

Supplementary Materials

Self-Assembled A-D-A Type Indacenodithiophene-based Small Conjugated Molecule/TiO₂ for Enhancing the Photocatalytic Activity

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Chemicals

4,9-dihydro-4,4,9,9-tetraoctyl-s-indaceno[1,2-b:5,6-b']dithiophene (IDT), 2-cyanoacetic acid, ammonium acetate, acetic acid was supplied by Jiaying Hepu Optoelectronics Technology Co., Ltd. (Zhejiang, China). TiO₂ was supplied by Energy Chemical (Shanghai, China). Nitrogen gas (N₂) was purchased from Siping Hongyuan Gas Co., Ltd. (Siping, China). Phosphate buffered saline (PBS) (pH = 7.2) was supplied by Beijing Solarbio Science & Technology Co., Ltd. (Beijing, China). Tryptic soy agar (TSA) and tryptic soy broth (TSB) were supplied by Qingdao Hope Bio-Technology Co., Ltd. (Qingdao, China). Isopropanol was purchased from Tianjin Fuyu Co., Ltd. (Tianjin, China). Propidium iodide (PI) and SYTO-9 were supplied by Invitrogen (American). Ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) was supplied by Changchun Tianjia Biological Technology Co., Ltd. (Changchun, China). Methanol, tetrahydrofuran (THF), acetic acid, toluene, hexane, K₂Cr₂O₇, NaN₃ and L-Ascorbic acid were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China). NIH3T3 cells were purchased from Huake Cell Biotechnology (Beijing, China). 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine (TEPM) were obtained from Sigma-Aldrich. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 3,4-Dihydro-2-methyl-1,1-dimethylethyl ester-2H-pyrrole-2-carboxylic acid-1-oxide (BMPO) were obtained from DOJINDO (Japan). Cell Counting Kit-8 (CCK-8), fetal bovine serum (FBS) and Dulbecco's modified eagle medium (DMEM) were supplied by HyClone (USA), PEAK SERUM (USA) and MCE (USA), respectively. The water used in all experiments was deionized (DI).

Preparation of the **bulk g-C₃N₄** (bg-C₃N₄). The bg-C₃N₄ was prepared by the thermal polymerization process. Typically, 1 g of urea was transferred into a 50 mL alumina crucible with a cover, and then heated at 550 °C for 4 h with a heating rate of 5 °C min⁻¹ under air atmosphere. After cooling to room temperature, the yellow products were milled into powder and collected for further characterization.

Photocatalytic degradation experiments

The photocatalytic activities of TiO₂, IDT-COOH and IDT-COOH/TiO₂ with varying IDT-COOH mass ratio were evaluated by degrading TC under visible light irradiation ($\lambda > 420$ nm). A 250W xenon lamp with a cut-off filter UV light ($\lambda < 420$ nm) was employed as the visible light source and the average light intensity of 80 mW cm⁻² was fixed. In detail, 16 mg of the

photocatalyst was dispersed into the 40 mL aqueous solution of TC (20 mg L⁻¹). The suspension solution was stirred in the dark for 1 h before irradiation to keep the adsorption-desorption equilibrium. At intervals of 30 min, aliquots of 3 mL were withdrawn and centrifuged. The concentrations of TC were detected by a UV-2550 spectrometer and the detection wavelength of TC was 357 nm. TOC were measured on a multi N/C 2100 (AnalytikJena AG, Germany) TOC analyzer.

Photocatalytic degradation pathway of tetracycline by IDT-COOH/TiO₂

Intermediate products obtained during photodegradation of TC over IDT-COOH/TiO₂ with visible light illumination were studied by HPLC-MS (HPLC: Agilent1100, China; MS: TSQ quantum Ultra, America). The intermediates with $m/z = 461, 477, 449$ and 309 were produced during photodegradation of TC under visible light illumination. Therefore, we can propose the TC photodegradation pathways (Fig. S10). The intermediate with $m/z = 416$ was produced after active radicals reacted with 1-(12, 13) double bond. Then, the 1-(2, 3) double bond of 2 structure was oxidized to form 3 ($m/z = 477$) molecule, and then the 4 ($m/z = 449$) molecule was produced in sequence by losing methyl groups. Further h^+ and $\cdot O_2^-$ attacked D to generate the 5 intermediate with $m/z = 309$ via decarboxylation reactions. Finally, through a series of open-ring reactions and the loss of functional groups, these small intermediate products were oxidized and decomposed into H₂O and CO₂.

Photocatalytic disinfection experiments

Photocatalytic disinfection performance of TiO₂, IDT-COOH and IDT-COOH/TiO₂ with varying IDT-COOH mass ratio was evaluated by inactivation of Gram-positive *S. aureus* (USA 300). Before test, all culture medium solution (TSA, TSB and PBS) and glassware were autoclaved at 121 °C for 30 min. First, *S. aureus* cells were cultured in TSB at 37 °C for 12 h and centrifuged to obtain ca. 10⁸ colony forming units per milliliter (cfu mL⁻¹) in PBS. The photocatalytic disinfection experiments were conducted under a 250 W xenon arc lamp equipped with an optical cutoff filter ($\lambda < 420$ nm). The temperature was kept at 30 °C and the visible light intensity was fixed at 80 mW cm⁻². The concentration of *S. aureus* for antibacterial test was ca. 10⁷ cfu mL⁻¹. At various illumination time intervals, 0.1 mL of tested sample was pipetted out, diluted by PBS serially and spread on TSA plates. Lastly, the cell numbers were counted to calculate the relative survival rate and cell density reduction of *S.*

aureus after incubation at 37 °C for 20 h. Dark control (*S. aureus* with 30% IDT-COOH/TiO₂) and light control (*S. aureus* without photocatalyst) were performed. All the tests were repeated for three times.

Rabbit plasma test

Staphylococcal coagulase is an important virulence factor for *S. aureus*. Coagulase converts host prothrombin to staphylothrombin, leading to activation of the protease activity of thrombin. It was predicted that coagulase could protect bacteria from phagocytic and immune defenses by causing localized clotting. The expression of coagulase of *S. aureus* was examined after the interaction between 30% IDT-COOH/TiO₂ and the bacteria. A tube coagulation assay based on freeze-dried rabbit plasma was performed. 30% IDT-COOH/TiO₂ (8 mg) was added to bacteria culture (20 mL) and allowed to react for 0, 0.5, 1, 1.5 and 2 h. Then 800 µL of reaction solution collected at different times were added to 500 µL of rabbit plasma in small ampules of glass tubes. The mixture samples were incubated at 37 °C for 6 h, and rabbit plasma coagulation was examined.

Fluorescence microscopy observation of bacteria

Furthermore, Fluorescent-based cell live/dead tests were carried out to explore the integrity of bacterial cell membranes. In brief, the bacterial liquids before and after 2 h irradiation treatment in the control and experimental groups were collected and centrifuged at 8000 rpm for 2 min with the supernatant being discarded. The obtained bacteria were dispersed in 50 µL sterile PBS solution and stained with 25 µL of SYTO-9 (6 mg mL⁻¹ in sterilized deionized water) and 25 µL of PI (6 mg mL⁻¹ in sterilized deionized water) solution for 15 min in the dark at room temperature. Lastly, 10 µL of stained bacterial liquid was taken out and dropped on the center of slide and then imaged using a laser scanning confocal microscope (Nikon Ti-s, Japan).

Growth studies

The *S. aureus* was used for the growth studies against 30% IDT-COOH/TiO₂. 8 mg 30% IDT-COOH/TiO₂ was dispersed in 20 mL of TSB solution in a 120 mL self-designed glass jacketed reactor containing bacteria solution (10⁷ cfu mL⁻¹). Aliquots were taken after every 2 h, 100 µL tested suspension sample was pipetted out and serially diluted using PBS and spread on nutrient TSA plates. After incubation at 37 °C for 18 h, the cell densities were checked to determine the survival bacterial numbers. The growth curves were plotted

accordingly. Samples without treatment of IDT-COOH were used as light control. The reaction was carried out in a GHX-3 photochemical reaction instrument equipped with a 250 W xenon arc lamp and an optical cutoff filter ($\lambda < 420$ nm). The visible light intensity was fixed at 80 mW cm^{-2} . The temperature was kept at $30 \text{ }^\circ\text{C}$ using a cryostatic tank.

Protein Leakage

Briefly, 10^7 cfu mL^{-1} of *S. aureus* was incubated with 30% IDT-COOH/ TiO_2 (0.4 mg mL^{-1}) and exposed to visible light sources (GHX-3, 250 W xenon arc lamp) for 2 h. The bacteria solution without PBDT-F-COOH was the control group. The solution was centrifuged at 12000 rpm for 2 min at $4 \text{ }^\circ\text{C}$. The supernatant liquid was transferred to a 96-well plate and the protein leakage concentrations were measured by the Enhanced BCA Protein Assay Kit (BL521A 500T, Biosharp, China) on a microplate reader.

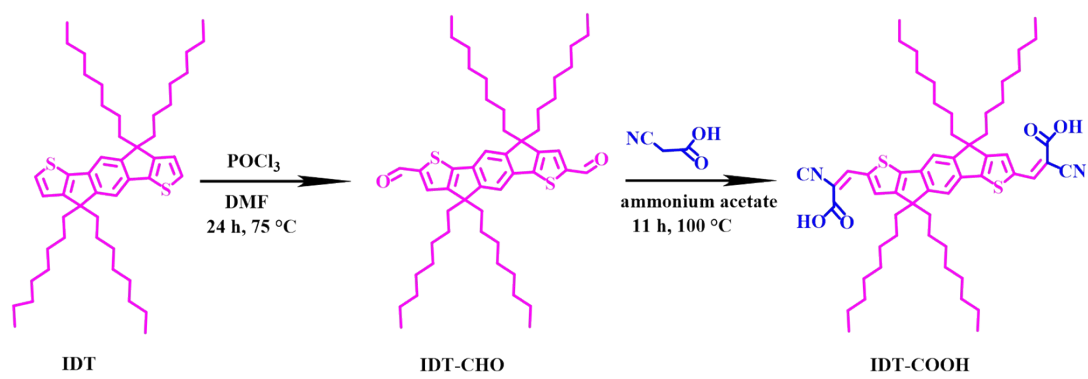
Active species trapping experiments

In order to explore the active species produced in photocatalytic process, isopropanol (10 mmol L^{-1}), $\text{K}_2\text{Cr}_2\text{O}_7$ (2 mmol L^{-1}), L-ascorbic acid (2 mmol L^{-1}), NaN_3 (2 mmol L^{-1}) and EDTA-2Na (0.5 mmol L^{-1}), were employed as the traps of hydroxyl radicals ($\bullet\text{OH}$), electrons (e^-), superoxide ($\bullet\text{O}_2^-$), $^1\text{O}_2$ and holes (h^+), respectively. Electron spin resonance (ESR) analyses were performed on the Bruker EMX-Plus spectrometer with the concentration of spin traps of DMPO, BMPO and TEMP being 0.22 mmol L^{-1} in deionized water.

Cell Toxicity Assay

The CCK-8 assay (Huake biotech, Beijing, China) was applied to study the cytotoxicity of the PBDT-F-COOH. First, the NIH3T3 cells were cultured with dulbecco's modified eagle medium (DMEM, HyClone) (6 mL) containing 1% penicillin-streptomycin solution (HyClone) and 10% fetal bovine serum (FBS, PEAK) in a humidified atmosphere containing 5% CO_2 at $37 \text{ }^\circ\text{C}$. The cell culture medium was refreshed every 3 days. Then, NIH3T3 cells ($5 \times 10^4 \text{ cells mL}^{-1}$) were cultured in DMEM ($100 \text{ }\mu\text{L}$) for 24 h on a 96-well plate so that they adhered to the plate wall, 5 replicates per well. Afterwards, DMEM was discarded and fresh DMEM medium containing IDT-COOH with different concentrations of $200 \text{ }\mu\text{g mL}^{-1}$, $400 \text{ }\mu\text{g mL}^{-1}$ and $800 \text{ }\mu\text{g mL}^{-1}$ was added in each well respectively. After 24 h co-cultivation, each well was incubated with $10 \text{ }\mu\text{L}$ CCK-8 solution at $37 \text{ }^\circ\text{C}$ for 2 h, the absorbance at 450 nm was measured using *Multimode Plate Reader*. No PBDT-F-COOH sample was added as control group. All experimental values are presented as means \pm SD. The statistical significance of the

difference was performed by Two-way ANOVA and Student's *t*-test using Graph-Pad Prism 7.0 software. A *P*-value <0.05 indicates statistical significance.



Scheme S1. The synthetic routes of IDT-COOH.



Fig. S1. Photographs of (a) amorphous IDT-COOH, (b) self-assembled IDT-COOH, (c) physically mixing 30% IDT-COOH/TiO₂, (d) 10% IDT-COOH/TiO₂, (e) 20% IDT-COOH/TiO₂, (f) 30% IDT-COOH/TiO₂ and (g) 40% IDT-COOH/TiO₂.

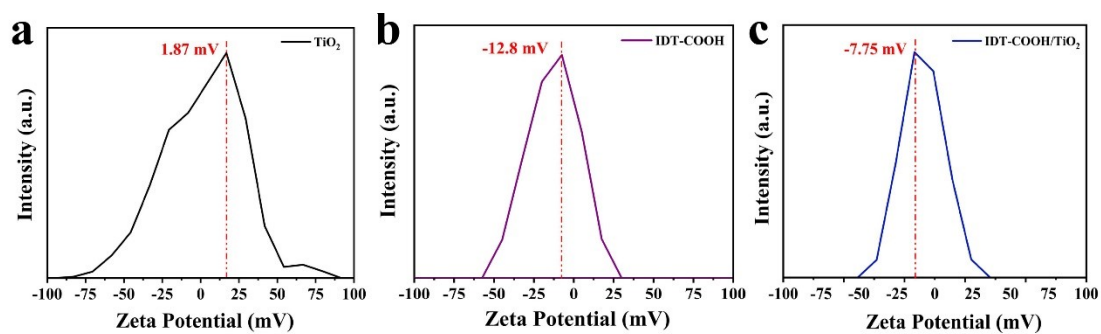


Fig. S2. Zeta potentials of (a) TiO₂, (b) IDT-COOH and (c) 30% IDT-COOH/TiO₂.

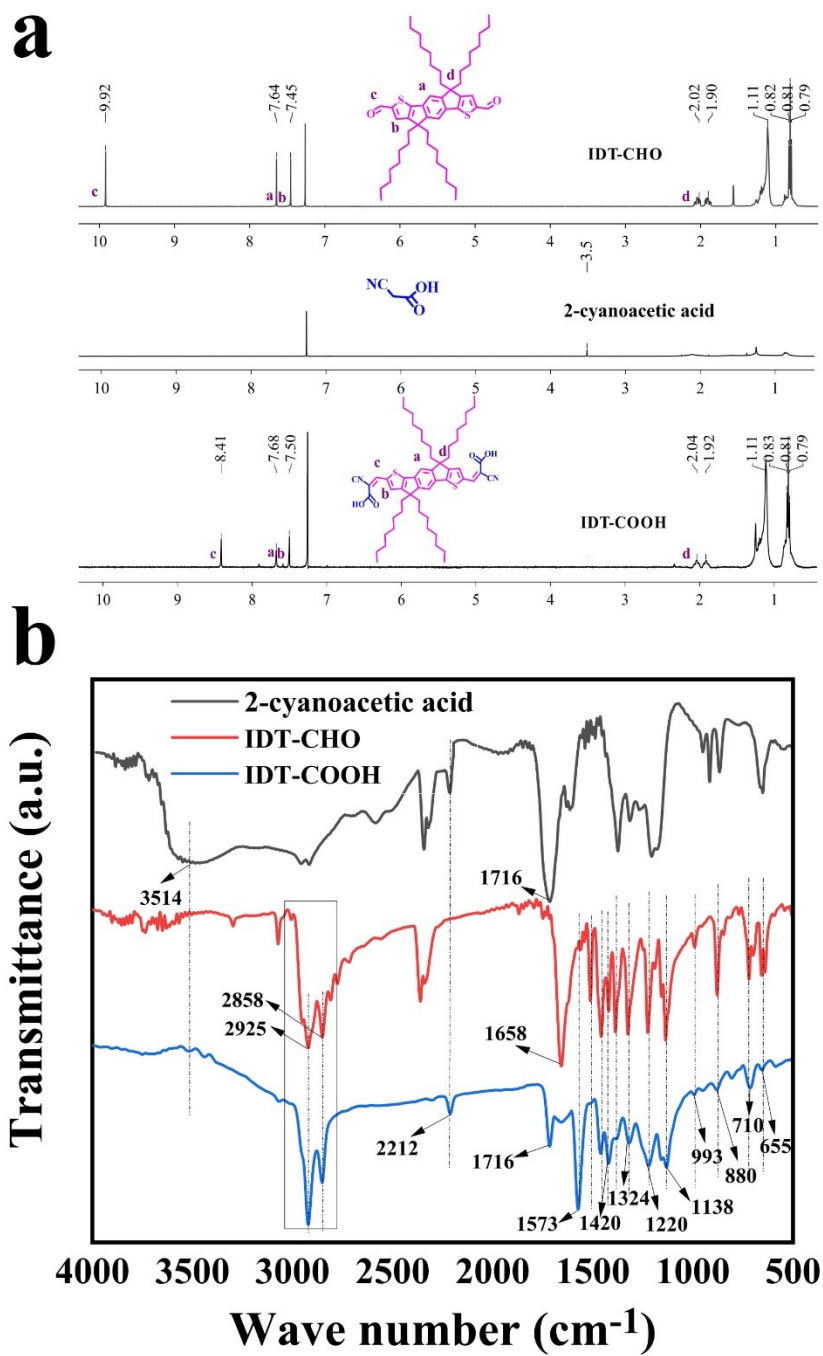


Fig. S3. (a) ^1H NMR and (b) FT-IR spectra of samples.

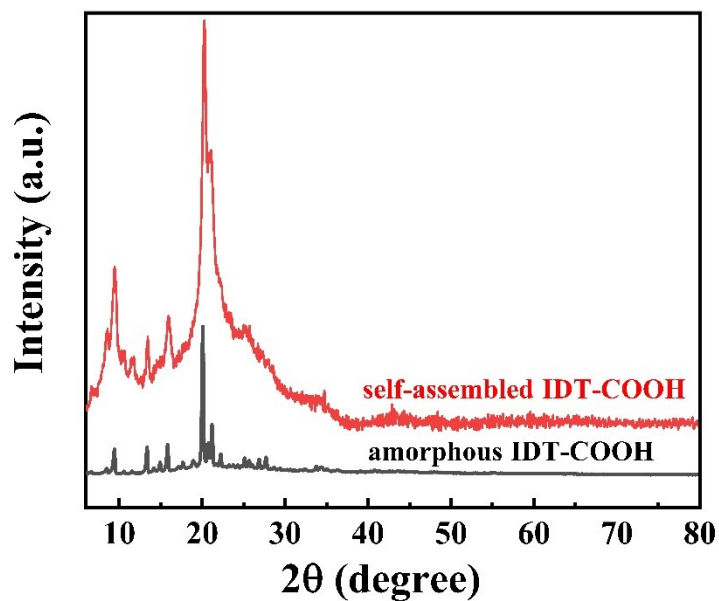


Fig. S4. XRD patterns of amorphous IDT-COOH and self-assembled IDT-COOH.

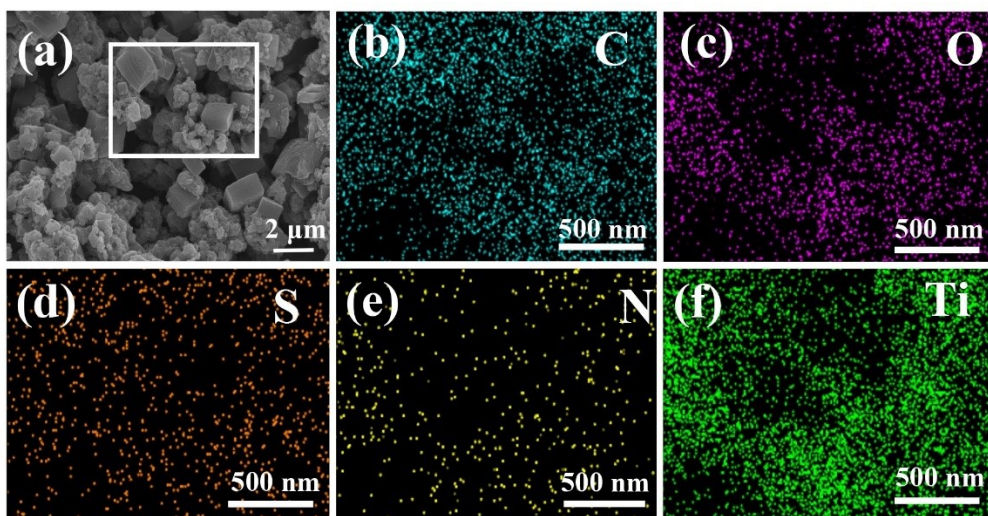


Fig. S5. SEM images of (a) IDT-COOH/TiO₂. The element mappings of (b) C, (c) O, (d) S, (e) N, (f) Ti.

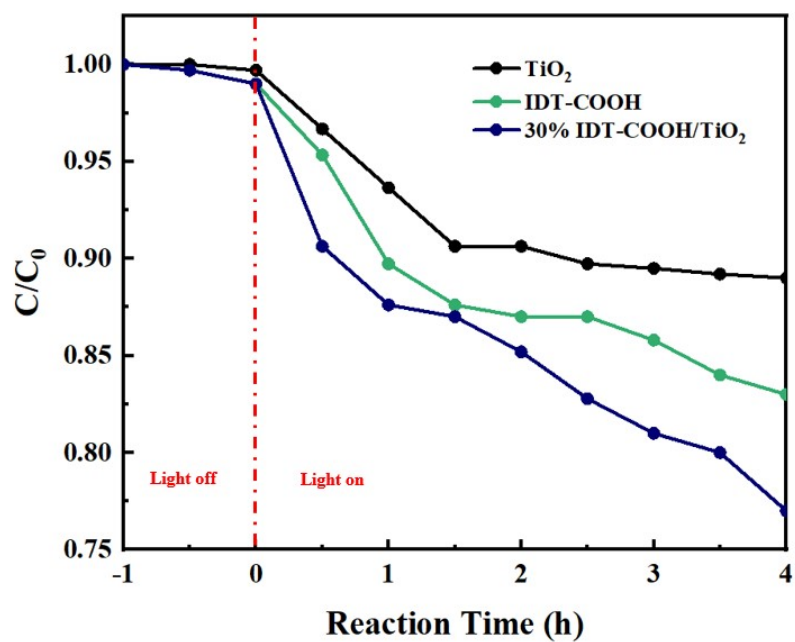


Fig. S6. Photodegradation toward BPA of TiO₂, IDT-COOH and 30% IDT-COOH/TiO₂

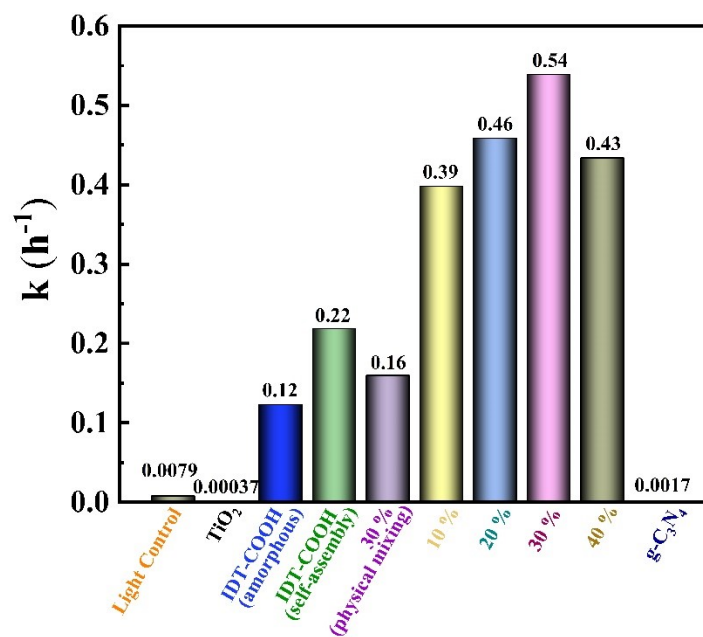


Fig. S7. Apparent rate constants k of samples for TC degradation.

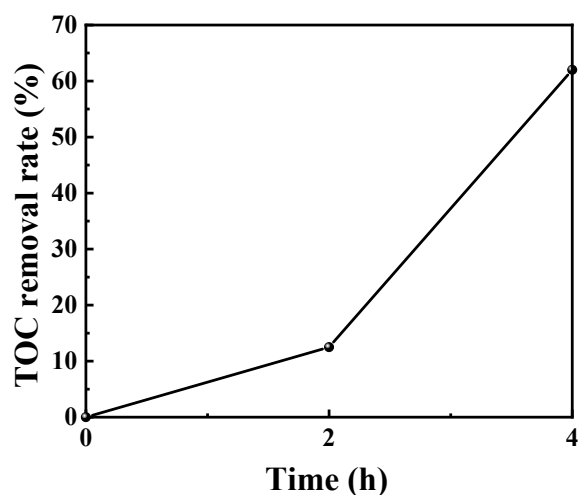


Fig. S8. TOC removal plots of TC over 30% IDT-COOH/TiO₂ under visible light irradiation.

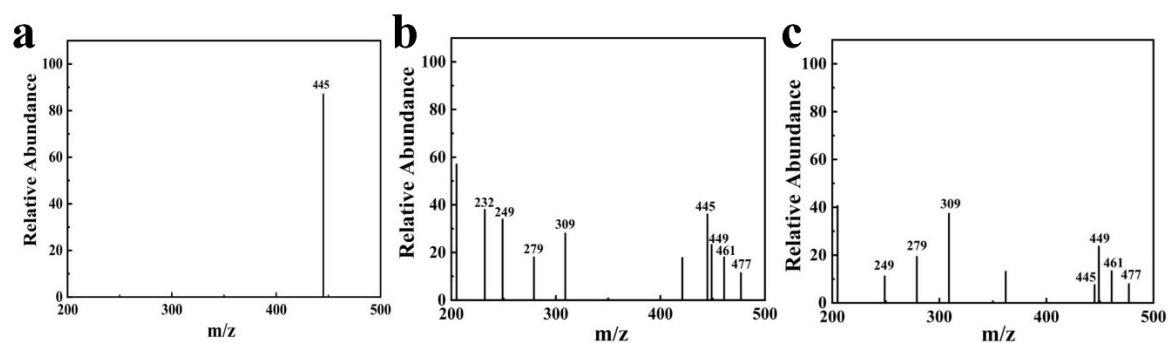


Fig. S9. HPLC-MS chromatograms of (a) TC and produced intermediates at (b) photodegradation reaction time 2 h and (c) 4 h.

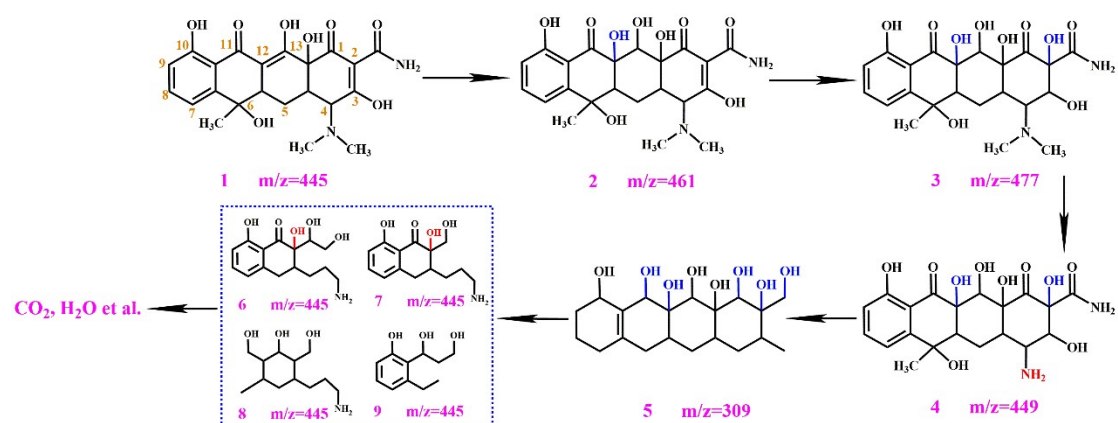


Fig. S10. Possible intermediate products (A-I) at the degradation process of TC over 30% IDT-COOH/TiO₂.

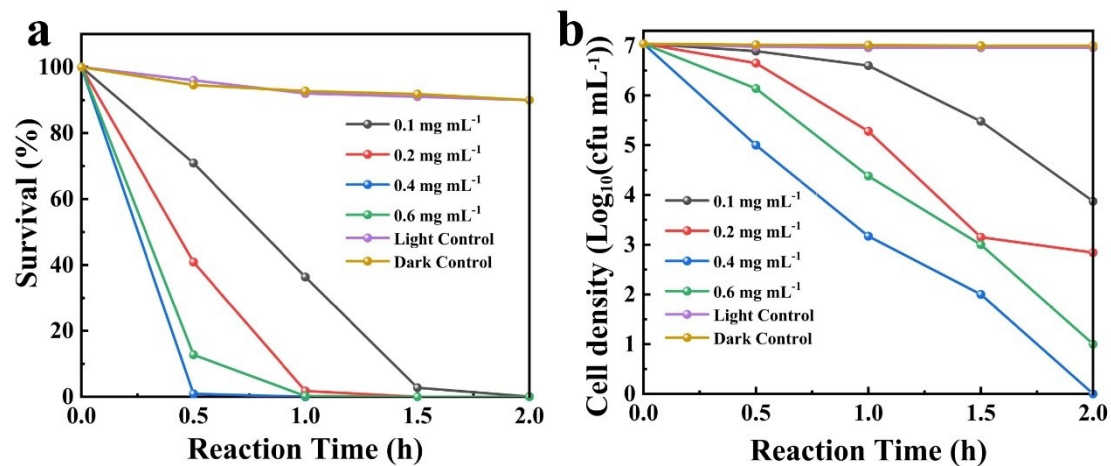


Fig. S11. Effect of 30% IDT-COOH/TiO₂ concentration on the photocatalytic inactivation of *S. aureus* (10⁷ cfu mL⁻¹).

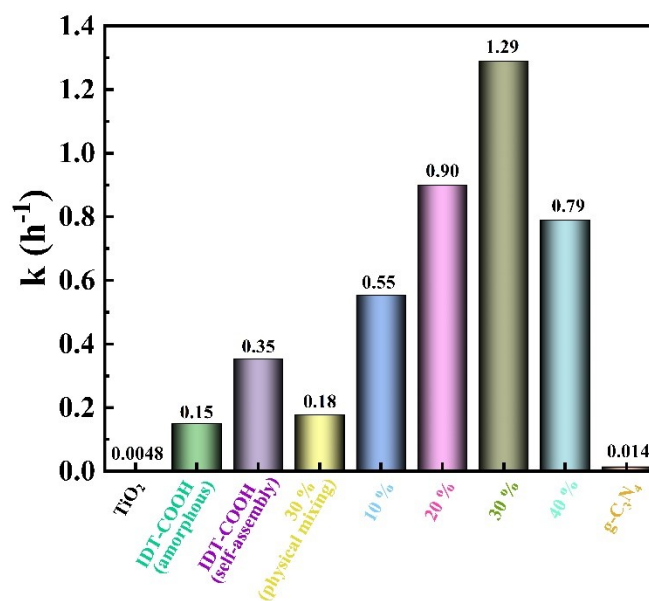


Fig. S12. Photocatalytic inactivation reaction rate constants (k) of samples against *S. aureus*.

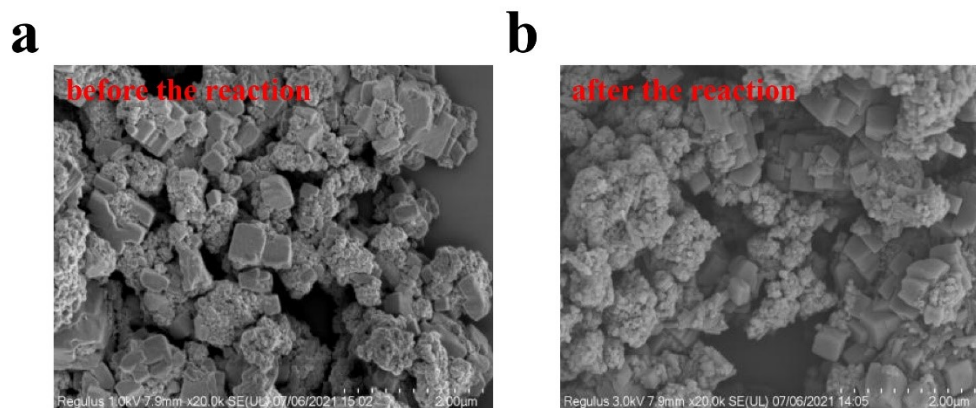


Fig. S13. SEM images of 30% IDT-COOH/TiO₂ (a) before and (b) after three runs.

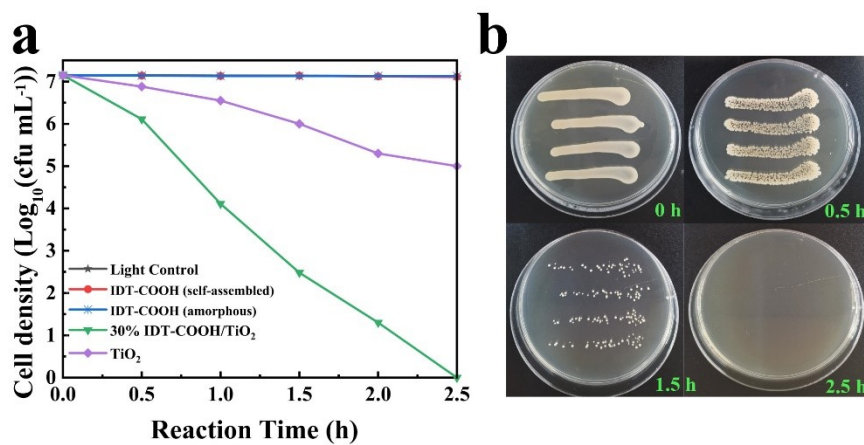


Fig. S14. Photocatalytic inactivation against *S. aureus* of TiO₂, amorphous IDT-COOH, self-assembled IDT-COOH and 30% IDT-COOH/TiO₂ (0.4 mg mL⁻¹) and images of colonies on an agar plate under sunlight illumination (Siping city of Jilin province, 10:00-13:00, December 1, 2021)

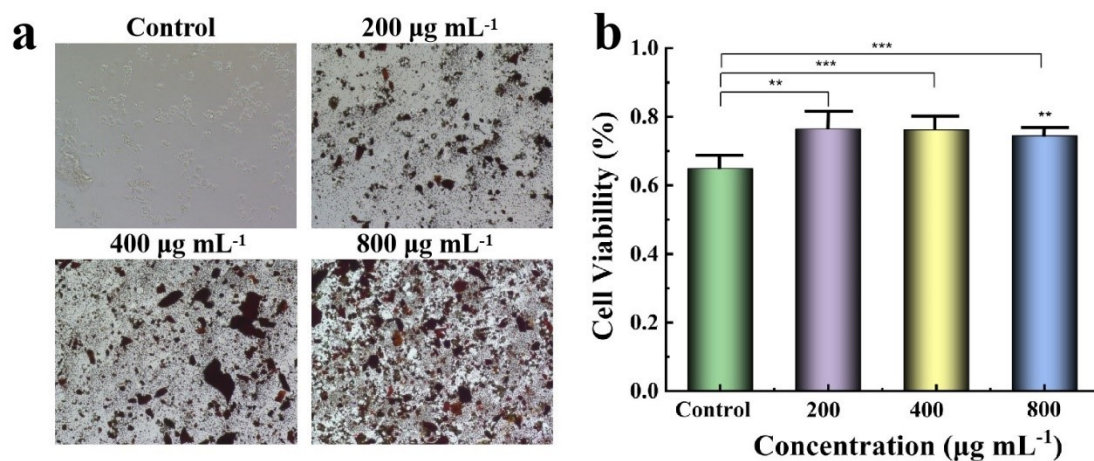


Fig. S15. (a) NIH3T3 cells images of cytotoxicity testing and (b) NIH3T3 cells viability after coculturing for 24 h with various concentrations of 30% IDT-COOH/TiO₂. The error bars indicate means \pm SD (n = 3).

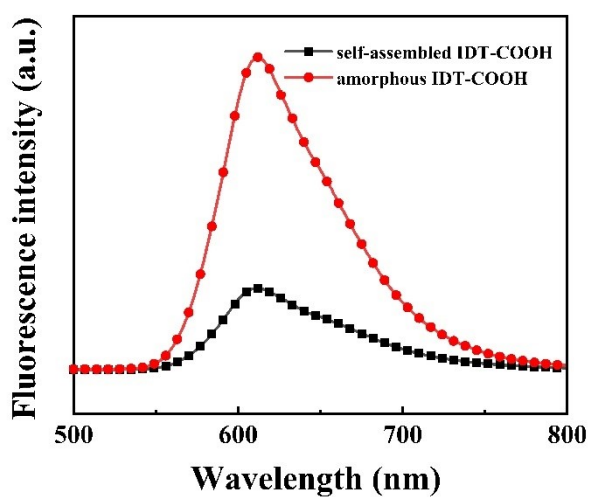


Fig. S16. Fluorescence spectra of self-assembly IDT-COOH and amorphous IDT-COOH.

Table S1. Representative Photocatalysts Based on Polythiophene (PTh)/TiO₂ with Their Concentration, Target Microorganisms, and Photocatalytic degradation Performances.

photocatalyst	concentration	light source	model pollutants	degradation efficiency	released year
P ₃ HT/TiO ₂ [1]	0.005 mg mL ⁻¹	UV	OG	~100% 1 h	2007
PTh/TNT [2]	1 mg mL ⁻¹	visible light	2,3-DCP	51% 420 min	2009
TiO ₂ /P3HT [3]	film	visible light	MO	88.5% 10 h	2009
P3HT/TiO ₂ [4]	1 mg mL ⁻¹	visible light	MeO	decrease in absorbance of MeO 10 h	2010
Polythiophene /TiO ₂ [5]	1 mg mL ⁻¹	UV-visible	MO	85.6% 2 h	2010
PT/TiO ₂ [6]	1 mg mL ⁻¹	visible light	MeO	80.3% 10 h	2010
PTh/TiO ₂ [7]	1 mg mL ⁻¹	visible light	MO	95.1% 10 h	2010
PTh/TiO ₂ [8]	1 mg mL ⁻¹	visible light	RhB	98% 10 h	2011
P3HT/TiO ₂ [9]	1 mg mL ⁻¹	visible light	MO	96% 10 h	2012
TiO ₂ -Mt/PTP-SDS [10]	0.5 mg mL ⁻¹	visible light	RhB	74.3% 1 h	2013
mTiO ₂ -P3HT [11]	coating	visible light	MO	~50% 3 h	2013
PTh/TiO ₂ [12]	1 mg mL ⁻¹	UV	Phenol	45% 2 h	2013
PProDOT/TiO ₂ [13]	0.4 mg mL ⁻¹	sunlight	MB	79.6% 7 h	2014
PProDOT-Me ₂ /TiO ₂ [13]	0.4 mg mL ⁻¹	sunlight	MB	62.8% 7 h	2014
poly(TPT)/TiO ₂ [13]	0.4 mg mL ⁻¹	sunlight	MB	90.5% 7 h	2014
poly(TMPT)/TiO ₂ [13]	0.4 mg mL ⁻¹	sunlight	MB	84.6% 7 h	2014
TiO ₂ -Cu/PTh [14]	0.6 mg mL ⁻¹	visible light	RhB	~100% 1.3 h	2015
Sn-TiO ₂ /PTh [15]	0.4 mg mL ⁻¹	visible light	NB	99.4% 1.75 h	2015
PTh-rGO-TiO ₂ [16]	0.25 mg mL ⁻¹	visible light	MB	63% 2 h	2016
FeTCCP-TDI-TiO ₂ [17]	1 mg mL ⁻¹	visible light	TC	99.2% 2 h	2016
Cu-TiO ₂ /polythiophene [18]	0.6 mg mL ⁻¹	visible light	RhB	99.4% 1.25 h	2017
PTh/Sn-TiO ₂ [19]	0.6 mg mL ⁻¹	visible light	CR	95% 2 h	2017
CT-g-ZnTAPc-2 [20]	0.5 mg mL ⁻¹	visible light	TC·HCl	~100% 1.7 h	2020
PTh/TiO ₂ -P90 [21]	0.5 mg mL ⁻¹	UV	MeO	98% 2.42 h	2021
FSTZP [22]	0.3 mg mL ⁻¹	visible light	TC·HCl	86% 1 h	2021
IDT-COOH/TiO ₂ (this work)	0.4 mg mL ⁻¹	visible light	TC	92.5% 4 h	

Table S2. Representative Photocatalysts Based on Organic Conjugated Molecules/TiO₂ with Their Concentration, Target Microorganisms, and Photocatalytic Disinfection Performances Under Visible Light

photocatalyst	concentration	bacteria	photocatalytic performance	released year	publication
ZnPc-TiO ₂ [23]	solution	<i>S. aureus</i>	80% inactivation 0.5 h	2010	Laser Phys. Lett.
MF ₂ POH@TiO ₂ [24]	100 mg mL ⁻¹	<i>S. aureus</i>	7 log inactivation 2 h	2010	Catal. Today
PANI-TiO ₂ [25]	0.1 mg mL ⁻¹	<i>E. coli</i>	strong inhibition	2014	Chem. Eng. J.
quercetin-TiO ₂ [26]	film	<i>H. maydis</i>	strong inhibition	2015	Mater. Lett.
TiO ₂ /PPIX/Hem [27]	film	<i>B. subtilis</i>	88% inactivation 1.7 h	2015	ACS Appl. Mater. Interfaces
PMMA/TiO ₂ [28]	film	<i>E. coli</i>	maximal inhibition zone diameters of 14±0.51 mm	2015	Photochem. Photobiol. Sci.
PANI@TiO ₂ /GN [29]	10 mg well ⁻¹	<i>E. coli</i>	maximal inhibition zone diameters of 17 mm	2016	RSC Advances
CuTCPP-TSI [30]	20 mg mL ⁻¹	<i>E. coli</i>	99.9% inactivation 3 h	2018	J. Magn. Magn. Mater.
TiO ₂ @4Si-Ce6-PEG [31]	10 umol/L	<i>E. coli</i>	2 log inactivation 3 h	2019	World J. Appl. Chem
F ₂ POH@qTiO ₂ [32]	1.0 mg mL ⁻¹	<i>S. aureus</i>	3-4 log inactivation 2 h	2019	Catalysts
PANI-TiO ₂ [33]	coating	<i>E. coli</i>	70% inactivation 0.5 h	2019	Synth. Met.
CuPc/TiO ₂ [34]	fabric	<i>E. coli</i>	100% inactivation 6 h	2019	Chem. Eng. J.
P ₃ -TiO ₂ [35]	film	<i>S. aureus</i>	80.4% inactivation 3 h	2019	Int. J. Mol. Sci.
CMP/TiO ₂ [36]	1.0 mg mL ⁻¹	<i>S. aureus</i>	100% inactivation 6 h	2021	Mater. Sci. Eng. C
TcPcZn-TiO ₂ [37]	film	<i>S. aureus</i>	76.5% inactivation 0.5 h	2021	ACS Omega
IDT-COOH/TiO ₂ (this work)	0.4 mg mL ⁻¹	<i>S. aureus</i>	100% inactivation 1.5 h 7 log inactivation 2 h		

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