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Application of single-atom Ti-doped g-C₃N₄ in photocatalytic H₂O₂ production†

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Synthesizing highly effective photocatalysts for hydrogen peroxide (H₂O₂) generation is still a challenge. In this work, the doping of graphite carbon nitride nanosheets with single-atom titanium, using TiCl₃ as a precursor, to form single Ti atom-doped graphitic carbon nitride (Ti-SAC/g-C₃N₄) photocatalysts can efficiently address this challenge. The photocatalytic activity is enhanced by increasing the concentration of titanium to 0.09%, and subsequently decreases with further increases in the concentration of titanium, thus confirming that the concentration of titanium atoms can modulate the performance of the single-atom catalysts. Furthermore, an in-depth investigation indicates that the bottom of the conduction band (CB) and the maximum of the valence band (VB) can be controlled by varying the concentration of titanium atoms. A high bottom of the CB is beneficial to increase the photocatalytic efficiency. Under acidic conditions and utilizing sacrificial agents, the H₂O₂ production rate of Ti-C₃N₄-100 can reach 356.45 μmol L⁻¹ h⁻¹ and is 2.44 and 2.13 times higher than that of BCN and g-C₃N₄, respectively. The electron spin resonance (ESR) spectra suggest that the generation of superoxide radicals is crucial in the photocatalytic process. This work provides a distinctive strategy to realize single titanium atom doping and offers new insights into structure–property relationships.

1. Introduction

Hydrogen peroxide (H₂O₂), a multifunctional oxidant, has been widely used in organic synthesis, bleaching, disinfection, environmental treatment and fuel cells due to its low cost and excellent eco-friendly properties.^{1–6} In general, there are two methodologies that have been employed to prepare H₂O₂. One is the anthraquinone oxidation (AO) method, which can manufacture H₂O₂ via Pd-catalysed cyclic hydrogenation and oxidation of alkyl-anthraquinones in organic solvents.⁷ However, the process is energy intensive and causes environmental pollution, thus seriously limiting its adoption.^{8,9} The second method uses photocatalytic techniques, which can sustainably convert solar energy to chemical energy without excess energy consumption and is an excellent alternative to the AO method.¹⁰ The key to success with photocatalytic H₂O₂ synthesis is to obtain highly efficient photocatalysts. Of these photocatalysts, graphitic carbon nitride (g-C₃N₄) has attracted extensive attention.¹¹ Although g-C₃N₄ catalysts can constantly produce H₂O₂ by taking advantage of visible light, the low production

rate and amounts obtained, due to its low carrier separation efficiency, immensely restrict the large-scale application of g-C₃N₄.^{12,13}

Recently, single atom-doped C₃N₄ photocatalysts have been investigated for enhanced photocatalytic performance.¹⁴ For instance, Zhang *et al.* synthesized single-atom Pt/C₃N₄ and found, using synchronous illumination X-ray photoelectron spectroscopy, that the Pt–N bond was cleaved to form Pt⁰ and a C=N bond under light irradiation.¹⁵ Xiao *et al.* embedded single atom Cu into a C₃N₄ matrix and the Cu–N_x species were found to immensely improve in-plane and interlayer separation transfer of charge carriers, resulting in an increase of the photocatalytic efficiency.¹⁶ Wang *et al.* prepared monatomic Ag dispersed mesoporous g-C₃N₄ to improve bisphenol A (BPA) degradation efficiency by utilizing the synergistic effect between silver and mesoporous g-C₃N₄.¹⁷ Titanium-doped photocatalysts, such as titanium dioxide^{18,19} and titanium carbide,^{20,21} are widely applied in photocatalysis due to their wide bandgaps. Indeed, the 3d orbitals of titanium are very helpful for reduction reactions due to their high energy, which is beneficial for the production of H₂O₂. Meanwhile, the photocatalytic activity of g-C₃N₄ for H₂O₂ preparation is also low owing to the high recombination rate and low electrical conductivity. Therefore, doping single titanium atoms into g-C₃N₄ is significant, to not only enhance the position of the bottom of the conduction band to reduce the recombination rate, but also to improve the electrical conductivity. However,

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the synthesis of single titanium atom-doped C_3N_4 is rarely reported because the titanium precursor easily forms TiO_2 during the reaction process. Therefore, it is highly desirable to synthesize a single titanium atom-doped C_3N_4 photocatalyst and investigate the relationship between the photocatalytic performance and the concentration of titanium atoms.

Herein, single titanium atom-doped graphitic carbon nitride catalysts have been synthesized by assembling melamine, cyanuric acid and $TiCl_3$. Single titanium atoms can be successfully embedded in the graphitic C_3N_4 matrix using $TiCl_3$ as the precursor due to its excellent chemical stability in solution. The photocatalytic activity exhibits a volcanic distribution in relation to the titanium concentration. The $Ti-C_3N_4-100$ sample, with 0.09% titanium content, exhibits the best catalytic performance. The H_2O_2 production rate of $Ti-C_3N_4-100$ can reach $356.45 \mu\text{mol L}^{-1} \text{h}^{-1}$ and is 2.44 and 2.13 times higher than that of BCN and $g-C_3N_4$, respectively. The mechanistic investigation indicates that the bottom of the conduction band (CB) and the maximum of the valence band (VB) can be controlled by altering the concentration of titanium atoms, and that $Ti-C_3N_4-100$ possesses the highest bottom of the CB and maximum of the VB. The more negative the bottom of the CB is, the better the photocatalytic efficiency is. This result demonstrates that the superoxide radical can be easily generated when the bottom of the CB is negative and the generation of the superoxide radical is crucial in the photocatalytic process. This work provides a distinctive strategy to realize single atom doping of titanium and offers new insight into structure-property relationships.

2. Experimental

2.1. Chemicals

All chemicals were obtained from commercial suppliers and used without further purification. Melamine (MA, 99%), cyanuric acid (CA, 98%), 1,4-benzoquinone (BQ, 99%), and titanium chloride solution ($TiCl_3$, 15–20%) were purchased from Aladdin Biochemical Technology co, Ltd (Shanghai, China). Isopropyl alcohol (IPA, 99.7%) was purchased from TianTai co, Ltd (Tianjin, China), potassium hydrogen phthalate and potassium iodide were purchased from BeiHua co, Ltd (Beijing, China).

2.2. Synthesis of photocatalysts

2.2.1. Synthesis of bulk carbon nitride (BCN). The BCN sample was synthesized by thermal polymerization of melamine. Typically, 1 g of melamine was heated in a quartz boat with a ramp rate of $5 \text{ }^\circ\text{C min}^{-1}$ in an air atmosphere at $600 \text{ }^\circ\text{C}$ for 2 h.

2.2.2. Synthesis of graphite carbon nitride ($g-C_3N_4$). Melamine (20.40 g) and cyanuric acid (20.00 g) at a ratio of 1:1 were mixed and dispersed in deionized water (400 mL) and stirred for 12 hours at $70 \text{ }^\circ\text{C}$ in a water bath. The obtained mixture was heated in an oven at $70 \text{ }^\circ\text{C}$ for 36 hours to prepare the precursors. The obtained precursors were thoroughly ground

and placed in crucibles, wrapped with tin foil, and placed in a muffle furnace. Subsequently, the above-mentioned precursors were heated to $600 \text{ }^\circ\text{C}$ at a rate of $5 \text{ }^\circ\text{C min}^{-1}$ for 2 hours to obtain a light yellow powder.

2.2.3. Synthesis of single atom Ti dispersed carbon nitride ($Ti-C_3N_4$). The preparation of the supramolecular precursors is consistent with the above section 2.0 g of the precursor was adequately dispersed in deionized water by stirring for 30 minutes. Then, 50 μL , 100 μL , and 250 μL of $TiCl_3$ solution were mixed with a solution of the precursor and stirred for 12 hours. Subsequently, the obtained mixtures were centrifuged, washed twice with deionized water, and dried. Finally, the obtained white powders were transferred into a crucible and heated at $600 \text{ }^\circ\text{C}$ in a muffle furnace for 2 hours at a rate of $5 \text{ }^\circ\text{C min}^{-1}$. The obtained samples were named as $Ti-C_3N_4-50$, $Ti-C_3N_4-100$, and $Ti-C_3N_4-250$, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were collected using a RigakuD/Max 2550 X-ray diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$). The surface morphologies were characterized using scanning electron microscopy (SEM) conducted with a JSM-7800F field emission scanning electron microscope at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) was conducted on a FEI Tecnai G2S-Twin with a field emission gun operating at 200 kV. An FEI-Titan Cubed Themis G2 300 with a spherical aberration corrector working at 300 kV was used to record high angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive spectroscopy (EDS) images. Fourier-transform infrared (FTIR) spectra were recorded in the range of $400\text{--}4000 \text{ cm}^{-1}$ using an IFS-66V/S FT-IR spectrometer with KBr pellets. Nitrogen adsorption/desorption measurements were carried out on Micromeritics 2020 analyzer at 77.35 K after the samples were degassed at $350 \text{ }^\circ\text{C}$ under vacuum. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALab 250 spectrometer with a monochromatic X-ray source (Al $K\alpha$ $h\nu = 1486.6 \text{ eV}$). The UV-vis diffuse reflectance spectra were recorded on a PerkinElmer Lambda 950. The steady-state emission spectra were obtained on a HORIBA FLUOROMAX-4 spectrophotometer. The time-resolved photoluminescence (PL) decay analysis was carried out on an Edinburgh Instrument FLS920 spectrophotometer. The electron paramagnetic resonance (EPR) spectra were obtained using a Bruker 300 EPR spectrometer under room temperature. The Ti content of the samples was determined using inductively coupled plasma (ICP) spectroscopy on a PerkinElmer Optima 3300 DV ICP instrument.

2.4. Photocatalytic experiments

2.4.1. Photocatalytic production of H_2O_2 . Typically, the as-synthesized catalyst (40 mg) was added to 50 mL of a mixed solution of water and isopropyl alcohol ($V_w:V_i = 9:1$) in a quartz glass reactor fitted with a temperature-controlled circulating water device ($25 \pm 1 \text{ }^\circ\text{C}$). Photocatalytic H_2O_2 production was performed under visible-light irradiation ($\lambda > 420 \text{ nm}$) with a 300 W Xenon lamp under air-equilibrated conditions for



120 min. Before the photoreaction, the pH of the above-mentioned mixture was adjusted to pH 3 with H_2SO_4 . Subsequently, the system was ultrasonically mixed for 30 minutes and stirred for one hour in the dark.

The concentration of H_2O_2 was determined with a traditional iodometric method.^{22,23}

This method involves mixing 0.5 mL each of 0.4 M potassium iodide solution and 0.1 M potassium hydrogen phthalate solution with 1 mL of the sample to be tested before waiting for them to fully react for 20 minutes. The mixed solutions were examined with UV visible spectroscopy.

2.4.2. Durability of catalysts test. The stability of the photocatalysts was examined using recycling tests (four runs). After each run, the photocatalysts were collected by centrifugation and washed three times, and finally dried at a temperature of 60 °C in an oven.

2.5. Photoelectric performance test

The as-synthesized samples were examined for their photoelectrochemical performance using a CHI-660e electrochemical system (China). A standard three-electrode model was adopted, in which the synthesized sample/FTO, standard silver electrode (Ag/AgCl), and Pt line served as the working electrode, reference electrode, and counter electrode, respectively. Na_2SO_4 (0.5 mM) was used as the electrolyte. For the fabrication of the working electrodes, 5 mg of the catalyst sample was dispersed into 500 μL of ethanol. This was followed by addition of 10 μL of Nafion solution. The resulting solution was applied uniformly to a 1.0 cm \times 1.0 cm ITO glass electrode and then dried for 6 h at 70 °C. The electrochemical impedance spectroscopy (EIS) spectra and transient photocurrent (I - T) of the prepared catalysts were measured at a stable open circuit potential.

3. Results and discussion

3.1. Morphology and structure

The Ti-SAC/ $g\text{-C}_3\text{N}_4$ photocatalysts were prepared by pyrolyzing the supramolecular precursors with the titanium atoms, which can effectively avoid the hydrolyzation of TiCl_3 and introduce titanium single atoms into the matrix of $g\text{-C}_3\text{N}_4$ (Fig. 1(a)). The morphologies and distribution of the elements of the as-synthesized samples were determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM and TEM images of $\text{Ti-C}_3\text{N}_4$ -100 reveal a curly laminar structure with a number of mesopores, as compared with BCN and $g\text{-C}_3\text{N}_4$ and shown in Fig. 1(b), (c), and Fig. S1 (ESI[†]), respectively. These pores can provide sufficient surface active sites to enhance the photocatalytic efficiency. Individual Ti atoms can be observed as bright spots in the high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, as seen in Fig. 1(d), suggesting that a quantity of single Ti atoms have been embedded in the $g\text{-C}_3\text{N}_4$ matrix.^{24–27} The concentration of Ti of $\text{Ti-C}_3\text{N}_4$ -100 is 0.09%, as determined using inductively coupled plasma (ICP) analysis, as seen in Table S1 (ESI[†]). The elemental mapping of $\text{Ti-C}_3\text{N}_4$ -100

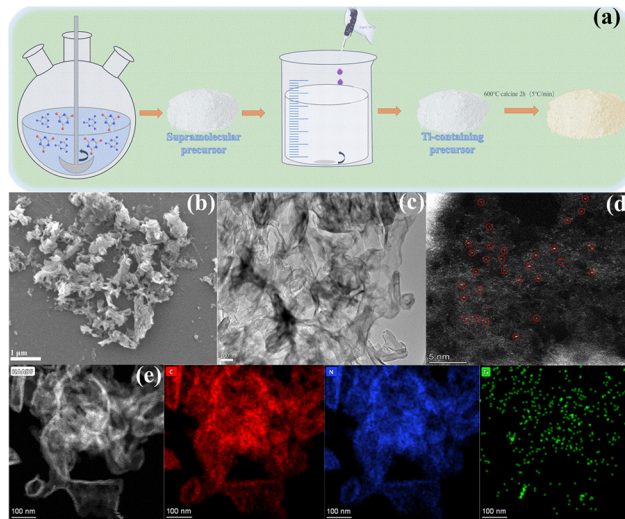


Fig. 1 (a) Schematic illustration of the preparation of $\text{Ti-C}_3\text{N}_4$ -100. (b) The SEM, (c) TEM, and (d) HAADF-STEM images of $\text{Ti-C}_3\text{N}_4$ -100. The (e) HAADF-STEM elemental mapping images of $\text{Ti-C}_3\text{N}_4$ -100.

further illustrates that C, N, Ti atoms are homogeneously distributed in the $g\text{-C}_3\text{N}_4$ nanosheets (Fig. 1(e)), consistent with the result of the HAADF-STEM.

The X-ray diffraction (XRD) patterns of BCN, $g\text{-C}_3\text{N}_4$ and the Ti-SAC/ $g\text{-C}_3\text{N}_4$ with different Ti contents are shown in Fig. 2(a). All the patterns demonstrate two characteristic peaks at 13.1° and 27.1°, respectively, which can be attributed to the typical diffraction peaks of $g\text{-C}_3\text{N}_4$ (PDF#50-1250). The first one is related to the in-plane ordering of repetitive heptazine units, corresponding to (100).²⁸ The second one is associated with the interlayer stacking of conjugated aromatic ring lamellar stacking of the graphite phase, ascribed to (200).²⁹ In contrast to BCN, the (002) peak of the $g\text{-C}_3\text{N}_4$ shows an obvious

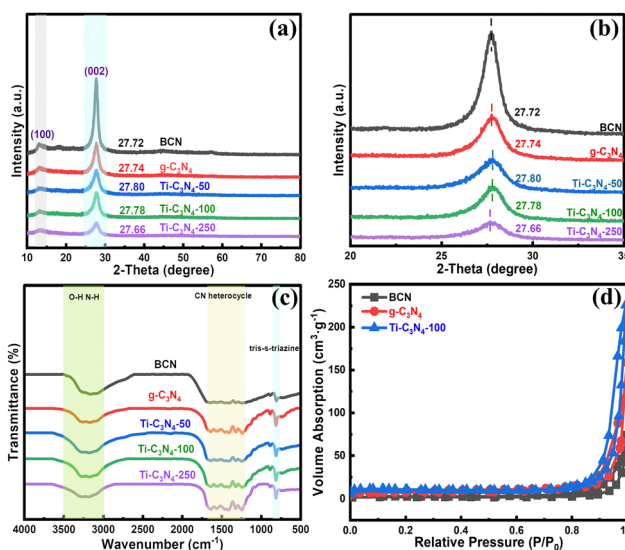


Fig. 2 (a) and (b) XRD patterns and (c) FTIR spectra of each sample. (d) The N_2 adsorption–desorption isotherms of BCN, $g\text{-C}_3\text{N}_4$ and $\text{Ti-C}_3\text{N}_4$ -100.



hypochromic shift owing to the increase of the interlayer distance, as shown in Fig. 2(b).¹⁶ The Ti-SAC/g-C₃N₄ samples exhibit different experimental results. The (002) peaks of Ti-C₃N₄-50 and Ti-C₃N₄-100 present slight bathochromic shifts in contrast to g-C₃N₄, which can be attributed to the shrinkage of the carbon nitride lattice due to Ti doping. However, the (002) peak of Ti-C₃N₄-250 presents a slight hypsochromic shift relative to g-C₃N₄, as the concentration of titanium is further increased. This indicates that further doping can give rise to the expansion of the lattice. No pure TiO₂ crystal phases can be detected for the Ti-SAC/g-C₃N₄ photocatalysts, implying that the titanium atoms have been embedded in the C₃N₄ matrix, consistent with the HAADF-STEM results.

To investigate the surface groups, the Fourier-transform infrared (FTIR) spectra were obtained (Fig. 2(c)). The absorption bands of the Ti-SAC/g-C₃N₄ photocatalysts are similar to that of pure bulk g-C₃N₄, according to previous reports, indicating that the introduction of titanium atoms cannot change the surface composition and structure of g-C₃N₄. The vibration bands at 1200–1700 cm⁻¹ should be attributed to the aromatic C–N stretching mode of the heterocycles.³⁰ The vibration peak centered at 806 cm⁻¹ corresponds to the respiratory mode of tri-s-triazine in C₃N₄.³¹ The broad absorption band in the range 3000–3400 cm⁻¹ can be ascribed to the typical N–H and O–H vibrations of uncondensed amino groups and adsorbed water molecules.³² respectively.

The nitrogen adsorption-desorption isotherm of the calcined BCN, g-C₃N₄ and Ti-C₃N₄-100 exhibit a type IV isotherm with an H₃ hysteresis loop, confirming the existence of mesopores, as shown in Fig. 2(d).³³ The Brunauer-Emmett-Teller (BET) surface area of Ti-C₃N₄-100 is calculated to be 32.98 m² g⁻¹, which is larger than that of BCN (4.73 m² g⁻¹) and g-C₃N₄ (24.98 m² g⁻¹), as seen in Table S2 (ESI†). The pore volume of Ti-C₃N₄-100 obtained from the N₂ adsorption volumes at the specific point (*P*/*P*₀ = 0.99) is 0.35 cm³ g⁻¹, higher than that of BCN (0.11 cm³ g⁻¹) and g-C₃N₄ (0.17 cm³ g⁻¹), as shown in Table S2 and Fig. S2 (ESI†). This observation can be ascribed to the introduction of titanium, which can lead to an increase in the number of structural defects and active edges in the melon units and further results in an increase of the surface area and pore volume. This result suggests that single titanium atoms can facilitate the formation of a mesoporous structure during polycondensation.³⁴

To further confirm the elemental distribution and chemical states of Ti-C₃N₄-100, X-ray photoelectron (XPS) characterization was performed. Fig. S3 (ESI†) exhibits the XPS spectra of C, N and Ti for BCN, g-C₃N₄ and Ti-C₃N₄-100. The C 1s peaks of BCN and g-C₃N₄ are doublets with binding energies of 284.8 eV, 288.3 eV and 284.8 eV, 288.3 eV, corresponding to the surface contaminated carbon (C–C/C=C) and the sp² hybrid carbon of the triazine ring (N–C=N)^{35,36} (Fig. S3b, ESI†). However, the C 1s peaks of Ti-C₃N₄-100 are triplets with binding energies of 284.8 eV, 288.2 eV and 286.5 eV. The first two peaks can be attributed to the surface contaminated carbon (C–C/C=C) and the sp² hybrid carbon of the triazine ring (N–C=N), consistent with BCN and g-C₃N₄. The third peak confirms the existence of

C–O bonds in the Ti-C₃N₄-100 sample.³⁷ Meanwhile, the N 1s peaks of BCN and g-C₃N₄ are triplets with binding energies of 398.7 eV, 399.4 eV, 401.3 eV and 398.4 eV, 399.2 eV, 401.2 eV (Fig. S3c, ESI†), which are attributed to the sp² nitrogen in the triazine rings (C–N=C), tertiary nitrogen (N–(C)₃), and C–NH_x.^{38,39} The introduction of titanium shifts the N 1s peaks to 398.4 eV, 399.6 eV, and 400.9 eV, which demonstrates that the binding energy of 399.6 eV in Ti-C₃N₄-100 is obviously higher than that of BCN and g-C₃N₄. The shift in the binding energies of the N elements implies that the titanium atoms in Ti-C₃N₄-100 can interact with the N atoms, confirming the formation of N–Ti bonds. The XPS spectrum of the Ti 2p peaks are not obviously visible due to low concentration, as shown by the ICP results (Fig. S3d, ESI†).

3.2. Photocatalytic performance

The photocatalytic performance strongly depends on the Ti concentration in the Ti-SAC/g-C₃N₄ sample used for H₂O₂ production (Fig. 3(a)). It is obvious that the photocatalytic activity of the Ti-SAC/g-C₃N₄ photocatalysts is higher than that of BCN and g-C₃N₄. The photocatalytic activity cannot be promoted until the concentration of the Ti atom reaches 0.09%. Ti-C₃N₄-100 shows the best photocatalytic performance and the H₂O₂ production rate can reach 356.45 μmol L⁻¹ h⁻¹, being 2.24 and 2.13 times higher than that of BCN and g-C₃N₄, respectively. The photocatalytic efficiency decrease at higher concentrations of Ti, which can be attributed to the decrease of the conduction band edge, as shown in our previous report.⁴⁰ The above-mentioned results suggest that the single atom Ti doping concentration can control the photocatalytic activity of the Ti-SAC/g-C₃N₄ material. Furthermore, recyclability experiments were performed with Ti-C₃N₄-100, whereby the catalyst was recovered using centrifugal separation and then reused in a four cycle run of further experiments (Fig. 3(b)). No significant changes in the crystal structure and chemical composition can be observed after four successive runs, confirming the excellent stability of the Ti-SAC/g-C₃N₄ photocatalysts (Fig. S4, ESI†). Furthermore, the H₂O₂ production rate of Ti-C₃N₄-100 is higher than that of other C₃N₄-based photocatalysts (Table 1), indicating that the Ti-SAC/C₃N₄ photocatalysts are promising photocatalysts for H₂O₂ production.

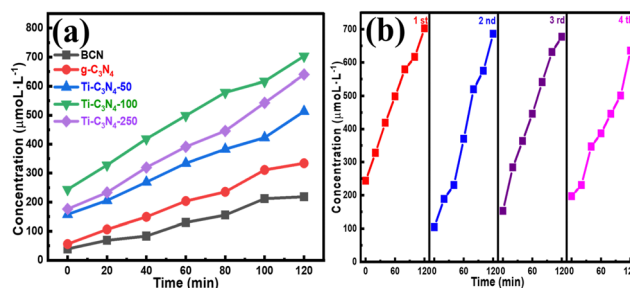


Fig. 3 (a) The photocatalytic hydrogen peroxide production performance of each sample. (b) Recycling performance of Ti-C₃N₄-100 photocatalyst.



Table 1 Comparison of H₂O₂ production with different photocatalysts

System	Dosage (g L ⁻¹)	Production (μM g ⁻¹ h ⁻¹)	Ref.
DCN	0.83	96.80	23
OCN	1.00	1200.0	41
g-C ₃ N ₄	4.00	125.0	7
CoP/CN	1.00	3200.0	42
CdS-GO	1.67	2560.0	43
ZnO/WO ₃	1.00	6788.00	44
Ti-C ₃ N ₄ -100	0.4	8911.25	

3.3. Photocatalytic mechanism

To further investigate the effects of single Ti atom-doping, the PL spectra, EIS spectra were obtained and relative photoelectrochemical experiments were conducted. Fig. 4(a) shows that doping with titanium atoms can effectively reduce the PL intensity, indicating that the doping of single titanium atoms can promote electron-hole pair separation and efficient charge transfer.⁴⁵ Subsequently, the time-resolved PL spectra were obtained to further verify the above-mentioned PL results (Fig. 4(b)). The average lifetime of Ti-C₃N₄-100 is significantly shorter than that of the BCN and g-C₃N₄, as shown in Table S3 (ESI[†]). This result suggests that the reduction of the excited state can take place by means of a non-radiative pathway, possibly through electron charge transfer to some advantageous defect states, thus further increasing charge transfer and separation.⁴⁶ Fig. 4(c) shows that the photo-generated current density of Ti-C₃N₄-100 is obviously higher than that of BCN and g-C₃N₄, confirming the high efficiency of charge separation and transfer.⁴⁷ In addition, the EIS spectra show that the diameter of the semicircles of Ti-C₃N₄-100 is the smallest of all the photocatalysts (Fig. 4(d)). This demonstrates that single Ti atom-doping is beneficial for photo-generated electron-hole

pair separation and charge transfer,⁴⁸ consistent with the PL and photoelectrochemical results.

To analyse in depth the mechanism of photocatalytic enhancement of Ti-SAC/g-C₃N₄, the absorption spectra of all samples were evaluated using ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS). Fig. 5(a) shows that the Ti-SAC/g-C₃N₄ photocatalysts have stronger absorption intensities in the ultraviolet and visible light region than BCN and g-C₃N₄. The absorption edges of the Ti-SAC/g-C₃N₄ photocatalysts are bathochromically shifted in contrast to those of BCN and g-C₃N₄, indicating that the introduction of single titanium atoms can effectively modulate the structure of the energy band.⁴⁰ In addition, the optical band gaps can be calculated in accordance with the Kubelka-Munk equation (Fig. 5(a) inset). The result indicates that the energy bandgaps (E_g) of the Ti-SAC/g-C₃N₄ photocatalysts are smaller than those of BCN (2.74 eV) and g-C₃N₄ (2.80 eV). E_g gradually decreases as the amount of TiCl₃ is increased to 100 μL, and slightly increases as the amount of TiCl₃ is further increased to 250 μL. The conduction band (CB) energies are determined using Mott-Schottky curves (MS) to investigate the effect that titanium single atoms have on the C₃N₄ matrix (Fig. 5(b)). Subsequently, the valence band (VB) potential of all photocatalysts were determined in agreement with the empirical formula (VB = CB + E_g) (Fig. 5(c)). The CB

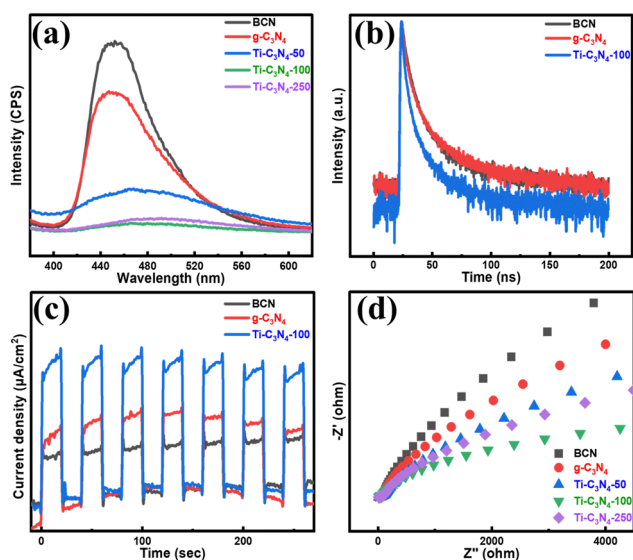


Fig. 4 (a) PL spectra of BCN, g-C₃N₄ and Ti-C₃N₄-100, (b) time-resolved PL spectra of BCN, g-C₃N₄ and Ti-C₃N₄-100, (c) photocurrent response, and (d) EIS spectra of BCN, g-C₃N₄ and Ti-C₃N₄-100.

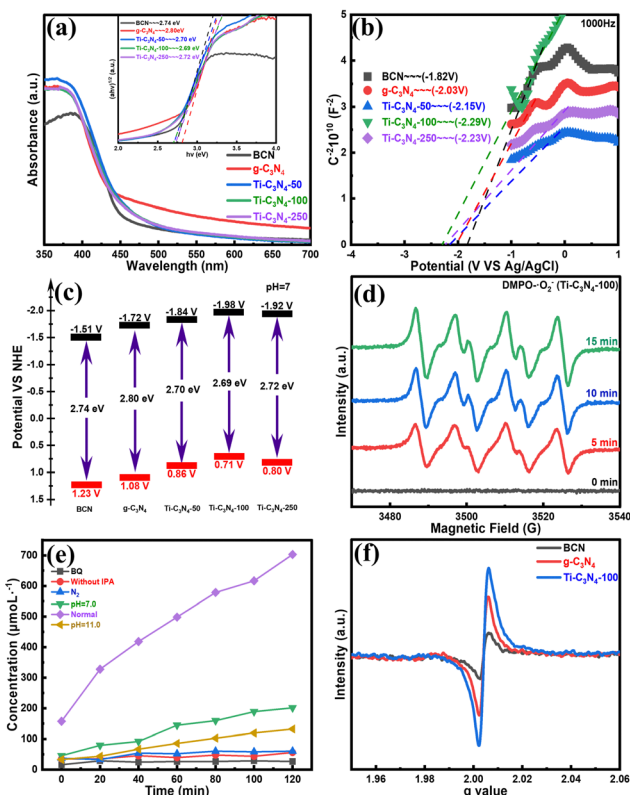


Fig. 5 (a) UV-vis diffuse reflectance spectra and band gap (higher-middle inset), (b) Mott-Schottky plots and (c) electronic band structures of all samples. (d) ESR spectrum of DMPO- O_2^- in the presence of Ti-C₃N₄-100, (e) photocatalytic performance of Ti-C₃N₄-100 under different conditions, and (f) EPR spectra of BCN, g-C₃N₄ and Ti-C₃N₄-100.



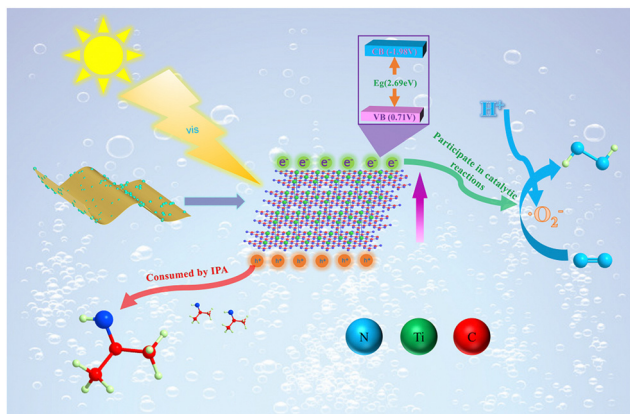


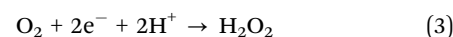
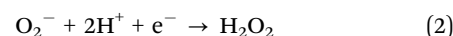
Fig. 6 Proposed photocatalytic mechanism for the Ti-C₃N₄-100 photocatalyst.

potentials of CB the Ti-SAC/g-C₃N₄ photocatalysts reveal a volcanic tendency, being more negative than that of g-C₃N₄. The CB potential is correlated with the production of photo-generated electrons, combining with O₂ to generate superoxide radicals. The superoxide radicals have an effect on the H₂O₂ production rate. The more negative the CB potential is, the higher the H₂O₂ production rate is. This result is observed by analyzing the concentration of single titanium atoms and the photocatalytic performance. Furthermore, the photogenerated holes can be fully consumed due to the presence of isopropyl alcohol, which facilitates the smooth progress of the 2-electron reaction of oxygen. Thus, it can be seen that varying the concentration of single titanium atoms can modulate the energy band structure and the light harvesting ability of the Ti-SAC/g-C₃N₄ photocatalysts.

Subsequently, a series of experiments were performed to further investigate the process of photocatalytic H₂O₂ production, confirming the primary photocatalytic active species. The ESR spectra exhibit the existence of superoxide radicals when 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) is employed as the scavenging agent (Fig. 5(d)). No DMPO·O₂⁻ peaks could be obtained in the dark. However, the significant signals of DMPO·O₂⁻ can be observed with the presence of Ti-C₃N₄-100 under visible light illumination. Next, radical capture experiments show that BQ obviously decrease the activity of Ti-C₃N₄-100, determining the predominant role of the superoxide radicals. Meanwhile, the decomposition of H₂O₂ can be inhibited owing to the presence of IPA. In addition, no H₂O₂ can be produced in an N₂ atmosphere, indicating that the presence of O₂ is required. The above-mentioned results expressly suggest that the formation of superoxide radicals is vital for the production of H₂O₂ (Fig. 5(e)), which is consistent with previous reports. Furthermore, the adsorption of O₂ is another important factor for the production of H₂O₂ due to the low concentration of O₂ in water. The electron paramagnetic resonance (EPR) spectra show that Ti-C₃N₄-100 exhibits a stronger EPR response than BCN and g-C₃N₄ (Fig. 5(f)), which leads to the adsorption of more O₂ molecules by Ti-C₃N₄-100 than by the BCN and g-C₃N₄ reaction systems. These results demonstrate

that doping single titanium atoms is not only beneficial to the delocalization of heptazine π-conjugated rings, resulting in a high mobility of charge transfer and separation, but also improves the adsorption of O₂ molecules.⁴⁹ The synergy of the two sides together promotes the photocatalytic effect of Ti-C₃N₄-100.

A possible photocatalytic mechanism for the Ti-SAC/g-C₃N₄ photocatalysts can be proposed on the basis of the above results (Fig. 6). Firstly, the introduction of single titanium atoms further reduces the band gap of C₃N₄, increasing the absorption of visible light. Secondly, the doping of the appropriate quantity of single titanium atoms can not only lead to a more negative CB, improving the reducing ability of the photocatalysts, but can also increase the adsorption of O₂ molecules in solution by Ti-SAC/g-C₃N₄. Thirdly, the photoinduced electrons are helpful for the formation of superoxide radicals, promoting the production of H₂O₂. Meanwhile, the photoinduced holes can be eliminated by IPA, decreasing the decomposition of H₂O₂. The photocatalytic process of H₂O₂ production can be summarized as follows:⁵⁰



4. Conclusions

Ti-SAC/g-C₃N₄ photocatalysts have been prepared by using TiCl₃ as the titanium source, owing to its excellent chemical stability in solution, to embed single titanium atoms into a C₃N₄ matrix. The photocatalytic activity experiments demonstrate that the Ti-C₃N₄-100 sample has the best catalytic performance. The H₂O₂ production rate can reach 356.45 μmol L⁻¹ h⁻¹, which is 2.44 and 2.13 times higher than BCN and g-C₃N₄, respectively. Further investigations demonstrate that the bottom of the conduction band (CB) and the maximum of the valence band (VB) can be controlled by varying the concentration of titanium atoms. The Ti-C₃N₄-100 sample has a concentration of 0.09% titanium and possesses the highest bottom of the CB and the highest maximum of the VB. The more negative the bottom of the CB is, the better the photocatalytic efficiency is. This study demonstrates that superoxide radicals can be easily generated when the bottom of the CB is negative, and the generation of superoxide radicals is crucial to the photocatalytic process. In addition, the doping of single titanium atoms can also form vacancies to enhance the adsorption of the O₂ molecules. These results provide a distinctive strategy to realize single atom-doping of titanium and offers new insights into the structure–property relationship.

Conflicts of interest

There are no conflicts to declare



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