Efficient inactivation of *Microcystis aeruginosa* by carbon mictube supported magnetic photocatalysts under visible light

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Boehm titration:

First, 0.5 g photocatalyst was dispersed in a mixture solution of 100 mL ethanol and NaCl by fully stirring at 25°C for 4 h. The pH value of the obtained suspension was subsequently adjusted to 4.0 with 0.1 M HCl or NaOH standard solution. Then, the solution was titrated from 4.0 to 9.0 with 0.1 M NaOH standard solution. The surface hydroxyl content was calculated as follows:

$$D = \frac{CVN_A \times 10^{-3}}{W} \quad \text{(S1)}$$

where D ($\times 10^{20} \cdot g^{-1}$) is the hydroxyl content on the surface of the sample; C is the concentration of the NaOH standard solution ($mol \cdot L^{-1}$); V is the volume of the consumed NaOH solution (mL) when the pH value was adjusted from 4.0 to 9.0; N_A is

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the Avogadro constant; and W is the mass of the samples (g).

MC-LR test method:

After filtration through a 0.22-μm membrane filter, the concentration of MC-LR was analyzed by high performance liquid chromatography (HPLC, HITACHI, Japan). The samples were separated on a C_{18} column (Waters, 150 × 4.6 mm) with a mobile phase of acetonitrile and 0.1% trifluoroacetic acid micro-pure water. The volume ratio was eluted from the initial ratio of 70:30 to 60:40, and the wavelength was set to 238 nm. The total operation time was 15 min (flow rate: 1 mL·min^{-1}). The degradation rate of MC-LR was determined using the following equation:

$$Removal\ rate\ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad \text{(S2)}$$

where C_0 and C_t represent the initial and residual concentrations of MC-LR (μg·L^{-1}), respectively. The identification of MC-LR and its intermediates was carried out in positive ion mode using HPLC–MS (Agilent, USA) under the conditions described above.

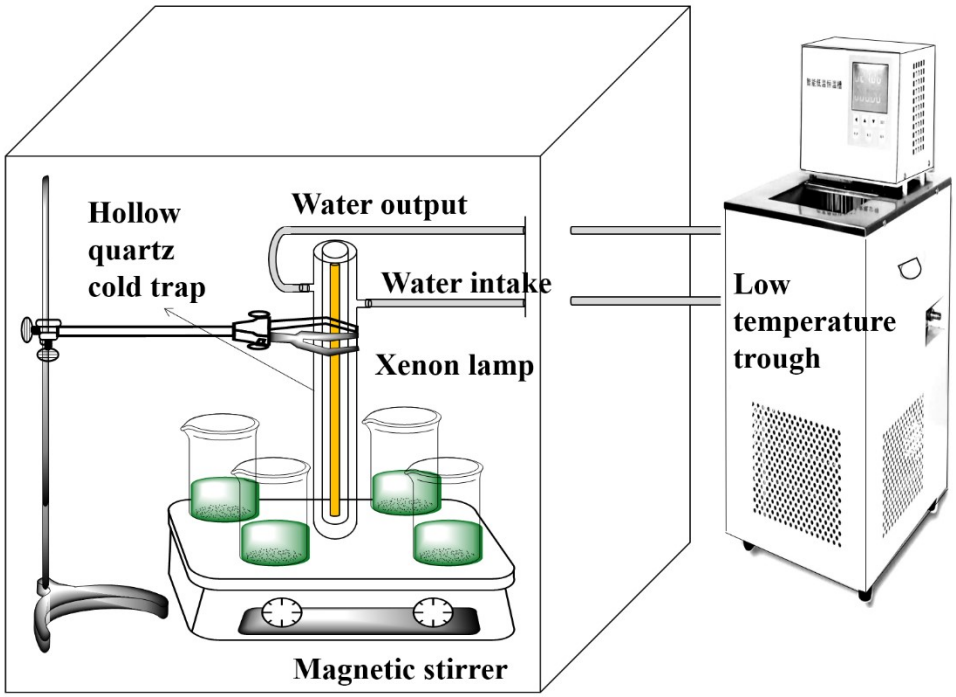

Fig. S1 Photocatalytic experimental device diagram

Table S1 Experimental design

	A: initial algal density (cells·mL^{-1})	B: dosage (g·L^{-1})	C: time (h)
−1	1×10^6	0.2	5
0	3×10^6	0.3	6
1	5×10^6	0.4	7

Table S2 Experimental operation

C-TiO_2				**C-TiO_2-Fe_3O_4**				**C-$TiFe_2O_4$**			
Initial algal density (cells·mL^{-1})	Dosage ($g·L^{-1}$)	Time (h)	Removal rate (%)	Initial algal density (cells·mL^{-1})	dosage ($g·L^{-1}$)	Time (h)	Removal rate (%)	Initial algal density (cells·mL^{-1})	Dosage ($g·L^{-1}$)	Time (h)	Removal rate (%)
1×10^6	0.	6	7	1×10^6	0.4	6	6	1 ×	0.4	6	6
3×10^6	0.	7	4	3×10^6	0.4	7	6	3 ×	0.4	7	7
5×10^6	0.	5	4	5×10^6	0.3	5	4	5 ×	0.3	5	3
1×10^6	0.	5	6	1×10^6	0.3	5	5	1 ×	0.3	5	4
5×10^6	0.	7	4	5×10^6	0.3	7	4	5 ×	0.3	7	4
5×10^6	0.	6	4	5×10^6	0.2	6	4	5 ×	0.2	6	3
5×10^6	0.	6	4	5×10^6	0.4	6	4	5 ×	0.4	6	4
1×10^6	0.	6	6	1×10^6	0.2	6	5	1 ×	0.2	6	4
3×10^6	0.	5	6	3×10^6	0.4	5	4	3 ×	0.4	5	5
3×10^6	0.	6	5	3×10^6	0.3	6	5	3 ×	0.3	6	5
3×10^6	0.	6	5	3×10^6	0.3	6	5	3 ×	0.3	6	5
3×10^6	0.	5	4	3×10^6	0.2	5	3	3 ×	0.2	5	4
3×10^6	0.	6	4	3×10^6	0.3	6	5	3 ×	0.3	6	5
3×10^6	0.	6	5	3×10^6	0.3	6	5	3 ×	0.3	6	5
3×10^6	0.	7	4	3×10^6	0.2	7	4	3 ×	0.2	7	5
3×10^6	0.	6	4	3×10^6	0.3	6	5	3 ×	0.3	6	5
1×10^6	0.	7	6	1×10^6	0.3	7	6	1 ×	0.3	7	6

Table S3 Structural data of the prepared materials

	Specific surface area ($m^2 \cdot g^{-1}$)	**Aperture (nm)**	**Pore volume ($cm^3 \cdot g^{-1}$)**
CMT	386.95	2.73	0.220
TiO_2	40.10	8.47	0.085
C-TiO_2	320.96	2.33	0.204
C-TiO_2-Fe_3O_4	224.62	3.45	0.194
C-$TiFe_2O_4$	260.02	3.05	0.198

Table S4 Surface hydroxyl content of the prepared materials

	Surface hydroxyl content (g^{-1})
CMT	2.7692×10^{20}
TiO_2	0.9632×10^{20}
C-TiO_2	4.214×10^{20}
C-TiO_2-Fe_3O_4	3.2508×10^{20}
C-$TiFe_2O_4$	4.634×10^{20}

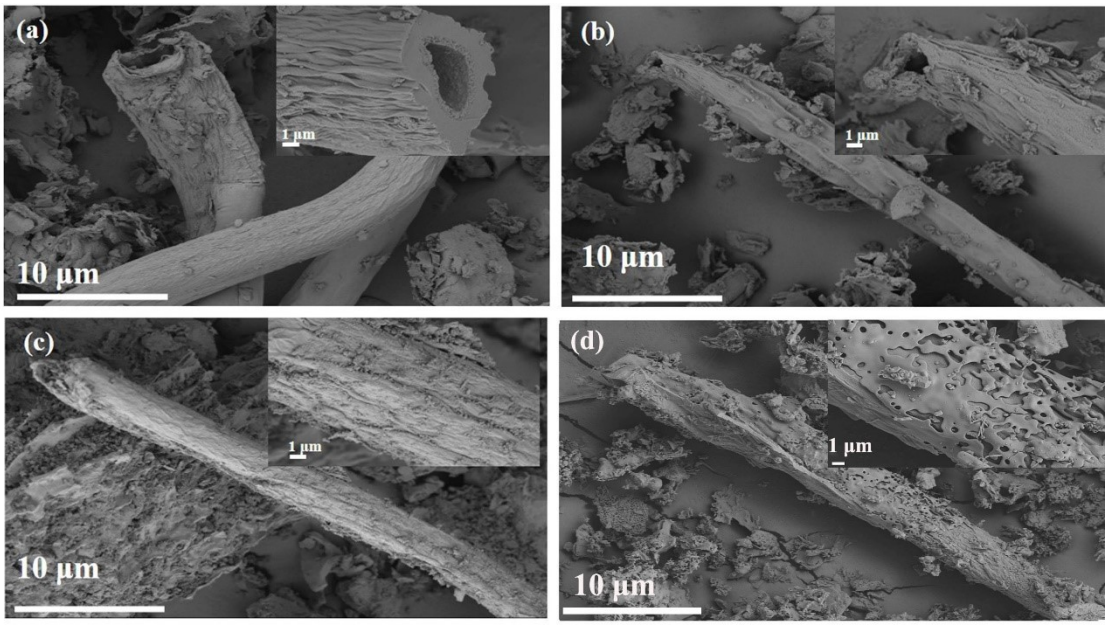

Fig. S2 SEM pattern of (a) CMT; (b) C-TiO_2; (c) C-TiO_2-Fe_3O_4; (d) C-$TiFe_2O_4$

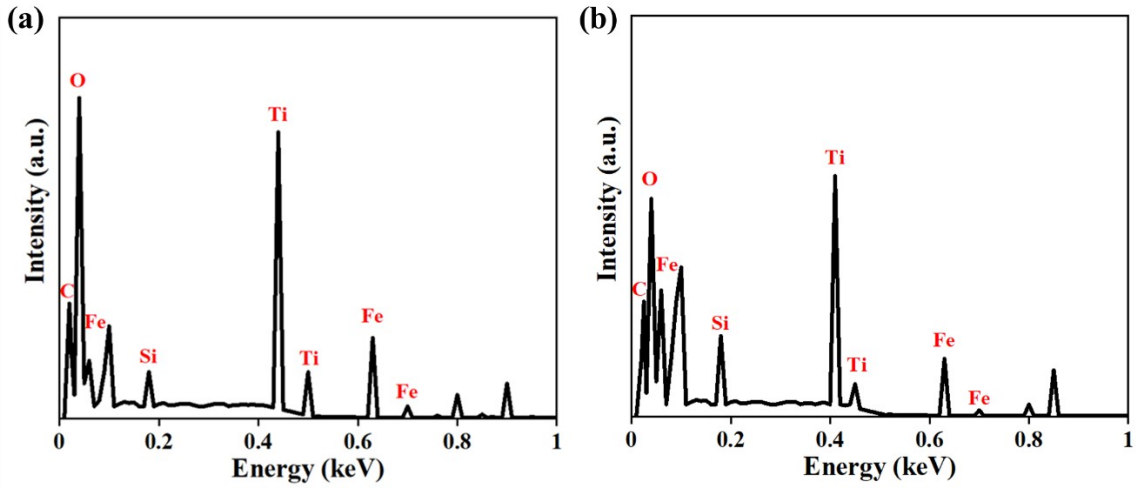

Fig. S3 EDX of (a) C-TiO_2-Fe_3O_4 and (b) C-$TiFe_2O_4$

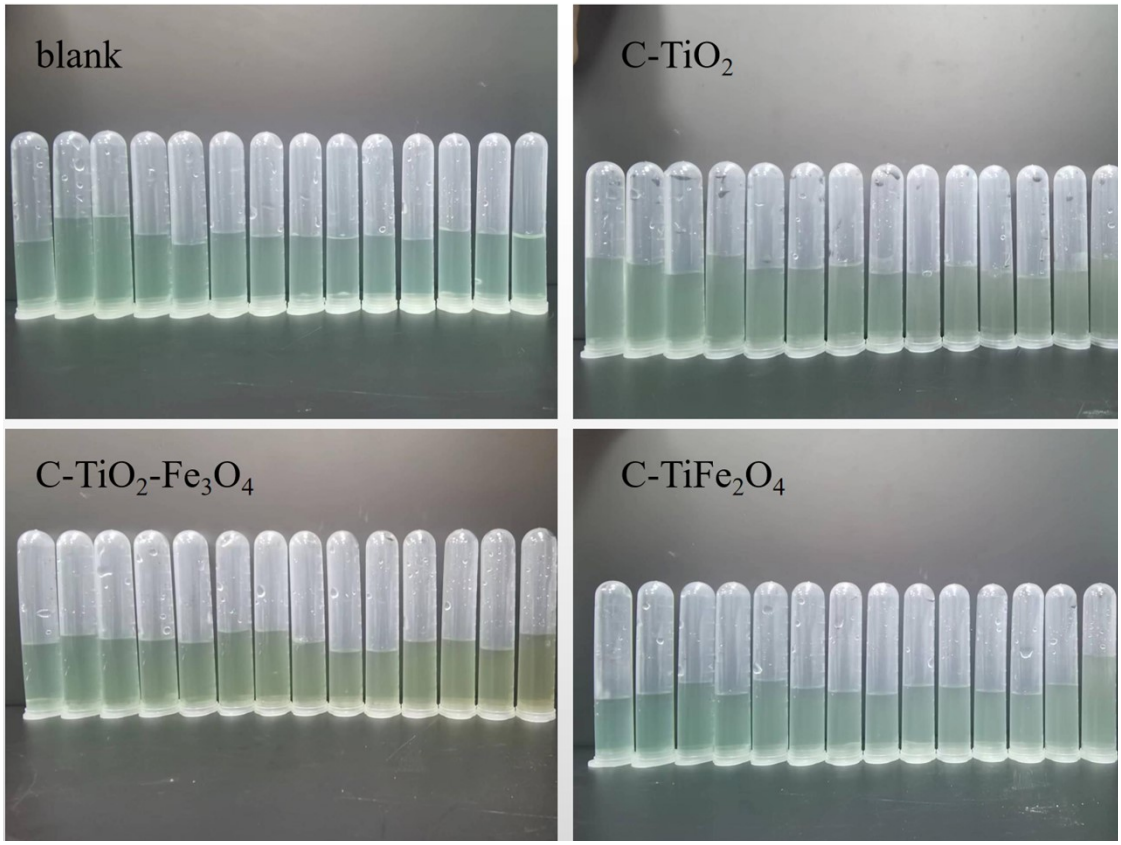

Fig. S4 Inactivation of *Microcystis aeruginosa* by the prepared materials

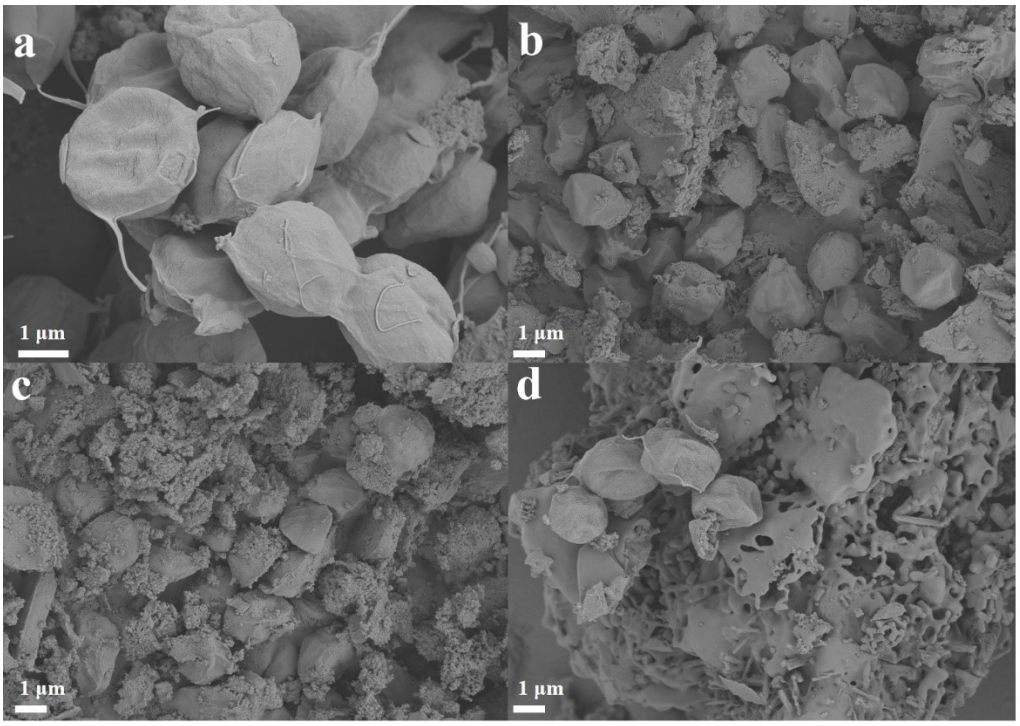

Fig. S5 SEM of (a) blank, (b) C-TiO_2, (c) C-TiO_2-Fe_3O_4, and (d) C-$TiFe_2O_4$ inactivation of *Microcystis aeruginosa* under photocatalysis

Photo-inactivation kinetics

The photo-inactivation kinetics of C-TiO_2-Fe_3O_4 and C-$TiFe_2O_4$ was analyzed using Langmuir-Hinshelwood (L-H) models (S3) and (S4). The mechanism is based on adsorption-surface reaction-desorption.

$$\frac{1}{k} = \frac{C_0}{k_1} + \frac{1}{k_1 k_c} \tag{S3}$$

The formula can be simplified to

$$-\ln(\frac{C_t}{C_0}) = k_1 k_c t = Kt \tag{S4}$$

where C_0 is the initial concentration of algal cells (cells·mL^{-1}); C_t is the concentration of algal cells at time t (cells·mL^{-1}); t is the reaction time (min); k is the reaction rate constant (min^{-1}); k_1 is the catalyst surface rate constant (cells·mL^{-1}·min); k_c is the adsorption equilibrium constant (cells·mL^{-1}); K is the surface reaction rate constant (cells·mL^{-1}·min).

Table S5 L-H model fitting parameter of (a) C-TiO_2, (b) C-TiO_2-Fe_3O_4 and (c) C-$TiFe_2O_4$

	1×10^6 cells·mL^{-1}		2.5×10^6 cells·mL^{-1}		5×10^6 cells·mL^{-1}		7.5×10^6 cells·mL^{-1}		1×10^7 cells·mL^{-1}	
	K	R^2	K	R^2	K	R^2	K	R^2	K	R^2
C-TiO_2	0.161	0.994	0.098	0.999	0.089	0.957	0.059	0.995	0.049	0.998
C-TiO_2-Fe_3O_4	0.084	0.951	0.084	0.974	0.079	0.979	0.078	0.987	0.073	0.950
C-$TiFe_2O_4$	0.115	0.994	0.103	0.999	0.052	0.962	0.047	0.993	0.045	0.930

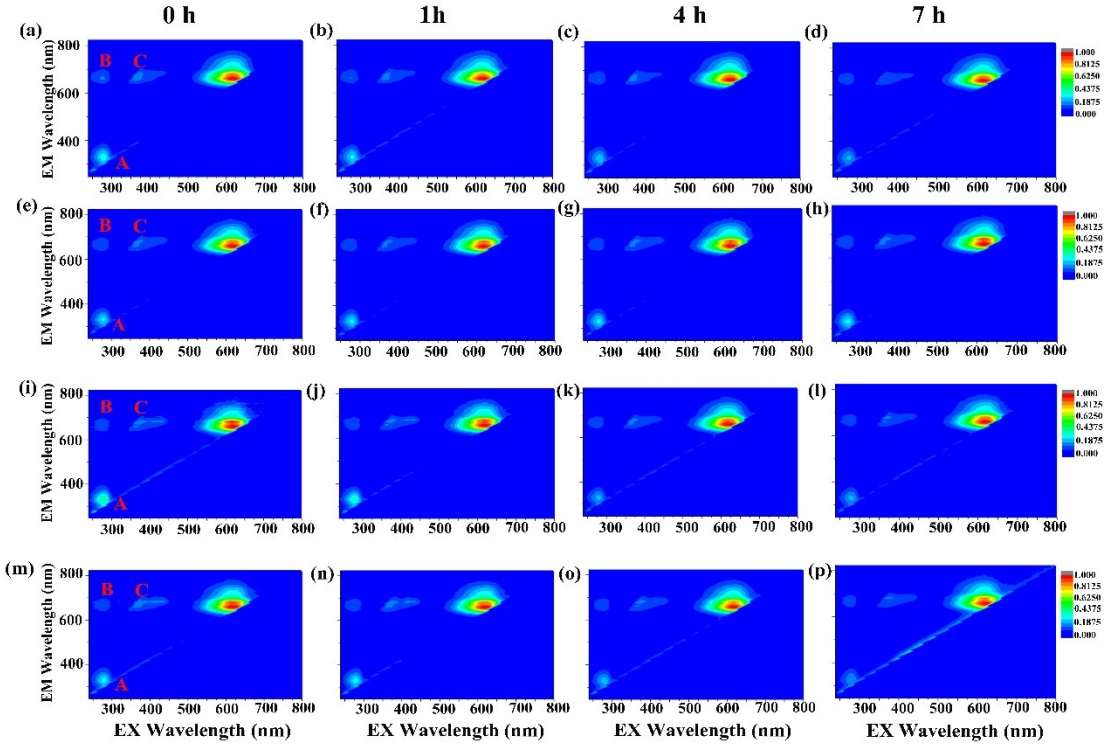

Fig. S6 Changes of extracellular organic matter during the inactivation of *Microcystis aeruginosa* by the prepared materials: (a, b, c, d) blank; (e, f, g, h) C-TiO_2; (i, j, k, l) C-TiO_2-Fe_3O_4; (m, n, o, p) C-$TiFe_2O_4$

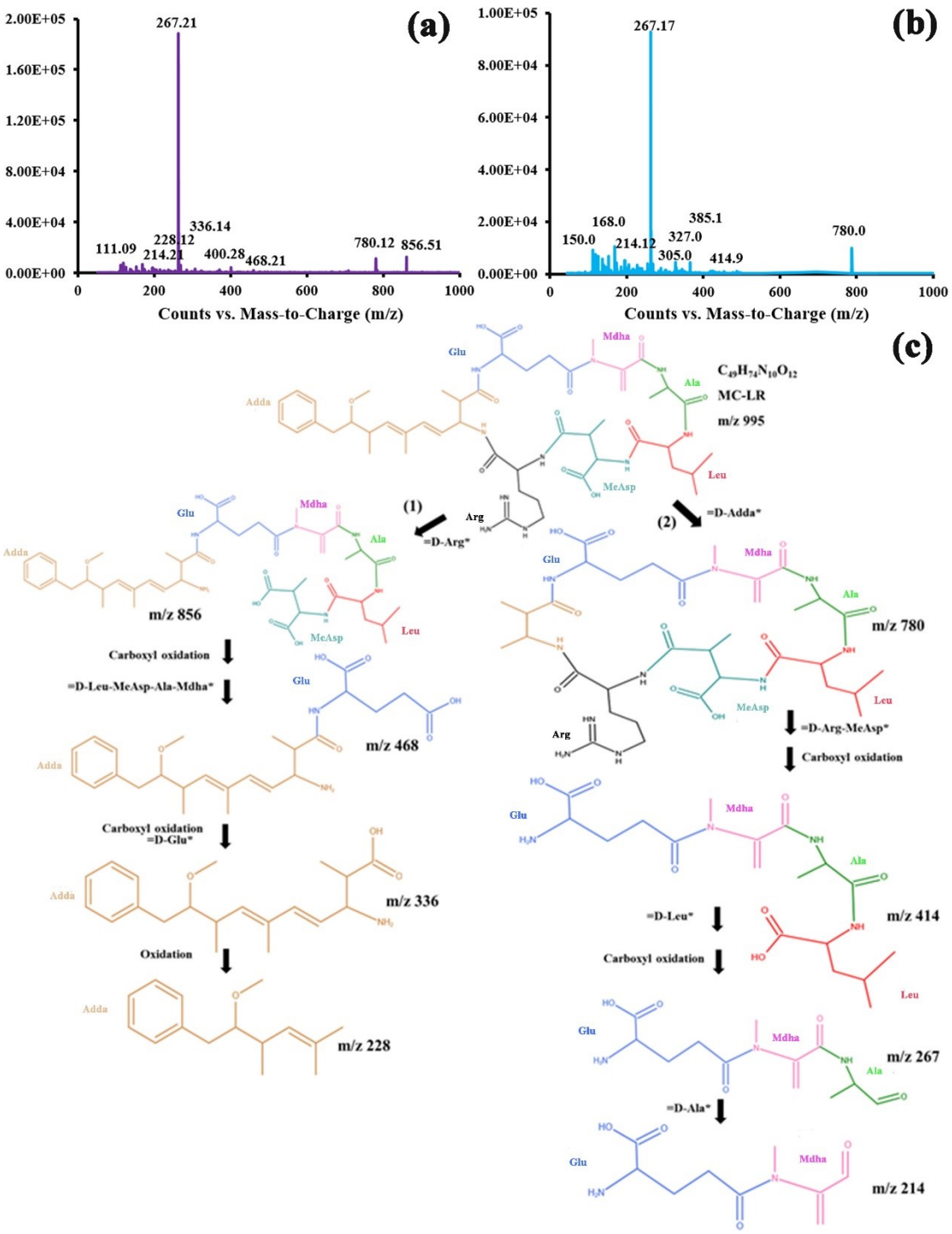

Fig. S7 LC-MS spectrum of the MC-LR solution with (a) 30 min and (b) 90 min photocatalytic process by C-$TiFe_2O_4$, (c) the possible degradation pathway of MC-LR during the photocatalytic degradation process by C-$TiFe_2O_4$

RSM results

Based on the Box-Behnken model (Table S1 and Table S2), the variables that have a greater impact on the inactivation of *Microcystis aeruginosa* (the catalyst dosage, initial algae density, and reaction time) were analyzed using RSM, as shown in Figs.

S8, S9, and S10. The RSM showed that the optimal reaction conditions of C-TiO_2 were as follows: reaction time: 6 h; catalyst dosage: 0.38 g·L^{-1}; initial algal density: 1×10^6 cells·mL^{-1}. The optimal reaction conditions of C-TiO_2-Fe_3O_4 were as follows: reaction time: 7 h; catalyst dosage: 0.29 g·L^{-1}; initial algae density: 1×10^6 cells·mL^{-1}. The optimal reaction conditions of C-$TiFe_2O_4$ were as follows: reaction time: 7 h; catalyst dosage: 0.39 g·L^{-1}; initial algae density: 1×10^6 cells·mL^{-1}; algae remove rate: 77.9%. Compared with other research results (Table S6), C-$TiFe_2O_4$ has the advantages of a low catalyst dosage and a relatively high deactivation rate.

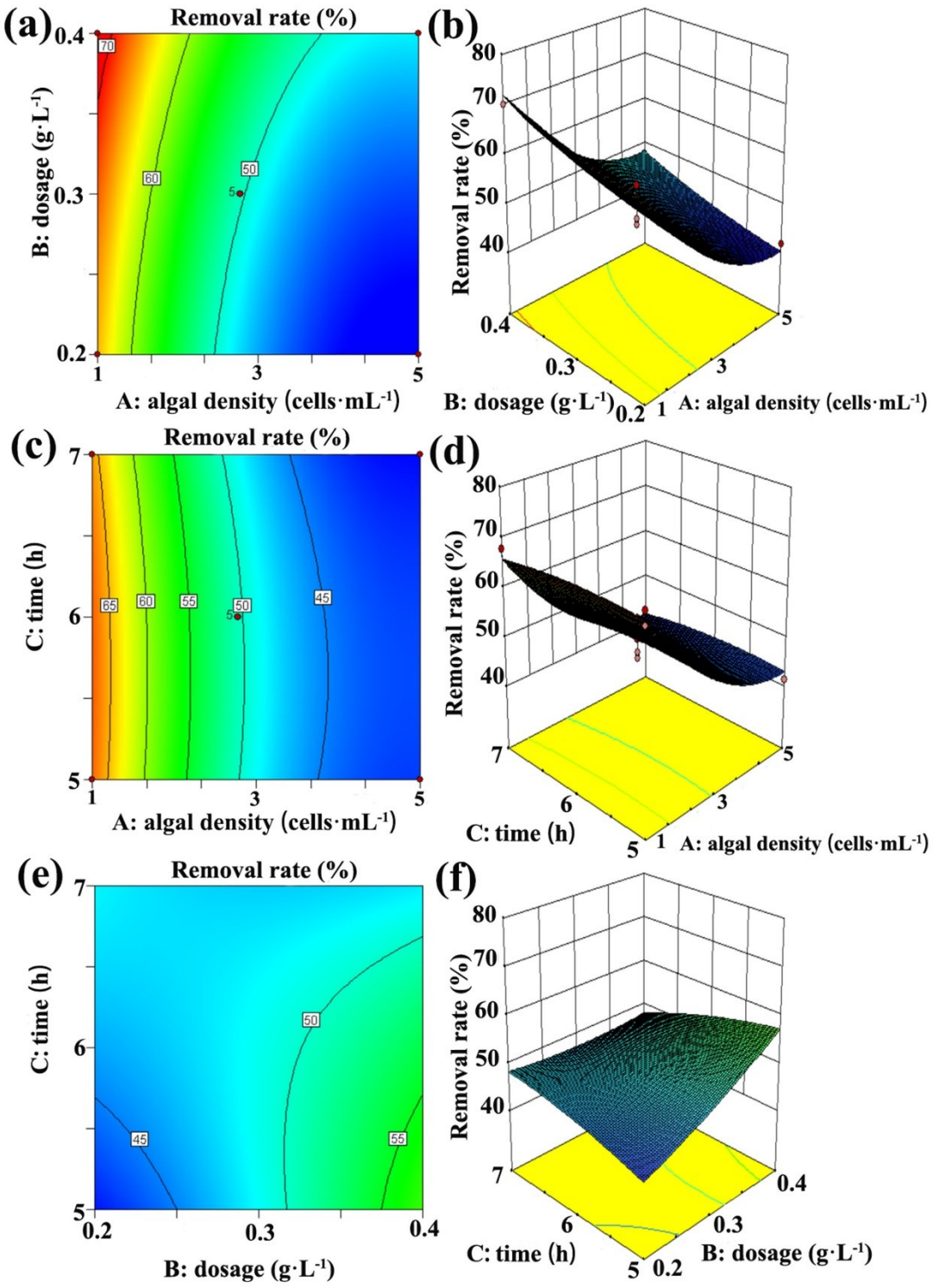

Fig. S8 Effect of the interaction of different variables on the inactivation of *Microcystis aeruginosa* by C-TiO_2

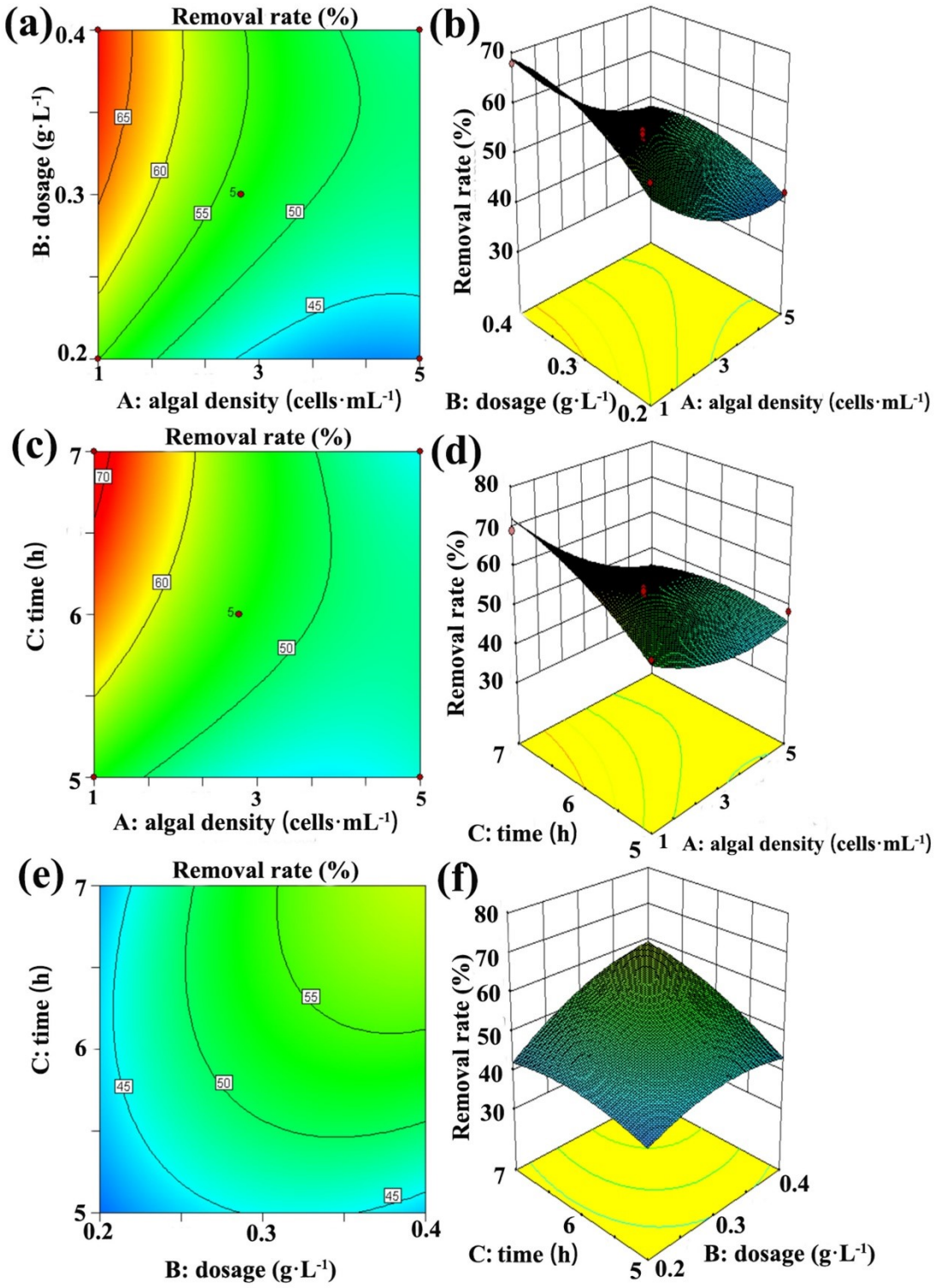

Fig. S9 Effect of the interaction of different variables on the inactivation of *Microcystis aeruginosa* by C-TiO_2-Fe_3O_4

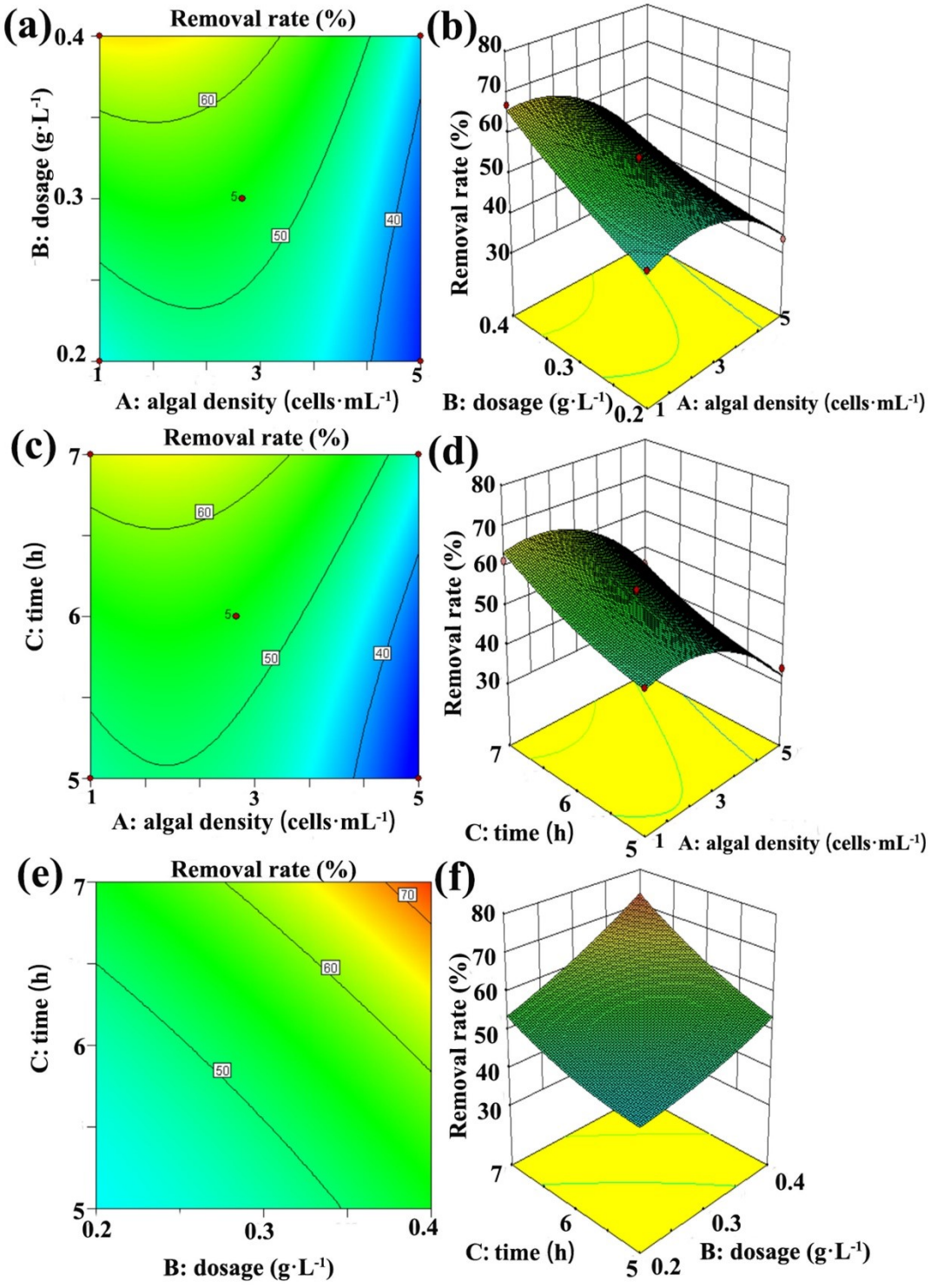

Fig. S10 Effect of the interaction of different variables on the inactivation of *Microcystis aeruginosa* by C-$TiFe_2O_4$

Table S6 Existing studies on the photocatalytic inactivation of *Microcystis aeruginosa*

	Algae density (cells·mL^{-1})	**Dosage (g·L^{-1})**	**Removal rate (%)**	**Time (h)**	**Reference**
F-Ce-TiO_2	2.7×10^6	4	98.1	9	[1]
TiO_2/g-C_3N_4	2.7×10^6	2	88.1	6	[2]
Ag_3PO_4/b-N-TiO_2	3.0×10^6	0.2	95	8	[3]
Ag-TiO_2	2.5×10^5	2.1	92	24	[4]
CeO_x/TiO_2-yFy	2.7×10^6	1	100	4	[5]
TiOX (X = N and P)	2.7×10^6	2	81.5	6	[6]
C-$TiFe_2O_4$	1.0×10^6	0.39	77.9	7	This work

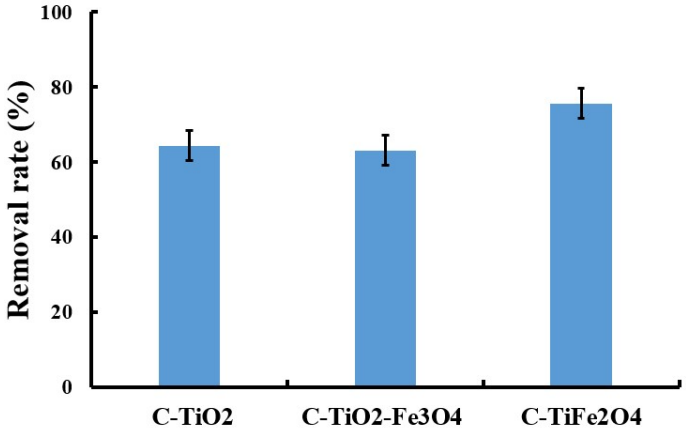

Figure S11 Validation results of the optimum conditions

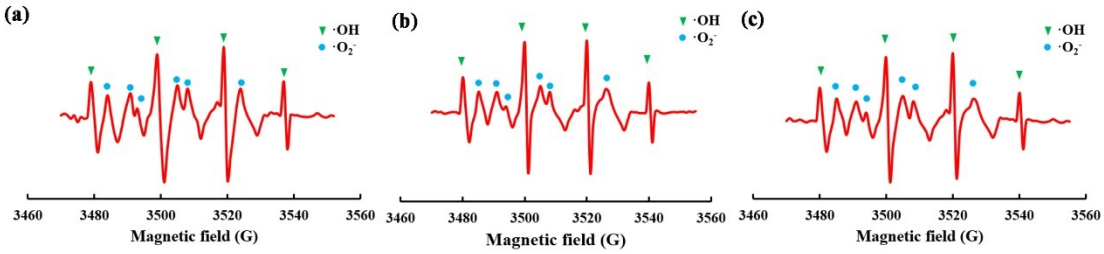

Figure S12 ESR spectra of (a) C-TiO_2, (b) C-TiO_2-Fe_3O_4, (c) C-$TiFe_2O_4$

Reference:

[1] Wang S, Zhang Y, Zhang T, et al. Readily attainable spongy foam photocatalyst for promising practical photocatalysis [J]. Applied Catalysis B: Environmental, 2017, 208: 75-81.

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implications [J]. Applied Catalysis B: Environmental, 2018, 226: 83-92.

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[6] Wang X, Song J, Li Y, et al. A highly efficient TiOX (X = N and P) photocatalyst for inactivation of *microcystis aeruginosa* under visible light irradiation [J]. Separation and Purification Technology, 2019, 222: 99-108.