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**Facile synthesis of carbon-doped mesoporous anatase TiO<sub>2</sub> for the enhanced visible-light driven photocatalysis†**

*Juming Liu,<sup>a,b</sup> Qiancheng Zhang,<sup>\*a</sup> Jucui Yang,<sup>b</sup> Huiyan Ma,<sup>a</sup> Moses O. Tade,<sup>c</sup> Shaobin Wang<sup>c</sup> and*

*Jian Liu<sup>\*c</sup>*

*<sup>a</sup> Key Lab of Industrial Catalysis of the Inner Mongolia Autonomous Region, Inner Mongolia University of Technology, Hohhot 010051, China. E-mail: [jzhang@imut.edu.cn](mailto:jzhang@imut.edu.cn)*

*<sup>b</sup> School of Energy and Power Engineering, Inner Mongolia University of Technology, Hohhot, 010051, China.*

*<sup>c</sup> Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia. E-mail: [jian.liu@curtin.edu.au](mailto:jian.liu@curtin.edu.au)*

**\* To whom correspondence should be addressed. E-mail: [jian.liu@curtin.edu.au](mailto:jian.liu@curtin.edu.au); [jzhang@imut.edu.cn](mailto:jzhang@imut.edu.cn)**

## Contents

Experimental section

**TABLE S1** Carbon species contents of different C-TiO<sub>2</sub> samples.

**Fig. S1** Energy-dispersive X-ray spectroscopy (EDX) of (a) C-TiO<sub>2</sub>-5 and (b) C-TiO<sub>2</sub>-21.

**Fig. S2** XRD patterns of C-TiO<sub>2</sub> synthesized in (a) pure N<sub>2</sub> atmosphere, (b) hypoxic atmosphere (5% O<sub>2</sub>, 95% N<sub>2</sub>) and (c) zero-air atmosphere (21% O<sub>2</sub>, 79% N<sub>2</sub>).

**Fig. S3** Nitrogen adsorption-desorption isotherm (left) and pore size distribution (right) of C-TiO<sub>2</sub>-5.

**Fig. S4** Raman spectrum of C-TiO<sub>2</sub>-5 in the range of 900-1800 cm<sup>-1</sup>.

**Fig. S5** UV-vis diffuse reflectance spectra of C-TiO<sub>2</sub> synthesized in (a) pure N<sub>2</sub> atmosphere, (b) hypoxic atmosphere (5% O<sub>2</sub>, 95% N<sub>2</sub>), (c) zero-air atmosphere (21% O<sub>2</sub>, 79% N<sub>2</sub>) and (d) P25.

**Fig. S6** TG and DSC curves of (a) C-TiO<sub>2</sub>-0, (b) C-TiO<sub>2</sub>-5 and (c) C-TiO<sub>2</sub>-21.

**Fig. S7** Photocatalytic degradation of methyl orange using different C-TiO<sub>2</sub> and P25 photocatalysts under visible light irradiation ( $\lambda > 400$  nm).

**Fig. S8** The cycling degradation experiments of MO on C-TiO<sub>2</sub>-0.

**Fig. S9** Recycling properties of C-TiO<sub>2</sub>-5 in photocatalytic degradation of MO.

**Fig.S10** XRD patterns of C-TiO<sub>2</sub>-5 (a) before cycling experiments and (b) after 3 rounds cycling experiments.

## Experimental Section

**Photocatalyst preparation.** All chemicals were used as received without further purification.

Distilled water was used for preparing all aqueous solutions. C-TiO<sub>2</sub> was prepared by combining the conventional sol-gel method followed with xerogel carbonization process. Typically, 10 mL of glacial acetic acid, 20 mL of anhydrous ethanol, and 7 mL of distilled water were mixed in a 200 mL flask with stirring for 10 min to obtain solution A. The pH of the solution A was adjusted to ca. 1.5 with HNO<sub>3</sub>. Meanwhile, 10 mL of titanium butoxide ( $\geq 99.0\%$ ) and 20 mL of anhydrous ethanol were mixed with stirring for 10 min to obtain solution B. The solution A was added into the solution B within 30 min, keeping the reaction mixture vigorously and magnetically stirred to form the sol. The sol was stirred continuously for 30 min and aged for 48 h at room temperature. After that, the sol was gradually heated to 70 °C and kept at this temperature for 30 min to form the gel. The gel was dried for 12 h at 100 °C to gain the xerogel, which was milled and put into a ceramic boat. Then, the xerogel was carbonized using a tube furnace at 400 °C with a ramping rate of 5 °C/min and held for 2 h to prepare the C-TiO<sub>2</sub> photocatalyst. The final products were allowed to cool to room temperature naturally. The carbonization was performed in pure N<sub>2</sub> atmosphere (0% O<sub>2</sub>, 100% N<sub>2</sub>), hypoxic

atmosphere (5% O<sub>2</sub>, 95% N<sub>2</sub>) and air atmosphere (21% O<sub>2</sub>, 79% N<sub>2</sub>), respectively. The gas flow rate was 100 mL/min, and the as-synthesized C-TiO<sub>2</sub> samples were labeled as C-TiO<sub>2</sub>-x (i.e. C-TiO<sub>2</sub>-0, C-TiO<sub>2</sub>-5 and C-TiO<sub>2</sub>-21), where “x” indicated the volume percentage of oxygen in the carbonization atmosphere.

**Photocatalyst characterization.** The thermal property of the as-prepared xerogel and C-TiO<sub>2</sub> samples were measured using a thermogravimetric analyzer (Linseis STA PT1600) with a temperature ramp up to 800 °C at the heating rate of 10 °C/min in air atmosphere. X-Ray diffraction (XRD) patterns were collected on a PANalytical Empyrean X-ray diffractometer with Cu K $\alpha$  radiation. The morphologies of C-TiO<sub>2</sub> was observed by the transmission electron microscopy (TEM, FEI tecnai F20). The sample for TEM measurements was suspended in ethanol and supported onto a holey carbon film on a Cu grid. Energy-dispersive X-ray spectroscopy (EDX, Brucker-QUANTAX 200) was performed, using an accelerating voltage of 20.0 kV. Nitrogen-sorption isotherms were collected by QuadraSorb Station 2 system (Quantachrome Ins) at 77 K. Prior to the measurement, samples were degassed at 300 °C for 3 h. The Brunauer-Emmett-Teller (BET) specific surface area was calculated using adsorption data at a relative pressure range of P/P<sub>0</sub> = 0.024-0.25. Pore size distribution was derived from the adsorption branch using Density Functional Theory (DFT) method. The total pore volume was estimated from the adsorbed amounts at a relative pressure (P/P<sub>0</sub>) of 0.99. X-Ray photoelectron spectroscopy (XPS) was accomplished using a PHI5000 VersaProbe X-ray photoelectron spectrometer using an Al K $\alpha$  X-ray beam (1486.6 eV). All binding energies were referenced to the C 1s neutral carbon peak, which was assigned the value of 284.8 eV to compensate for surface charge effects. To investigate the local chemical state of functional groups on the surface, curve fitting of the raw data of the Ti 2p, O 1s and C 1s spectra was performed using the public

software package XPSPEAK v4.1. Argon-ion etching of the C-TiO<sub>2</sub> was carried out for 5 min, which corresponds to a sputtering rate of ca. 2.0 nm/min for SiO<sub>2</sub>. Diffuse reflectance spectra were recorded in the range of 250-800 nm in reference to barium sulphate (BaSO<sub>4</sub>) using a UV-Vis spectrometer (UV-3600, Shimadzu). Raman spectra were acquired with a Laser Confocal Micro-Raman Spectroscopy (LabRAM HR800, Horiba Jobin Yvon) equipped with a 532 nm green laser source.

**Photocatalytic degradation experiment.** The photocatalytic activity of C-TiO<sub>2</sub> was evaluated using methyl orange (MO) degradation in aqueous solution under visible light irradiation. The light source was a 300 W Xenon arc lamp and the short wavelength components ( $\lambda < 400$  nm) of the light were cut off using a glass optical filter. Typically, 1.0 g of as-prepared C-TiO<sub>2</sub> catalyst was added to 200 mL of 20 mg/L MO solution in a 400 mL beaker. Prior to irradiation, the suspensions were magnetically stirred for 1 h to achieve adsorption-desorption equilibrium for MO. Thereafter, the suspensions were illuminated with the above-mentioned light source. To determine the change in MO concentration in solution during the process, a few milliliters of the solution were taken from the reaction mixture, subsequently filtered through a millipore filter (pore size 0.22  $\mu$ m) to remove the catalyst completely. After that, this solution was analyzed on a UV-Vis spectrometer. The absorbance of MO solution was determined by UV-Vis spectrometry at 464 nm. The concentration of MO was obtained according to the linear relation between the absorbance and the concentration of MO solution. P25 (DeGussa), as a typical reference TiO<sub>2</sub> for the evaluation of C-TiO<sub>2</sub> photocatalyst activity, was used for comparison under the same conditions.

The photocatalytic activity of C-TiO<sub>2</sub> was also evaluated by measuring their efficiency in photocatalytic decomposition of phenol in aqueous solution under visible-light irradiation with the wavelength longer than 450 nm. In a typical experiment, 0.5 g of as-prepared C-TiO<sub>2</sub> catalyst was

added to 100 mL of 20 mg/L phenol solution in a 250 mL beaker. Prior to irradiation, the suspensions were magnetically stirred for 1 h to achieve adsorption-desorption equilibrium for phenol. Thereafter, the suspensions were illuminated with the above-mentioned 300 W Xenon arc lamp and the short wavelength components ( $\lambda < 450$  nm) of the light were cut off using a glass optical filter. During the 180-minute long illumination, a few milliliters of solution together with the solid catalyst was drawn out every 20 minutes to determine the concentration of the remaining phenol using UV-visible spectrophotometer by measuring of absorbance at 270 nm. The solution was separated from the catalyst through syringe filtration (pore size 0.22  $\mu$ m). The concentration of phenol was obtained according to the linear relation between the absorbance and the concentration of phenol solution. P25 (DeGussa) was also used for comparison under the same conditions.

TABLE S1 Carbon species contents of different C-TiO<sub>2</sub> samples

Sample	Carbonization atmosphere	Carbon species content <sup>a</sup> (wt %)
C-TiO <sub>2</sub> -0	Pure N <sub>2</sub> atmosphere (0% O <sub>2</sub> , 100% N <sub>2</sub> )	17.4%
C-TiO <sub>2</sub> -5	Hypoxic atmosphere (5% O <sub>2</sub> , 95% N <sub>2</sub> )	4.4%
C-TiO <sub>2</sub> -21	Zero-air atmosphere (21% O <sub>2</sub> , 79% N <sub>2</sub> )	2.6%

<sup>a</sup> Determined by TG/DSC.

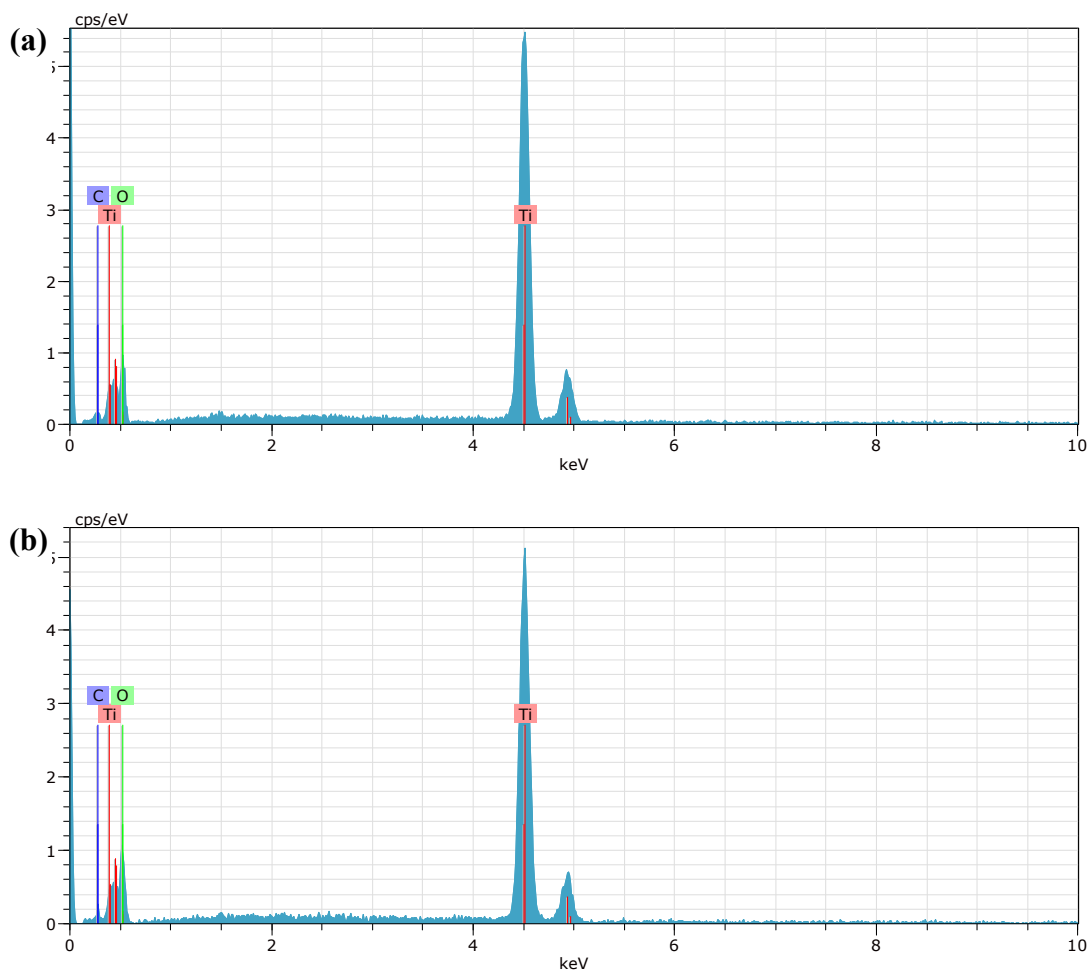


Fig. S1 Energy-dispersive X-ray spectroscopy (EDX) of (a) C-TiO<sub>2</sub>-5 and (b) C-TiO<sub>2</sub>-21.

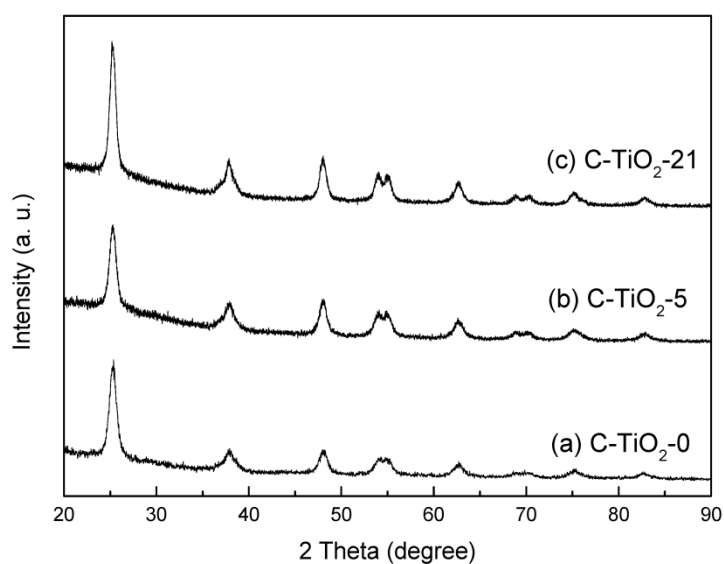


Fig. S2 XRD patterns of C-TiO<sub>2</sub> synthesized in (a) pure N<sub>2</sub> atmosphere, (b) hypoxic atmosphere (5% O<sub>2</sub>, 95% N<sub>2</sub>) and (c) zero-air atmosphere (21% O<sub>2</sub>, 79% N<sub>2</sub>).

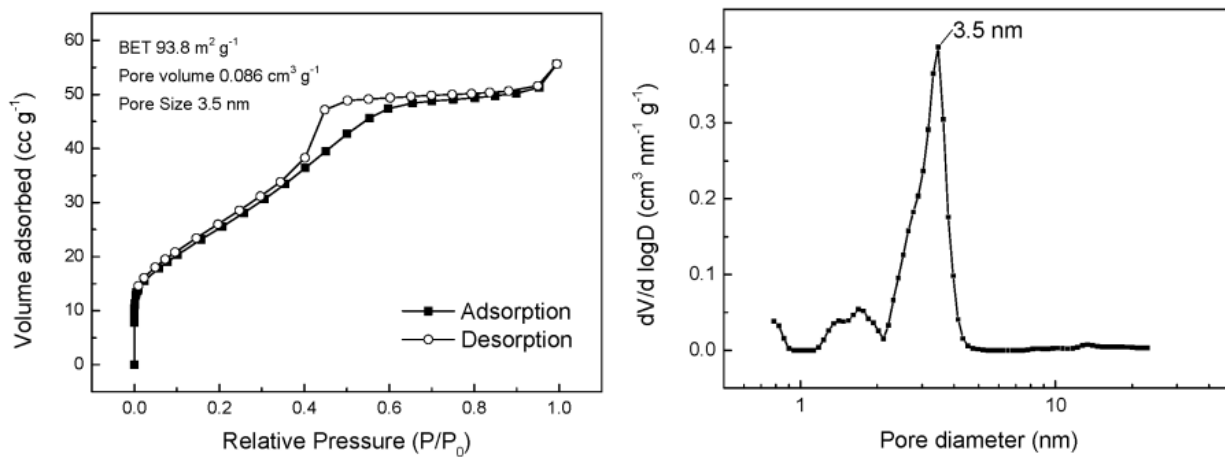


Fig. S3 Nitrogen adsorption-desorption isotherm (left) and pore size distribution (right) of C-TiO<sub>2</sub>-5.

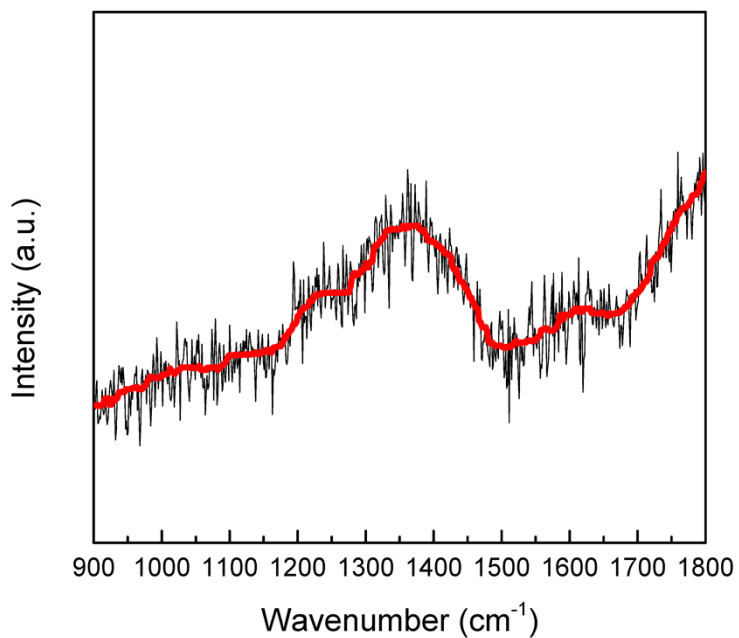


Fig. S4 Raman spectrum of C-TiO<sub>2</sub>-5 in the range of 900-1800 cm<sup>-1</sup>.

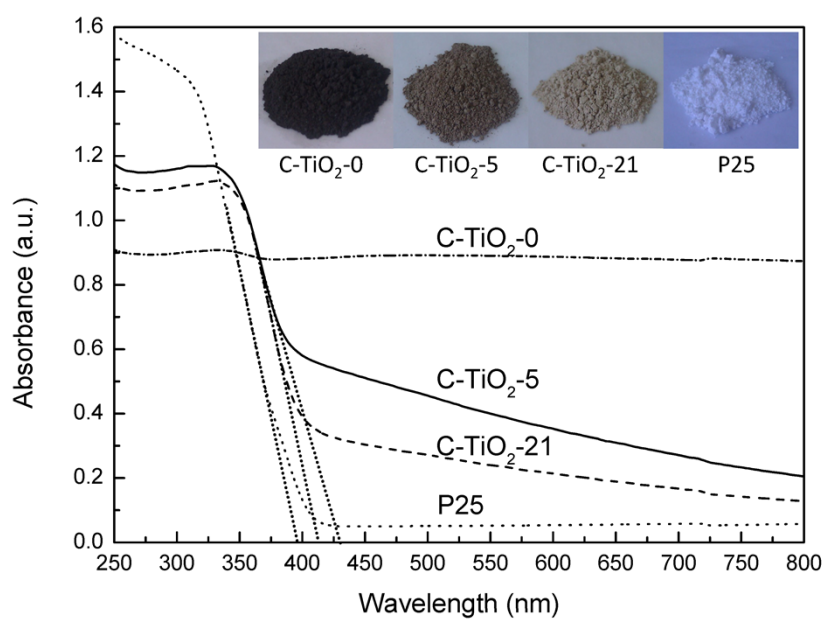


Fig. S5 UV-vis diffuse reflectance spectra of C-TiO<sub>2</sub> synthesized in (a) pure N<sub>2</sub> atmosphere, (b) hypoxic atmosphere (5% O<sub>2</sub>, 95% N<sub>2</sub>), (c) zero-air atmosphere (21% O<sub>2</sub>, 79% N<sub>2</sub>) and (d) P25.

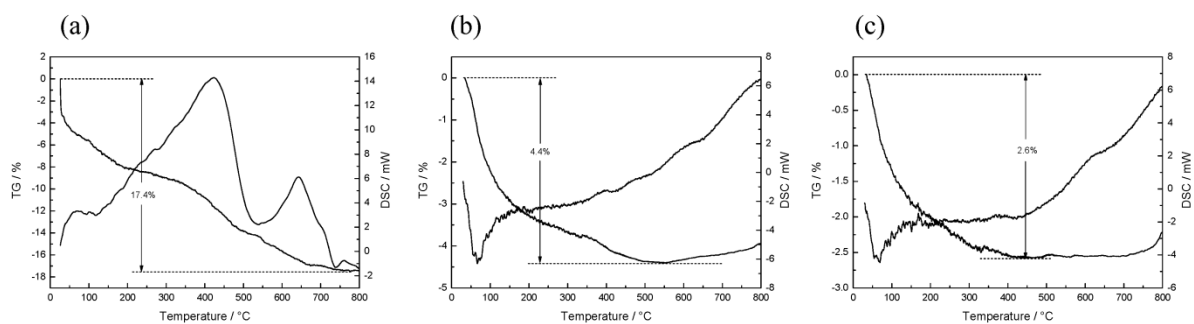


Fig. S6 TG and DSC curves of (a) C-TiO<sub>2</sub>-0, (b) C-TiO<sub>2</sub>-5 and (c) C-TiO<sub>2</sub>-21.



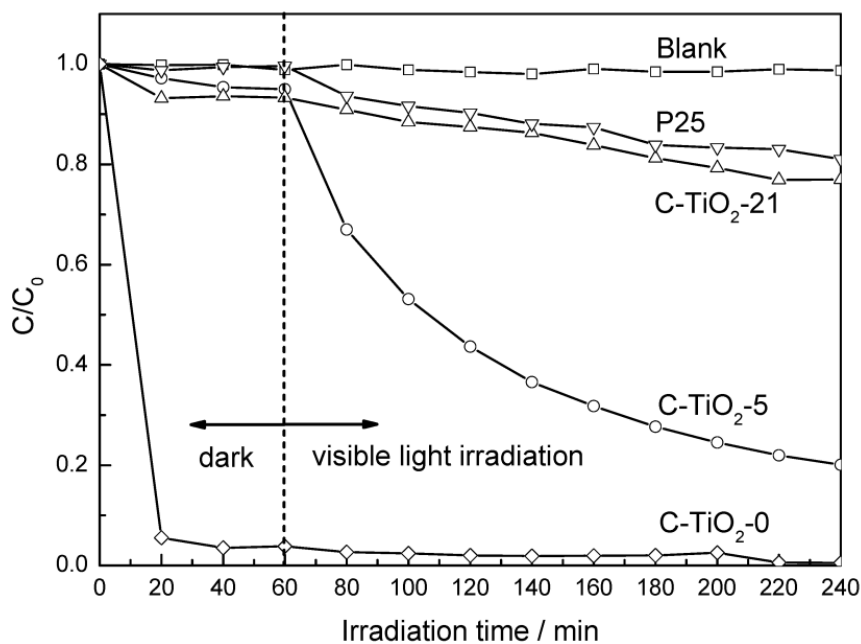


Fig. S7 Photocatalytic degradation of methyl orange using different C-TiO<sub>2</sub> and P25 photocatalysts under visible light irradiation ( $\lambda > 400$  nm).

Notably, C-TiO<sub>2</sub>-0 showed a strong adsorption of MO in the dark without any further photocatalytic activity under visible light, which is due to the formation of more residual carbon species with high adsorbability under pure nitrogen heat treatment atmosphere. The cycling degradation experiments of MO on C-TiO<sub>2</sub>-0 were further performed and confirmed that the C-TiO<sub>2</sub>-0 photocatalyst only has adsorption capacity as shown in Fig. S8. Too much residual carbon species seemed adverse for the photocatalytic degradation, which might be due to that the surface of TiO<sub>2</sub> was covered by residual carbon species and the photocatalysis reaction was restrained. C-TiO<sub>2</sub>-21 had a low photocatalytic activity under visible light, and the decolorization efficiency was only 23% in 3 h.

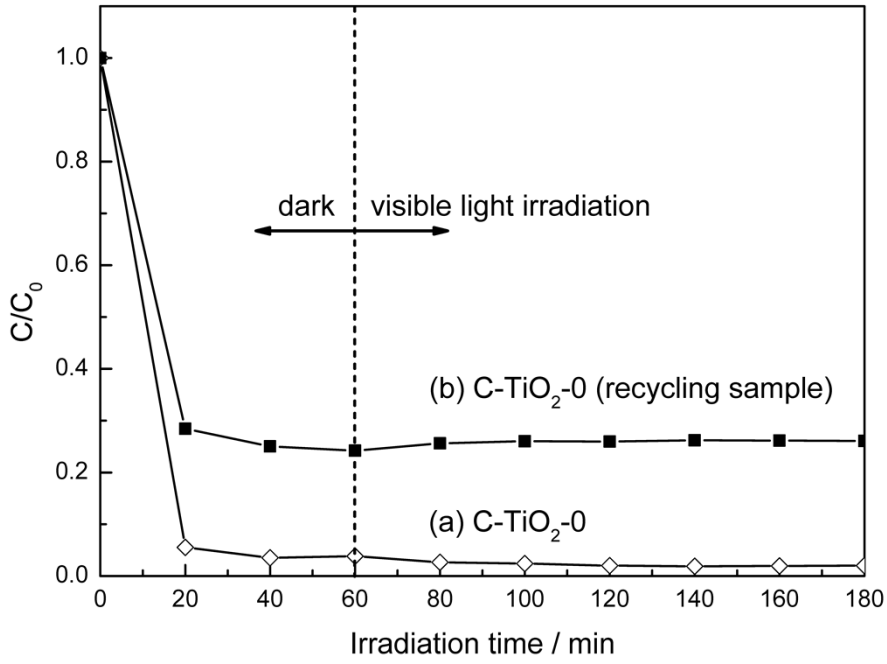


Fig. S8 The cycling degradation experiments of MO on C-TiO<sub>2</sub>-0.

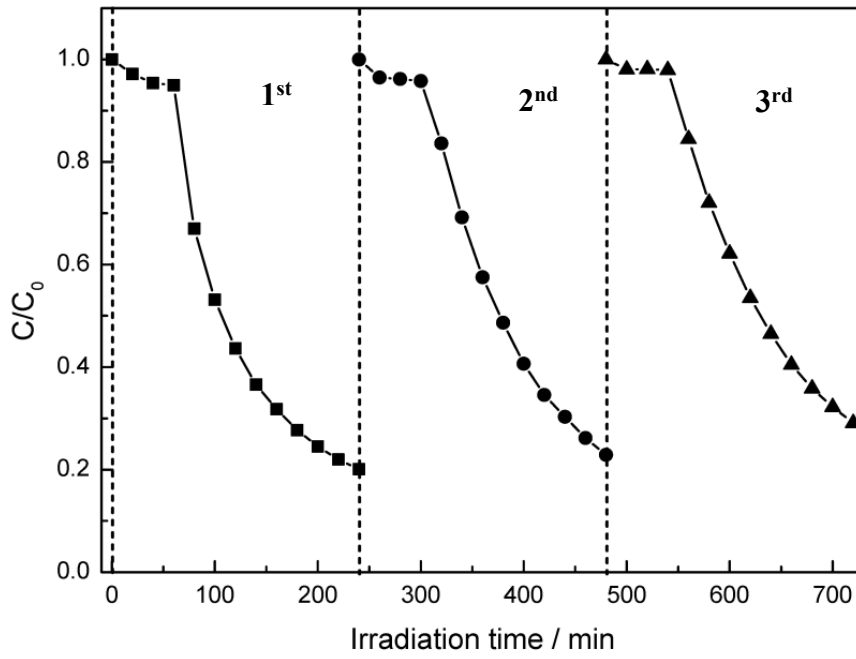


Fig. S9 Recycling properties of C-TiO<sub>2</sub>-5 in photocatalytic degradation of MO.

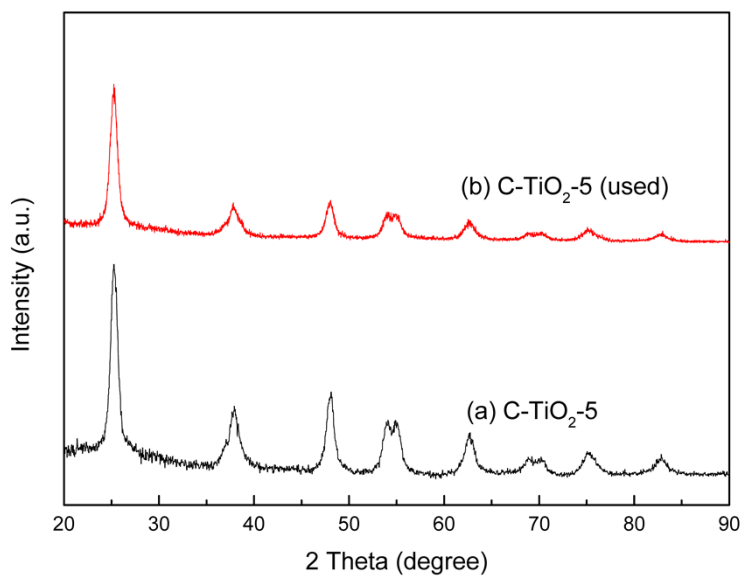


Fig.S10 XRD patterns of C-TiO<sub>2</sub>-5 (a) before cycling experiments and (b) after 3 rounds cycling experiments.

XRD analysis of the used C-TiO<sub>2</sub>-5 sample confirmed that the photocatalyst is very stable and no obvious change in structure was found (Fig. S10).