SUPPORTING INFORMATION FOR

Stepwise preparation of Ti-doped functionalized carbon nitride nanoparticles and hybrid TiO_2/graphitic-C_3N_4 for detection of free residual chlorine and visible-light photocatalysis

1. Experimental Section

1.1. Chemicals

Tetrabutyl titanate (chemically pure, CP) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Urea, citric acid monohydrate (CA), methylene blue (MB) and oleic acid were all analytical reagents (AR), and also afforded by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Quinine sulfate was bought from Aladdin Industrial Corporation (Shanghai, China). Sodium hypochlorite solution (1.37M) was purchased from Xilong Chemical Co. Ltd. (Guangdong, China). Ultrapure water was dealt with Milli-Q system (Millipore, Bedford, MA, USA). Other reagents were all analytical and were used without further purification.

1.2. Stepwise preparation of Ti-CNNPs and TiO_2/g-C_3N_4

Typically, a simple one-step oil-thermal tactic was taken to prepare Ti-CNNPs. 2.0 g CA, 2.0 g urea and 40 mL oleic acid were put into a three neck flask. Then, 1.5 mL tetrabutyl titanate (TBT) was added into the system. The mixture was stirred at 180 °C for 30 min at 2000 rpm. After the reaction was finished, the flask was naturally cooled to room temperature. The collected sediment was sufficiently washed with *n*-hexane and ethanol, then dried at 50 °C in a vacuum drier for 12 h.

The TiO_2/g-C_3N_4 composites were prepared by running to the second step following the oil-thermal treatment. The obtained Ti-CNNPs were calcined further at 500 °C for 1 h in a muffle furnace. The product was collected and ground into power. The same two-step strategy was performed to prepare g-C_3N_4 and TiO_2 using corresponding precursors.

Table S1 shows the comparison of total preparation time of various TiO_2/g-C_3N_4 composites. It clearly indicates that our two-step strategy greatly shortens the experimental time.

1.3. Quantum yield measurement

The quantum yield (QY) of the prepared Ti-CNNPs was measured according to the established procedure, by comparing the integrated fluorescence (FL) intensity and the absorbance value of the product with the reference quinine sulfate. The quinine sulfate (literature QY_R=0.54 at an excitation wavelength of 360 nm) was dissolved in 0.1 M H_2SO_4 (refractive index η of 1.33), and the obtained Ti-CNNPs was dissolved in ultrapure water (η=1.33). The absorbencies in 10 mm fluorescence cuvettes were kept under 0.1 at the corresponding excitation wavelength. The quantum yield of the Ti-CNNPs was measured by the following equation:

$$QY = QY_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta 2}{\eta_R^2}$$

Where "I" is the measured and integrated emission intensity, "η" is the refractive index of the solvents, and "A" is the absorbance corresponding to excitation wavelength. The subscript "R" refers to the reference of known quantum yield.

1.4. Detection of free residual chlorine by using Ti-CNNPs solution

The FL intensity of 0.62 mg/mL Ti-CNNPs solution was measured with the addition of different concentration of ClO^- to obtain the FL intensity–concentration calibration curve (F–C curve) as well as the LOD of this method. The concentration of ClO^- was set at 0, 0.5. 1, 2, 4, 6, 8, 10, 12, 15, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μM. The selectivity of ClO^- was examined by adding some common ions such as Cl^-, SO_4^{2-}, ClO_4^-, Br^-, ClO_3^-, NO_2^-, F^-, BrO_4^-, IO_3^-, $C_2O_4^{2-}$, HCO_3^-, NO_3^-, HPO_4^{2-}, AC^-, PO_4^{3-}, CO_3^{2-}, Zn^{2+}, K^+, Ca^{2+}, Na^+, Ba^{2+}, Mg^{2+}, Mn^{2+}, NH_4^+, $Ni^{2+}$and Ag^+ under identical conditions. The final concentration of ClO^- or the examination ions are all 100 μM. In the interference experiments, the Ti-CNNFs aqueous solution was mixed with ClO^- in the absence or presence of interferential ions, and corresponding fluorescence intensity was recorded to evaluate the interference. The final concentration of ClO^- and interfering ions were all 30 µM.

1.5. Visual light photocatalytic activity test

The visual light photocatalytic activities of those prepared materials mentioned above were investigated by degrading methylene blue (MB) aqueous solution under visible light (420-800 nm). In each experiment, 40 mg of the prepared materials was dispersed into 50 mL of 6 mg/L MB solution and kept stirring at 800 rpm in the dark ambience for 60 min to establish an adsorption-desorption equilibrium between catalyst and MB solution. The suspension was then exposed to 420-800 nm light from a 35 W xenon lamp. Three milliliter of suspension was sampled every 30 min and centrifuged at 10000 rpm for 5 min to separate the catalyst. The supernatant was taken to measure the UV-vis spectrum of MB in time. The maximum absorbance at the wavelength of 655 nm was recorded.

2. Characterization Section

Transmission electron microscopy (TEM) images were taken on a Tecnai G2 F20 instruments (FEI, America). Scanning electron microscopy (SEM) images were obtained on a Zeiss supra 55 (Germany). X-ray diffraction (XRD) spectra were recorded by a Bruker DAVINCI D8 ADVANCE diffractometer (Germany). A Magna-IR 750 Fourier transform infrared spectrometer (Nicolet, America) was performed to acquire FT-IR spectra. X-ray photoelectron spectroscopy (XPS) spectra were carried out on a Thermo ESCALAB 250Xi multifunctional imaging electron spectrometer (Thermo Fisher). Fluorescence spectra were obtained by a Cary Eclipse FL spectrophotometer (Varian, America). Nitrogen adsorption-desorption isotherm measurements were conducted at 77 K using a Gemini 2390 surface area analyzer (America). All samples were pretreated by degassing at 200 °C for 6 h to remove any adsorbed species. The elemental composition was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer Nexion 300, America) and an elemental analyzer (Flash2000, Thermo Electron Corporation, America). UV-2550 spectrophotometer (Shimadzu, Japan) was used to record the UV-vis spectra. UV-vis diffuse reflectance spectra (UVDRS) were carried out on a solid UV-vis-DH-2000-

BAL spectrophotometer (Ocean optics, shanghai, China). Xenon lamp (35 W, Guangzhou Popnow electronic technology Co., Ltd, China) was used to afford 420-800 nm visual light.

3. Supporting Figures

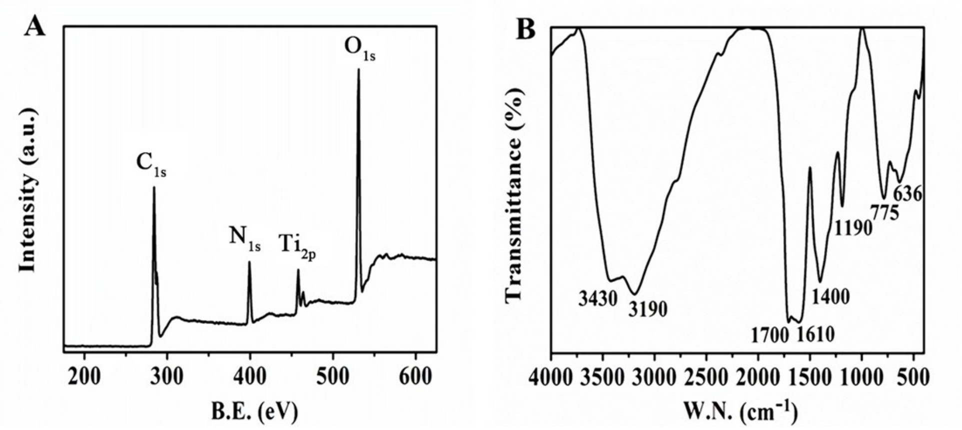


Fig. S1. (A) XPS spectrum and (B) FT-IR spectrum of the Ti-CNNPs.

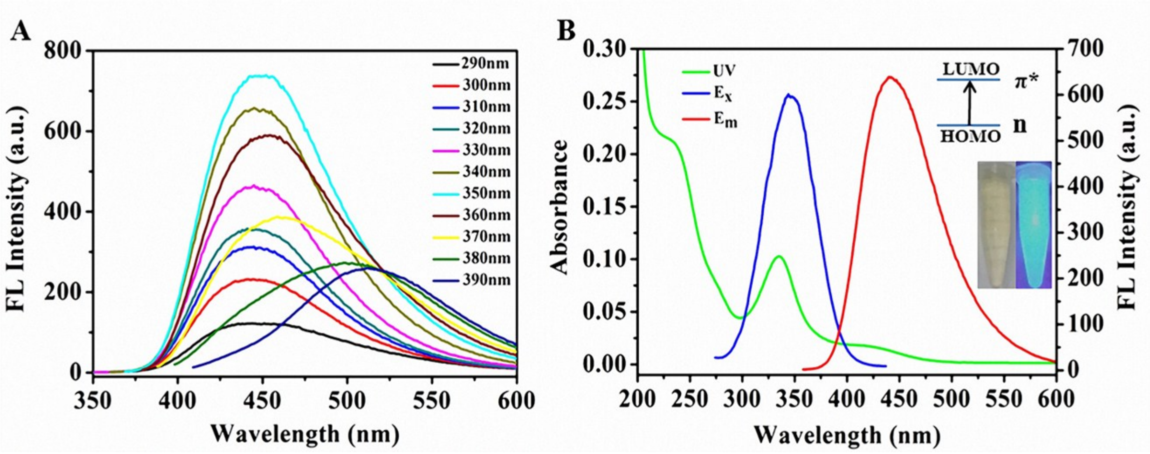


Fig. S2. (A) Excitation-dependent emission spectrum and (B) UV-vis spectrum and FL excitation, emission spectrum of of the Ti-CNNPs. Inset of B, the photographs under illumination of nature (left) and UV (365 nm, right) light.

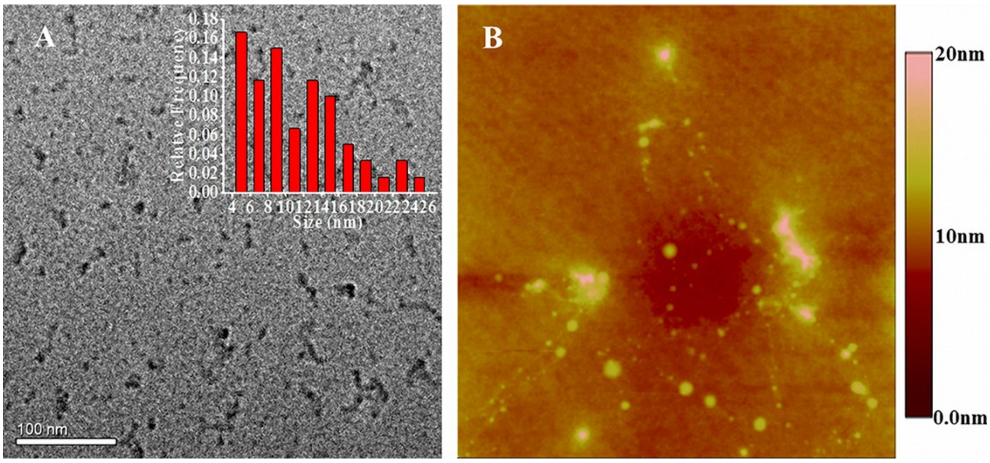
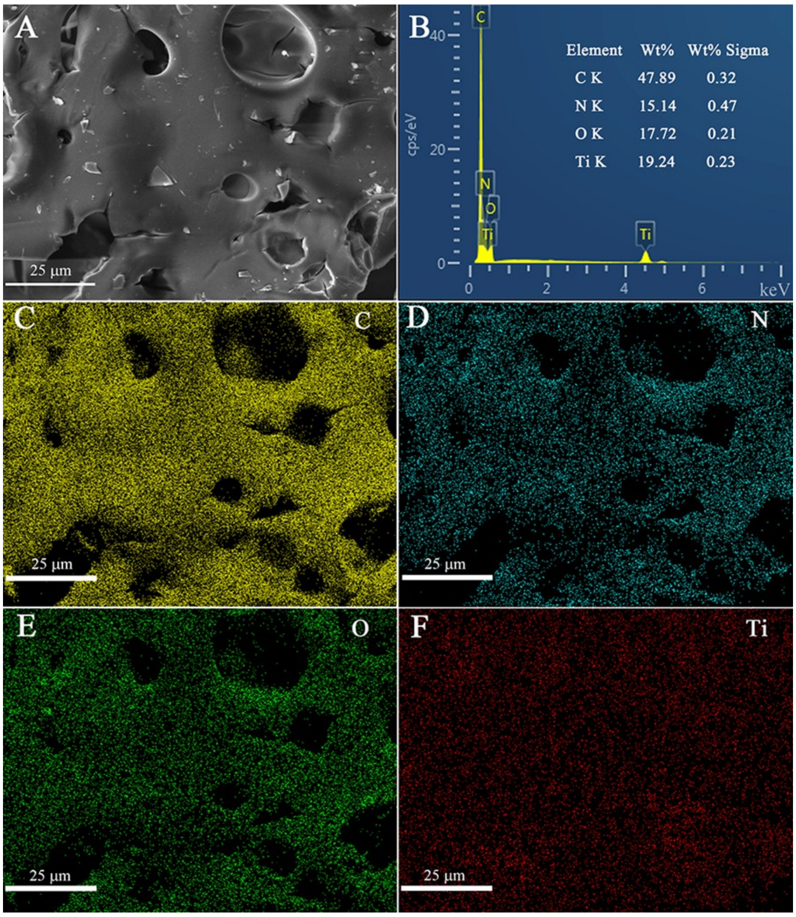


Fig. S3. (A) High-resolution transmission electron microscopy (HRTEM) and (B) atomic force microscopy (AFM) images of Ti-CNNPs.



Element	Wt%	Wt% Sigma
C K	47.89	0.32
N K	15.14	0.47
O K	17.72	0.21
Ti K	19.24	0.23

Fig. S4. SEM (A), EDS pattern (B), C element (C), N element (D), O element (E), and Ti element (F) maps of the TiO_2/g-C_3N_4 composites.

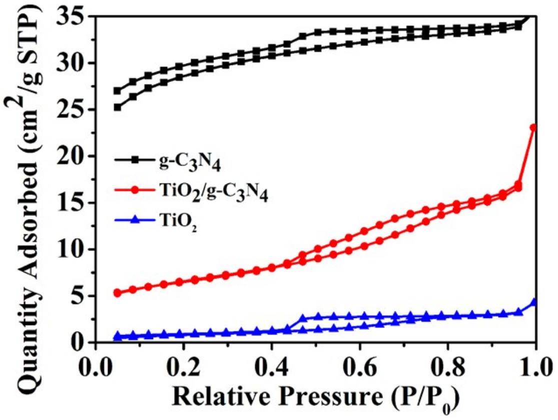


Fig. S5 Nitrogen adsorption-desorption isotherms.

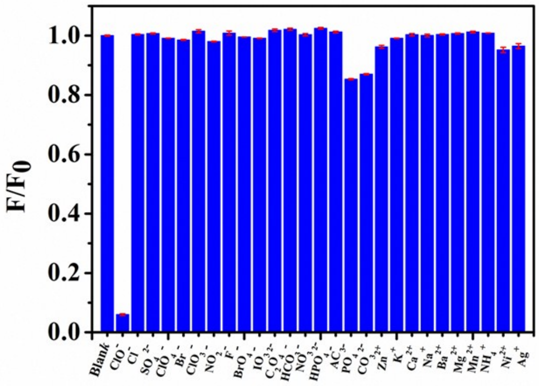


Fig. S6. Selectivity experiments for determination of HClO by Ti-CNNPs.

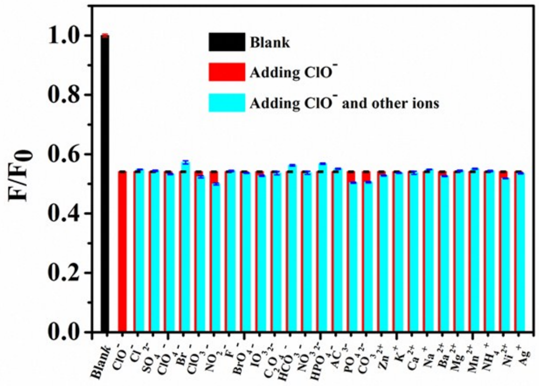


Fig. S7. Interference experiments for the determination of HClO by Ti-CNNPs.

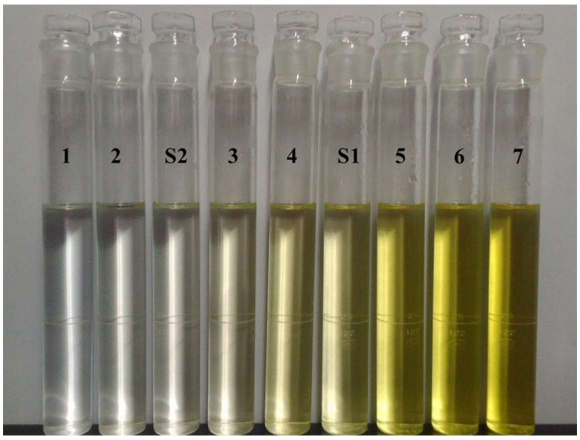


Fig. S8. Colorimetric method for the determination of HClO by Ti-CNNPs.

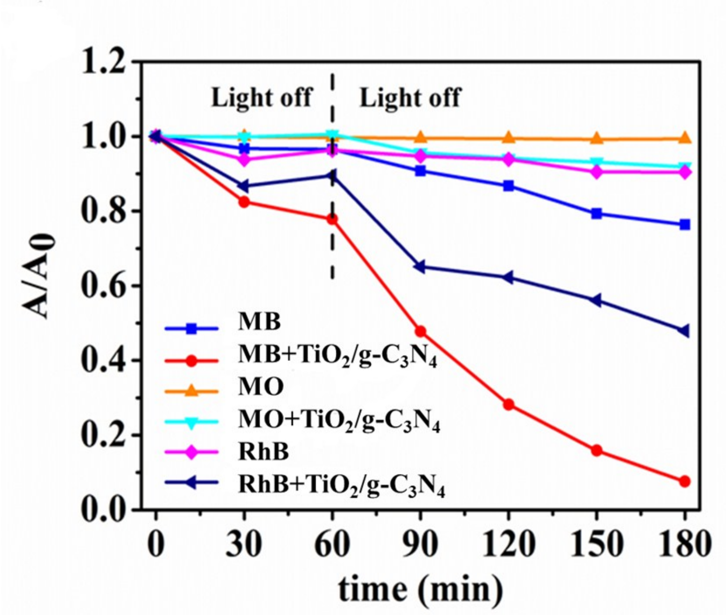


Fig. S9. Degradation of methylene blue (MB), methyl orange (MO) and rhodamine B (RhB) by the obtained $TiO_2/g\text{-}C_3N_4$.

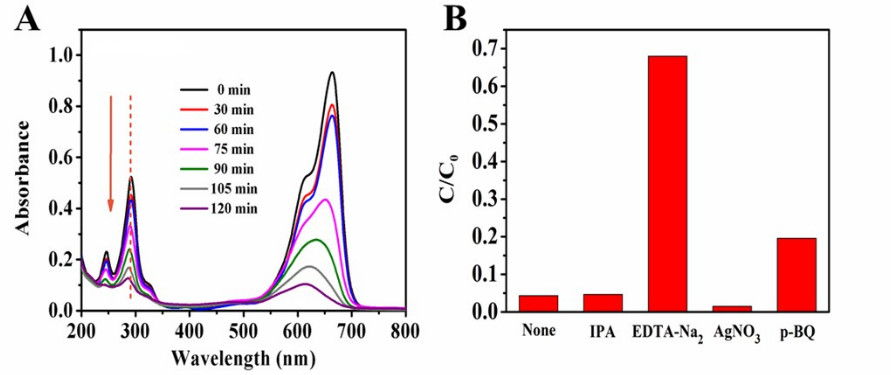


Fig. S10. Absorbance change of MB (A) with the variation of irradiation time and (B) by the additives.

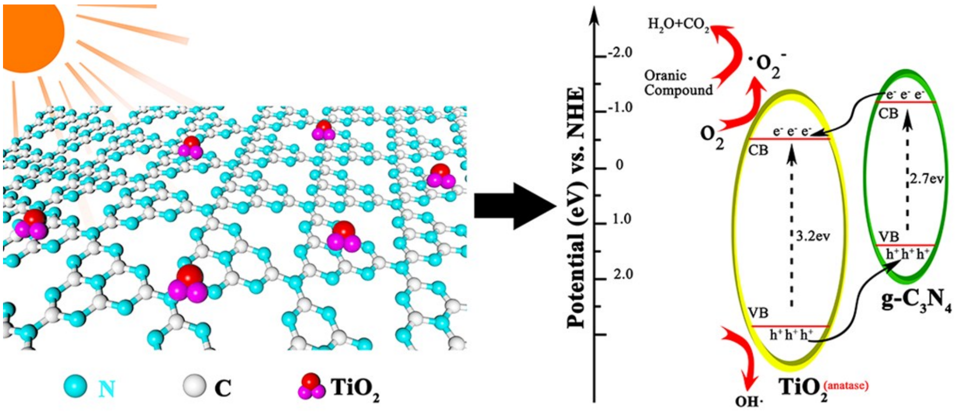


Fig. S11 Schematic diagram of photocatalytic mechanism of the TiO_2/g-C_3N_4 composite

4. Supporting Tables

Tables S1 Comparison of experimental time on preparing the TiO_2/g-C_3N_4 composites.

Ref.	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	Our work
time /h	32.5	61	57.5	48	41.5	34	19	29	88.5	38	66.5	10

Table S2 Comparison of sensing performance of different fluorescent probes for HClO.

Fluorescence probe	LOD (μM)	LR (μM)	Ref.
DFPT	0.7	0.7-70	[12]
GO-C_6NH_2	3.5	3.5-130	[13]
HA [a]	0.7	0.7-32	[14]
RBH1-UCNPs	0.32	0.32-120	[15]
CDs-RhB	4	4-140	[16]
Ti–CNNPs	0.203	0.203-70	This work

[a] 2-(2-(5-(4-Aminophenoxy)carbonyl)amino)-N-[2-(2-acetoxyethoxy)ethyl]-3-amino-1,8-naphthalimide.

Table S3 Determination of HClO in two tap water samples.

Sample	Found (μM)	RSD (%, n = 6)	Added (μM)	Total found (μM)	RSD (%, n = 6)	Recovery (%)
Sam. 1	0.73	4.2	1.0	1.64	3.3	91.03
			2.0	2.66	2.9	96.67
			3.0	3.69	2.0	98.74
Sam. 2	2.07	3.2	2.0	3.95	3.2	93.91
			4.0	6.09	4.2	100.60
			6.0	8.04	2.7	99.55

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