Supporting information

A Strong Hydrangeas-like Au-TiO_2 Catalyst for Round-the-Clock Degradation of Oxalic Acid in the Presence of Ozone

Ling Wu,[a] Zhenyue Zhao,[a] Haidong Yu,[a] Mingxi Wang,[b] Guisheng Li,[c] Hexing Li[c] and Jiabao Yan*[a]

[a] Hubei Province Key Laboratory of Coal Conversion and New Carbon Materials, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China.

[b] Key Laboratory for Green Chemical Process of Ministry of Education, School of Chemical and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430205, China.

[c] The Education Ministry Key Lab of Resource Chemistry, Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, China.

E-mail: yanmener@wust.edu.cn (J. Yan)

Preparation of hydrangeas-like Au-TiO_2

Hydrangeas-like Au-TiO_2 was prepared by solvothermal process combining with subsequent deposition-precipitation method. In a typical synthesis of TiO_2, 9.4 mL glycerol, 20 mL absolute ethanol and 1 mL titanium tetrachloride were mixed in a 100 mL beaker. The clear precursor solution was then transferred to a 50 mL autoclave, followed by keeping in an oven at 110°C for 48 h. After naturally cooling down to room temperature, the product was filtered, washed several times with absolute ethanol, dried at 80°C, and then calcined at 500°C for 2 h at a heating rate of 2.0°C min^{-1}.

Au NPs were deposited on TiO_2 by a simple deposition-precipitation method, similar to the procedures reported elsewhere[1, 2]. Firstly, 0.5 g TiO_2 was added into a beaker with 40 mL ultra-pure water. The pH of the suspension was adjusted to *ca.* 7.6 with 1 M hydrochloric acid or potassium hydroxide and measured by a pH-meter (PHS-25C). Then, appropriate amount of chloroauric acid solution was added to the suspension for obtaining Au-TiO_2 with various gold loadings (0.5 % Au-TiO_2, 1.0% Au-TiO_2, 1.5% Au-TiO_2, and 2.0% Au-TiO_2, the Au weight loading of the samples is expressed in $[m_{Au}/(m_{Au} + m_{TiO2})] \times 100\%$). The pH of the suspension was adjusted to *ca.* 7.6 again, and then placed in a constant temperature water bath with stirring at 60°C for 4 h. Next, the suspension was filtrated and washed with ultra-pure water until the pH to *ca.* 7. After filtration, the sample was dried at 60°C for 8 h and calcined in a muffle furnace at 300°C for 4 h.

Catalyst characterization

Powder X-ray diffraction (XRD) measurements were carried out in a parallel mode using a D/Max-rB rotating-target X-ray diffractometer (Cu K_α radiation). The morphologies of the products were observed by scanning electron microscopy (SEM, S-4700) and transmission electron microscopy (TEM, JEM-2100 UHR). The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). All the binding energy values were calibrated by using C1s = 284.8 eV as a reference. The diffuse reflectance spectra of the samples over a range of 200-700 nm were recorded by a UV 2550 UV-Vis-NIR system equipped with a Labsphere diffuse reflectance accessory using $BaSO_4$ as a reference.

Measurement of catalytic activity

The degradation of oxalic acid (OA) aqueous solution under light irradiation and in the dark was performed for evaluating the catalytic activity of the prepared pure TiO_2 and Au-TiO_2. All the experiments were carried out in a homemade cylindrical glass reactor with a quartz cap, a sampling port, a gas inlet and a gas outlet. Visible light ($420 < \lambda < 780$ nm) was irradiated by a 300 W xenon lamp (CEL-HXF300, China) with a cut-off filter from the top of the reactor. Ozone (O_3) was generated from ultrapure oxygen by an ozone generator (Anseros COM-AD-01, Germany).

In a typical experiment, 150 mL OA solution was added into the reactor with the initial concentration of 100 ppm. 45 mg of catalyst was added into the reactor and magnetically stirred in the dark for 30 min, in order to achieve adsorption-desorption equilibrium before reaction. The catalytic reaction was performed under visible light irradiation or in the dark, both with continuously ozone bubbling. At given time intervals, the reaction suspension was sampled and centrifuged to remove the solid catalyst for further determining the concentration of residual OA molecules and the total organic carbon (TOC) in solution. For comparison, photolysis (Vis), single ozonation (O_3), and photocatalysis (TiO_2/Vis and Au-TiO_2/Vis) were also carried out under the similar reaction conditions.

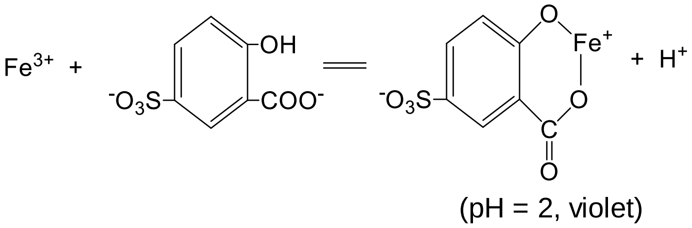
Determination of Oxalic Acid Concentration by fading spectrophotometric method

The concentration of oxalic acid (OA, $H_2C_2O_4$) is usually determined by permanganometry method[3-5] and high performance liquid chromatography (HPLC) method[6-8], but these two methods have some limitations. The classical potassium permanganate titration method is time-consuming and its sensitivity is relatively low. Although the HPLC method is with high sensitivity and low detection limit, but the instrument is too expensive. Some spectrophotometry methods have also developed for determination of OA, such as catalytic kinetic spectrophotometry[9, 10], extraction spectrophotometry[11]. In the present study, a fast and simple fading spectrophotometric method was used, similar to that reported by Zhai[12]. Such a spectrophotometric method is based on that OA can react with Fe(III)-sulfosalicylate (FeSSA) complex which exhibits a characteristic absorption peak centered at 505 nm [13-18], and replaces the ligand of sulfosalicylate to form a more stable Fe(III)-oxalate complex, thereby leading to a bleaching effect. The bleaching degree is proportional to the concentration of the OA added over a defined range.

Reagent and solutions for the fading spectrophotometric method

All chemicals used were analytical reagent grade. All solutions were prepared with ultra-pure water.

HCl solution (0.01 M) was obtained by appropriately diluting concentrated hydrochloric acid (*ca.* 12 M) with ultra-pure water. 0.01 M $FeCl_3$ (III) solution was prepared by dissolving 0.6758 g iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, M = 270.29 g mol^{-1}) with 0.01 M HCl solution in a beaker. It was then transferred into a 250-mL volumetric flask, and diluted up to the mark with 0.01 M HCl solution. 0.01 M 5-sulfosalicylic acid (SSA) solution was prepared by dissolving 0.2545 g 5-Sulfosalicylic acid dihydrate ($C_7H_6O_6S \cdot 2H_2O$, M = 254.21 g mol^{-1}) with ultra-pure water in a beaker. It was transferred into a 250-mL brown volumetric flask and diluted up to the mark with ultra-pure water. Fe(III)-sulfosalicylate (FeSSA) complex solution was prepared by mixing $FeCl_3$ (III) solution (5 mL, 0.01M) and 5-sulfosalicylic acid (SSA) solution (5 mL, 0.01 M) in a 50-mL volumetric flask:



The mixture was diluted up to the mark with 0.01 M HCl solution.

OA solution (1 g L^{-1}) was prepared by dissolving 1.0000 g oxalic acid ($H_2C_2O_4$, M = 90.03 g mol^{-1}) with ultra-pure water in a beaker. It was transferred into a 1000-mL calibrated flask and diluted up to the mark with ultra-pure water. OA solution of other concentrations were obtained by appropriately diluting the high concentration OA solution (1 g L^{-1}).

Drawing of standard curve

In order to obtain standard curve, the absorbance spectra of OA solutions with various concentrations (10 mg L^{-1}, 20 mg L^{-1}, 40 mg L^{-1}, 60 mg L^{-1}, 80 mg L^{-1}, 100 mg L^{-1}) were measured by a UV-Vis spectrophotometer (UV-2550, China) with ultra-pure water as a reference. 2 mL FeSSA solution was evenly mixed with 2 mL OA solution in a centrifuge tube, and then was transferred into a quartz cell (1 cm) for absorbance measurement.

Determination of OA concentration in catalytic process

During the catalytic process with Au-TiO_2 catalysts in the dark and under visible light irradiation, the OA concentration was measured. At given time intervals, 5 mL reaction suspension was sampled and centrifuged twice to completely remove the solid catalysts. Then, the clear reaction solution (2 mL) and the prepared FeSSA complex solution (2 mL) were mixed thoroughly, and the absorbance spectrum was measured immediately. The value of OA concentration was calculated by substituting the absorbance value at λ=505nm into the obtained standard curve equation.

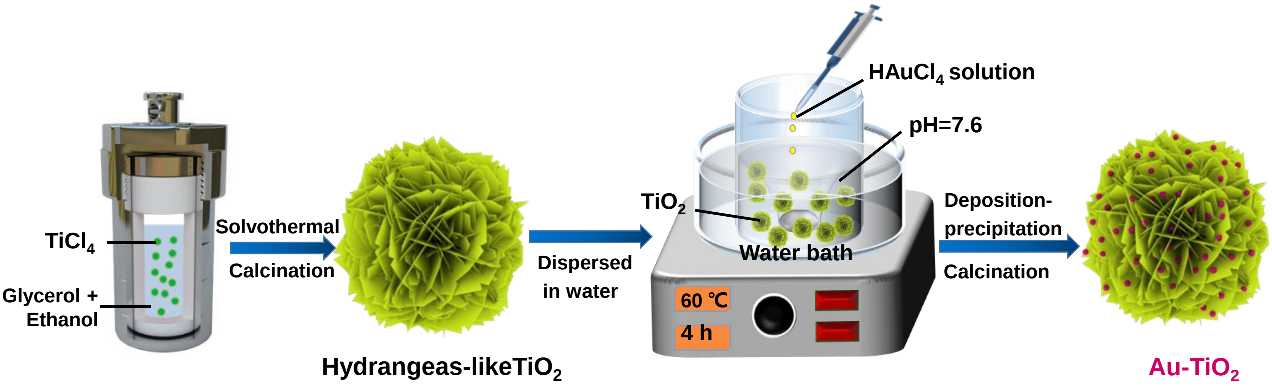


Fig. S1 Schematic illustration for the preparation of Au NPs decorated hydrangeas-like TiO_2.

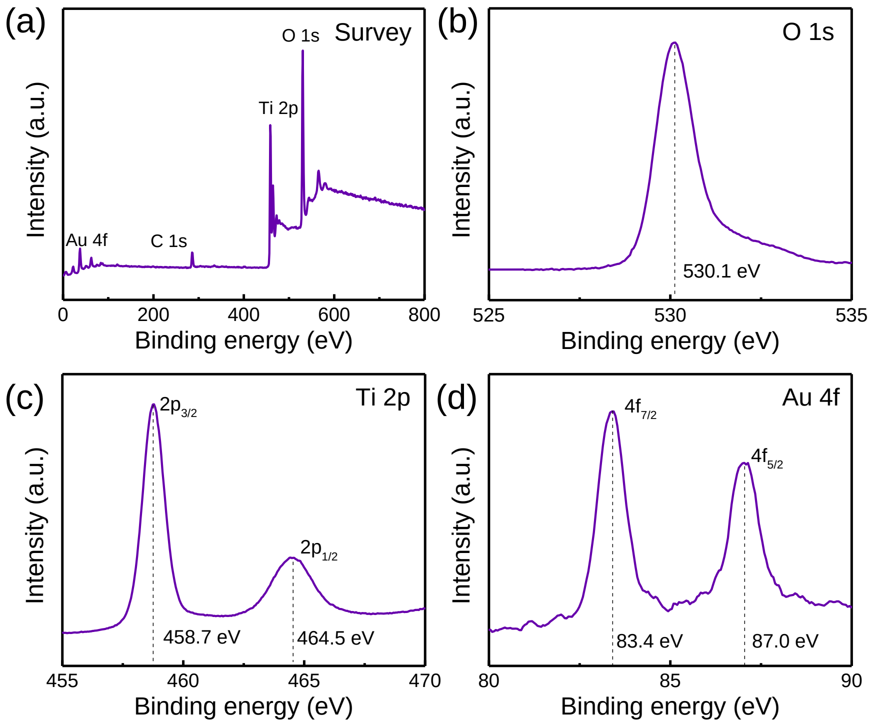


Fig. S2 XPS spectra for 1.5% Au-TiO_2: (a) general scan spectrum, high-resolution spectra of (b) O1s, (c) Ti2p, and (d) Au4f.

The elemental composition and chemical state of Au-TiO_2 were investigated by X-ray photoelectron spectroscopy (XPS). The general scan spectrum over a large energy range at low resolution is shown in Fig. S2. It was detected that the obtained Au-TiO_2 catalyst contains Ti, O, Au, and C. The high-resolution spectra of O1s, Ti 2p and Au 4f are presented in Fig. S2b-d. For O1s XPS spectrum, the peak at 530.1 eV is ascribed to the lattice oxygen O^{2-} in the TiO_2. With regard to Ti 2p spectrum, two peaks at 458.7 eV (Ti2$p_{3/2}$) and 464.54 eV (Ti 2$p_{1/2}$) are attributed to the Ti^{4+} in anatase TiO_2. Au 4f spectrum in Fig. S2d exhibits two peaks at 83.4 eV and 87.0 eV, corresponding to the binding energy of Au 4$f_{7/2}$ and 4$f_{5/2}$ level, respectively[19]. It reveals that Au NPs on the surface of hydrangeas-like TiO_2 exist in metallic gold state, which is well supported by the aforementioned XRD results. Comparing with the binding energy of bulk Au (84.0 eV), a negative shift (about 0.6 eV) was observed in the Au-TiO_2 catalyst, due to the electron transfer from TiO_2 to Au when they are in contact with each other[20]. It demonstrates that the Au NPs are interacting with the TiO_2, which is beneficial to the electron transfer at their interface in the process of photocatalytic ozonation, leading to a high degradation efficiency towards organic pollutants.

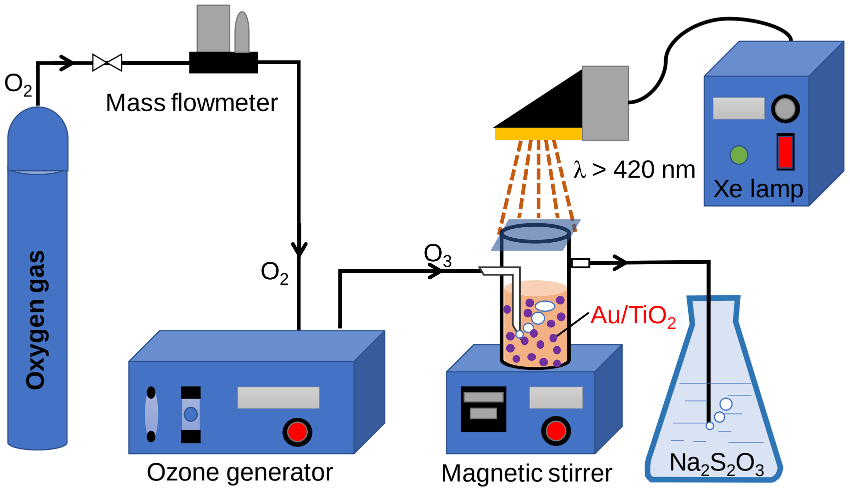


Fig. S3 Experimental setup for photocatalytic and catalytic ozonation with the prepared Au-TiO$_2$

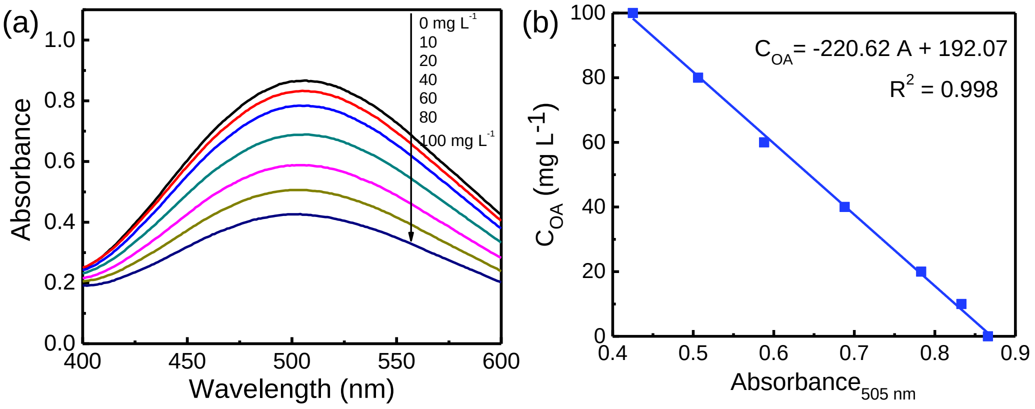


Fig. S4 (a) Absorption spectra of mixtures of FeSSA and OA with various OA concentrations, (b)the corresponding standard curve line of OA.

The absorbance spectra of OA solutions with various concentrations were presented Fig. S4a. It can be seen that the prepared FeSSA solution exhibits a broad absorbance peak centered at the wavelength of 505 nm (Fig. S4a, 0 mg L^{-1}). The absorbance values at 505 nm are gradually decreased from 0.425 to 0.866 with the increase of the concentration of OA solutions added. The corresponding standard curve was shown in Figure S4b. It is linear in the OA concentration range of 0-100 mg L^{-1}. The regression equation is C_{OA} = -220.62 A + 192.07 with correlation coefficient of 0.998, where C_{OA} is the concentration of OA in mg L^{-1} and A is the absorbance value at 505 nm.

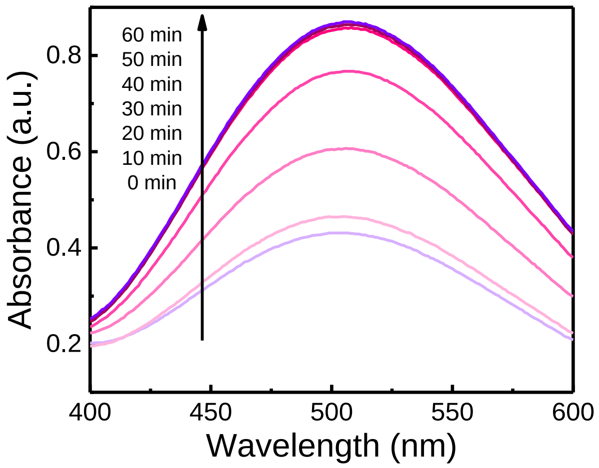


Fig. S5 UV-visible spectral changes of the mixture of FeSSA and oxalic acid (OA) solution as a function of reaction time in the process of 1.5% Au-TiO_2/Vis/O_3 (initial volume of solution : 150 mL; initial OA concentration: 100 ppm; catalyst dosage: 45 mg; gas flow rate: 40 mL min^{-1}; ozone concentration: 6.3 mg L^{-1}; light wavelength: 420-800 nm; light intensity: 330 mW cm^{-2}).

Degradation rate

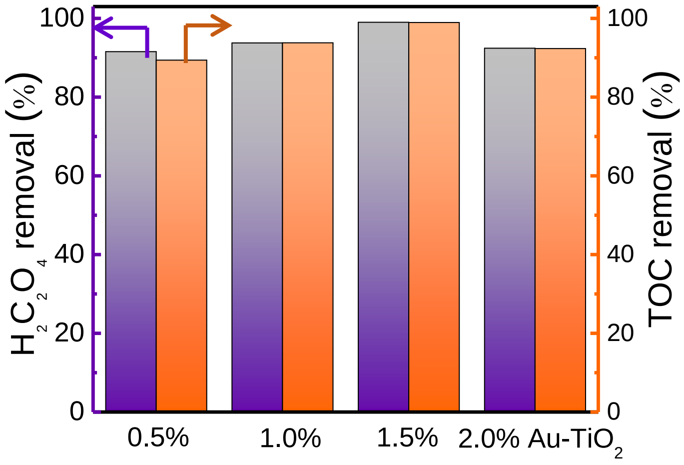


Fig. S6 OA removal efficiency and total organic carbon (TOC) removal efficiency in Au-TiO_2/Vis/O_3 for 60 min (initial volume of solution : 150 mL; initial OA concentration: 100 ppm; catalyst dosage: 45 mg; gas flow rate: 40 mL min^{-1}; ozone concentration: 6.3 mg L^{-1}; light wavelength: 420-800 nm; light intensity: 330 mW cm^{-2}).

Fig. S6 shows the comparison of OA removal efficiency and TOC removal efficiency in Au-TiO_2/Vis/O_3 process. The OA removal efficiency (D(%)) was calculated by D(%) = 100(C_0 – C_{60})/C_0, and the TOC removal efficiency (TOC(%)) was calculated by TOC(%) = 100(TOC_0 – TOC_{60})/TOC_0, where C_0 and C_{60} are the initial (0 min) and final (60 min) concentration of OA, and TOC_0 and TOC_{60} are the initial (0 min) and final (60 min) TOC of the reaction solution.

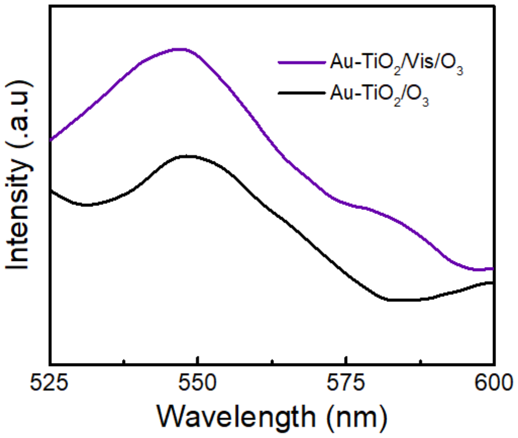


Fig. S7 •O_2^--trapping photoluminescence spectra in NBD-Cl solution in Au-TiO_2/O_3 and Au-TiO_2/Vis/O_3 for 20 min (initial volume of solution: 150 mL; initial NBD-Cl concentration: 20 ppm; initial pH: 3; catalyst dosage: 20 mg; gas flow rate: 20 mL min^{-1}; light wavelength: 420-800 nm; light intensity: 330 mW cm^{-2})

The existence of •O_2^- radical in catalytic ozonation and photocatalytic ozonation with the prepared Au-TiO_2 was further proved by a photoluminescence probing technique, in which 4-chloro-7-nitrobenzo-2-oxa-1,3-dizole (NBD-Cl) was used as a probe molecule to react with •O_2^- to form a fluorescent product.[21-22] In this experiment, NBD-Cl aqueous solution (20 ppm, 150 mL, pH = 3) was transferred to a reactor containing 45 mg of Au-TiO_2, and continuously stirred at 500 rpm. For photocatalytic ozonation, Xe lamp with a cut-off filter ($420 < \lambda < 780$ nm) was turned on, and ozone was bubbled into the reaction system at the same time. For catalytic ozonation, only ozone was continuously bubbled in the dark. After reaction for 20 min, the suspension was sampled and centrifuged to remove the solid catalyst. Next, 1 mL of clear sample solution was mixed with 2 mL of acetonitrile, and immediately measured the fluorescence emission spectra with a fluorescence spectrometer (PerkinElmer, LS55). The excitation wavelength was 470 nm, and emission scans were carried out between wavelength ranges of 480 and 680 nm. The emission slit and excitation slit were set to 5 nm and 15 nm, respectively.

Comparison of catalytic degradation of OA with previous study

Table S1 Comparison of catalytic degradation of OA in the presence of ozone under visible light irradiation or in the dark

Catalyst	Reaction conditions					D%[a]	TOC%[b]	Ref.
	λ/nm	O_3 flow rate/ mg h^{-1}	Catalyst dose/g L^{-1}	C(OA)/ mg L^{-1}	t/min			
WO_3(100)	420-800	120	0.1	180	60	98.6%	-	[23]
WO_3	>410	450	2	900	60	-	62%	[24]
	Dark	450	2	900	240	-	~ 20%	
$BiVO_4$	420-800	120	0.1	90	30	84.4%	-	[25]
	Dark	120	0.1	90	30	24.0%		
g-C_3N_4	>400	500	0.5	10	120	80.0%	-	[26]
	Dark	500	0.5	10	120	20.8%	-	
g-C_3N_4	420-800	180	1	90	30	85%	-	[27]
	Dark	180	1	90	30	~ 1%	-	
Fe_2O_3/Al_2O_3	Dark	720	1.25	720	180	28%	-	[28]
FeOOH	Dark	27	2	0.9	30	54%	-	[29]
N-doped layered nanocarbons	Dark	150	0.1	50	45	100%	-	[30]
reduced graphene oxide	Dark	300	0.1	100	60	90%	-	[31]
Au-TiO_2	420-800	15	0.3	100	60	99%	99%	This study
	Dark	15	0.3	100	60	84%	-	

a: Degradation rate of oxalic acid; b: Total organic carbon (TOC) removal rate

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