Amorphous TiO₂ Doped with Carbon for Visible Light Photodegradation of Rhodamine B and 4-Chlorophenol

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ABSTRACT

Visible light photocatalytic activity of amorphous TiO₂ doped with carbon is prepared by a facile sol-gel route for the first time. The most active sample with mesostructure of amorphous phase, high surface area (273 m²·g⁻¹) and large pore volume (0.33 cm³·g⁻¹) is identified by X-ray diffractometer, Raman spectrometer, transmission electron microscope and N₂ adsorption-desorption isotherms. In addition, the most active sample is characterized by Fourier transform-infrared spectrometer, X-ray photoelectron spectrometer, UV-Vis diffuse reflectance spectrometer and luminescence spectrometer. The results show that the most active sample with oxygenic groups has a narrower bandgap and lower recombination of electron-hole, due to the carbon doping and phase of amorphous. Effective photodegradation capability and stability of rhodamine B and colorless 4-chlorophenol are verified by photocatalytic tests under visible light irradiation. A possible mechanism of amorphous TiO₂ doped with carbon for visible light photocatalysis is proposed. The findings of this paper will provide new insights to design visible light-induced photocatalyst based on amorphous TiO₂ for organic removal.

Keywords: Amorphous TiO₂; Carbon-doping; Visible light photocatalysis; Organic removal

1. Induction

Titanium dioxide (TiO_2) has been extensively investigated as a photocatalyst due to its high stability, strong redox ability, and low cost [1, 2]. However, the large band gap of TiO_2 (3.2 eV for anatase [3] and 3.0 eV for rutile [4]) restricts its photocatalytic activity to the **ultraviolet** range (about 5% of the total solar energy). Only less than 2.2% of the photoconversion efficiency **can** be obtained by the TiO_2 under AM 1.5 global solar irradiation [5]. Therefore, studies to extend the photocatalytic activity of TiO_2 to **the** visible light range have become a hot issue in recent years.

Two promising strategies have been proposed to enhance the visible light harvesting capability of TiO_2 : **(1) Coupling** with small band gap metallic compounds (CdSe [6], CdS [7]) or noble metals (Au [8, 9], Pt [10], Ag [11]) to form donor states below the conduction band of TiO_2 [12]; **(2) Adjusting** the valence band by doping nonmetal elements (C [13], N [14], B [15]) into TiO_2 to form acceptor states above the valence band. Among these nonmetal elements, carbon has been proved to be an excellent candidate for extending the absorption spectrum of TiO_2 to the visible light region (about 45% of the total solar energy) [16-18].

On the other hand, more attention has been recently attracted by defective or disordered TiO_2 for photocatalysis [19] and photoelectrochemical water splitting [20], owing to its narrower bandgap and enhanced absorption of visible light. Chen et al. [19] prepared black TiO_2 with ~ 1.0 eV bandgap by introducing disorder in surface layer of TiO_2 through high-pressure hydrogenation. Naldoni et al. [21] reported the synthesis of black TiO_2 nanoparticles with defective core/disordered shell morphology, which exhibited the bandgap of 1.85 eV. It is well matched with visible light spectrum. Zuo and Hoang et al. [20, 22] demonstrated the defect on

TiO₂ was the key factor for the reduction of bandgap. Inspired by these studies, it seems possible to fabricate the visible light-driven TiO₂ by introducing surface disorder and point defect.

Amorphous TiO₂ contains more disorders and defects than that in the crystalline phase [23, 24]. Based on the above-mentioned discussion, the amorphous TiO₂ may be promising for visible-light photocatalysis. However, some researches [25, 26] demonstrated that the amorphous TiO₂ only had a rather weak ultraviolet photocatalytic activity, because the defects on the surface and in the bulk could act as electron-hole traps. On the other hand, through H₂O₂ sensitization, Zou et al.[27] observed higher photodegradation capability of amorphous TiO₂ sol under visible light than that of anatase TiO₂ and P25, due to the suppression of the recombinations of electron-hole pairs. It was also reported recently that the coupling metal ions and metal oxides with amorphous TiO₂ could significantly strengthen the photodecomposition capability of dyes [28, 29]. However, there is no report on degradation of colorless organic pollutants by amorphous TiO₂ composites under visible light irradiation.

Herein, we prepare mesoporous carbon-doped amorphous TiO₂ with high BET surface area, large pore volume and reduced bandgap via a facile sol-gel process. The carbon-doped amorphous TiO₂ exhibits excellent photodecomposition capability of rhodamine B (RhB) and colorless 4-chlorophenol under visible light irradiation. High stability of the photocatalyst is also verified by the cyclic photocatalytic tests. To the best of our knowledge, this is the first time for the investigation of nonmetal-doped amorphous TiO₂. It introduces new insights for the design of visible-light photocatalyst based on amorphous TiO₂ for effective degradation of organic contaminants in water.

2. Experimental methods

2.1. Photocatalyst preparation

In a typical experiment, 1.0 mL deionized water (resistivity $>18 \text{ M}\Omega\cdot\text{cm}$) was mixed with 25.0 mL benzyl alcohol (99.5%, Sinopharm Chemical Reagent) under stirring at room temperature to form a clear solution. Benzyl alcohol was selected as carbon source, due to its high affinity with oxides or hydroxides of titanium. Then 5.0 mL titanium (IV) isopropoxide (97%, Sigma-Aldrich) was slowly added to the clear solution. After 30 min stirring, the clear solution turned to be turbid. Subsequently, 0.5 g sodium borohydride (98%, Sinopharm Chemical Reagent) was gradually dissolved into the suspensions, which was kept stirring for 6 h at room temperature. After reaction, the mixture was isolated by centrifugation and washed thoroughly with deionized water/ethanol. Then, it was dried under vacuum oven at 60°C overnight. Finally, the photocatalyst was obtained by thermal treatment at different temperature under vacuum furnace for 2 h. During the process of thermal treatment, the carbon species could be doped into TiO_2 . According to different treatment temperatures (300, 400, 500 and 600°C), the corresponding samples were labeled as S-300, S-400, S-500 and S-600, respectively. And the carbon content of samples was adjusted by controlling the temperature of thermal treatment. Meanwhile, the commercial P25 (Evonik Deguss) was used as a reference sample to estimate the photo-activity of the prepared samples.

2.2. Photocatalyst characterization

X-ray diffraction (XRD) patterns of the samples with different calcination temperatures were collected by a X-ray diffractometer (Philips, X Pert PRO MPD) operated at 35 kV and 45 mA with Cu K α radiation ($\lambda = 0.15418 \text{ nm}$). Transmission electron microscopy (TEM) analysis was carried out with a FEI Tecnai G² F30 operated at 300 kV. Samples for TEM observation

were suspended in ethanol and then supported on a Cu grid. N₂ adsorption-desorption isotherms were measured at 77 K with a Micromeritics ASAP2020. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. The pore volume and pore size distribution were derived from the adsorption branch of the isotherm through the Barrett-Joyner-Halenda (BJH) model. Fourier transform-infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum One B. The analysis of X-ray photoelectron spectroscopy (XPS) for samples were carried out with a Thermo ESCALAB 250 with Al K α X-ray ($h\nu=1486.6$ eV) radiation operated at 150 W. The energies of the peaks were calibrated by fixing the position of the C 1s peak at 284.6 eV. The UV-Vis diffuse reflectance spectra (DRS) of samples were achieved by a spectrophotometer (Shimadzu, UV2550), using the BaSO₄ as the reflectance sample. Photoluminescence (PL) spectra were measured on a luminescence spectrometer (Jasco, FP-6500) at room temperature under the excitation light at 315 and 515 nm, respectively.

2.3. Photocatalyst activity

Photocatalytic activity of sample was evaluated by measuring the decomposition of the aqueous solution of RhB (95%, Aladdin Reagent) and 4-chlorophenol (99%, Aladdin Reagent). A 300 W xenon lamp (Beijing NBeT) equipped with a 400 nm cut-off filter was used as light source. For the degradation of RhB, 25 mg of each catalyst was suspended in 50 mL of RhB solution ($C_0=5$ mg/L), and the mixture was stirred for 30 min to reach an adsorption equilibrium in the dark before irradiation. The removal rate of RhB was monitored by measuring the changes in the absorption maxima of the solution with a UV/Vis spectrophotometer. The temperature of the reactor was maintained at 25 °C by continuous circulating water. For the degradation of 4-chlorophenol ($C_0=5$ mg/L), similar experimental method was employed, except that 50 mg of the catalyst was added. The removal rate of 4-chlorophenol was monitored by the HPLC system

(Waters Baseline 810) with a Waters 486 tunable UV absorbance detector and a Supelco LC-18-DB column (250 mm×4.6 mm). The eluent consisted of methanol and water (40:60, v/v) and the flow rate was set at 1.0 mL/min.

On the other hand, the photocatalytic activity of the catalyst samples was also evaluated by comparing the apparent reaction rate constants (k). The k could be calculated as:

$k = -(1/t) \cdot \ln(C/C_0)$, where k was the apparent reaction rate constant; C_0 and C were the initial concentration and the reaction concentration of targeted organic substances, respectively.

In the cyclic photocatalytic tests, the used catalyst was recycled by centrifugation. And the stability of the photocatalyst was assessed by the above-mentioned photocatalytic test for three cycles.

2.4. Analysis of hydroxyl radicals

The presence of hydroxyl radicals in photocatalytic reaction was detected by PL technology using terephthalic acid as a probe molecule. The experimental methods were similar to those used in the estimation of photocatalytic activity except that the aqueous solution of organic pollutant was replaced by an aqueous solution of 5×10^{-4} M terephthalic acid and 2×10^{-3} M NaOH. The solution was analyzed after filtration on a luminescence spectrometer (Jasco, FP-6500) at room temperature under the excitation light at 315 nm.

3. Results and discussion

3.1. Structure and morphology

1 It is widely agreed that the **crystalline phase** of TiO_2 highly depends on the calcination
2 temperature. Fig. 1a shows the XRD patterns of TiO_2 samples with different calcination
3 temperatures. The absence of any clearly characteristic peaks in the diffraction pattern of the
4 S-300 and S-400 **suggest** their amorphous nature. With increasing calcination temperature, the
5 amorphous-to-crystalline transition is observed. The diffraction peaks of S-500 and S-600 are
6 mainly attributed to TiO_2 (B) phase (JCPDS, NO. 46-1238), containing a little of anatase phase
7 (JCPDS, NO. 21-1272).

8 To confirm the crystalline phase of the TiO_2 samples, Raman spectrum is further adopted
9 because it provides sensitive and non-destructive characterization for the crystal structure feature
10 [30]. As illustrated in Figure 1b, the peaks at 127, 264 and 423 cm^{-1} are attributed to the
11 characteristic peaks of TiO_2 (B) [31], while peaks located around 200 and 633 cm^{-1} can be
12 assigned to the presence of anatase phase [32]. Meanwhile, it is also observed that the intensity
13 of Raman peaks decrease sharply from S-600 to S-500, and can be barely found in S-400 and
14 S-300. The results confirm that the S-600 is highly crystallized, and the S-500 is poorly
15 crystallized. On the contrary, the S-400 and S-300 are dominated by the amorphous TiO_2 phase.

Fig.1

17 The morphology and textural structure of the samples are investigated by TEM and N_2
18 adsorption-desorption isotherms, as shown in Fig. 2. The TEM image of S-300 (Fig. 2a)
19 indicates that the sample consists of a large amount of **nanoparticles with an average diameter of**
20 **5.06 nm**. And the porous structure is formed by the agglomeration of **nanoparticles**. The average
21 pore size which is calculated from the adsorption data based on Barret-Joyner-Halenda model is
22 4.9 nm (Fig. 2b (inset)). It is **in agreement with** TEM image of S-300. The full width at half

1 maximum of the pore size distribution is 1.2 nm, indicating a very narrow pore size distribution.
2 Furthermore, the S-300 possesses a high BET surface area of $273 \text{ m}^2\cdot\text{g}^{-1}$ and a large pore volume
3 of $0.33 \text{ cm}^3\cdot\text{g}^{-1}$. As illustrated in Fig. 2b, the isotherm of S-300 exhibits a typical type H2 of IV
4 isotherm curve that is characteristic of mesoporous structure. The morphology and structure of
5 S-400 (Fig. 2c, d) are shown to be similar to that of S-300 to some extent; however, its BET
6 surface area and pore volume are decreased to $204 \text{ m}^2\cdot\text{g}^{-1}$ and $0.25 \text{ cm}^3\cdot\text{g}^{-1}$, respectively (Table
7 1). The large BET surface area and pore volume not only promote the absorption and utilization
8 of incident light, but also provide more active sites, which are beneficial for photocatalysis [32].
9 Besides, the mesoporous structure allows light waves to penetrate more deeply into the catalyst
10 and results in high mobility of photo-induced carriers [33]. As can also be found, the desorption
11 isotherms of the S-300 and S-400 are delayed until relative pressure becomes close to the fluid
12 cavitation pressure, indicating the non-uniformity of local component, which is in good
13 agreement with that for mesoporous carbonaceous-inorganic composite materials [34, 35]. This
14 implies that there may be carbon species in the S-300 and S-400 prepared in our study, which
15 will be discussed detailedly in characterizations of XPS and FTIR.

16 However, the S-500 and S-600 demonstrate distinctly different textural properties as
17 compared with S-300 and S-400. The nanoparticles in S-500 and S-600 aggregate so severely
18 that we even cannot distinguish the porous structure from the TEM images (Fig. 2e, g). Their
19 BET surface area decrease to 105 and $101 \text{ m}^2\cdot\text{g}^{-1}$, while pore volume decreases to 0.13 and 0.15
20 $\text{cm}^3\cdot\text{g}^{-1}$ for S-500 and S-600, respectively (Table 1). The textural difference can be ascribed to
21 the collapse of some pores, the shrinkage of framework and the severe aggregation of primary
22 particles during the annealing process. The respective selected area electron diffraction for the
23 samples annealed at different temperatures is presented in Fig. 2a, c, e, g (inset). As can be seen,

the diffraction rings of samples reveal that S-300 and S-400 are dominated by amorphous phase; in contrary, better crystallization has been obtained for the S-500 and S-600. The results are in accordance with the XRD and Raman characterizations.

Fig. 2

Table 1

The bonding characteristics of functional groups on different samples are identified by FTIR **spectrometer**, as illustrated in Fig. 3a. For S-300, a sharp peak at 1623 cm^{-1} and broad peaks at $3000\text{-}3600\text{ cm}^{-1}$ are easily distinguished, which can be ascribed to the bending mode of water and the stretching vibration of surface-adsorbed water molecules, surface hydroxyl groups on the samples, respectively [36]. The characteristic peaks of carboxy C-O (at 1205 and 1319 cm^{-1}), the bending mode of carboxy OH (at 1450 cm^{-1}) and alkoxy C-O (at 1043 cm^{-1}) are also observed on S-300[37]. With the elevation of annealing temperature, the intensity of peaks corresponding to the water (both surface and interior) and oxygen functional groups become weaker from S-300 to S-600. It indicates that the oxygen functional groups on the samples are decreased with increased temperatures, which are **in agreement with** the element analysis of different samples (Supplementary data Table S1), where the oxygen content of samples are decreased with the elevation of annealing temperature. The oxygen functional groups play an important role in the photocatalysis because these groups can be trapped by the holes generated under light irradiation. The **recombinations** of electron/hole pairs are suppressed consequently [37]. Absorption peak at 635 cm^{-1} represents the formation of Ti-O-Ti network [38]. The existence of carbon on S-300 is clearly identified by the distinctive peak at 802 cm^{-1} , which is in accord with previous studies, where the carbon-modified crystalline TiO_2 was successfully

synthesized [18]. Moreover, the weak peaks of the bending of alkene C-H (at 1205 cm^{-1}) and the stretching of alkene C-H (at 2970 cm^{-1}) are also observed on S-300[37]. Similar carbonaceous species have also been observed in lots of carbon-titania materials, indicating that S-300 is composed of TiO_2 doped with the carbon [39].

XPS is carried out to further investigation of the element chemical state of the samples. Fig. 3b describes the full survey spectrum of S-300, in which the elements of Ti, C and O can be clearly identified, with the binding energies of C 1s, Ti 2p and O 1s electrons at approximately 284.8, 457.8 and 531.3 eV, respectively [16]. It is noted that the characteristic peak of the element of boron is undetected, which reveals the nonexistence of boron on samples (Supplementary data Fig. S1). The C 1s fine XPS spectrum of S-300 is shown in Fig. 3c. As can be seen, the C 1s signal is well fitted by three contributions: an uppermost contribution at 284.5 eV is attributed to C-C, while contributions at 286.1 and 288.5 eV are ascribed to the C-O-C (and C-OH) and C=O (and COO), respectively [40]. The characteristic peak of Ti-C bond cannot be found in the C 1s spectrum, which rules out the carbon doping in the TiO_2 lattice. The Ti 2p core level spectrum represents the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ binding energies of 458.5 and 464.3 eV, respectively [41] (Supplementary data Fig. S2). The spin-orbital splitting of 5.8 eV between Ti $2p_{3/2}$ and $2p_{1/2}$ peaks is consistent with pure TiO_2 [33, 42]. However, the Ti 2p binding energies are slightly lowered in S-300 compared with bulk TiO_2 (459.4 and 465.1 eV) [42] or anatase TiO_2 (458.8 and 464.5 eV) [43], indicating the transfer of partial charge from the functional groups on carbon surface to the Ti (IV) centers in the TiO_2 [16]. Fig. 3d shows the O 1s fine XPS spectrum of S-300, which can be deconvoluted into three peaks at 530.1, 531.7 and 533.5 eV, corresponding to the Ti-O, hydroxyl O on the TiO_2 surface and C-O-C, respectively [44,45].

The results from XPS analysis are in coincidence with that by FTIR characterization. It further demonstrates that the S-300 is amorphous TiO₂ modified with carbon species.

Fig. 3

3.2. Optical properties and photocatalytic efficiency

Fig. 4a describes the UV-Vis diffuse reflectance spectra of various samples as compared with commercial P25. It can be seen that all samples exhibit a remarkable optical absorption in the visible light region and the absorption intensity of visible light increases with the raising of calcination temperature. This is due to the fact that carbon content would be increased with elevating the calcination temperatures (Table 1), which can strengthen the absorption of visible light [33, 46]. Supposing the samples as indirect semiconductor, plotting of the modified Kubelka-Munk function [47] against the photo energy of exciting light yields the bandgap energies of 1.94, 2.49, 3.05 eV for S-300, S-400 and P25, respectively (Figure 4b, Table 1). The light absorption of TiO₂ in S-500 and S-600 containing higher carbon content are severely shielded by the carbon species, thus the calculations of their bandgap energies are not possible[33, 48]. Generally, the bandgap narrowing **can** be attributed to the substitute of the oxygen site in TiO₂ lattice by the carbon with low electronegativity, which results in the upward shift of the valence band [49, 50]. However, the bonding of O-Ti-C is not identified in this study (Fig. 3), thus the substitution of carbon for oxygen in TiO₂ lattice cannot be supposed to account for the narrowing of bandgap for S-300. Nevertheless, three 2p bands of carbon atom still lie in the bandgap of TiO₂, which can significantly reduce the energy for electronic transition from the valence band to the conduction band [51]. Therefore, the bandgap narrowing of S-300 is partially ascribed to the isolated C 2p **state** in the bandgap of TiO₂ [18]. Besides, as discussed in Section

of 3.1, the S-300 is dominated by amorphous phase; the defects and disorders derived from amorphous TiO₂ also contribute to the narrowing of the bandgap [19, 20, 52].

PL spectrum is used to investigate the fate of photo-generated carriers (electron/hole). Fig. 4c depicts the PL intensities of different samples by using 315 nm UV light as excitation light source. The intensities of PL signals for S-300 and S-400 are much lower than that of P25, illustrating that the recombination of electron and hole is effectively hindered [36]. The effective inhibition of electron-hole recombination can be attributed to three pathways. Firstly, the carbon-doping promotes the formation of oxygen vacancies—the well-known electronic traps [53]; while the hole can be trapped by the carbon, thus the PL intensity decreases. Secondly, amorphous phase of S-300 and S-400 indicates the presence of defective sites and disorders, which are favorable for the separation of photo-induced carriers [21, 22, 52]. At last, the surface hydroxyl groups can be trapped by the holes to form hydroxyl radicals which can suppress the recombination of photo-generated carriers [36]. Interestingly, the PL intensities of S-500 and S-600 are shown to be almost negligible, mainly due to that the higher amount of carbon on the TiO₂ suppresses the exciting light source to reach the surface of TiO₂ [48]. Even weaker PL intensities are observed for the S-500 and S-600 under the excitation of visible light at 515 nm (Fig. 4d). On the contrary, much stronger intensities of PL signals are obtained for S-300 and S-400, indicating S-300 and S-400 can be effectively excited by the irradiation of visible light.

Fig. 4

The photocatalytic activities of different samples are estimated by the degradation of RhB in an aqueous solution under visible light irradiation ($\lambda > 400$ nm). As shown in Fig. 5a, although P25 cannot be excited by visible light, it still displays 71% degradation of RhB within 60 min,

possibly due to the photosensitization mechanism of the RhB. On the other hand, S-300 achieves as high as 95% of the photocatalytic efficiency, indicating the high photo-activity of S-300 under visible light irradiation. The temporal absorption spectrum changes of RhB clearly demonstrate the decomposition process of RhB during the visible light irradiation (Fig. 5b). The Fig. 5b inset displays that the maximum absorption of spectrum shifts rapidly from 554 nm to 497 nm after 20 min irradiation, implying the removal of the *N*-ethyl groups from RhB; after that, the conjugated chromophore structures gradually decompose under continuous illumination of visible light [54]. For S-500 and S-600, it is observed that the removal of RhB is mainly due to initial adsorption on the samples, and the contribution from photocatalytic degradation is negligible.

To minimize the influence of photosensitization on the photocatalytic efficiency, colorless 4-chlorophenol is employed as targeted pollutant for evaluating the photocatalytic activity of different samples. Fig. 5c presents that about 94% of 4-chlorophenol can be decomposed by S-300 after irradiation for 60 min, which is much higher than the 49% removal obtained by P25. Interestingly, the photodegradation curves of S-500 and S-600 exhibit relatively flat pattern during the irradiation, which are similar to the degradation behavior for RhB (Fig. 5a). It further confirms that the removal of RhB and 4-chlorophenol by S-500 and S-600 is mainly caused by adsorption rather than photocatalytic decomposition. This is not surprising because it is already shown in Fig. 4c and 4d that the S-500 and S-600 are difficult to be excited by the visible light. The photodegradation reaction kinetic of 4-chlorophenol is investigated by pseudo-first-order model. As shown in Fig. 5d, the apparent rate constant (k) of S-300 for the photodegradation of 4-chlorophenol reaches to 0.046 min^{-1} , which is 4.18 times higher than that of P25 (0.011 min^{-1}), and 3.53 times higher than the S-400 (0.013 min^{-1}), respectively. These results indicate the much higher photocatalytic activity of S-300. Moreover, the value of total organic carbon (TOC) is

adopted to further investigate the mineralization of RhB and 4-chlorophenol. Fig. S3 exhibits that TOC removal efficiencies of S-300 in the mineralization of RhB and 4-chlorophenol are 41% and 32%, respectively, which are higher than those of S-400 and P25. However, the mineralization efficiencies of organic pollutants are much lower than those of degradation efficiencies. That is because that the complete mineralization of organic pollutants does not go through one step and needs more irradiation time. Fig. S4 also shows that even after three cycles of repeated use, the photocatalytic activity of the S-300 for decomposition of RhB and 4-chlorophenol is still maintained, demonstrating the excellent stability of S-300 for applications in water treatment.

Fig. 5

3.3. Mechanism of visible light photocatalysis

To understand the active species involved in the photocatalytic process, hydroxyl radicals are detected by PL technology using terephthalic acid as a probe molecule. As shown in Fig. S5, a gradual increase in PL intensity centered at 425 nm is observed with increasing irradiation time, which indicates the production of $\cdot\text{OH}$ radicals [55]. Fig. 6 displays the possible mechanism of photocatalysis. Firstly, the acceptor impurity energy level is formed above the valence band maximum due to the **interstitial** doping of carbon in TiO_2 . As the C 2p electrons with higher energy are located in the bandgap of TiO_2 , the energy required for electronic transition is reduced, which extends the absorption spectrum to the visible light region [18, 51]. Secondly, the defects and **disorders** in amorphous TiO_2 may introduce the localized donor energy level under the conduction band minimum, further narrowing the bandgap of the TiO_2 [21, 52]. Therefore, electronic transitions from both the C 2p modified valence band and the

localized donor energy level to the conduction band, and from the C 2p modified valence band to the localized donor energy level, are jointly responsible for the absorption of visible light. The process of visible light photocatalysis can thus be summarized to the following steps: (1) electron-hole pairs are generated by visible light excitation; (2) transitions of electrons take place simultaneously from the C 2p modified valence band and the localized donor energy level to the conduction band, and from the C 2p modified valence band to the localized donor energy level; (3) the electrons and holes reaching the surface of **photocatalyst** react with H_2O , OH^- , and O_2 , leading to the formation of reactive oxygen species ($\cdot\text{OH}$, $\cdot\text{O}_2^-$ and H_2O_2); (4) the reactive oxygen species as well as the electrons and holes participate in the redox reactions together, and the decomposition of RhB and 4-chlorophenol is achieved.

Fig. 6

4. Conclusions

Effective visible light-activity mesoporous carbon-doped amorphous TiO_2 with high BET surface area and large pore volume has been obtained by a **facile** sol-gel route. The carbon-doped and amorphous phase jointly contribute to narrower bandgap and lower recombination of electron and hole pairs, which lead to unexpected photodegradation capability of RhB and 4-chlorophenol under visible light illumination. The findings of this investigation provide new insights to design visible light-induced photocatalyst based on amorphous TiO_2 for decontamination of water.

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Figure List:

Fig. 1. X-ray diffraction (XRD) patterns (a) and Raman spectra of samples with different calcination temperatures (b).

Fig. 2. TEM images contained selected area electron diffraction patterns (inset) and N₂ adsorption-desorption isotherms included pore size distributions (inset) with different annealing temperatures. (a), (b) S-300; (c), (d) S-400; (e), (f) S-500; (g), (h) S-600.

Fig. 3. FTIR spectra of samples (a), XPS survey spectra of samples (b), C 1s (c) and O 1s (d) fine XPS spectrum of S-300.

Fig. 4. Diffuse reflectance UV-Vis spectra (a), modified Kubelka-Munk functions (b) and PL spectra of samples under UV-315 nm (c) and visible light-515 nm (d).

Fig. 5. The changes in the absorption maxima of samples (a) , the temporal absorption spectrum change (b) and the corresponding maximum absorption band shift (b, inset) of S-300 of photocatalytic degradation of RhB; photocatalytic degradation efficiencies (c) and the corresponding photocatalytic kinetic curves (d) of 4-chlorophenol, as well as the P25 for comparison.

Fig. 6. Schematic illustration showing the possible mechanism for photocatalytic degradation of organic pollutants (RhB or 4-chlorophenol).

1 **Table List**

2 **Table 1**

3 Phase structure, BET surface area, pore parameter, carbon content and bandgap of different
4 samples

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a **c** **b** **d**

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3 samples

Sample	Phase content ^[a]	Bandgap ^[b] (eV)	S _{BET} (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)	C ^[c] (wt %)
S-300	amorphous	1.94	273	4.90	0.33	26.54
S-400	amorphous	2.49	204	5.30	0.25	28.01
S-500	TiO ₂ (B)+anatase	-	105	5.00	0.13	30.79
S-600	TiO ₂ (B)+anatase	-	101	6.10	0.15	31.80
P25	anatase+rutile	3.05	66	7.30	0.12	-

4 [a] Phase content is obtained by XRD patterns and Ramman spectra, as show in Fig 1. [b] The
5 bandgap is determined by the plot of $(ah\nu)^{1/2}$ vs $h\nu$, as shown in Fig. 4b. [c] Carbon content is
6 determined by XPS analysis, as show in Table S1.

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