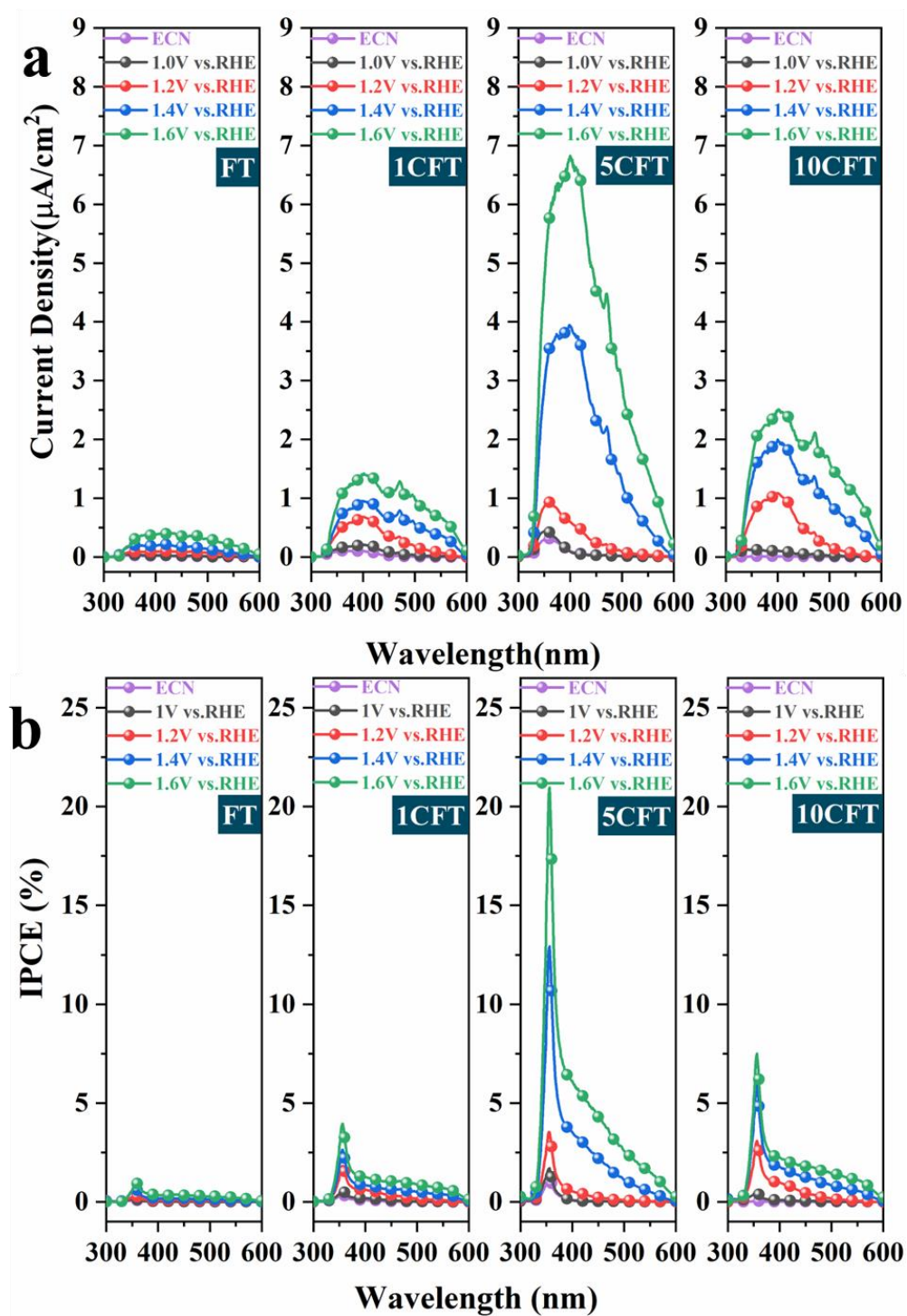


Figure S3. (a) Photocurrent density versus the monochromatic light; (b) IPCE values of FT, 1CFT, 5CFT, 10CFT under different bias

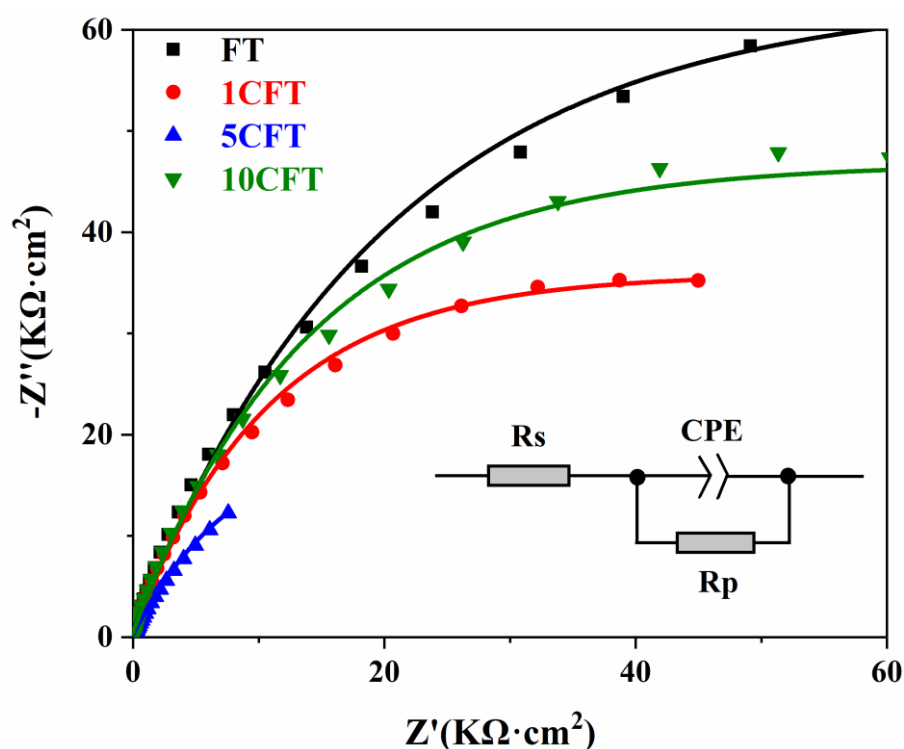


Figure S4 Electrochemical impedance spectroscopy (EIS) and Equivalent Circuit of Fe_2O_3 nanorods and Ce doped Fe_2O_3 nanorods samples

Table S3 Fitting data for each component in the fitted circuit for each sample

samples	R_s	$\text{CPE}-\sigma$	$\text{CPE}-m$	R_p
FT	2.0722	2.1915×10^{-5}	0.88228	1.6133×10^5
1CFT	1.2783	2.7865×10^{-5}	0.85492	0.89992×10^5
5CFT	1.1421	15.332×10^{-5}	0.75145	0.79914×10^5
10CFT	1.877	1.4352×10^{-5}	0.87341	1.0574×10^5

R_p is expressed as the resistance of the charge transfer between redox pairs occurring on the surface of the sample. The non-Faraday electrode capacitance owing to charge accumulation on the Fe_2O_3 surface is represented by a constant-phase element (CPE). R_p in parallel with the CPE is indicated by two charge paths for the electrons at the surface of the sample. The resistance R_s in series with both R_p and CPE represents the voltage drop in the electrolyte between the working electrode and reference electrode.

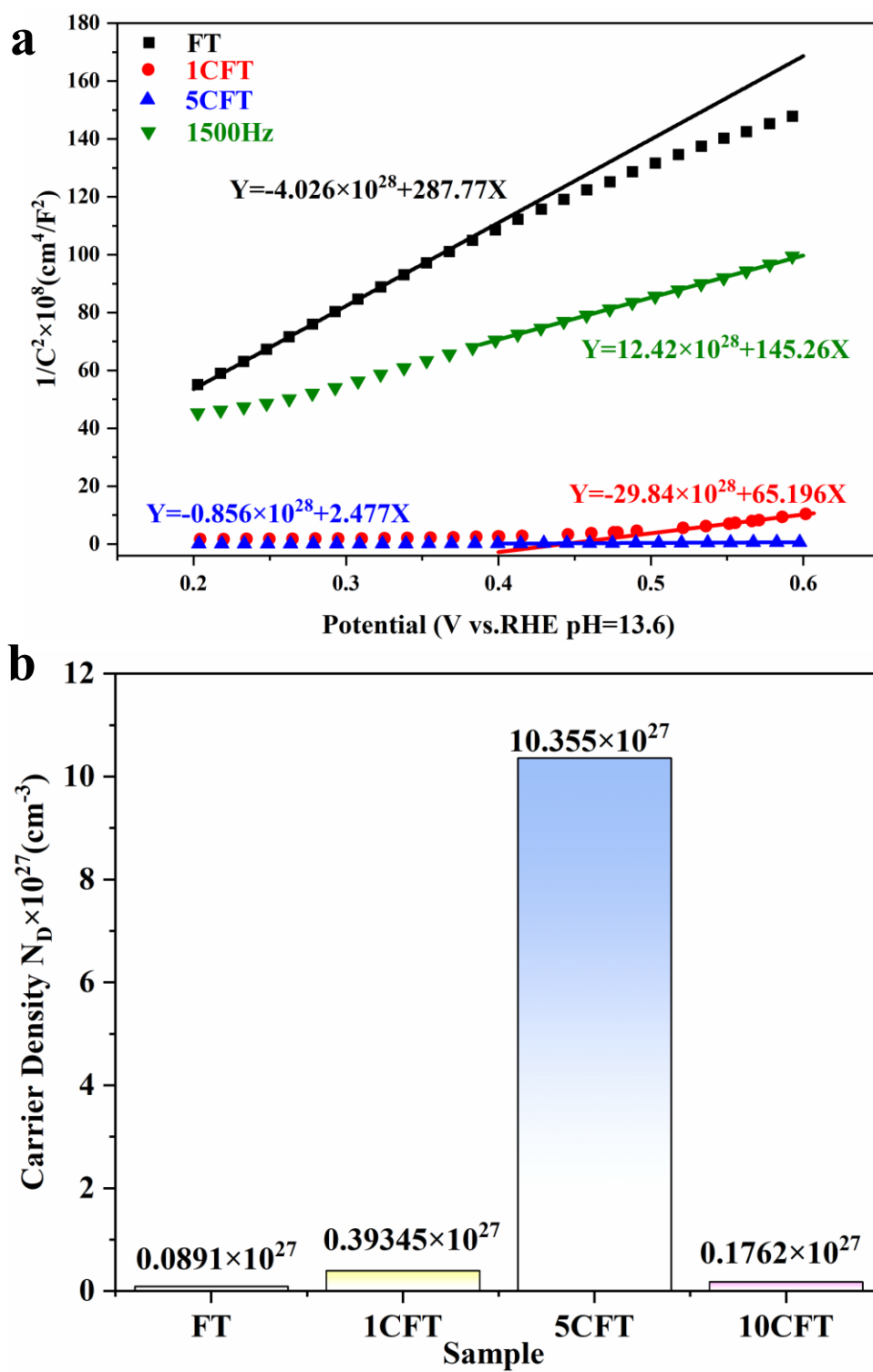


Figure S5. (a) Mott-Schottky plots collected at 1.5 kHz at a linear potential region between 0.2 to 0.6V vs. RHE and (b) Calculated carrier densities of Fe_2O_3 (FT) and Ce-doped Fe_2O_3 (1CFT, 5CFT, 10CFT).

References

- [1] S. Kim, E. An, I. Oh, J.B. Hwang, S. Seo, Y. Jung, J.-C. Park, H. Choi, C.H. Choi, S. Lee, CeO₂ nanoarray decorated Ce-doped ZnO nanowire photoanode for efficient hydrogen production with glycerol as a sacrificial agent, *Catalysis Science & Technology*, 12 (2022) 5517-5523.
- [2] P. Senthilkumar, D.A. Jency, T. Kavinkumar, D. Dhayanithi, S. Dhanuskodi, M. Umadevi, S. Manivannan, N.V. Giridharan, V. Thiagarajan, M. Sriramkumar, K. Jothivenkatachalam, Built-in Electric Field Assisted Photocatalytic Dye Degradation and Photoelectrochemical Water Splitting of Ferroelectric Ce Doped BaTiO₃ Nanoassemblies, *ACS Sustainable Chemistry & Engineering*, (2019).
- [3] Y. Tan, S. Zhang, R. Shi, W. Wang, K. Liang, Visible light active Ce/Ce₂O/CeO₂/TiO₂ nanotube arrays for efficient hydrogen production by photoelectrochemical water splitting, *International Journal of Hydrogen Energy*, 41 (2016) 5437-5444.