Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for:

Control of Chemical State of Cerium in Doped Anatase TiO_2 By Solvothermal and its Application in Photocatalytical Water Reduction

Juliana Fonseca de Lima, Mohammad Hilni Harunsani, David James Martin, Dan Kong, Peter W. Dunne, Diego Gianolio, Reza J. Kashtiban, Jeremy Sloan, Osvaldo Antonio Serra, Junwang Tang and Richard I. Walton

S1: Synthesis

Table S1: Amounts of starting materials used for n%Ce-TiO_2 synthesis

Ce conc./%	$Ce(NO_3)_3.6H_2O$ in ethanol (0.5 M)/mL	Ti isopropoxide in ethanol (0.5M)/mL	Lactic acid/mL (where used)
0	-	50	1
0.5	0.25	49.75	
1	0.5	49.5	
5	2.5	47.5	
10	5	45	
15	7.5	42.5	

As stated in the text the reactions were performed with and without the lactic acid.

S2: Powder XRD

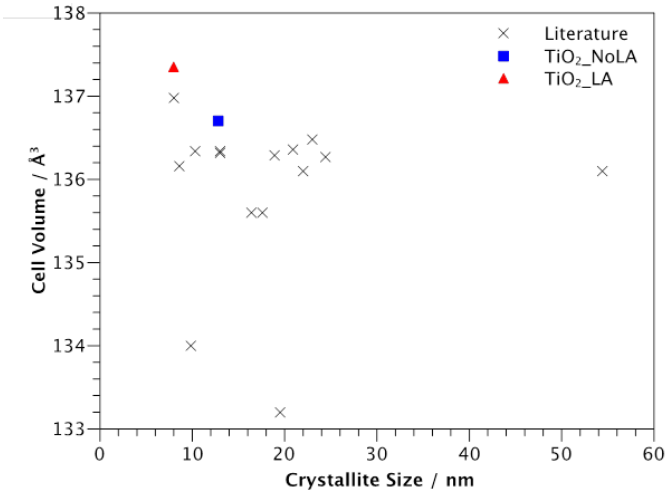

Figure S1: Plot of lattice parameters of anatase TiO_2 from the literature[1-8] compared to samples of TiO_2 made in the presence (LA) and absence (NoLA) of lactic acid in our work.

1. Z. Matěj, L. Matějováb, and R. Kužel, *Powder Diffr.*, 2013, **28**, S161.

2. V. Swamy, A. Kuznetsov, L. S. Dubrovinsky, R. A. Caruso, D. G. Shchukin and B. C. Muddle, *Phys. Rev. B*, 2005, 71, 184302.

3. J. Xie, D. Jianga, M. Chena, D. Lia, J. Zhua, X. Lua, C. Yan, *Colloids Surf, A: Physicochem. Eng. Aspects 2010, **372**, 107.*

4. T. Tong, J. Zhang, B. Tian, F. Chen, D. He, M Anpo, *J. Colloid Interface Sci.*, 2007, **315**, 382.

5. V. Stengl, S. Bakardjieva, N. Murafa, Mater. *Chem Phys.*, 2009, **114**, 217.

6. J. Fang, X. Bi, D. Si, Z. Jiang, W. Huang, *Appl. Surf. Sci.*, 2007, **253**, 8952.

7. L. Matějová, K. Kočí, M. Reli, L. Čapek, A. Hospodková, P. Peikertová, Z. Matěj, L. Obalová, A. Wach, P. Kustrowski, A. Kotarba, *Appl. Catal. B*, 2014, **152-153**, 173

8. T. López, F. Rojas, R. Alexander-Katz, F. Galindo, A. Balankin and A. Buljan, *J. Solid State Chem.*, 2004, **177**, 1873,

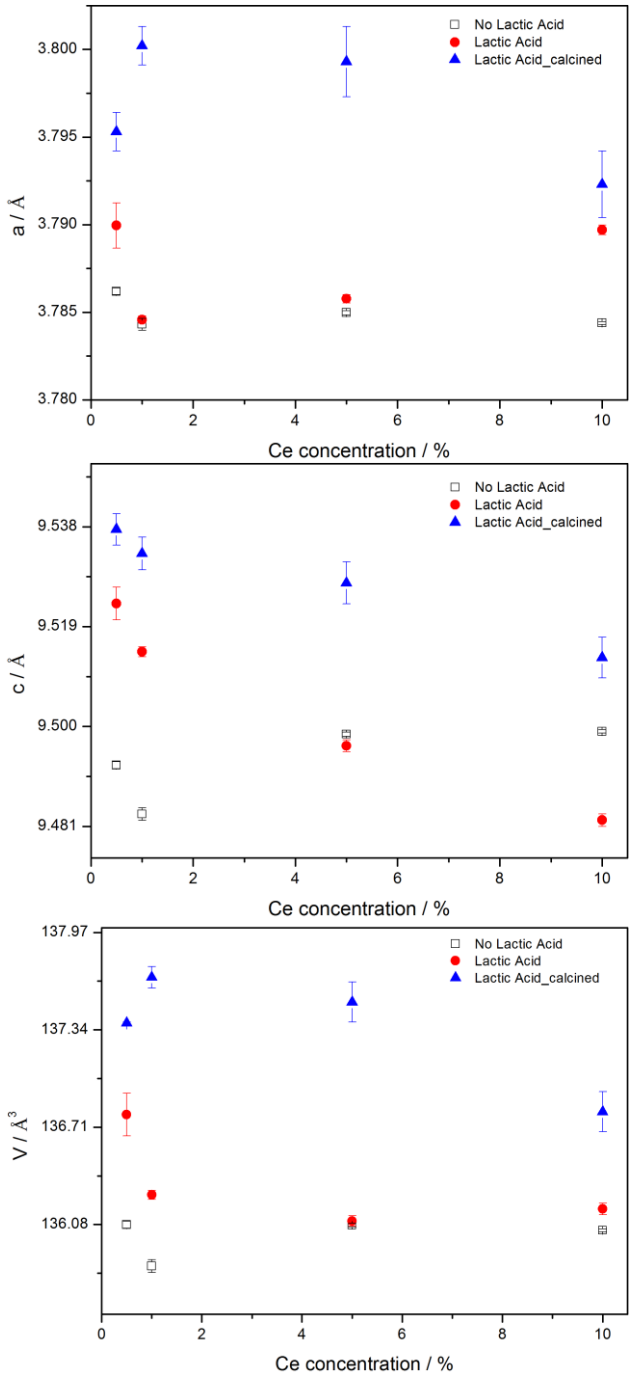

Figure S2: Refined lattice parameters of Ce-TiO_2 materials prepared in lactic acid after being calcined

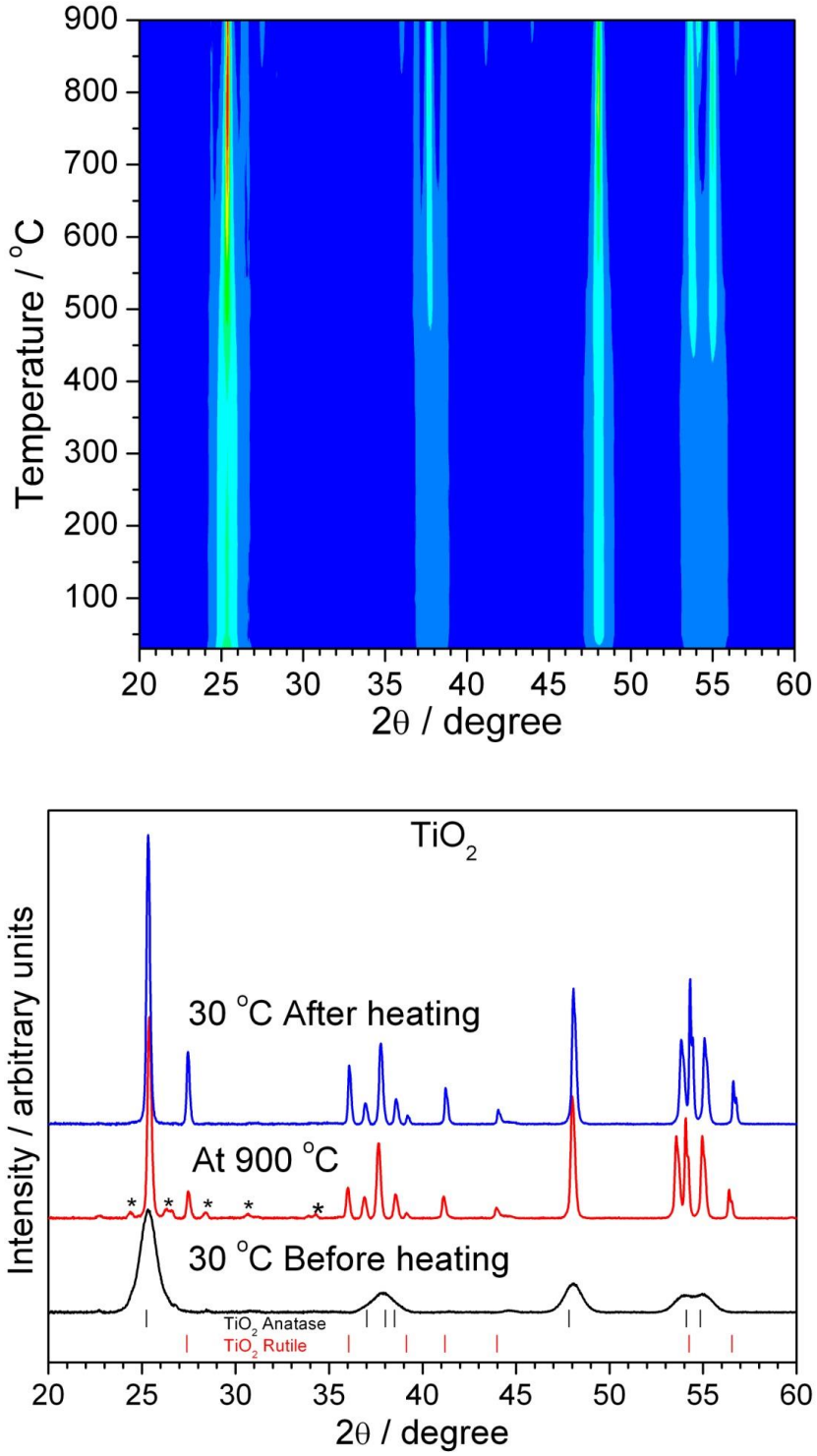

Figure S3: (a)* In situ *powder XRD measured during heating of TiO_2 with the appearance of rutile at ~825 ^oC (b) individual XRD patterns measured before during and after heating. * shows peaks due to the sample holder dut to sample movement with the phase transition.

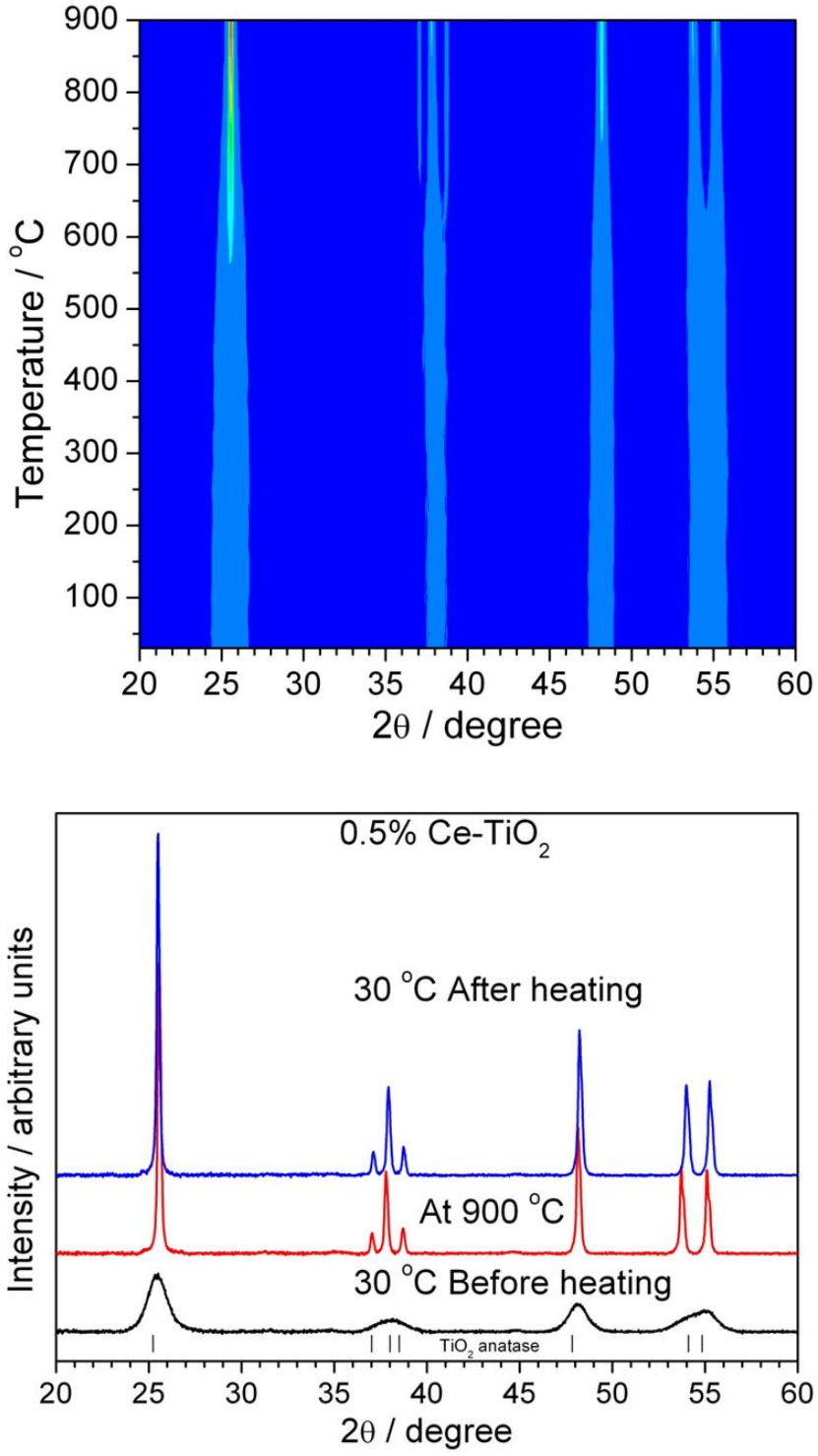

Figure S4: (a)* In situ *powder XRD measured during heating of 0.5%Ce-TiO_2 with no appearance of rutile (b) individual XRD patterns measured before during and after heating.

S3: BET adsorption isotherms

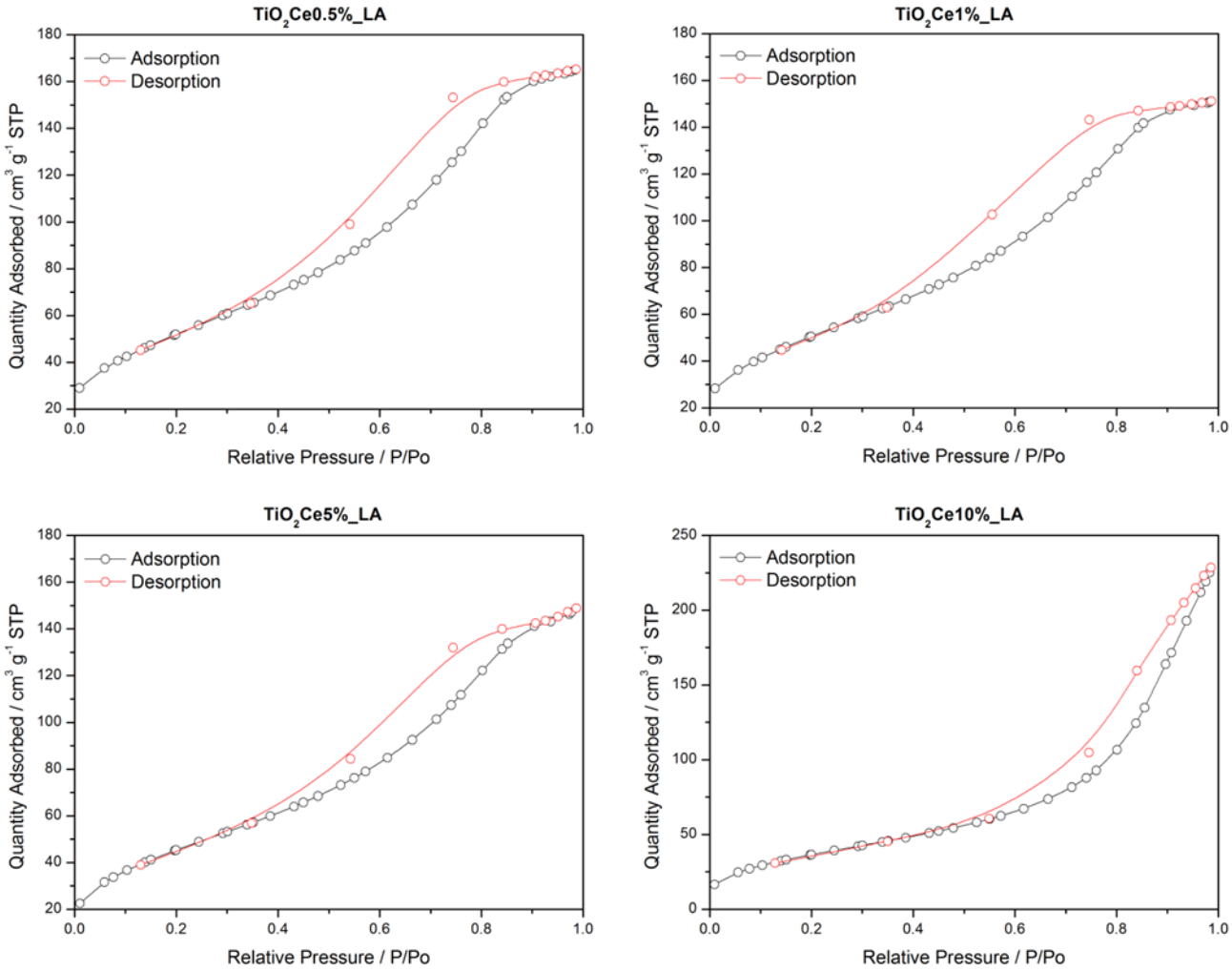

Figure S5: BET isotherms of materials prepared in the presence of lactic acid

S4: ICP Analysis

Table S2 Atomic composition of Ce-TiO2 samples(lactic acid) from ICP analysis. Note: Ce concentration = [Ce / (Ce+Ti)] × 100

Intended Ce concentration / %	**Ce / at. % (Expected value)**	**Ti / at. % (Expected value)**	**Measured Ce conc. / %**
0.5	0.14 (0.17)	28.67 (33.17)	0.49
1	0.30 (0.33)	28.44 (33)	1.05
10	2.08 (3.33)	19.16 (30)	10.86
15	3.38 (5)	20.32 (28.33)	14.26

S5: EELS Mapping

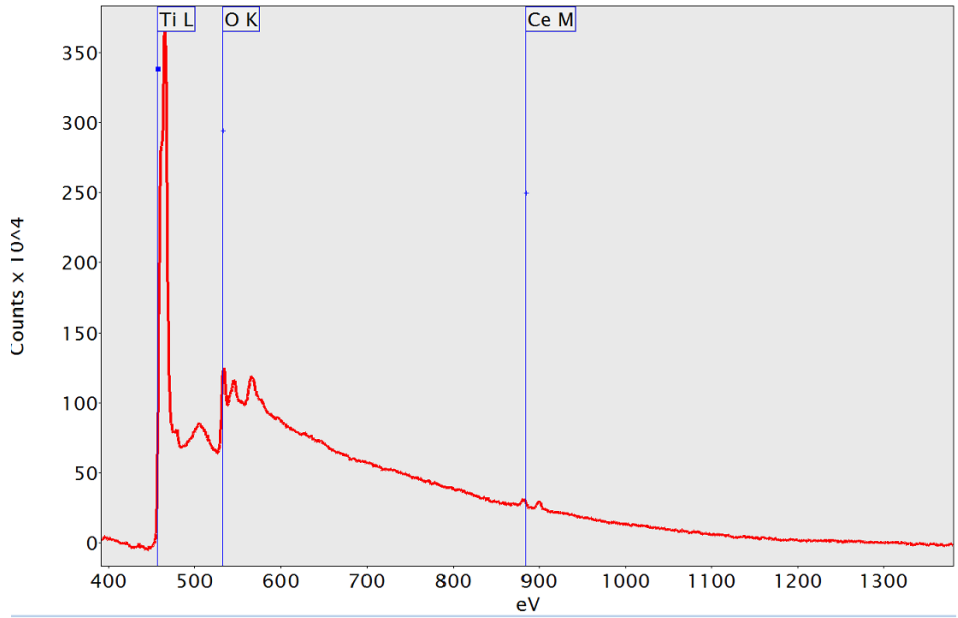

Figure S6: Typical EELS spectrum showing edges analysed

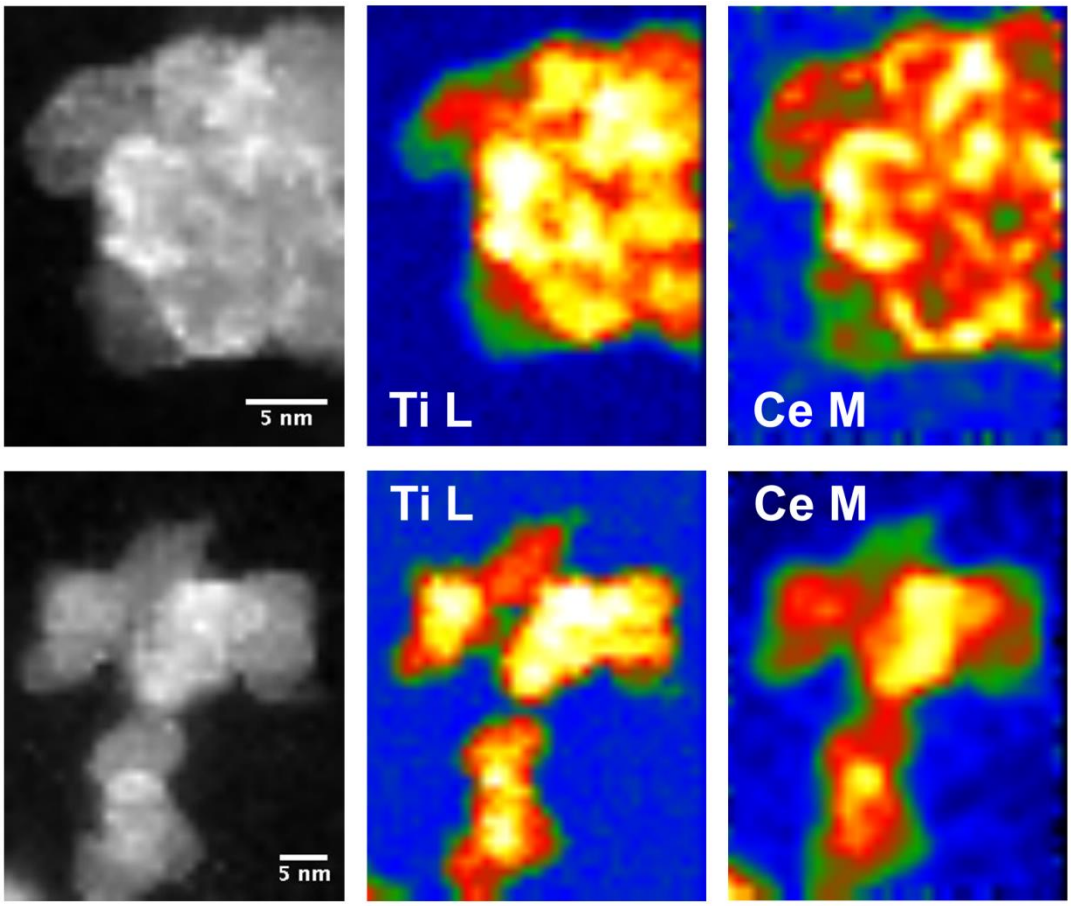

Figure S7: Further EELS maps of 10%Ce-TiO_2 showing the homogeneity of the sample.

S6: Thermogravimetric Analysis

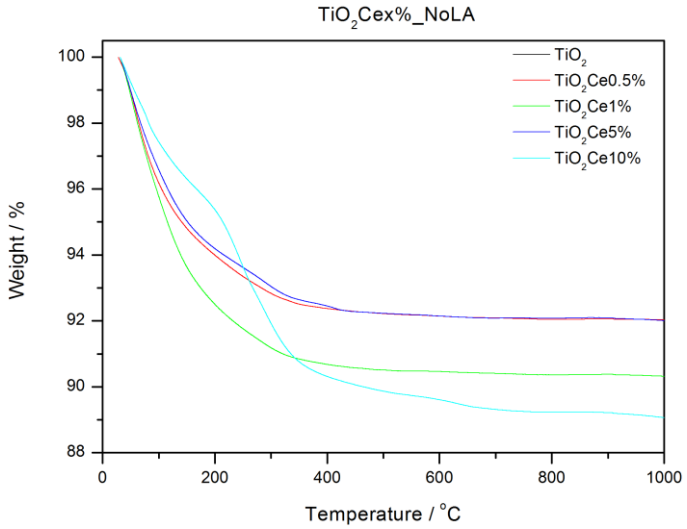

Figure S8: TGA of samples prepared in the absence of lactic acid

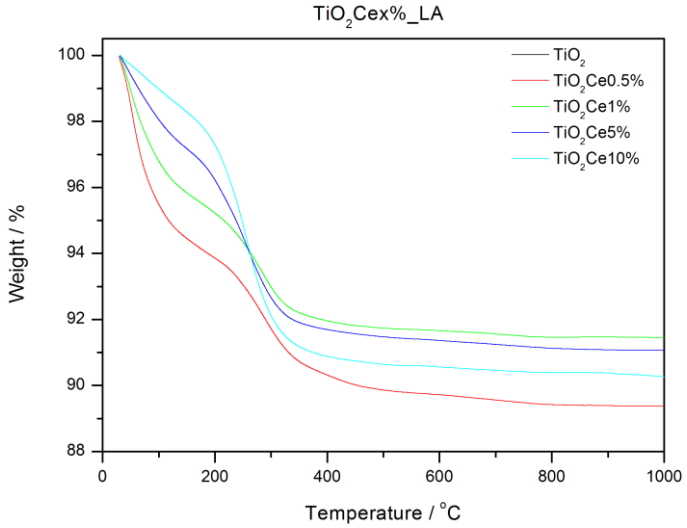

Figure S9: TGA of samples prepared in the presence of lactic acid

S7: UV-Visible Diffuse Reflectance Spectroscopy

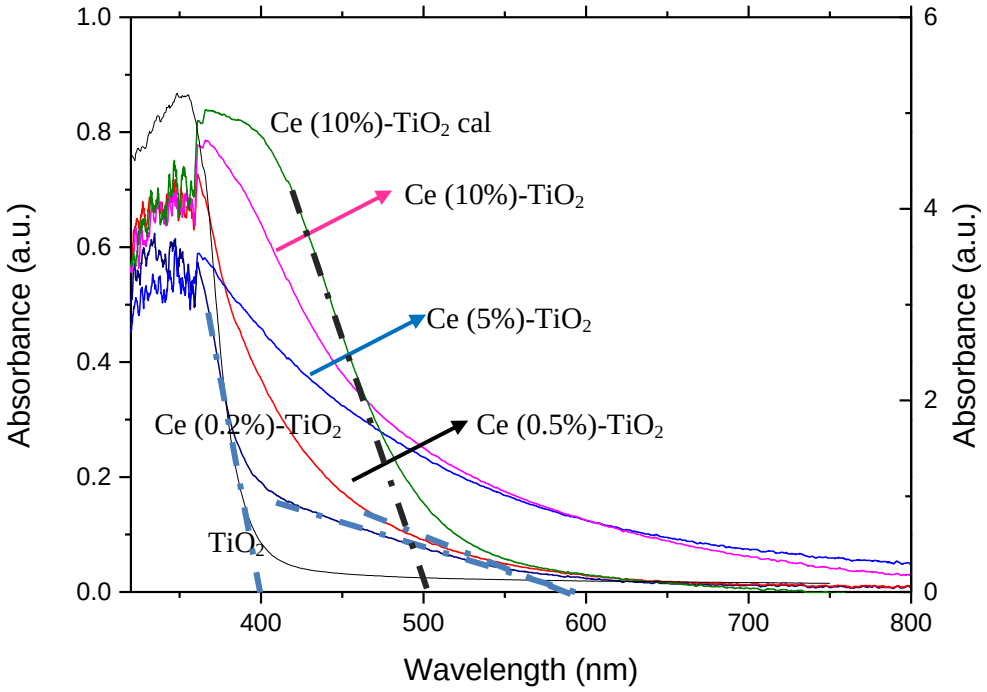

Figure S10: Diffuse reflectance UV-Vis spectroscopy. Dotted lines represent extrapolation of the linear region to estimate band gap.