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Electronic Supplementary Information

Uniform titania-supported Ce(III) carbonate cluster catalysts for degradation of reactive oxygen species

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Contents:

Experimental Methods:

S1.1. Reagents and precursors:

Chemicals were obtained from commercial sources and used without purification. The chemicals were obtained from $Ce(NO_3)_3{\cdot}6H_2O$ (Thermo Scientific, REacton 99.99%), $(NH_4)_2CO_3$ (Sigma Aldrich, ACS grade), benchmark Aeroxide P25, ~27 nm TiO_2 photocatalyst (Acros Organics) and Methylene Blue Hydrate (TCI Chemicals, >70%). Ultrapure deionized water 18 Mohm was used for the chemical manipulations and photocatalysis tests.

S.1.2. Synthesis of $MgCO_3$:

$Mg(NO_3)_2{\cdot}6H_2O$, (897 mg, 3.5 mmol) was dissolved in 10 mL of deionized water. 672 mg of $(NH_4)_2CO_3$ (7 mmol) was dissolved in 10 mL of deionized water. The $(NH_4)_2CO_3$ solution was poured into the magnesium salt solution (during the course of 5 seconds) under rapid stirring (700 RPM), and was allowed to stir at room temperature for 25 h, at a pH of 9. The obtained precipitate was centrifuged for 5 min at 20,000 RPM, redispersed and washed three times with deionized water. The final centrifugation was performed at 20,000 RPM for 10 min, and the precipitate was collected as a wet paste, which was dried at 60 °C for further analysis. ICP/MS characterization shows a Mg composition of 24.6 wt. % in the dried material.

S1.3. Synthesis of Mg-Ce mixed carbonate precursor:

$Mg(NO_3)_2{\cdot}6H_2O$ (3.375 mmol, 865.4 mg) and $Ce(NO_3)_3{\cdot}6H_2O$ (0.125 mmol, 54.25 mg) were dissolved in 10 mL deionized H_2O. Separately, a solution of $(NH_4)_2CO_3$ (7.125 mmol, 684 mg) was dissolved in 10 mL deionized water. The $(NH_4)_2CO_3$ solution was added (during the course of 5 seconds) into the metal-nitrate salt solution and allowed to rapidly stir (700 RPM) at room temperature for 25 h. The obtained precipitate was centrifuged for 5 min at 20,000 RPM, redispersed, and washed twice with deionized H_2O. The final centrifugation was performed at 20,000 RPM for 10 min, and the precipitate was collected as a wet paste. The obtained Mg-Ce mixed carbonate precursor was first dried at room temperature and to obtain fine powder subsequently further dried at 60°C for 5 hours. Based on the total weight of the 60 ^{o}C heat-treated samples as well as the Ce content measured by ICP-MS, the Ce yield of the syntheses (defined as the Ce contained in the final product divided by the initial Ce added to the synthesis) was 91.4% for the Mg-Ce mixed carbonate precursor.

S1.4. Synthesis of Ce-carbonate deposited onto TiO_2:

Mg-Ce mixed carbonate (2 mg) and P25-TiO_2 (4 mg) were carefully weighed and added to 100 mL of deionized H_2O. The mixture was sonicated for 5 min to obtain a homogenous suspension, which was stirred overnight for about 12 h in the dark. The suspension was again sonicated for 5 min to further homogenize the suspension. The uniform dispersion was divided into two 50 mL aliquots, each of which comprised 1 mg Mg-Ce mixed carbonate and 2 mg TiO_2 in solution. The 50 mL dispersion aliquot was centrifuged at 20,000 RPM for 15 min. The solid part was carefully separated from the supernatant using a Pasteur pipette to remove the supernatant. Both the solid and supernatant were carefully stored for further experiments. The supernatant pH was 7.8.

S1.5. Photocatalysis tests of Ce-carbonate deposited onto TiO_2:

S1.5.1. Photocatalysis test at basic pH using supernatant: The obtained Ce-carbonate deposited onto TiO_2 (consisting of a 2 mg TiO_2 basis) was redispersed in 99 mL of the collected supernatant at pH 7.8 during the centrifugation step. The dispersion was sonicated for 5 min to further homogenize it, and 1 mL 10^{-3} M methylene blue dye solution was added. The solution was transferred to the photoreactor, and was stirred in the dark for 30 min. After 30 min, 1.5 mL of the solution was removed as a t=0 reference. This small sample was centrifuged for 3 min at 14,000 RPM. The remaining solution was placed covered on top with a watch glass, and it was stirred in the photoreactor. Lights were turned on, and the timer on the photoreactor was set to 1 h. After one hour time periods, a 1.5 mL aliquot was removed and centrifuged (14,000 RPM for 3 min). These small aliquots were characterized via UV-vis spectroscopy (scan rate 2000, 1.1 interval, 0.033 s per scan, 200 nm – 800 nm) in order to measure the dye concentration. The same procedure was used to perform photocatalysis tests at pHs of 7, 8.2, and 9.2 (pH was controlled with dilute NaOH solution), except that instead of using supernatant, an aqueous solution of controlled pH was used as the redispersion medium. A control experiment was also conducted wherein a dilute aqueous Na_2CO_3 solution used to adjust the pH to 8.2 for the photocatalysis test, instead of NaOH, to rule out the role of any specific base in the observed photocatalytic activity tests.

S1.5.2. Photocatalysis test at pH 6: The Ce-carbonate deposited onto TiO_2 synthesis steps were the same as discussed above, except that for the photocatalysis test, pH 6 deionized water (equilibrated with atmosphere – no pH adjustment was required) was used. The remaining photocatalysis test steps were the same.

S1.6. Preparation of Ce-carbonate deposited onto TiO_2 TEM grids for characterization: The other half 50 mL aliquot in the S1.3. step was also centrifuged at 20000 RPM for 15 min to separate the liquid from the Ce carbonate nanoparticles deposited on TiO_2. The solid was dispersed in the same pH or supernatant solution as used for the photocatalysis test, so as to prepare the sample for TEM characterization. The solution was sonicated, and vortex mixed to achieve a uniform suspension. About 20 µL of suspension was drop cast on Lacey carbon 400 mesh Cu grids (Ted Pella, Inc 01824). The sample was dried at room temperature. The deposited cerium carbonate TiO_2 samples used in the photocatalysis tests were analyzed using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) sensitive to the atomic number and electron energy loss spectroscopy (EELS) was also performed.

S1.7. Preparation of Ce-carbonate deposited onto TiO_2 at pH 6 control TEM grid: To further confirm the observed photocatalysis activity is due to the role of pH, a control TEM experiment at pH 6 was also performed for which the grid was prepared using the following protocol. Mg-Ce mixed carbonate precursor (2 mg) and TiO_2 (4 mg) were dispersed in 100 mL of deionized-H_2O and sonicated for 5 min. The resulting suspension was stirred overnight, and was subsequently sonicated for 5 min, to further homogenize the suspension. The suspension was portioned into 50 mL aliquots. Each of these separate 50 mL suspensions was centrifuged at 20,000 RPM for 15 min, to collect the Ce-carbonate deposited onto TiO_2 solid, by carefully removing the supernatant using a Pasteur pipette from the top. To this solid, 40 mL of pH 6 deionized water was added. The suspension was vortex mixed for 2 min, sonicated for 5 min, and again vortex mixed for 1 min, followed by hand shaking while transporting the sample to the centrifuge. The resulting well mixed suspension was centrifuged at 20,000 RPM for 15 min and the pH 6 supernatant was carefully removed via Pasteur pipette. This entire vortex mixing, sonication, and centrifugation procedure was repeated once more to obtain the final solid. The obtained solid was again redispersed in pH 6 water. About 20 μL of the suspension was drop cast on a Lacey carbon 400 mesh Cu grid (Ted Pella, Inc 01824). The sample was dried at room temperature. The Ce-carbonate-nanoparticle-on-TiO_2 samples used in the photocatalysis were analyzed using HAADF-STEM and EELS.

S.1.8. Characterization:

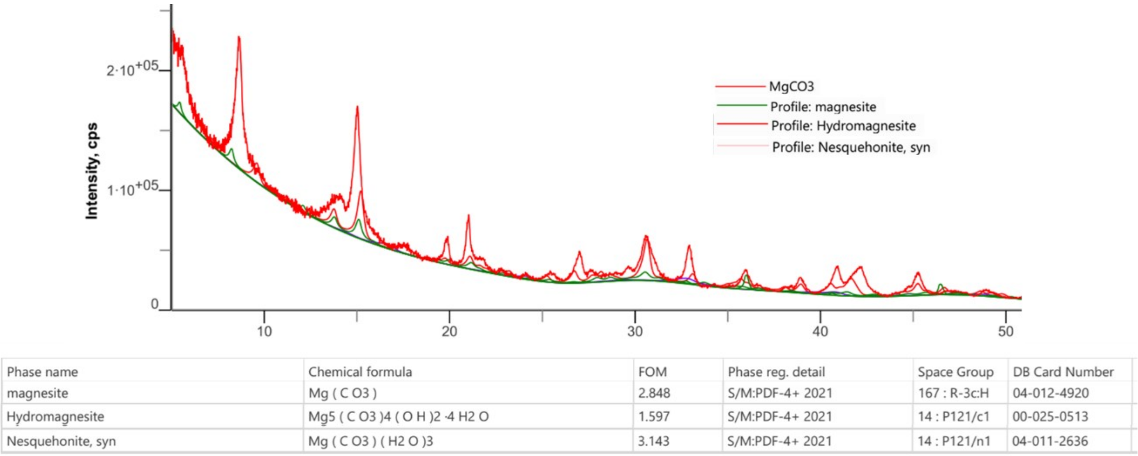
X-ray diffraction (XRD) pattern was recorded using Rigaku MiniFlex diffractometer with Cu $K\alpha$ radiation. UV-vis absorbance was measured using a Varian Cary 400 UV-Vis spectrometer. Ultrasonication was conducted in a Branson 3510 bath at room temperature. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded using Nicolet FT-IR spectrometer from Thermo scientific with diamond crystal plate. The pH of suspensions was measured using a Hanna pH electrode HI11312. CHN analysis was performed using 2400 CHN Elemental Analyzer by Perkin Elmer. ICP was performed by Galbraith Laboratories Inc. Photocatalysis tests were performed in a photoreactor equipped with 14 UV lamps (145-155 total Lux) operating at a wavelength of 254 nm (Luzchem LZC-4VB, Canada). Centrifugation was performed using a Beckman Coulter Avanti J-25 centrifuge equipped with a Beckman JA-20 rotor (serial number 02U 010612).

S.1.8.1. HAADF-STEM of Ce-carbonate deposited onto TiO_2:

All imaging and EELS were performed at the National Center for Electron Microscopy-Lawrence Berkeley National Laboratory. The Ce-carbonate deposited onto TiO_2 sample used in the pH dependent photocatalysis was characterized on a FEI-Tecnai TF20 transmission electron microscope at an accelerating voltage of 200 kV. HAADF-STEM imaging of the Ce-carbonate deposited onto TiO_2 sample was performed at a camera length of 140 mm and 100 μm C2 aperture. EELS experiments were performed on a Gatan Tridiem image filter. Multiple HAADF-STEM images and EELS were collected on different region of the sample.

S.1.8.2. HAADF-STEM on Mg-Ce mixed carbonate:

The Mg-Ce mixed carbonate starting precursor was analyzed in FEI-Tecnai TEM at an accelerating voltage of 200 kV. HAADF-STEM was performed using 100 μm C2 aperture. EELS experiments were performed on a Gatan Tridiem image filter. Multiple HAADF-STEM images and EELS were collected on different regions of the sample.



Phase name	Chemical formula	FOM	Phase reg. detail	Space Group	DB Card Number
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Hydromagnesite	Mg5 (C O3)4 (O H)2 ·4 H2 O	1.597	S/M:PDF-4+ 2021	14 : P121/c1	00-025-0513
Nesquehonite, syn	Mg (C O3) (H2 O)3	3.143	S/M:PDF-4+ 2021	14 : P121/n1	04-011-2636

Figure S1: Powder X-ray diffraction (PXRD) pattern of Mg-Ce mixed carbonate.

Table S1. ICP elemental analysis of Mg-Ce mixed carbonate precursor.

Sl. No.	Analysis	Result (Weight%)
1.	Cerium	6.64
2.	Magnesium	13.7

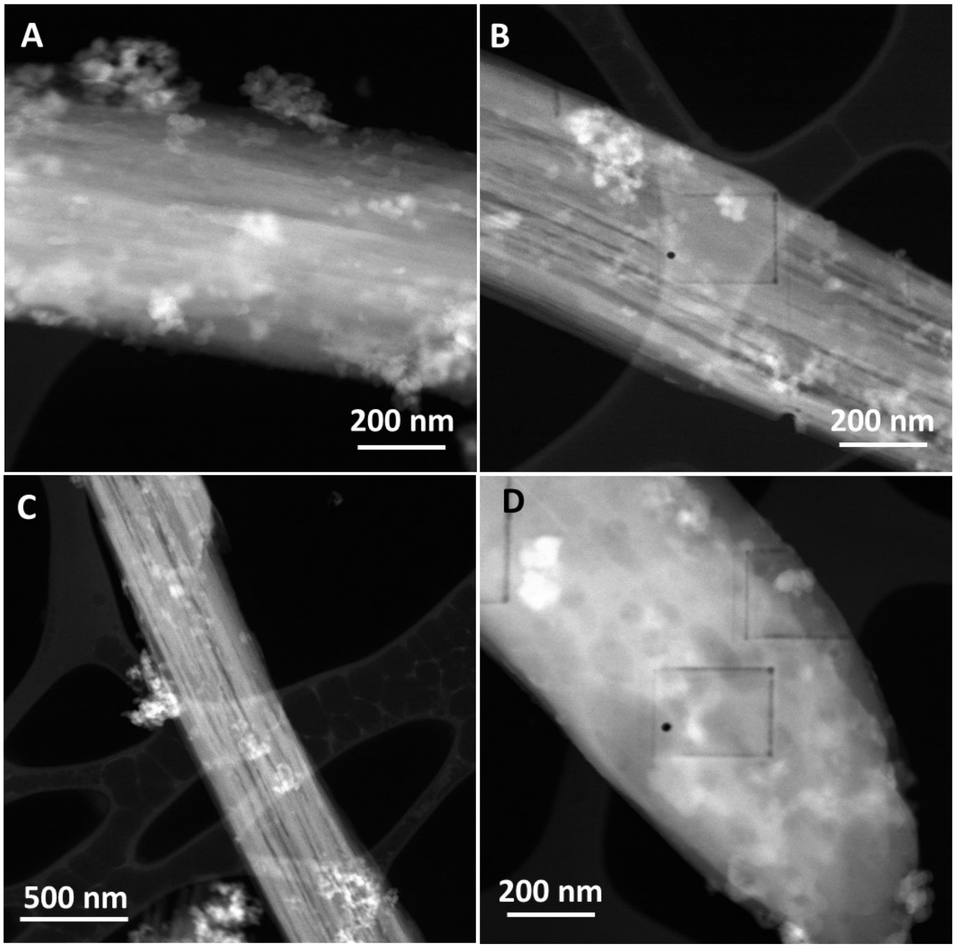

Figure S2: (A-D) HAADF-STEM images of Mg-Ce mixed carbonate precursor. The squares and black dots in (B) and (D) arise from beam damage due to focusing the electron beam on the image during the initial focusing of the beam in HAADF-STEM mode on the sample.

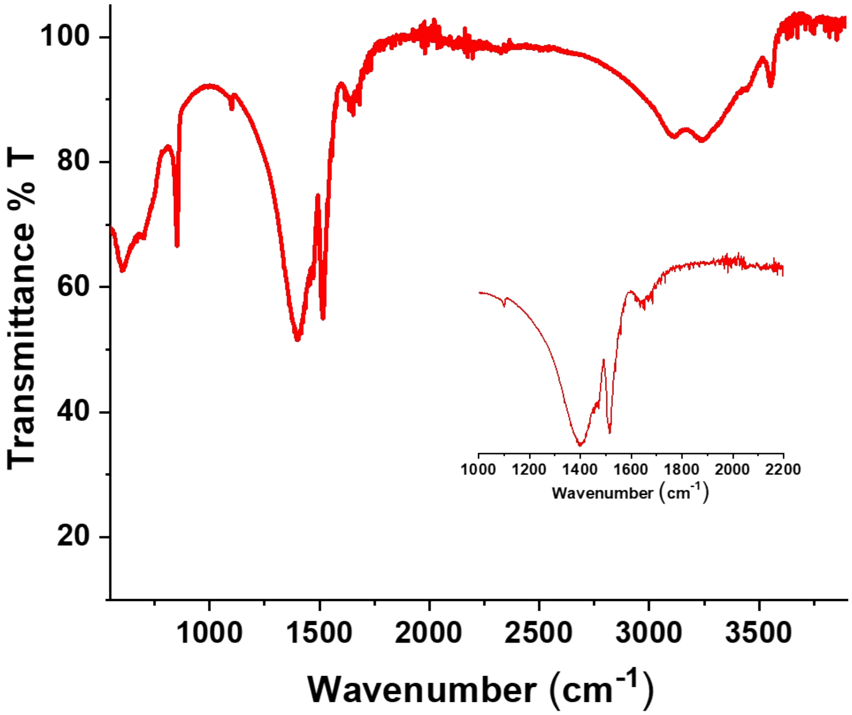

Figure S3: Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrum of Mg-Ce mixed carbonate precursor.

Figure S4: Optical photograph of Ce-carbonate deposited onto TiO_2 showing white contrast characteristic of Ce^{3+} and, more specifically, a lack of Ce^{4+} in the material.

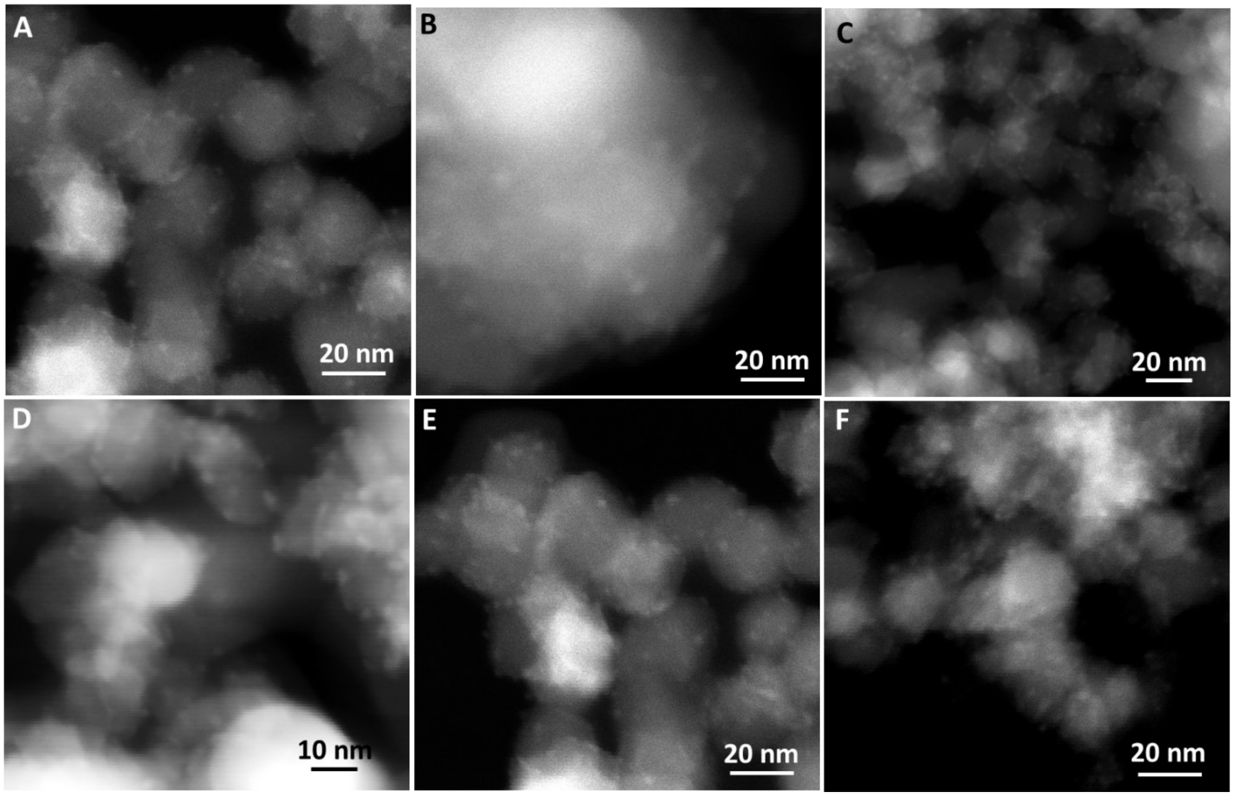

Figure S5: (A-F) HAADF-STEM images of Ce(III) carbonate deposited onto TiO_2.

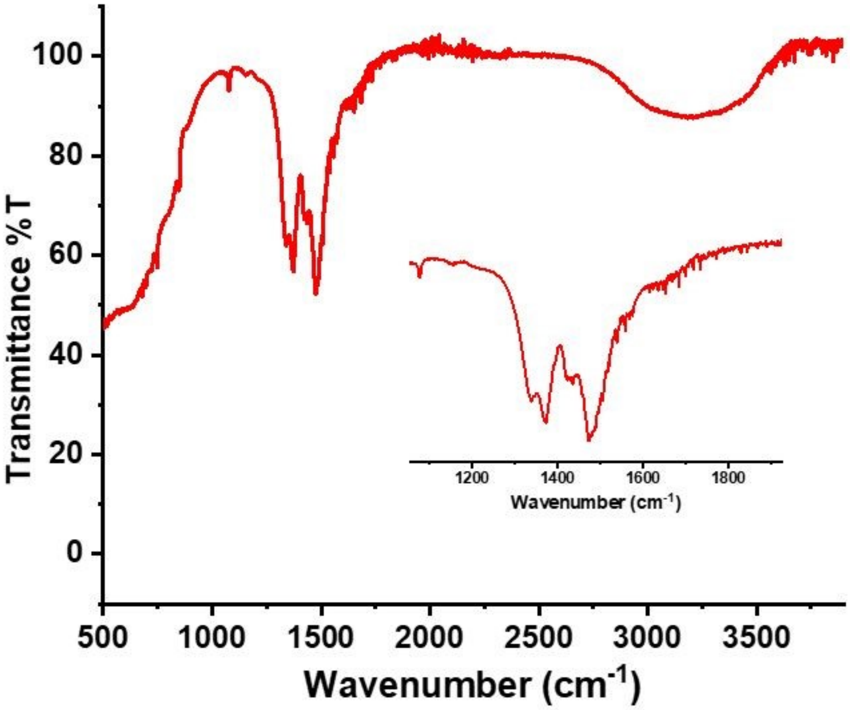

Figure S6: ATR-FTIR spectrum of Ce-carbonate deposited onto TiO_2.

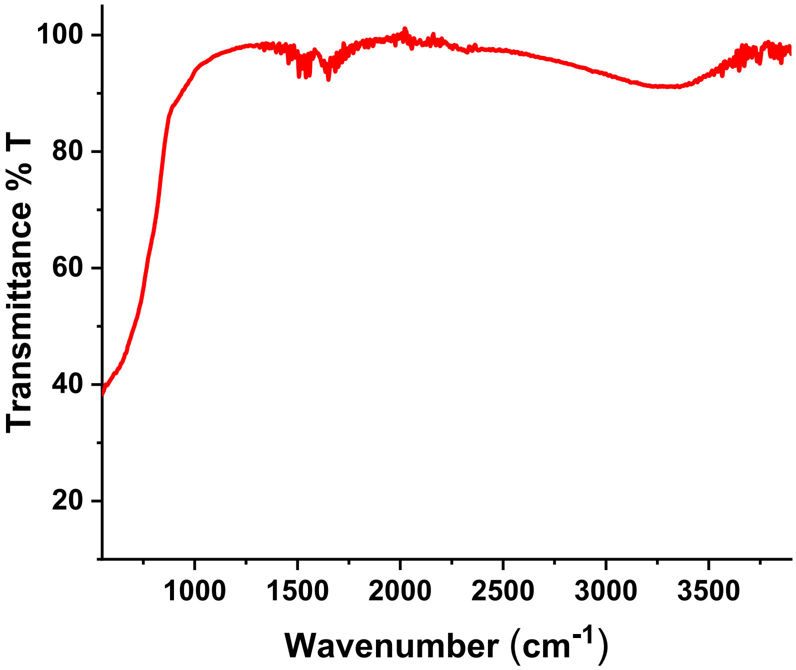

Figure S7: ATR-FTIR spectrum of pristine TiO_2 (P25).

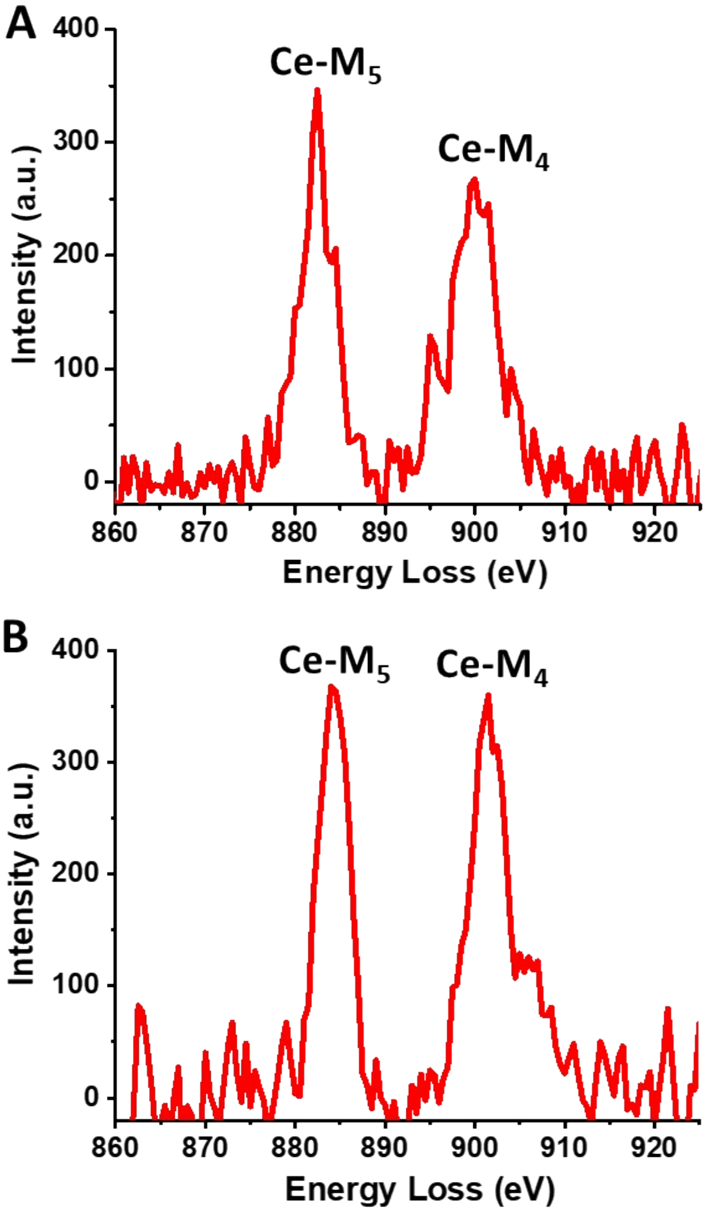

Figure S8: Ce-M_4/M_5 EELS data upon (a) initial and (b) prolonged exposure to the electron beam. The initial M_4/M_5 ratio is 0.77 characteristic of Ce^{3+} oxidation state in (a), whereas in (b) this ratio is 0.98. These data demonstrate that prolonged exposure of Ce(III) carbonate deposited on TiO_2 under the electron beam synthesizes Ce(IV), which we surmise to be due to the established decomposition of Ce(III) carbonate to Ce(IV) oxide as a result of beam damage.[1–3]

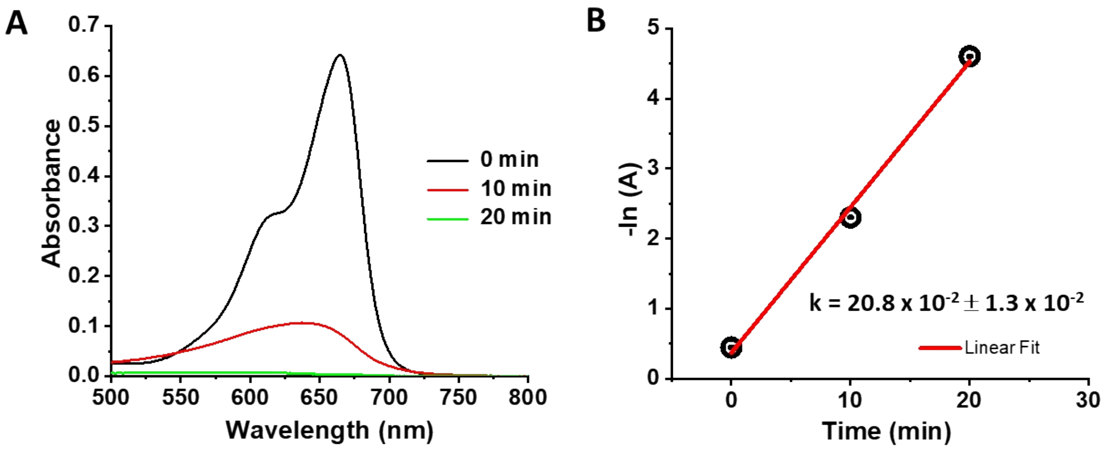

Figure S9: (A) UV-visible absorption spectrum of methylene blue dye photodegradation in the presence of Ce-carbonate deposited onto TiO_2 photocatalyst at pH 6. (B) Pseudo-first-order rate constant of the corresponding methylene blue dye photodegradation.

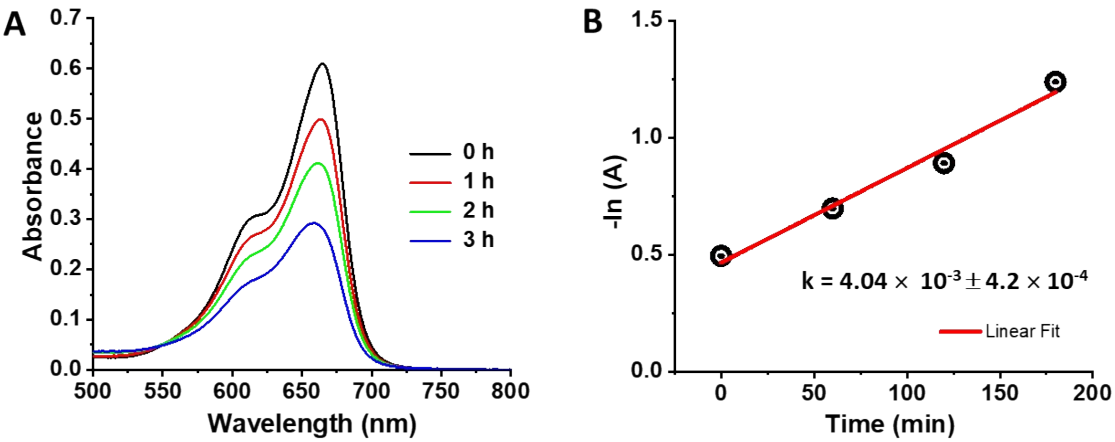

Figure S10: (A) UV-visible absorption spectrum of methylene blue dye photodegradation in the presence of Ce-carbonate deposited onto TiO_2 photocatalyst at pH 7. (B) Pseudo-first-order rate constant of the corresponding methylene blue dye photodegradation.

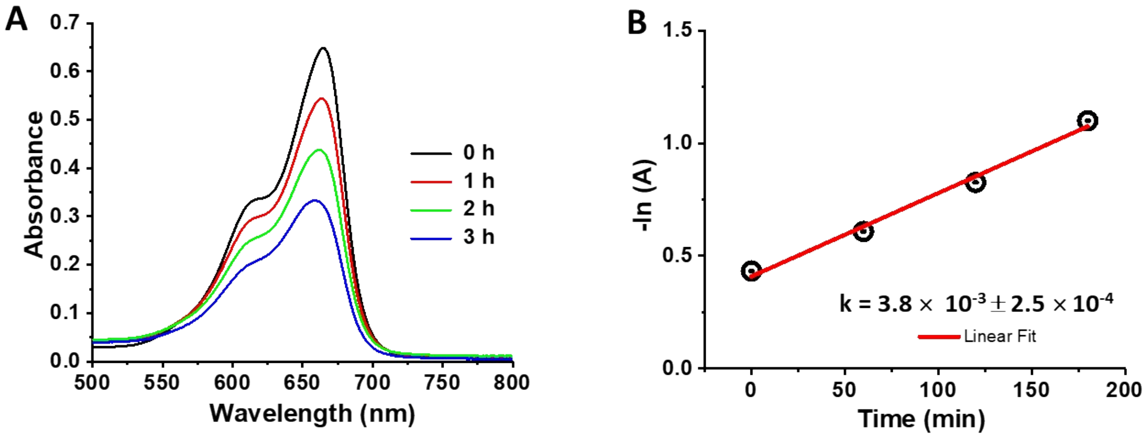

Figure S11: (A) UV-visible absorption spectrum of methylene blue dye photodegradation in the presence of Ce-carbonate deposited onto TiO_2 photocatalyst at pH 7.8. (B) Pseudo-first-order rate constant of the corresponding methylene blue dye photodegradation.

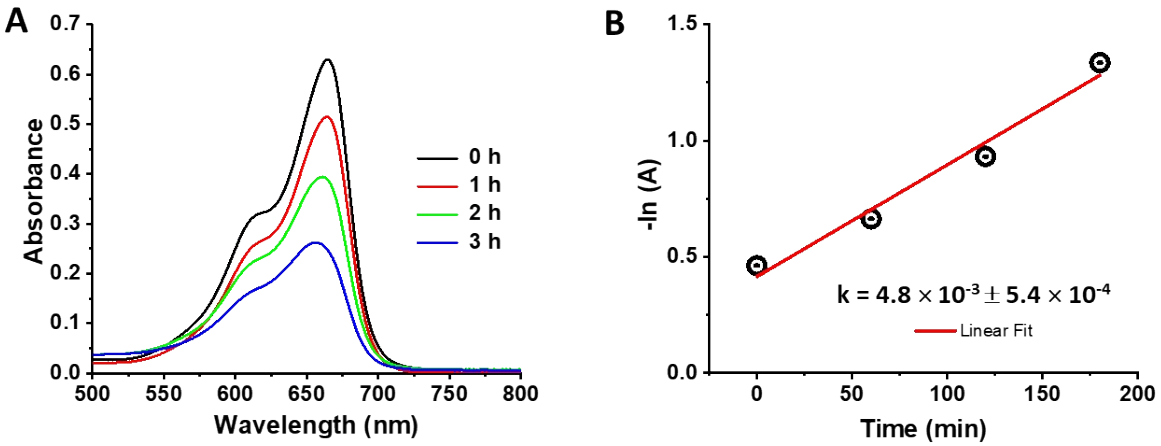

Figure S12: (A) UV-visible absorption spectrum of methylene blue dye photodegradation in the presence of Ce-carbonate deposited onto TiO_2 photocatalyst at pH 8.2. Dilute NaOH solution was used to equilibrate the pH to 8.2. (B) Pseudo-first-order rate constant of the corresponding methylene blue dye photodegradation.

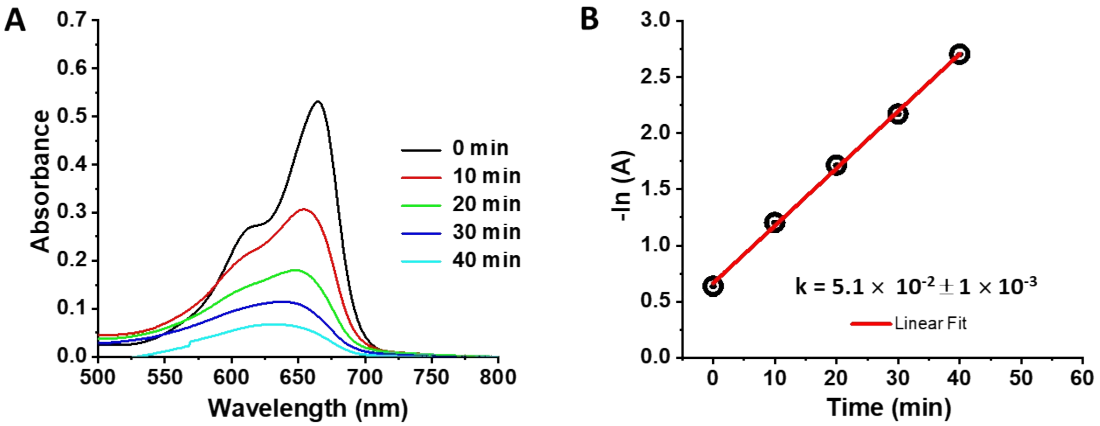

Figure S13: (A) UV-visible absorption spectrum of methylene blue dye photodegradation in the presence of Ce-carbonate deposited onto TiO_2 photocatalyst at pH 9.2. Dilute NaOH solution was used to equilibrate the pH to 9.2. (B) Pseudo-first-order rate constant of the corresponding methylene blue dye photodegradation.

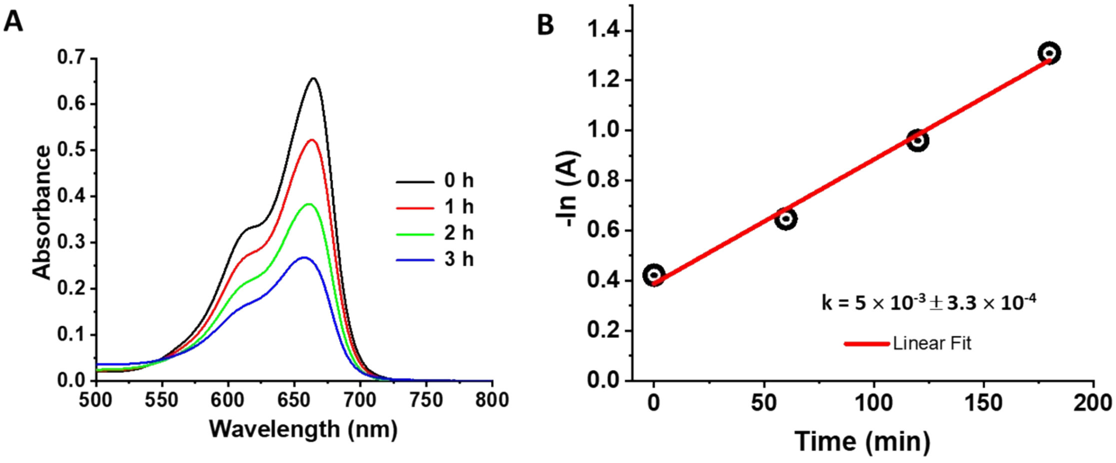

Figure S14: (A) UV-visible absorption spectrum of methylene blue dye photodegradation in the presence of Ce-carbonate deposited onto TiO_2 photocatalyst at pH 8.2. Dilute Na_2CO_3 solution was used to equilibrate the pH to 8.2. (B) Pseudo-first-order rate constant of the corresponding methylene blue dye photodegradation.

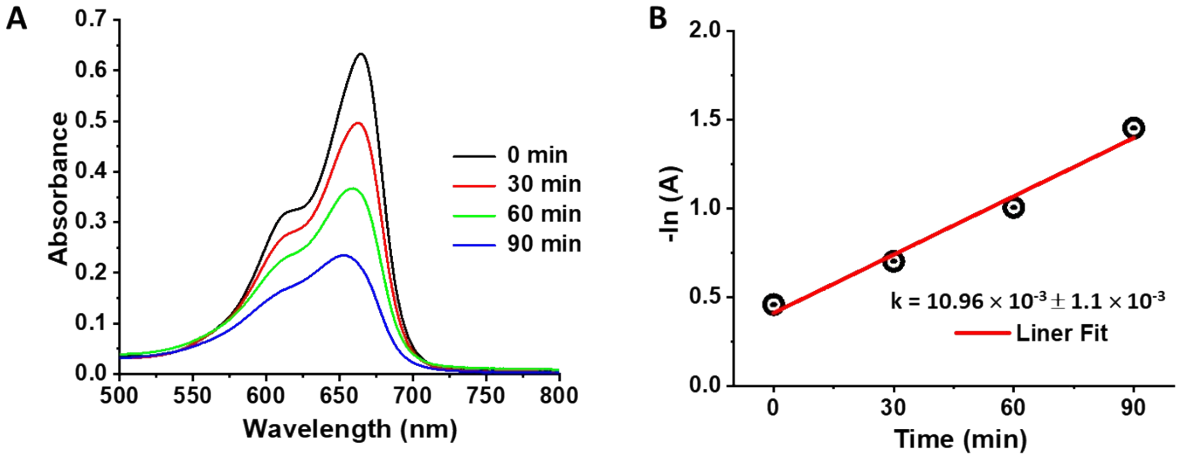

Figure S15: UV-visible absorption spectrum of methylene blue dye photodegradation in the presence of $Ce_2(CO_3)_3 \cdot 8H_2O$ with same amount of active Ce mass determined using ICP as Ce-carbonate deposited onto TiO_2. Experimental: 1.0 mg of $Ce_2(CO_3)_3 \cdot 8H_2O$ and 13.3 mg of TiO_2 were dispersed in 100 mL of deonized water by first sonicating for 7 min and subsequently stirring for 15 min. A uniform suspension was thus made, and under rapid stirring, 15.1 mL of the uniform suspension was withdrawn with a pipette and added to a photoreactor. In this fashion, 0.15 mg of $Ce_2(CO_3)_3 \cdot 8H_2O$ were added to the reactor. This is the same amount of Ce as added in an photocatalysis experiment involving 1 mg of Mg-Ce mixed carbonate. To this suspension, we added 83.9 mL of deionized water and sonicated the mixture for 5 min. 1 mL of 10^{-3}M methylene blue was added, and the mixture was stirred in the dark for 30 min, prior to initiation of photocatalysis with lights on, using the standard procedure.

References:

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3 K. Song, H. Schmid, V. Srot, E. Gilardi, G. Gregori, K. Du, J. Maier and P. A. van Aken, *APL Mater.*, 2014, **2**, 032104.