

Supplementary Material (ESI)

Carbon-doped Titania Flakes with Octahedral Bipyramid Skeleton Structure for the Visible-light Photocatalytic Mineralization of Ciprofloxacin†

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1. Experimental details

All chemical reagents were of analytical grade and used without further purification.

1.1 Preparation of C-doped TiO₂ flacks (CTF) with dominant {001} facets

Titanium carbide solid powder (TiC, particle size: 2~4 μm, Aladdin Reagent Company) was employed as the TiO₂ precursor. In a typical synthesis procedure, 0.9 g of TiC powder was added into 10 mL of HF (40%) to form suspension. After stirring for half an hour, 10 mL of HNO₃ (68%) was added. After stirring for an hour, 10 mL of ultrapure water was added. After continuously stirring for half an hour, the mixed suspension was transferred to an 80 mL Teflon-lined autoclave and heated at 180 °C for 30 hours. After the reaction, the products were collected by centrifugation and washed with ultrapure water for several times, and then were dried overnight at 80 °C in air.

1.2 Preparation of C-doped TiO₂ sheets (CTS) with dominant {001} facets

The preparation of CTS with dominant {001} facets was based on the previous work.¹ In a typical synthesis route, 2.5 mL of HF, 10 mL of HNO₃ and 18 mL of ultrapure water were mixed under vigorous stirring to form solution. Then, 0.9 g of TiC powder was added into the solution. After stirring for an hour, the suspension was transferred to an 80 mL Teflon-lined autoclave and heated at 180 °C for 30 hours. After the reaction, the products were collected by centrifugation and washed with ultrapure water for several

times, and then were dried overnight at 80 °C in air. The calculation of the percentage of {001} facets was carried out according to previous publication.²

1.3 Characterizations

Scanning electron microscopy (SEM) images were performed on S-4800 (Hitachi, Japan) equipment. Transmission electron microscope (TEM) tests were carried out on JEM 2100 (JEOL, Japan). X-ray diffraction (XRD) patterns were recorded at room temperature with an X'pert PROMPD diffractometer (PANalytical, Holland) with copper K α 1 radiation. X-ray photoelectron spectroscopy (XPS) analyses were tested on a PHI5300 analyzer (Perkin Elmer, America) with aluminum K α radiation. The nitrogen adsorption measurements were carried out at 77 K using an ASAP 2010 analyzer (Micromeritics, USA), and the Barrett-Joyner-Halenda (BJH) pore diameter distribution curves were obtained from the desorption branch and specific surface areas were obtained according to the Brunauer-Emmett-Teller (BET) model. Ultraviolet-visible (UV-vis) absorption spectroscopies were recorded by a UV-2450 spectrophotometer (Shimadzu, Japan) equipped with an integrating sphere, and the baseline correction was done using a calibrated sample of barium sulfate.

1.4 Photocatalytic activity test

The photocatalytic experiment was carried out in a photo reaction system (Fig. S9). A 1000 W Xe lamp equipped with a 420 nm cut-off glass filter (removing the UV irradiation below 420 nm wavelength), positioned in the center of a water-cooled quartz jacket, was used to offer visible light irradiation. At the side of quartz jacket, a 50-mL cylindrical vessel was used as the reactive bottle to load reaction solution. The distance between lamp and reactive bottle was 40 mm. In the bottom of the reactive bottle, a magnetic stirrer was equipped to achieve effective dispersion. Air was bubbled through the reaction solution from the bottom of the reactive bottle to ensure a constant dissolved oxygen concentration and fully dispersed catalyst particles. The photocatalytic activity of samples was evaluated by the mineralization of CIP solution without investigating the degradation intermediates in detail. Photocatalyst powder (50 mg) was added into 50 mL CIP solution with the concentration of 50 mg/L to form suspension. During photocatalysis, the suspension was stirred continuously. At given time interval, a certain volume of suspension was taken out and immediately centrifuged to eliminate solid particles. Total organic carbon (TOC) of filtrate was measured by using a Shimadzu TOC-VCPH analyzer.

2. Calculation methods and details

Theoretical investigations were performed by first-principles calculation based on the periodic density functional theory (DFT), as implemented in CASTEP code.³ The plane wave basis and the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE)⁴ were employed for calculating exchange-correlation energy. Vanderbilt ultrasoft pseudopotential⁵ was applied to approximate the interactions between the ions and valence electrons. The atomic configurations of C, O and Ti generated from it were $2s^22p^2$, $2s^22p^4$ and $3s^23p^63d^24s^2$, respectively. The Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm⁶ was adopted to optimize the atomic positions. During the relaxations, all structures have been relaxed to the criteria, 5.0×10^{-6} eV/atom for maximum energy total energy change, 0.01 eV/Å for maximum force, 0.02 GPa for maximum stress, and 5.0×10^{-4} Å for the maximum displacement, respectively. A kinetic energy cutoff in the plane wave basis was set as 440 eV. Their k-point meshes were set at $11 \times 11 \times 9$ for the TiO₂ bulk unit cell, and $7 \times 7 \times 3$ for the C-doped TiO₂ bulk unit cell, using Monkhorst-Pack scheme.⁷

To avoid the well-known underestimated band gap problem of transition metal oxide, a rotationally invariant LDA+U approach^{8,9} was introduced to evaluate the on-site Colulomb interaction for Ti 3d electrons, which provided a reasonable electronic structure of pure anatase TiO₂ and C-doped anatase TiO₂.

The optimized lattice parameters of pure bulk anatase TiO₂ is a=3.791 Å, c=9.795 Å, which is in agreement with experimental values, a=3.784 Å, c=9.515 Å.¹⁰ Note that the parameters calculated based on PBE is larger.¹¹ With extensive tests, the appropriate Hubbard U we identified is 7.8 eV, the same parameter as Ref.12. The correctional band gap of bulk anatase is 3.24 eV, which is very close to the experimental data 3.20 eV.¹³ And the value is 2.16 eV without LDA+U correction. The same correction was adopted to the calculation of C-doped anatase TiO₂ system. The content of elements in C-doped anatase sample we synthetized was identified by XPS element analyses where the atomic percent of Ti and O atoms are 24.64% and 47.63%, respectively. Therefore the ratio of Ti and O atoms approximately equals 4:7. Thus, to illustrate the contribution of reducing band gap by impurity energy levels (IELs) qualitatively with less calculation, the C-doped system we simulated was Ti₄O₇C.

Reference

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3. Figures

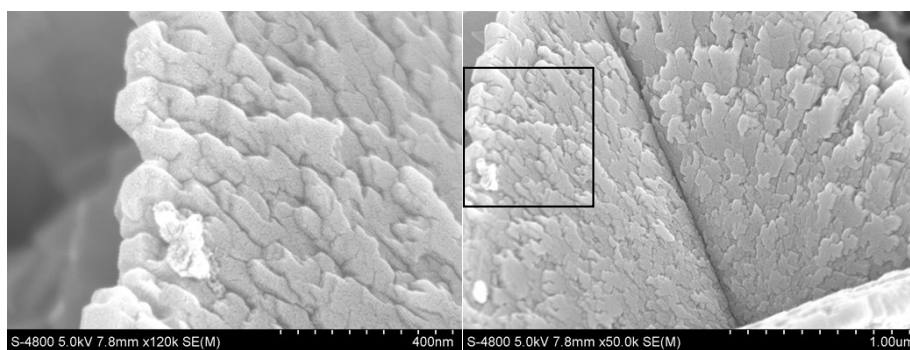


Fig. S1. The high-magnification SEM images of CTF (the left image is the high-magnification in the area marked with black square in the right image)

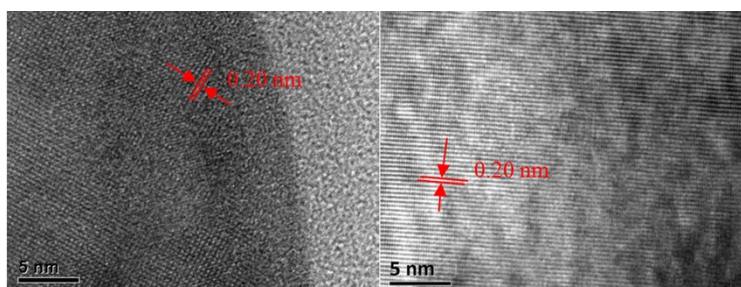


Fig. S2. HRTEM images of CTF (left) and CTS (right).

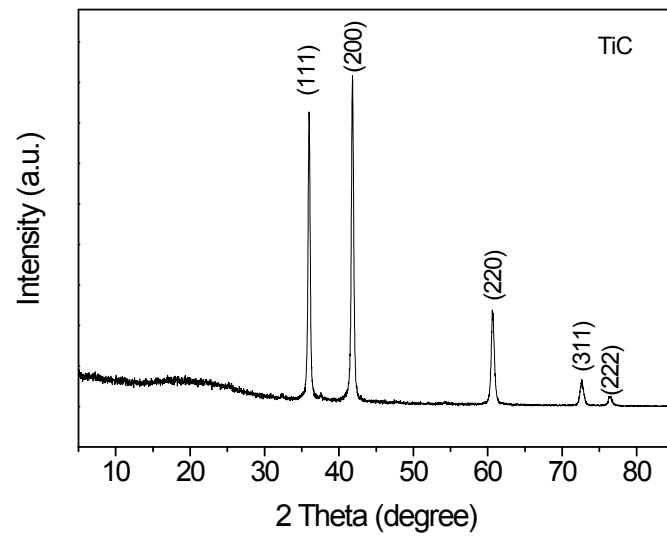


Fig. S3. XRD pattern of TiC precursor

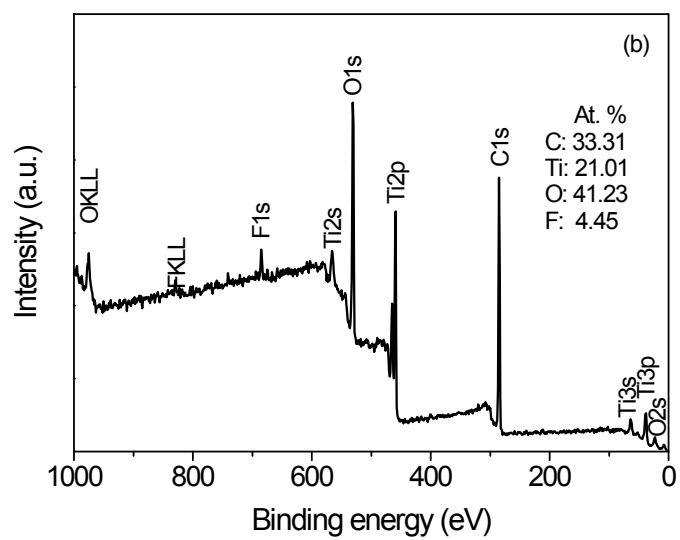
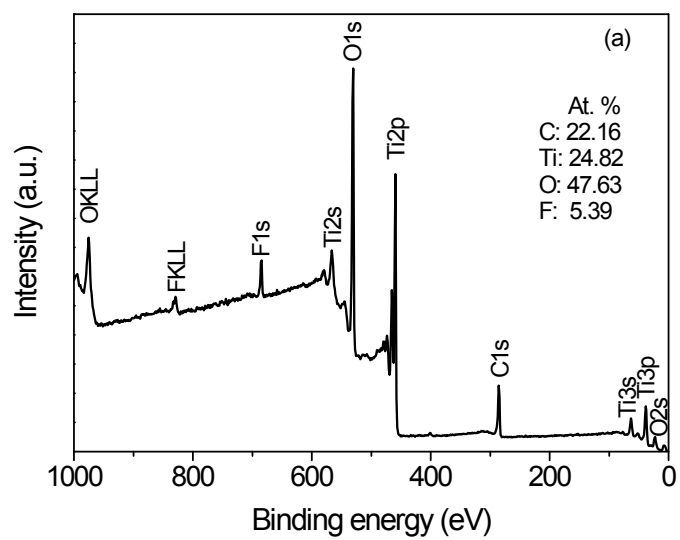


Fig. S4. XPS patterns of CTF (a) and CTS (b).

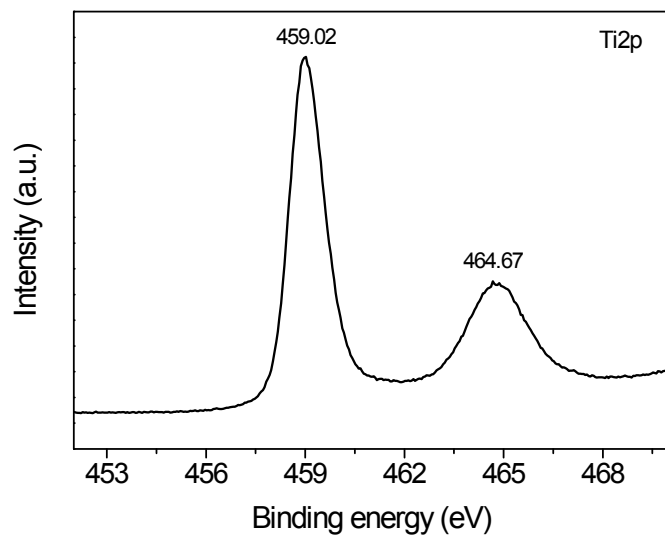


Fig. S5. High-resolution Ti2p XPS spectrum of CTF

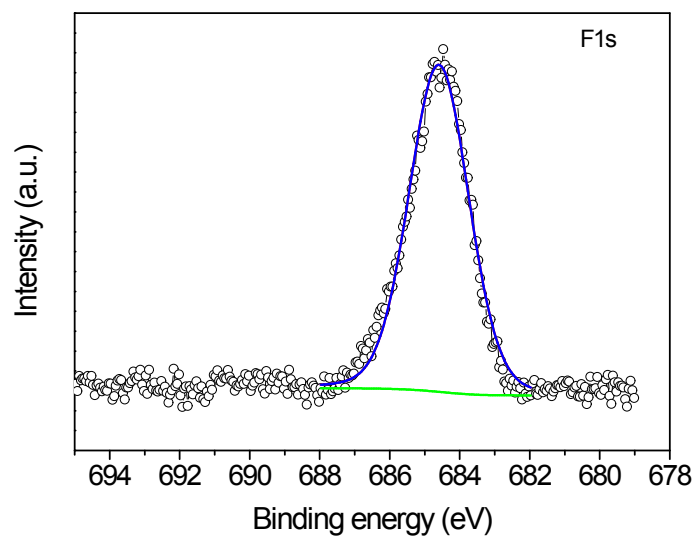


Fig. S6. high-resolution F1s XPS spectrum of CTF



Fig. S7. The optical photographs of all samples.

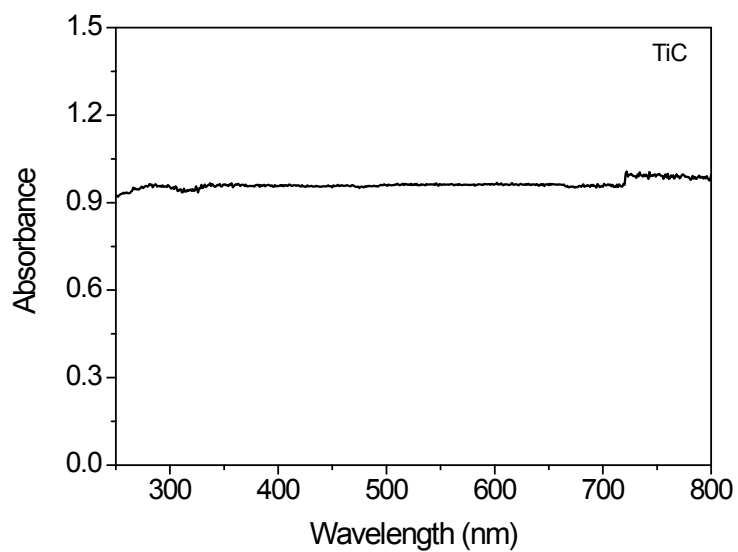


Fig. S8. UV-visible spectrum of TiC precursor

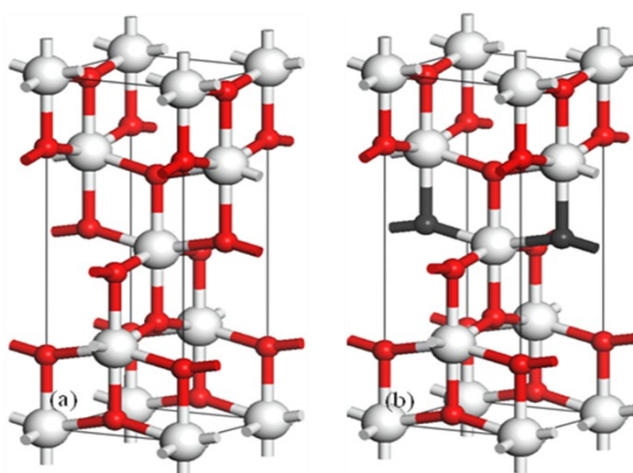


Fig. S9. Supercell model for (a) intrinsic anatase and (b) C-doped anatase.
The white, red and black balls represent the Ti, O and C atoms, respectively.

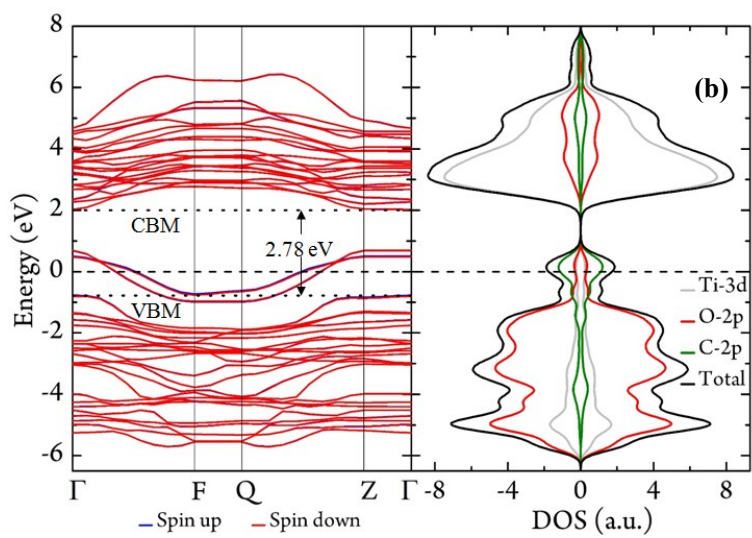
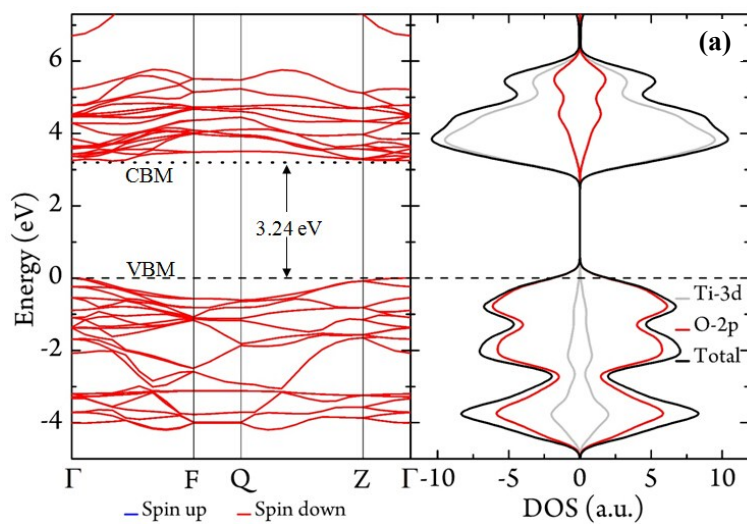


Fig. S10. Band structure and projected spin density of states of the pure anatase TiO₂ (a) and C-doped anatase TiO₂ (b). The dashed line represents the Fermi level.

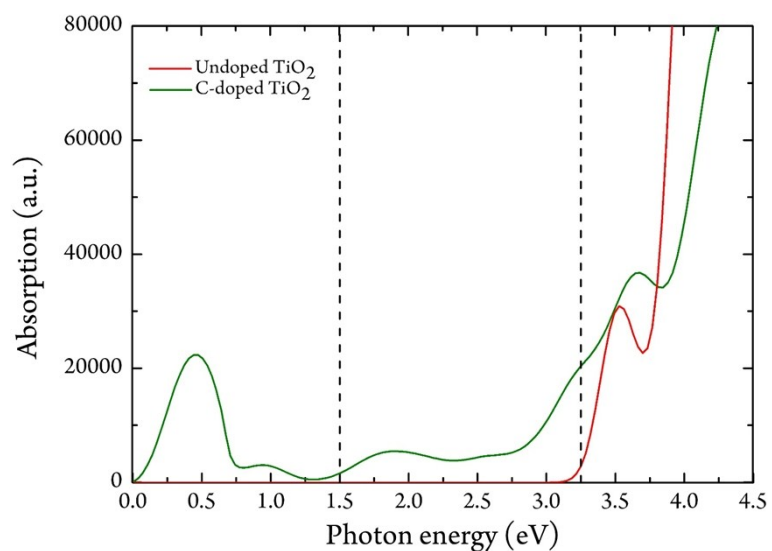


Fig. S11. Calculated optical absorption spectra of the pure and C-doped anatase TiO_2 .

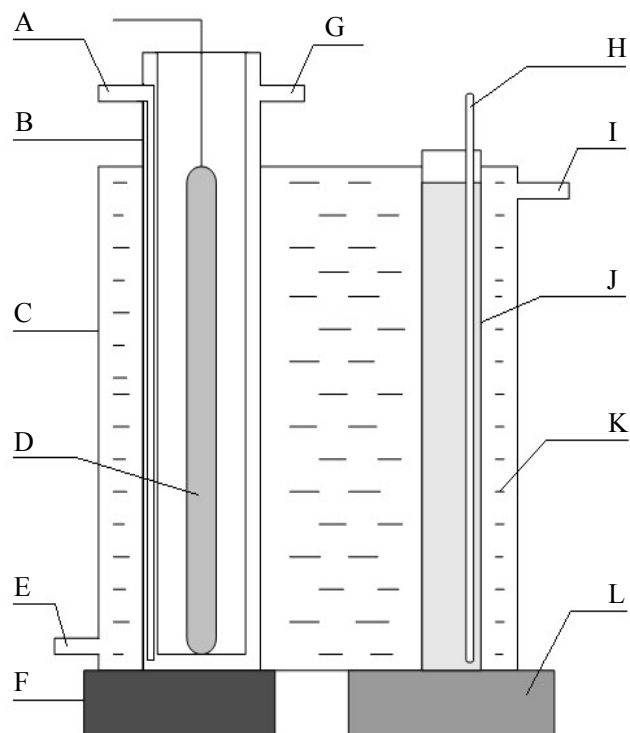


Fig. S12. Schematic illustration of the photo reaction system: (A) cooling water inlet 1; (B) water-cooled quartz jacket; (C) water container; (D) lamp; (E) cooling water inlet 2; (F) stow-wood; (G) cooling water outlet 1; (H) air inlet; (I) cooling water outlet 2; (J) reactive bottle; (K) cooling water; (L) magnetic stirrer

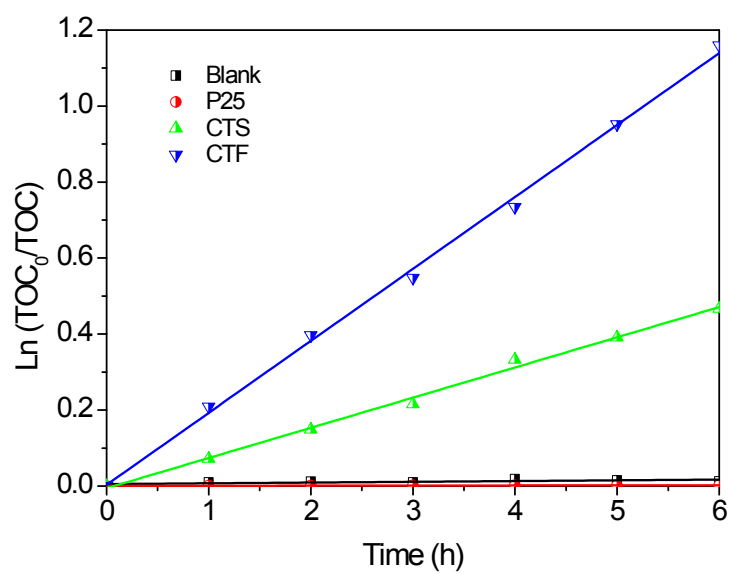


Fig. S13. Photocatalytic reaction kinetics of CIP mineralization ($\text{Ln}(TOC_0/TOC)$ -time curves).