Electronic Supplementary Information for

Inherent Enantioselective Adsorption and Photocatalytic Removal of L-Phenylalanine on Cerium Phosphate Films†

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1. Material and Methods

1.1. Chemicals

P25 TiO_2 (CAS: 13463-67-7) was purchased from Holland Moran, rhabdophane-phase $CePO_4$ (CAS:13454-71-2) was purchased from Alfa-Aesar, 2-Propanol (CAS:67-63-0) was purchased from Bio-Lab, Tetraethyl-orthosilicate (CAS:78-10-4) was purchased from Sigma-Aldrich, Ludox (CAS:7631-86-9) was purchased from Sigma-Aldrich, Hydrochloric acid 32% (CAS:7647-01-0) was purchased from Bio-Lab, Triton TX-100 (CAS:9002931) was purchased from DAEJUNG, n-Hexanol (CAS:111-27-3) was purchased from Sigma-Aldrich, Cyclohexane (CAS:110-82-7) was purchased from Sigma-Aldrich, Cerium chloride heptahydrate ($CeCl_3*7H_2O$) (CAS:18618558) was purchased from Sigma-Aldrich, HPLC water (CAS:6795-25) was purchased from Macron, Ammonium hydroxide (NH_4OH) (CAS:1336-21-6) was purchased from Frutarom, and Sodium hydrogen phosphate (Na_2HPO_4) (CAS:13100876) was purchased from Merck.

1.2. Synthesis of Monazite-Phase $CePO_4$

The synthesis of Monazite-Phase $CePO_4$ was based on an adaptation of two known syntheses of hydroxyapatite and TiO_2 using microemulsions as microreactors.[1,2]

Monazite-phase $CePO_4$ was prepared by mixing three solutions according to the following description; Solution 1 contained 10 ml triton X-100, 10 ml n-hexanol, and 40 ml cyclohexane, solution 2 contained 0.653 g cerium chloride ($CeCl_3$) in 3 ml HPLC-grade water, and solution 3 contained 0.44 ml ammonium hydroxide (NH_4OH), 2.36 ml HPLC-grade water and 0.2385 g sodium hydrogen phosphate (Na_2HPO_4).

After mixing each solution (until complete solvation), solutions two and three were added dropwise and simultaneously into solution one, under constant stirring. Following 24 hours of stirring at room temperature, the resulting suspension was centrifuged for 10 minutes at 8,000 RPM (app. 13,000 g) at 4°C. The separated particles were washed with ethanol, HPLC-grade water and ethanol again, with centrifugation at the same conditions, following each washing step. The resulting solids were then dried for 1 hour at 100°C, and calcined for 2 hours at 450°C. Finally, the solid was ground into a powder.

1.3. Film Preparation

1.3.1. Silicon Binder Preparation

In order to homogenously coat glass plate substrates with the catalysts, a binder solution was prepared according to the following steps: 1.42 ml Tetraethyl-orthosilicate were added into a glass vessel. 2.17 ml of room temperature Ludox, 34 µl 32%w hydrochloric acid, and 6.37 ml 2-propanol were added dropwise and sequentially to the vessel, with 2-propanol added in two steps: First,

approximately 2 ml was added until the solution became milky, waiting until the solution became clear, and then adding the rest, again dropwise. The solution was stirred overnight.

1.3.2. Catalyst-Binder Film Deposition

Four different catalysts were weighed (240.1 mg P25 TiO_2, 703.5 mg rhabdophane $CePO_4$, 703.8 mg monazite $CePO_4$) for the preparation of the film coating. Each catalyst was added to an empty vial. The powders were vortexed for a few minutes. Then, 1 ml of HPLC-grade water was added to each vial, and again vortexed. The vials were ultrasonicated for 30 minutes. Next, 0.537 ml binder solution and 1.314 ml n-propanol were added to each vial (to obtain a 1:3 SiO_2 : Catalyst molar ratio). The vials were stirred, ultrasonicated again for 45 minutes and left under stirring. 1”x0.5” glass plates were cut from microscope slides, washed in water and placed in a UV-Ozone cleaning system (UVOCS) for 5 minutes, following by drying at 120°C in an oven.

The clean glass plates were coated with the catalyst-binder suspension using spin-coating (Setcas LLC) by the following steps: 80 µl catalyst-binder solution was deposited slowly and uniformly on the glass plate, accelerated at 200 RPM/sec and spun 10 seconds at 500 RPM, after which the spinning was accelerated again (500 RPM/sec) to 2000 RPM for 30 seconds. After depositing the first layer, the films were annealed for 30 minutes at 120°C. Next, another layer was deposited with 80 µl of suspension, accelerated at 200 RPM/sec and spun 10 seconds at 500 RPM, after which the spinning was accelerated again (500 RPM/sec) to 1000 RPM for 30 seconds. This was followed by a second annealing step.

2. Experimental

2.1. Catalyst Characterization

The glass plates coated with catalyst-binder films were characterized by SEM-EDS, shown in Figures S1-S3, and XRD, shown in Figure S4.

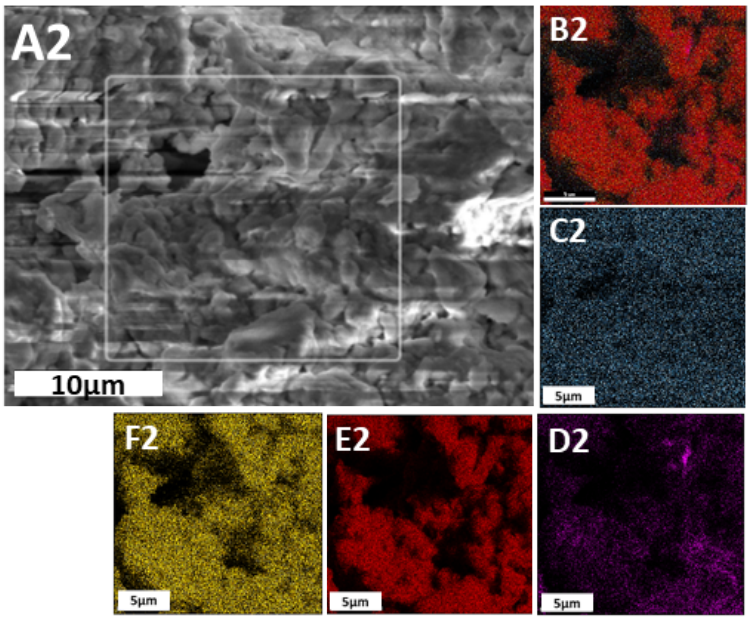

Figure S1 Micrograph (A2) and atomic distribution maps of films of rhabdophane-phase $CePO_4$ in a silica binder. Elemental overlays (B2) and distributions of Ce (C2), Si (D2), O (E2), and P (F2) are shown.

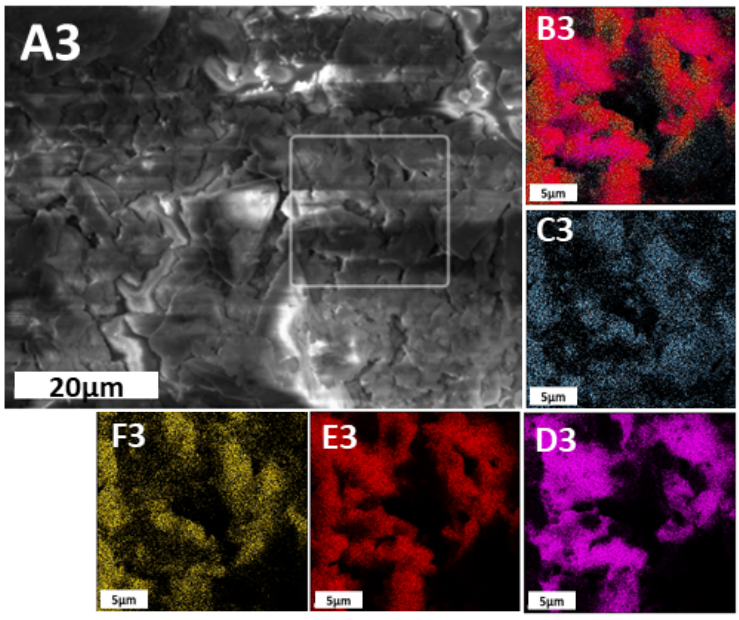

Figure S2 Micrograph (A3) and atomic distribution maps of films of monazite-phase $CePO_4$ in a silica binder. Elemental overlays (B3) and distributions of Ce (C3), Si (D3), O (E3), and P (F2) are shown.

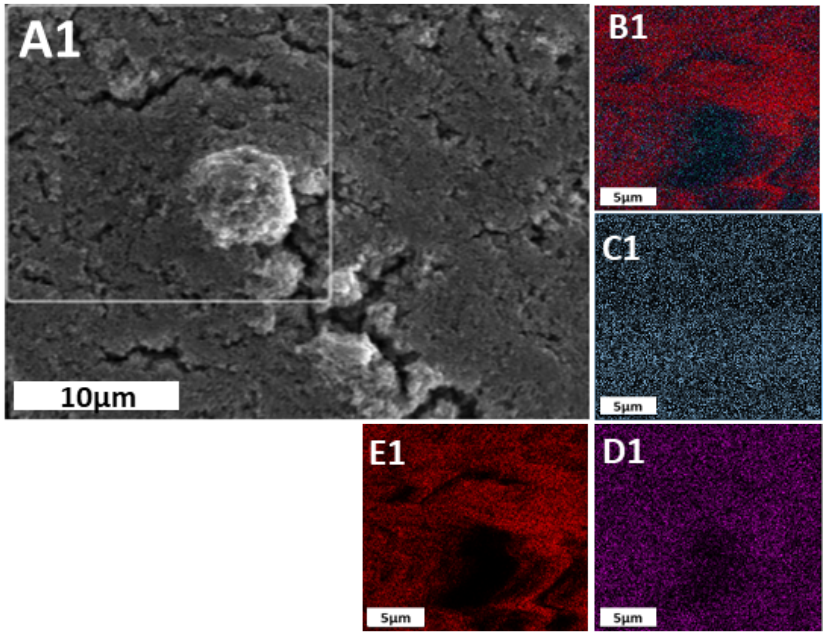

Figure S3 Micrograph (A1) and atomic distribution maps of films of P25 in a silica binder. Elemental overlays (B1) and distributions of Ti (C1), Si (D1), and O (E1) are shown.

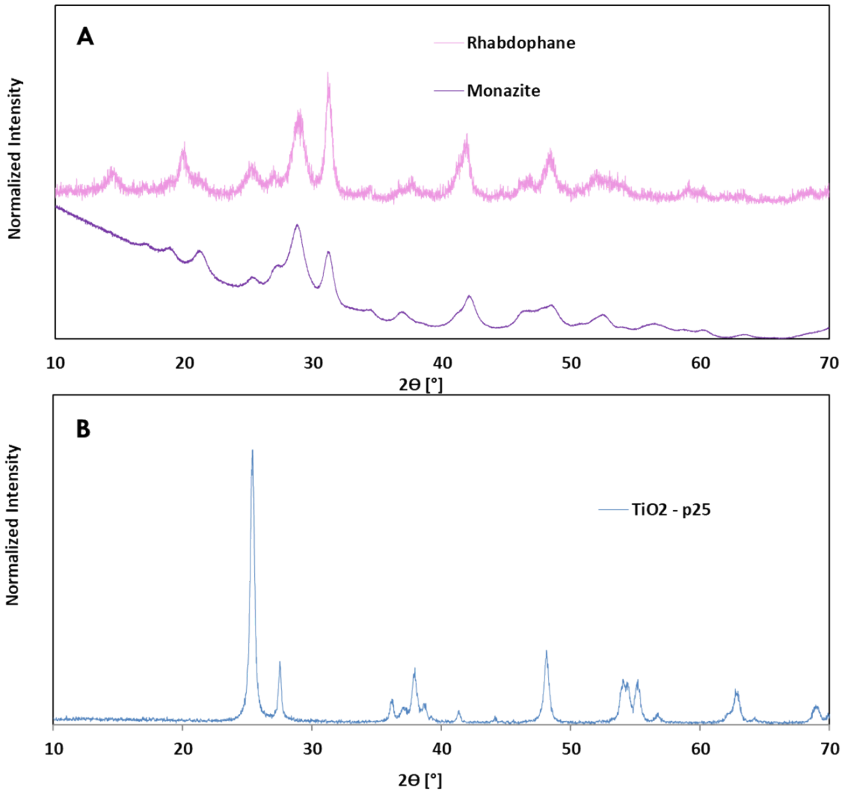

Figure S4 XRD patterns of (A) rhabdophane (commercial) and monazite (synthesized) $CePO_4$, and (B) P25 TiO_2

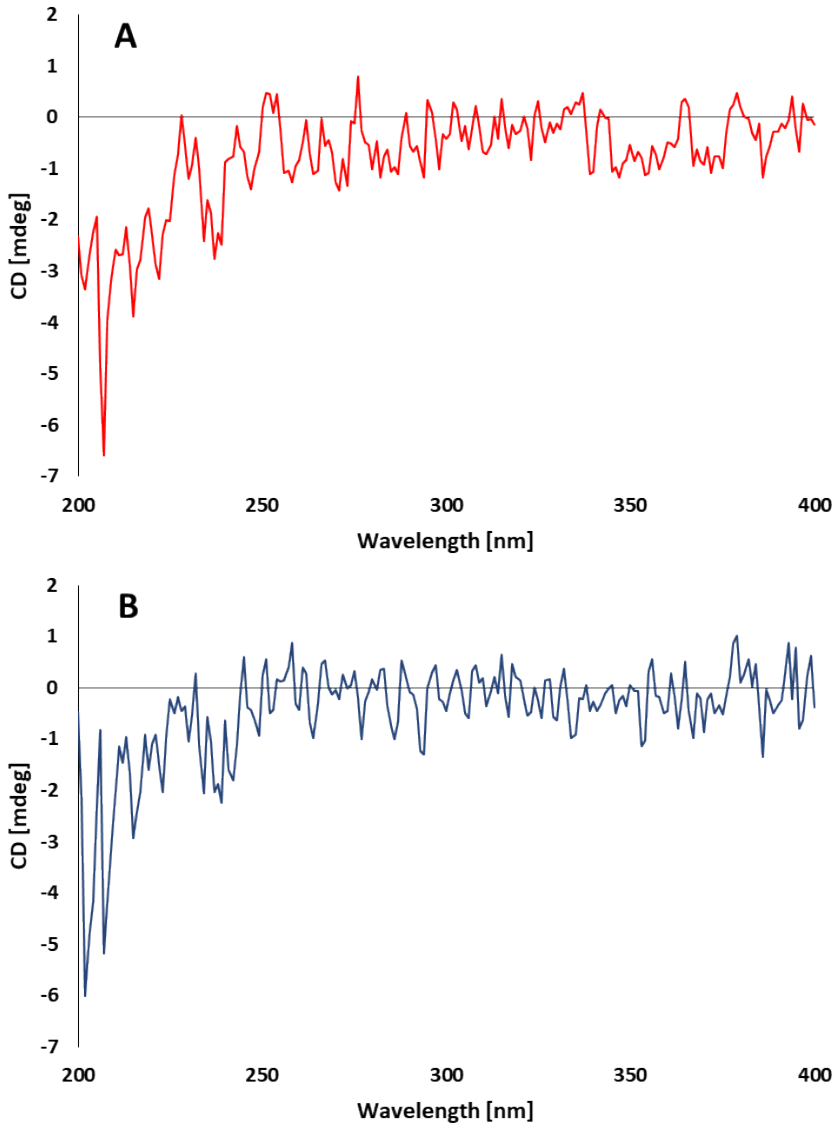

Figure S5 Circular dichroism traces of (A) rhabdophane-phase $CePO_4$ and (B) monazite-phase $CePO_4$. Measurements were performed on pellets containing 1.4% wt $CePO_4$ powder in KBr.

Circular dichroism measurements were performed on pellets composed of 70 mg KBr mixed with 1.2 mg of the relevant catalyst powder, and pressed at 10 tonnes for 1 hour (Figure S5). Measurements were performed according to the process outlined by Kuroda et al.[3]

2.2. Adsorption experiments

2.2.1. Racemic Experiments

A racemic solution of L- and D-phenylalanine (PA) was prepared by adding 50 mg L-PA and 50 mg D-PA into 250 ml of HPLC-grade water. The solution was mixed. Each catalyst film was placed in a specially designed Teflon holder inside a Carousel 12 Plus Reaction System (R.B. Radley & Co. Ltd.) tube, with 20 ml of racemic

solution added. The Carousel system was stirred at 900 RPM at room temperature for 48 hours without illumination. Samples were collected at different times and analyzed using HPLC.

2.2.2. Enantiopure Experiments

Two enantiopure solutions of L- and D-phenylalanine (PA) were prepared by adding either 40.6 mg L-PA or 40.2 mg D-PA (separately) into 100 ml of HPLC-grade water. Each catalyst film was placed in a specially designed Teflon holder inside a Carousel tube and 20 ml of one enantiopure solution was added. The Carousel system was stirred at 900 RPM at room temperature for 48 hours without illumination. Samples were collected at different times and analyzed using HPLC.

2.3. Photocatalytic Experiments

2.3.1. Racemic Experiments

A racemic solution of L- and D-phenylalanine (PA) was prepared by adding 50.1 mg L-PA and 49.9 mg D-PA into 250 ml of HPLC-grade water, under mixing. Each catalyst film was placed in a specially designed Teflon holder inside a Carousel tube and 20 ml of the racemic solution was added. The Carousel system was stirred at 900 RPM at room temperature. The tubes were stirred overnight without illumination for initial adsorption. Three samples were collected at different times. Then, each tube was illuminated by a 365 nm UV LED at a flux of 8 mW/cm^2. Samples were taken periodically up to 150 hours and analyzed using HPLC.

2.3.2. Enantiopure Experiments

Two enantiopure solutions of L- and D-phenylalanine (PA) were prepared by adding either 50.1 mg L-PA or 49.9 mg D-PA (separately) into 250 ml of HPLC-grade water. The solutions were mixed. Each catalyst film was placed in a specially designed Teflon holder inside a Carousel tube and 20 ml of one enantiopure solution was added. The Carousel system was stirred at 900 RPM at room temperature. The tubes were stirred overnight without illumination for initial adsorption. Three samples were collected at different times. Then, each tube was illuminated by a 365 nm UV LED at a flux of 8 mW/cm^2. Samples were taken periodically up to 150 hours and analyzed using HPLC.

2.4. HPLC Protocol

Before using HPLC analysis, the UV-absorption spectrum of PA was measured by a Shimadzu UV-2600 spectrophotometer (Figure S6). The phenylalanine characteristic peaks were found to be at 257nm and ~205nm. Since the 205 nm peak showed a higher signal, it was chosen for HPLC analysis.

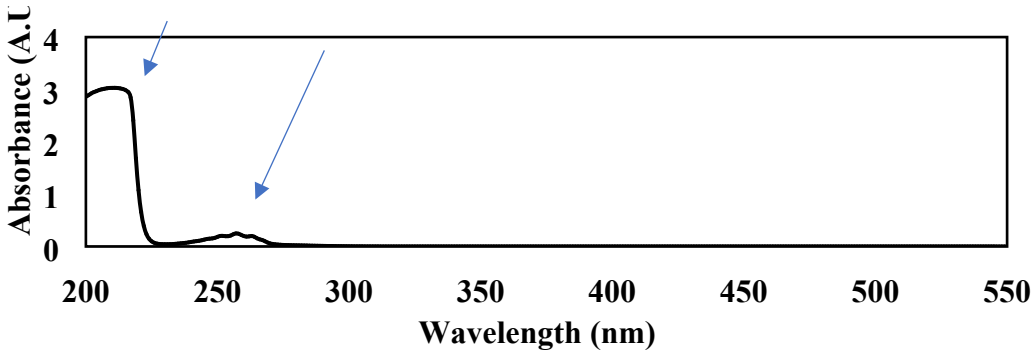

Figure S6 Phenylalanine absorbance spectrum in water

The mobile phase used in the HPLC was prepared by mixing 70%v HPLC-grade methanol, 30%v HPLC-grade water, and 0.03%v formic acid. The mixture was sonicated for 1 hour before measurement. An Astec Chirobiotic T 15 cm x 4.6 mm column was used, with a Supelco C18 pre-column. Each run was set to an isocratic flow rate of 0.5 ml/min for 10 min. The monitoring wavelength of the detector was set to 205 nm.

2.5. HPLC Calibration Curves

Figure S7 shows the HPLC chromatograms for enantiopure L-PA (S7A), enantiopure D-PA (S7B), and racemic PA (S7C).

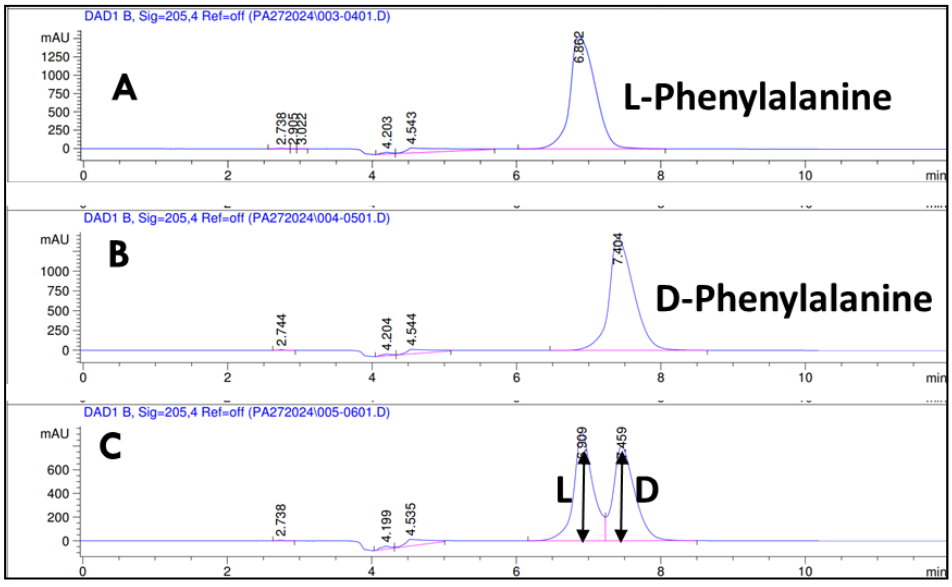

Figure S7 The HPLC chromatogram of (A) enantiopure L-PA, (B) enantiopure D-PA, and (C) racemic PA.

A calibration curve was prepared using the height of the relevant peaks from the chromatogram, as peak area was deemed too susceptible to deviations due to degradation product peaks. Figure S8 presents the calibration for a racemic solution.

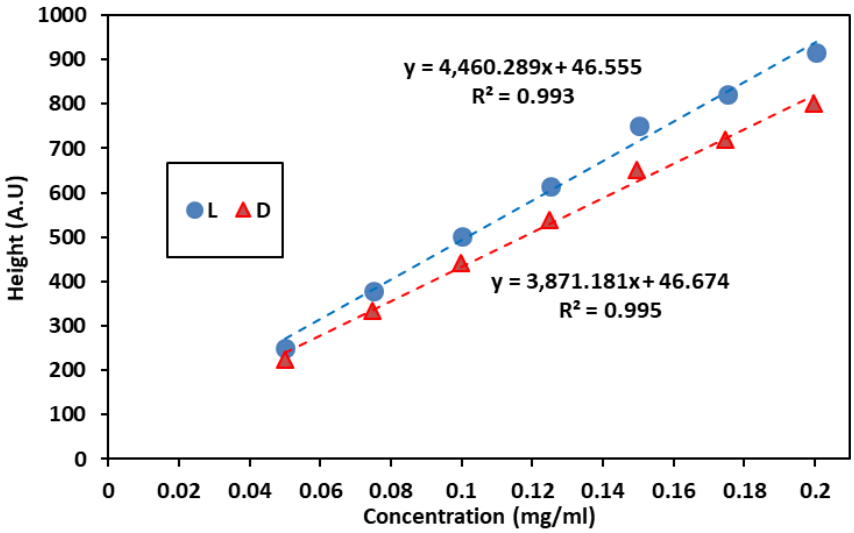

Figure S8 Racemic solution calibration curves for L- and D-PA

3. Exemplary Chromatograms

Exemplary chromatograms are presented here (Figures S9, S10 and S11) for both the adsorption and photocatalytic experiments, showing the peaks for both enantiomers (for racemic solutions) or each enantiomer (single-enantiomer solutions) at the start and end of the experiments.

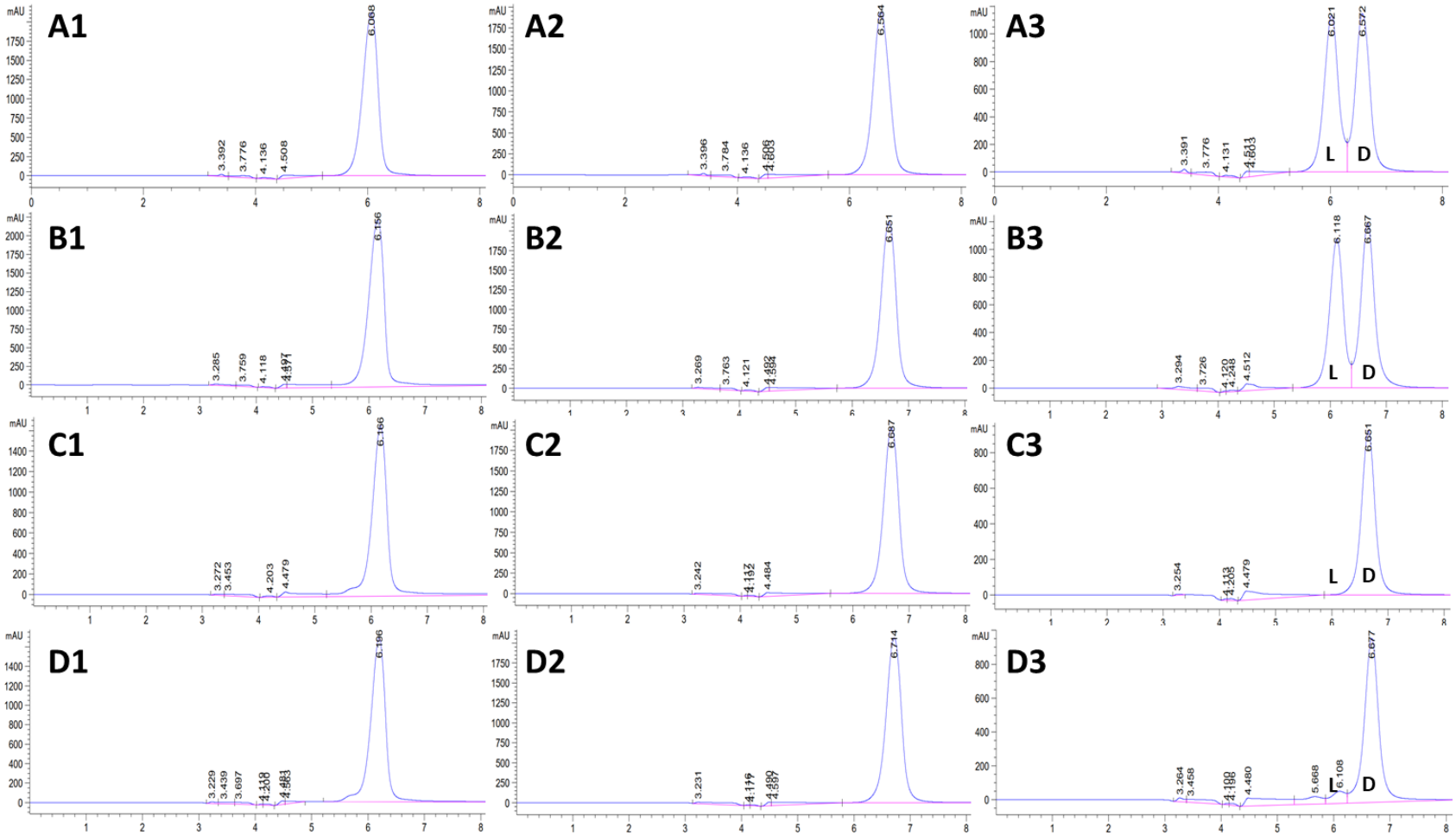

Figure S9 Chiral HPLC chromatograms of phenylalanine (A) before adsorption, and (B-D) after 48 hours of adsorption under dark conditions on (B) P25, (C) rhabdophane $CePO_4$ and (D) monazite $CePO_4$ films. (1) denotes experiments in solutions of only L-phenylalanine, (2) experiments of only D-phenylalanine, and (3) experiments in racemic mixtures.

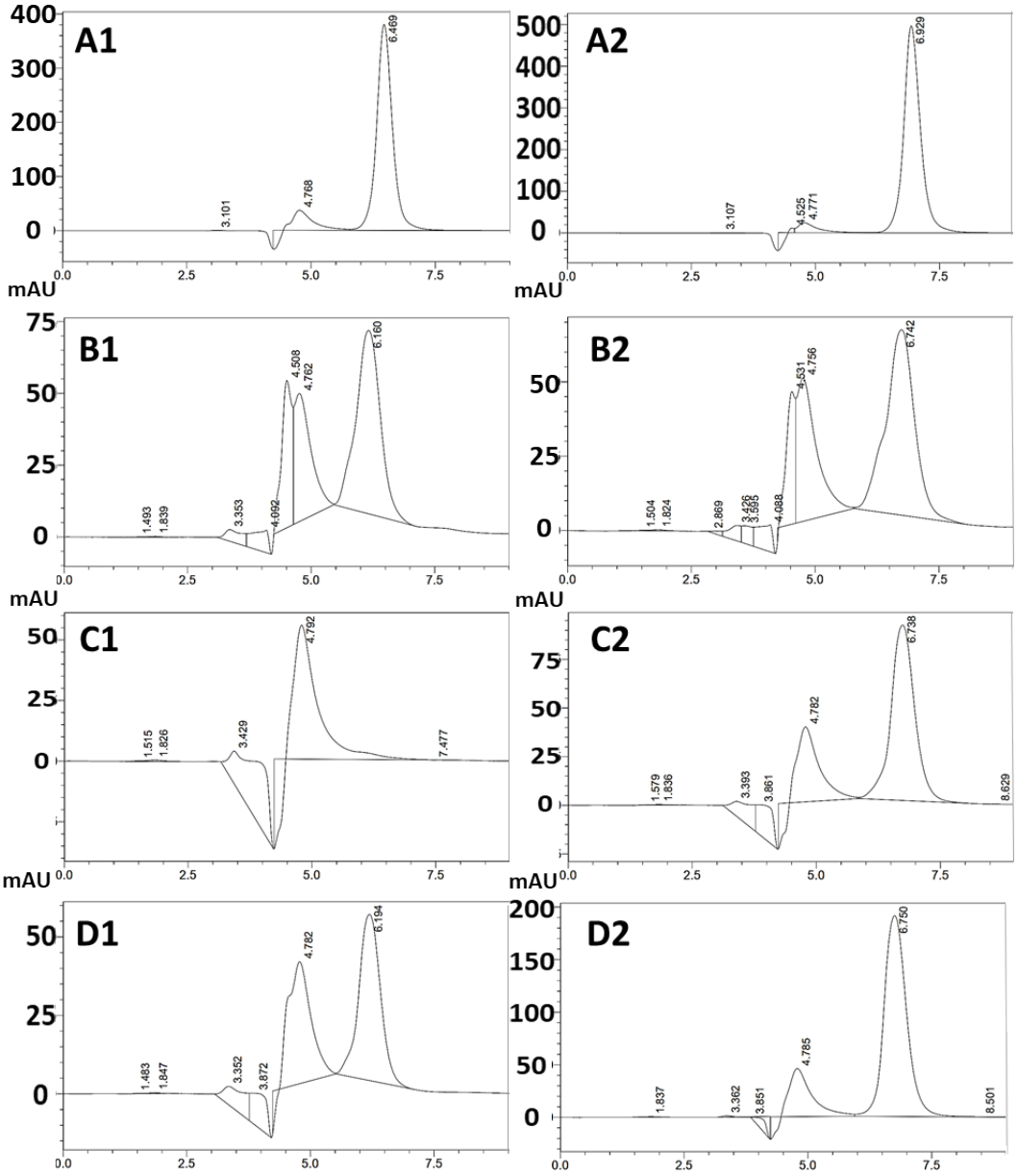

Figure S10 HPLC chromatograms of phenylalanine (A) before reaction, and (B-D) after 150 hours of photocatalytic reaction on (B) P25, (C) rhabdophane $CePO_4$ and (D) monazite $CePO_4$ films. (1) denotes experiments in solutions of only L-phenylalanine, and (2) experiments of only D-phenylalanine.

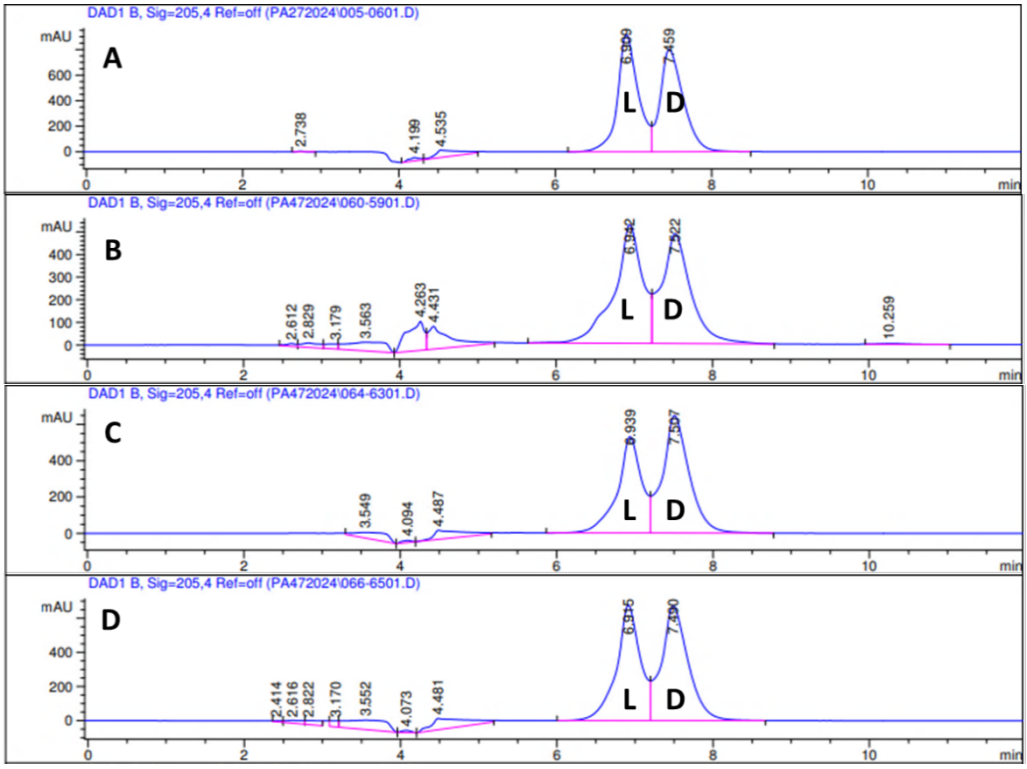

Figure S11 Chiral HPLC chromatograms of racemic mixtures of phenylalanine (A) before reaction, and (B-D) after photocatalytic reaction on (B) P25, (C) rhabdophane $CePO_4$ and (D) monazite $CePO_4$ films.

4. Control Experiments

Control experiments were performed in order to rule out spontaneous photolysis (Fig. S12), dark hydrolysis (Fig. S13) and selective adsorption on the silica binder (Fig. S14).

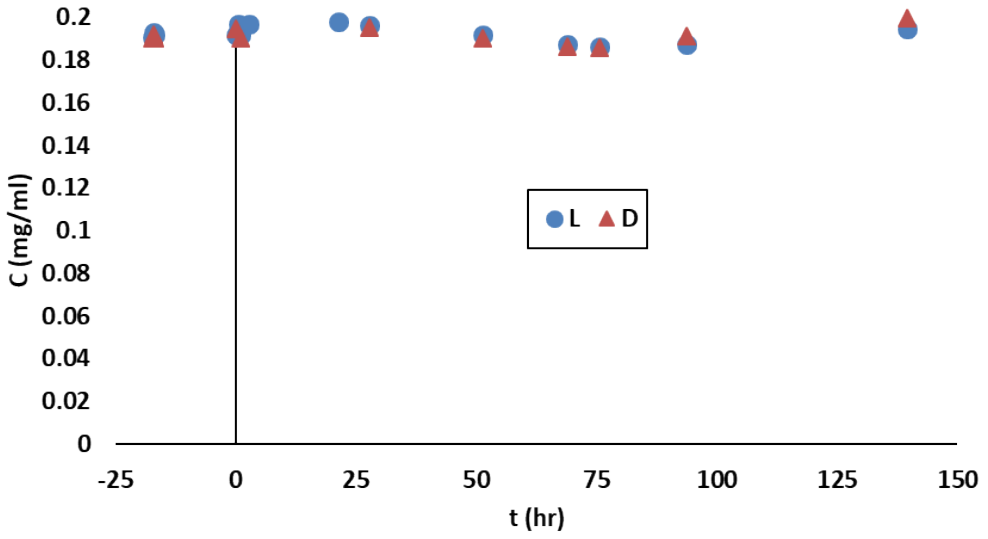

Figure S12 Photolysis under 365 nm irradiation of L- and D-PA in the absence of a catalyst

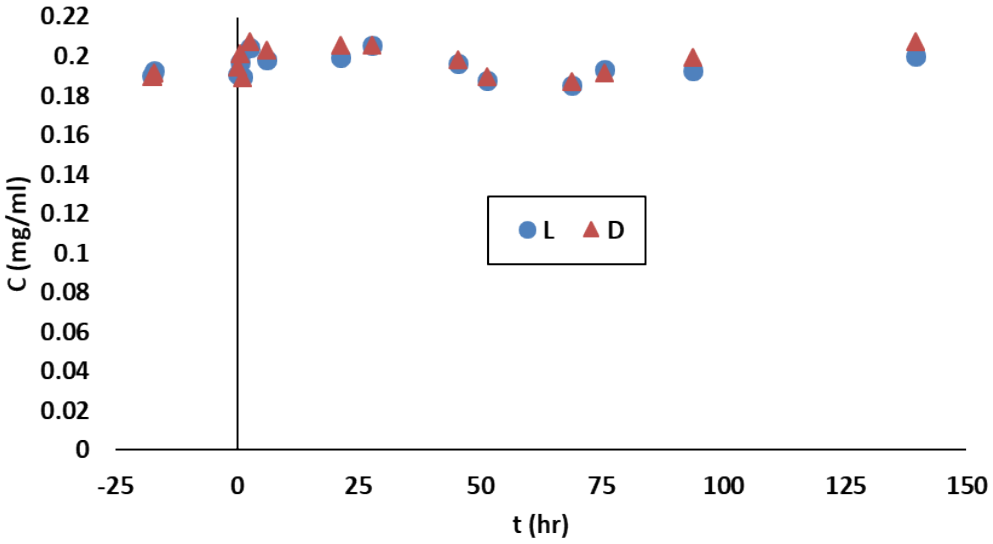

Figure S13 Dark hydrolysis of L- and D-PA in the absence of a catalyst

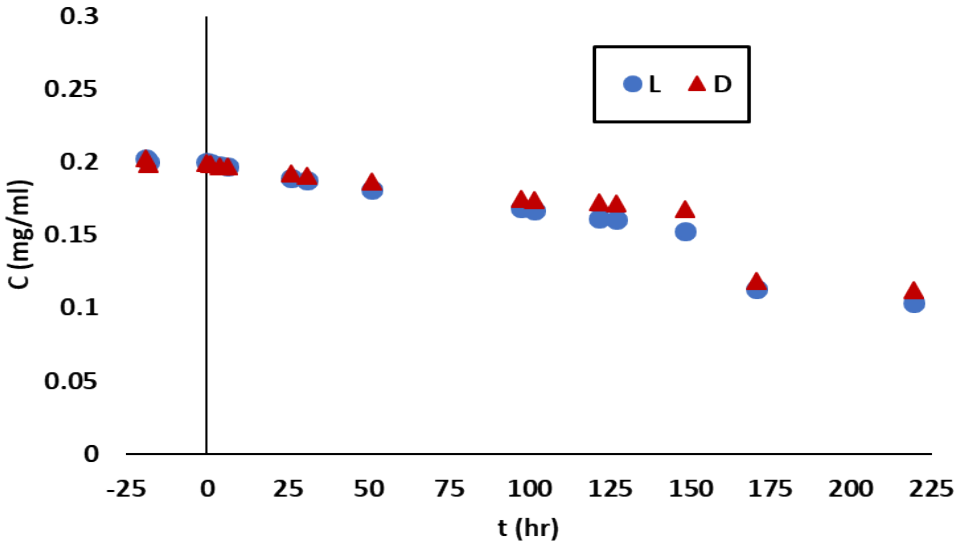

Figure S14 Adsorption of L- and D-PA on a film of SiO_2 binder

5. Kinetic Rate Constants Assuming 1st-order Kinetics

Presenting ln(C/C0) versus reaction time yielded, for most cases, a linear dependence (Figures S15-S17). Based on this apparent 1st-order behavior, the kinetic rate constants were calculated (Table S1).

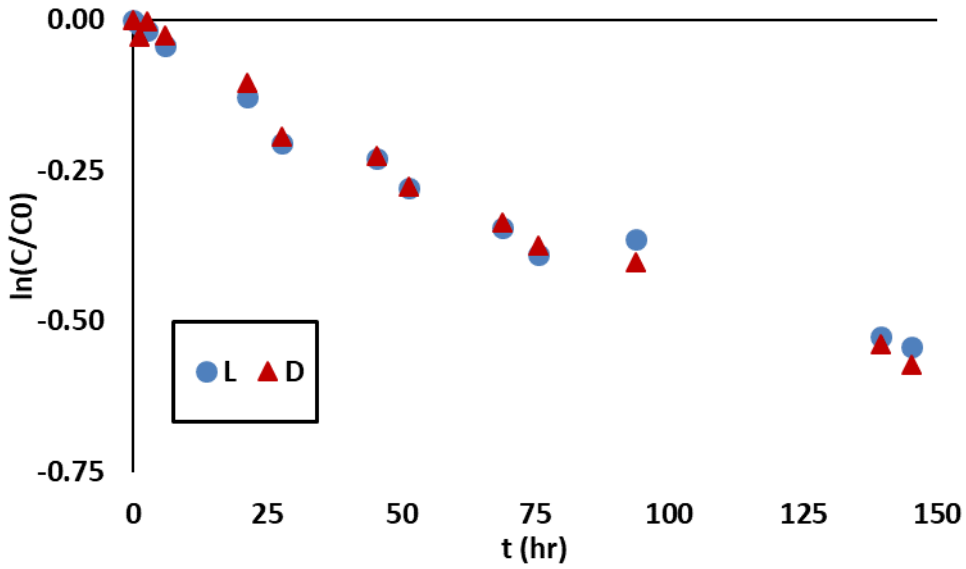

Figure S15 1st-order kinetic model fitting of a photocatalytic reaction in a racemic solution using a P25 film.

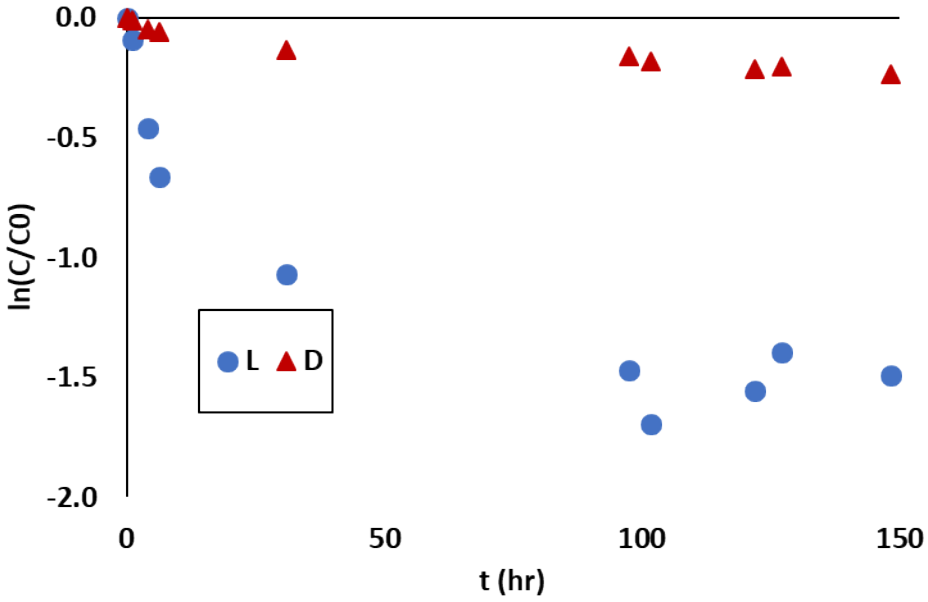

Figure S16 1st-order kinetic model fitting of a photocatalytic reaction in a racemic solution using a rhabdophane $CePO_4$ film.

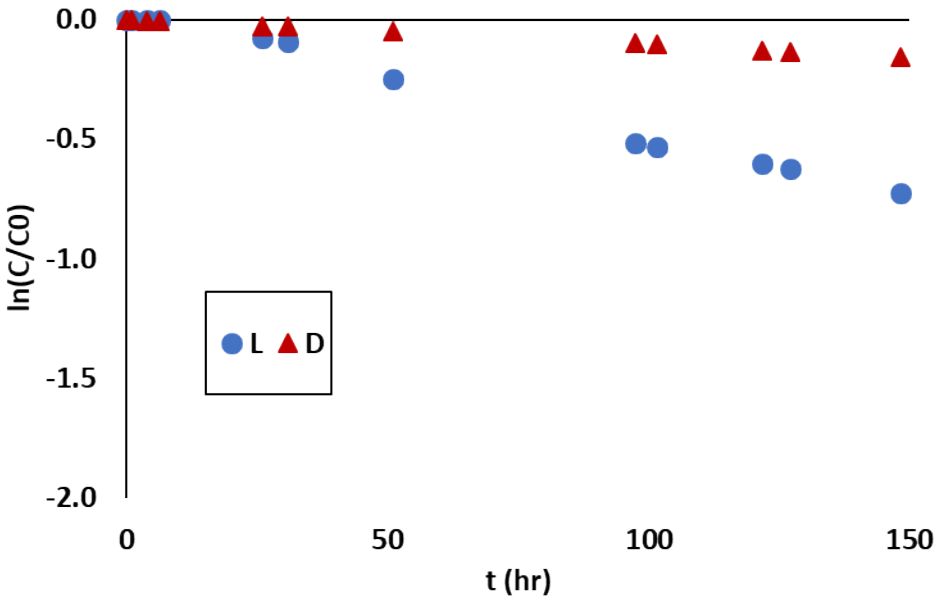

Figure S17 1st-order kinetic model fitting of a photocatalytic reaction in a racemic solution using a monazite $CePO_4$ film.

Table S1 Average calculated kinetic constants for both enantiopure and racemic photocatalytic experiments, shown with standard deviation

Catalyst		k_L [1/hr]	k_D [1/hr]
P25	Enantiopure	0.0120 ±0.00005	0.0159 ±0.0046
	Racemic	0.0036 ±0.002	0.00375 ±0.00025
Rhabdophane $CePO_4$	Enantiopure	0.0119 ±0.0002	0.0055 ±0.0017
	Racemic	0.0093 ±0.0045	0.0013 ±0.0004
Monazite $CePO_4$	Enantiopure	0.0127 ±0.0016	0.0028 ±0.0004
	Racemic	0.0062 ±0.0037	0.0012 ±0.0004

6. Citrulline adsorption experiments

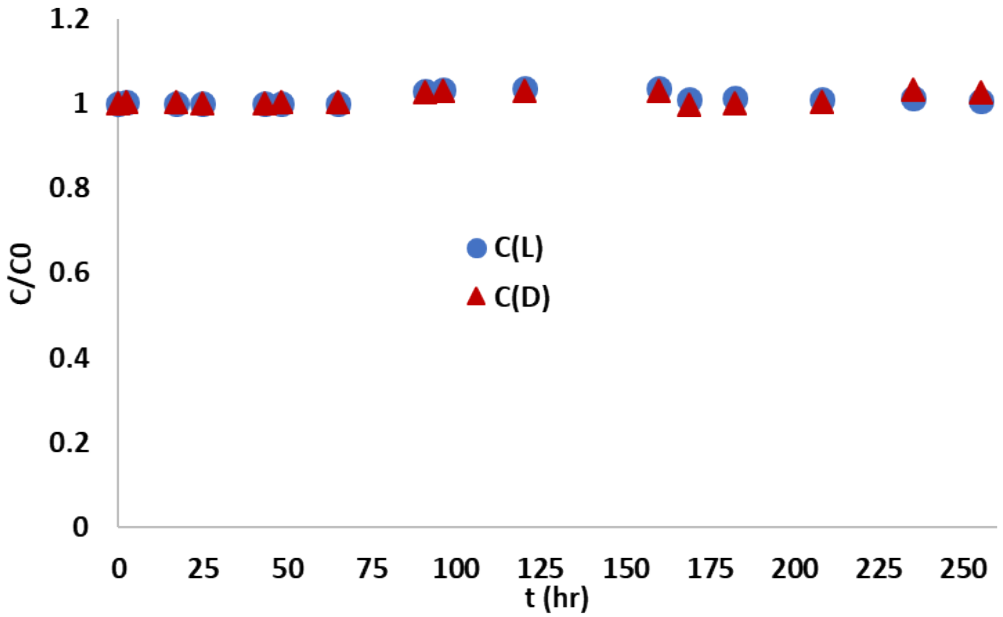

Figure S18 Adsorption of a citrulline racemic solution using a titania P25 film.

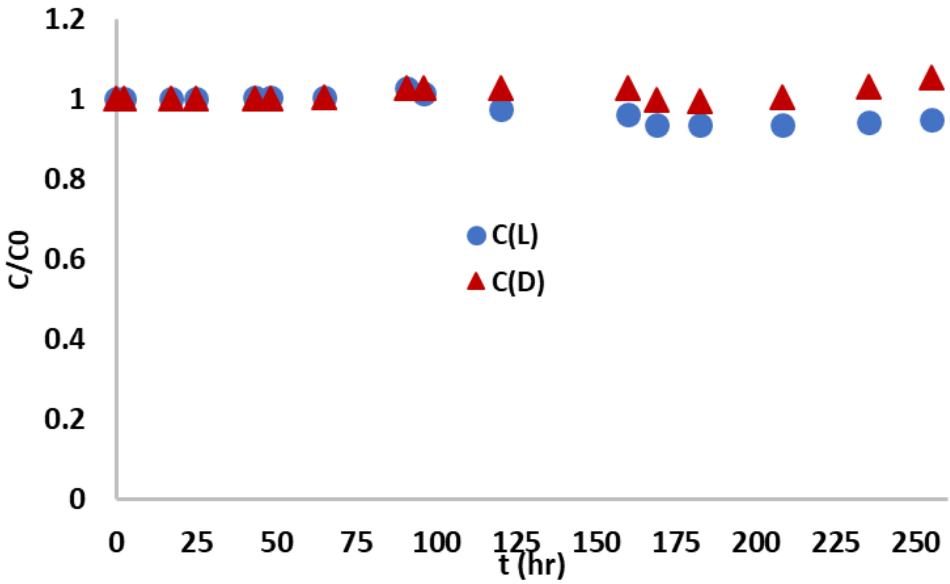

Figure S19 Adsorption of a citrulline racemic solution using a rhabdophane $CePO_4$ film.

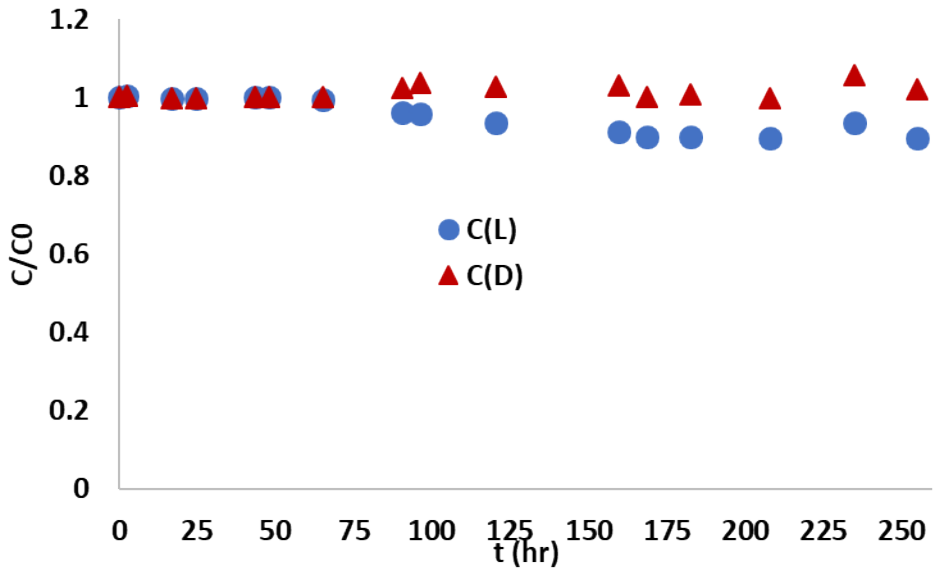

Figure S20 Adsorption of a citrulline racemic solution using a monazite $CePO_4$ film.

7. References

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2. V. Chhabra, V. Pillai, B. K. Mishra, A. Morrone, D. O. Shah, *Langmuir*, 1995, **11**, 3307–3311.

3. R. Kuroda, T. Honma, *Chirality*, 2000, **12**, 269-277.