Enhanced Adsorption and Photocatalysis by Introduction of C into N, Zr/TiO₂

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The introduction of carbon (C) into TiO₂ may facilitate charge transfer and thus improve its photocatalytic activities. In this paper, C was introduced into N, Zr/TiO₂ via ultrasound and calcination using glucose as carbon precursor. The as-prepared C@N, Zr/TiO₂ was characterized by SEM, TEM, XRD, UV-Vis DRS, and XPS. The adsorption abilities of the materials were evaluated using two anion dyes [methylene blue (MB) and basic violet (BV)] and two cation dyes [titan yellow (TY) and congo red (CR)] as model pollutants. The photocatalytic activities were investigated through the degradation of Ciprofloxacin (CIP) under simulated sunlight irradiation. The results revealed that the appropriate introduction of carbon may improve the adsorption abilities and the photocatalytic activities of non-carbonaceous materials. Furthermore, several samples exhibited selective adsorption abilities for cation dyes, which suggested the potential application of the as-prepared materials for the selective removal of co-existing pollutants.

Keywords TiO₂, carbon, photocatalysis, adsorption

Introduction

Environmental pollution is becoming increasingly serious as the result of continually expanding industrial development. Therefore, formerly localized environmental issues have grown into global challenges that affect all of humanity in the 21st century. Photocatalysis comprises an environmentally compatible technique with the potential to solve environmental problems by employing ambient solar light. TiO₂ has been extensively studied as a photocatalyst due to its high efficiency, low cost, non-toxicity, anti-photocorrosion, and so on. However, the application of TiO₂ has been constrained due to its wide band gap and high recombination rate of photo-induced electrons and holes.

The introduction of new elements into TiO₂ via doping has been verified as a suitable technique to overcome these two shortcomings. Many elements have been investigated in this regard, including noble elements (Au, Ag, Pt, Rh),^[1-5] transition metals (Zn, Fe, Ni, Cu, Co),^[6-10] rare earth elements,^[11] as well as other metals.^[12,13] In view of the various characteristics of metals and non-metals, co-doping with these elements has also been explored, encompassing C, N, F, S, P, B, and metal elements.^[14-24] Among non-metal elements, C has garnered significant attention due to its unique properties. It has been experimentally and theoretically verified that C doping into TiO₂ can enable visible light responses. Wang *et al.*^[25] speculated and calculated via DFT theory when C substitutes O atoms in TiO₂, C2p will overlap O2p orbitals and thus reduce the bad gap of TiO₂ to improve its photocatalytic activities. On the other hand, C doping may improve the adsorption abilities of TiO₂, which facilitates the attraction of contaminants by photocatalysts to improve photocatalytic activity.^[26] Additionally, C

doping may also enhance the conductivity of TiO₂, which assists electron transport between the surface and interior, thus prolonging the separation of photo-induced electrons and holes.^[27]

Numerous studies on carbon doped TiO₂ have been reported, including Chen and co-workers,^[28] who prepared C–N-co-doped anatase TiO₂ photocatalysts via a sol-gel method. They observed an obvious red shift of the absorption edge of TiO₂, and the photocatalytic activities of TiO₂ were greatly improved as the result of C and N doping. Ruzybayev *et al.*^[29] prepared N–C co-doped TiO₂ thin films through a reactive pulsed laser deposition technique. The band gap of the co-doped TiO₂ thin film was reduced by ~1.00 eV in contrast to undoped TiO₂ film that was prepared by the same technique. Lei and co-workers^[30] synthesized C, N, and S co-doped TiO₂ samples via a sol-gel method by employing butyl titanate as the titanium source and thiourea as the dopant. The results indicated that the doping of anatase TiO₂ samples with C, N, and S not only broadened the light adsorption spectrum into the visible region (>400 nm) to make it active under visible light, but also promoted the separation of photo-induced carriers to enhance its efficiency under visible light irradiation.

Ciprofloxacin (CIP), which is a common quinolone antibiotic, has been widely used in medicine and animal husbandry. Most CIP is released into environment in its original form, because it can only be metabolized by <25% in the human body. Furthermore, CIP is mostly non-biodegradable in the ambient environment and it has been detected in remote areas at sea, as well as in cemeterial soils following long distance transport.^[31,32] It was learned that CIP is toxic to bacteria and induces drug resistance in bacteria,^[33] which poses a threat to the environment and human health. Currently, CIP cannot be completely degraded with typical water treatment technologies.

Dye infused water is difficult to deal with due to its perfused color, complicated composition, anti-oxidation properties, and bio-toxicity. Similarly to CIP, dye water is non-biodegradable^[34-36] in the ambient environment. Due to its unique capabilities, adsorption has been applied to the treatment of dye water and attracted much attention.

In our previous work, co-doped (N and Zr) TiO₂ was synthesized^[37] and endowed with visible light activity by narrowing the band gap. However, the adsorption ability was obviously not improved. Much research has shown that the adsorption abilities of TiO₂ may be improved through the introduction of C. At the same time, the photocatalytic activities of TiO₂ may be enhanced by multi-element doping. In this paper, we introduced C into N, Zr co-doped TiO₂ using glucose as carbon source and investigated the effects of the carbon content, as well as calcination temperature on the adsorption and photocatalytic activities of various samples. We employed two cation dyes (methylene blue and basic violet), two anion dyes (titan yellow and congo red), and CIP as model pollutants, to investigate the adsorption and photocatalytic activities of the materials, respectively. The results revealed that the appropriate introduction of carbon not only increased its adsorption properties, but also enhanced its photocatalytic activities.

Experimental

Reagents

All the chemicals used in the study were analytical grade and used without any further treatment.

Preparation of N, Zr co-doped TiO₂

N, Zr co-doped TiO₂ was prepared according to a previous reference.^[38] Acetic acid (0.5 mL) was dissolved in 20 mL of ethanol and stirred for 10 min. Subsequently, 2 mL of tetrabutyl titanate was added dropwise into the solution and stirred for an additional 10 min to complete the mixture. Afterwards, 8.04 mL of zirconium acetate was added dropwise with stirring, followed by 5.0 g of urea. The mixed solution was annealed at 300 °C until the water had completely evaporated. Next, the sample was cooled to room temperature and milled for 20 min; whereafter, the N, Zr co-doped TiO₂ was obtained, in which the molar ratios of nitrogen and zirconium to titanium were N/Ti = 0.5% and Zr/Ti = 1.0%, respectively.

Synthesis of C@N, Zr/TiO₂

Firstly, a certain amount of glucose was dissolved into 10 mL of deionized water, after which the as-prepared N, Zr, co-doped TiO₂ was added to the solution and exposed to ultrasound for 30 min to form a homogeneous solution, followed by drying under 60 °C for 12 h and cooling down to room temperature. Secondly, the mixture was annealed for 3 h under different temperatures (under nitrogen protection). The amount of carbon in the materials was denoted via the quantity of glucose added (mg). According to the different calcination temperatures and carbon amounts in the samples, as-prepared materials were denoted as T-temperature-carbon amount. For example, T-450-0 denotes the sample was calcined at 450 °C without glucose addition, whereas T-600-5 denotes the sample was calcined at 600 °C and the addition of glucose was 5 mg.

Characterization

The crystal structure was characterized by a D8 Advance X-ray diffractometer (Bruker, German) with Cu K α radiation source (λ = 0.15406 Å) operated at 25 mA and 35 KV. The data

was recorded between 10°–80° at a speed (2 θ) of 0.02 between 10°–80°. The materials were observed via a JSM-6390LV (Japan) scanning electronic microscope and JEM-2100 (JEOL, Japan) high resolution transmission electron microscope. The elemental composition of the material was determined via ESCALA260Xi X-ray photoelectron spectroscopy with an Al KLA260Xi X-ray phot (set at 225 W), operated at 15 A and 15 kV. The UV-VIS DRS was recorded by a Lambda 950 (Perkin Elmer, USA) spectrometer, with BaSO₄ as reference and scanned at 300–800 nm. The Brunauer-Emmett-Teller specific surface areas (SBET) and the porosity of the samples were evaluated on the basis of nitrogen adsorption isotherms measured at -196 °C using Micromeritics ASAP 2020 (USA) gas adsorption. Zeta potential analysis was conducted on a ZETASIZER Nano-ZS potentiostat. The UV-VIS spectra of the dyes were measured on a TU-1900 double-beam UV-Vis Spectrophotometer (Beijing, China), scanned from 200–800 nm. The CIP concentration was measured on a Waters1525-2998 HPLC with a C18 column (5 μ m, 4.6 x 150 mm) and DAD detector.

Selective adsorption

The selective adsorption abilities of the materials were evaluated by selecting two cation dyes [basic violet (BV) and methylene blue (MB)] and two anion dyes [titan yellow (TY) and congo red (CR)] as model pollutants. The adsorption experiments were carried out as follows: 50 mL of the dye solution and 10 mg of as-prepared materials with a concentration of 10 mg·L⁻¹ were introduced into quartz bottle and stirred for 90 min to obtain an adsorption-desorption balance. During the process, 4 mL of the solution was extracted and centrifuged for 10 min at a speed of 10000 r·min⁻¹. Afterwards, the absorbance of the supernatant was measured using a TU-1900 double-beam UV-Vis spectrophotometer. The absorption peaks of the four dyes BV, MB, TY, and CR were 582, 664, 336, and 498 nm, respectively. Within 0–20 mg·L⁻¹, the relationship between the absorbance of the dye solution and concentration obeyed the Beer-Lambert law. As a result, the adsorption rate (r) was calculated according to Eq. (1):

$$r = \frac{C_0 - C}{C_0} = \frac{A_0 - A}{A_0} \quad (1)$$

where C_0 or A_0 is the initial concentration or absorbance of the dye solution, and C or A is the concentration or absorbance of the dyes following a certain interval.

Photocatalytic activities

The photocatalytic activities of the materials were evaluated using Ciprofloxacin (CIP) as model pollutant under simulated sunlight irradiation. The experiments were conducted in a HXSEI photoreactor (Kaifeng, China). A 200 W xenon lamp was set in a quartz cold trap and cooled with circulating water. The experiments were carried out as follows: 50 mL of the CIP solution with concentration of 10 mg·L⁻¹ was deposited into a quartz bottle, as along with 10 mg of the as-prepared materials, and stirred for 60 min in the dark to obtain an adsorption-desorption balance, after which the light was turned on. At 30 min intervals, 4 mL of the reaction solution was extracted and poured through a 0.22 μ m filter to capture any material in the solution. The CIP concentration was determined using a Waters HPLC system, which consisted of a 1525 pump and 2998 PDA detector. The HPLC conditions included a reverse phase C18 column (5 μ m, 4.6 mm x 250 mm), wherein the mobile phase was composed of a methanol and 0.25 mmol·L⁻¹ phosphoric acid solution (V:V = 3:7), in which the pH of the phosphoric acid solution was adjusted to 3 using triethylamine.

The flow rate was controlled at $1.0 \text{ mL} \cdot \text{min}^{-1}$ and the detection wavelength was set at 278 nm. A good linear relationship between the peak area (s) and the concentration (c) of CIP was obtained from $0\text{--}20 \text{ mg} \cdot \text{L}^{-1}$, and the degradation rate (r) was calculated according to Eq. (2):

$$r = \frac{C_0 - C}{C_0} = \frac{S_0 - S}{S_0} \quad (2)$$

where C_0 or S_0 is the initial concentration or peak area of the CIP solution, and C or S is the concentration or peak area of the CIP solution at a certain interval once the light had been turned on.

Results and Discussion

XRD analysis

XRD analysis was applied to determine the crystalline composition and structure. The XRD spectra of the samples with different carbon content and calcination temperatures are displayed in Figure 1. It can be seen that the samples at 450°C and 600°C were amorphous and anatase, respectively. When temperature was increased to 750°C and 900°C , the crystal form was transformed to rutile. All of the diffraction peaks were consistent with JCPDS No. 21-1276. Diffraction peaks could be observed at 27.5° , 36.1° , 39.1° , 41.5° , 44° , 54.2° , and 56.6° (2θ), which indicated that the sample possessed a tetragonal structure. No peak attributed to C, N, or Zr could be observed, which was likely due to their low concentrations and uniform dispersion in TiO_2 . When comparing T-900-5 to T-750-5 in Figure 1a, it can be observed that most of the T-900-5 diffraction peaks were weaker than those of T-750-5, which indicated that too high a temperature may destroy the TiO_2 crystal to a certain extent.

Figure 1 (a) XRD patterns of the samples at different calcination temperatures, (b) samples with different carbon content at 750°C .

In order to investigate the effects of carbon on the crystallinity of the samples, XRD analysis of samples with different carbon content at 750°C were carried out, with the results displayed in Figure 1b. It can be seen that the positions of the diffraction peaks did not change for various samples obviously, indicating that the carbon content had little effect on the crystal form. On the other hand, the intensities of the peaks increased dramatically in the 5% carbon content sample (T-750-5), and decreased clearly in the 10% and 15% carbon content samples (T-750-10 and T-750-15), showing that the introduction of the appropriate amount carbon may improve crystallinity, whereas excessive carbon plays a contrary role.

SEM and TEM analysis

The morphology of the samples was characterized by SEM and TEM in Figure 2, where Figure 2a is a SEM image of the T-750-5. It may be seen that the sample was comprised of long

strips, where several long uniform strips aggregated into bunches. Each strip was approximately $15\text{--}20 \mu\text{m}$ in length and $1.5\text{--}2.0 \mu\text{m}$ in width. Figure 2b is a TEM image of the T-750-5 sample, which revealed that the strips possessed a porous structure. Numerous porous structures could be observed at the end of the strip, which was beneficial for adsorption. The width of the strip was about $1.5 \mu\text{m}$, which was consistent with the SEM results.

Figure 2 (a) SEM and (b) TEM images of T-750-5.

XPS analysis

XPS was carried out to investigate what the elements states were in the samples, with XPS images of the T-750-5 displayed in Figure 3. A survey scan (Figure 3a) showed that the surface of the T-750-5 was comprised of Ti, O, N, Zr, and C. The peak of Zr was very low due to its limited concentration. High-resolution (HR) XPS spectra of Ti2p, O1s, C1s, N1s, and Zr3d are presented in Figures 3b–3f. The Ti2p peaks could be fitted with two types of Ti species. One existed at 458.6 and 464.4 eV , which were attributed to the Ti-O band.^[39] The other existed at 457.3 and 463.3 eV , which were attributed to the Ti-N band,^[40] which indicated that N was connected with Ti in the TiO_2 crystal rather than an O atom. The O1s peak was fitted with two peaks, existing at 530.5 and 532.3 eV , respectively. The peak of 530.5 eV was assigned to Ti-O link, derived from the O atom in the TiO_2 crystal. The peak of 532.3 eV was assigned to Ti-OH,^[30] which was derived from the OH that was absorbed onto the surface. The N1s peak could be fitted with three peaks, existing at 396.2 , 399.6 , and 401.4 eV , respectively. The peak of 396.2 eV could be assigned to Ti-N band,^[39] which indicated that

Figure 3 XPS images of T-750-5: survey scan (a), Ti2p (b), O1s (d), C1s (d), N1s (e), and Zr3d (f).

some of the N atoms entered into TiO₂ crystal lattice via the substitution of an O atom, which was consistent with Ti peaks of 457.3 and 463.3 eV. It was reported that the band gap of TiO₂ could be narrowed by doping N into TiO₂ crystal lattice, replacing the O atom.^[39,40] Hence, it might be theorized that the band gap of the material might be narrowed, as the peak of Ti-N band was found. The 399.6 eV peak could be attributed to Ti-O-N, indicating that some of the N atoms existed interstitially within the TiO₂ crystal. The peak of 401.4 eV was assigned to the N-H band^[39,40] (likely coming from urea, the precursor of nitrogen), and Zr3d peaks existed at 184.6 and 182.5 eV, which were attributed to the Zr-O band.^[41,42]

The C 1s peak was fitted by three peaks, existing at 284.8, 286.3, and 288.1 eV, respectively. The peak at 284.8 eV was primarily attributed to the carbon tape and non-oxygenated carbon,^[39] which was derived from ambient absorbed carbon. The peaks at BEs of 286.3 and 288.1 eV were assigned to C-O and C=O groups,^[39,43] which confirmed that there were carbon-containing groups on the surface of the sample. However, no peak at 281 eV (Ti-C band) was observed, which indicated that the carbon did not enter into the TiO₂ phase. As a result, it can be inferred that carbon was connected to TiO₂ via a Ti-O-C link.^[44] Earlier studies indicated that the chemical Ti-O-C bond at the interface exhibited high strength.^[45] Hence, the as-prepared C@N, Zr/TiO₂ might be expected to display high structural stability. On the other hand, electron transfer via Ti-O-C between TiO₂ and C extended greatly the separation of photo-induced charge carriers and prolonged the carrier lifetime.^[46] That is to say, the structures were favorable for the transfer of light-excited charges^[47] and improved the photocatalytic activity. Furthermore, the colors of the sample changed from brown to dark following the introduction of carbon, while non-carbon containing samples were light yellow, which suggested electronic interactions and different bonding in C@N, Zr/TiO₂.^[47]

UV-Vis DRS analysis

The capacity for light adsorption is a critical factor for photocatalysts. The color of the N, Zr/TiO₂ was light yellow, whereas the colors of C@N, Zr/TiO₂ were from dark brown to black, depending on the carbon content of the sample, which is beneficial for light adsorption. The UV-Vis diffuse reflectance spectra of T-750-0, T-750-5, and P25 are displayed in Figure 4. It may be seen that there was no visible light adsorption for P25, whereas for T-750-0 and T-750-5, obvious visible light adsorption was observed from 400–800 nm. Further, T-750-5 showed higher adsorption abilities, in contrast to T-750-0, in the visible light area. In another words, T-750-0 and T-750-5 could utilize visible light more efficiently than P25, particularly for T-750-5. Thus, the conclusion was drawn that the introduction of carbon improved the visible light adsorption efficiency.

Figure 4 UV-Vis diffuse reflectance spectra.

BET surface area

The BET surface area is also a key factor in adsorption and for photocatalytic activities. Studies on N₂ gas adsorption/desorption were conducted, where all of the samples showed similar nitrogen adsorption-desorption isotherms, as well as pore size distribution curves. The nitrogen adsorption-desorption isotherm of T-750-5 is displayed in Figure 5a, which exhibited an IV (Brunauer Deming Deming Teller classification) style, with a H₃ hysteresis loop. The pore size distribution curve was calculated by the BJH equation in Figure 5b. It indicated that most of the pores were mesoporous, which was consistent with the TEM results. The calcination temperature and carbon content influenced the BET surface areas, pore volume, and average pore size, with the results presented in Table 1. At the same calcination temperature (750 °C), the introduction of carbon increased the catalyst surface area significantly. In contrast to the non-carbon sample (T-750-0), the surface areas of carbon-containing samples (T-750-5, T-750-10, T-750-15) increased by over 30%. In addition, the surface area decreased slightly along with the increased carbon content. The calcination temperature played a very important role in the BET surface area as well. The surface area was observed to increase with the temperature when it was below 750 °C, which began to decrease at 900 °C. Moreover, all of the surface areas of the as prepared materials were higher than that of P25 (about 50 m²·g⁻¹). The pore volume was altered similarly to the changes in the BET surface area.

Figure 5 (a) Nitrogen adsorption-desorption isotherms (b) corresponding pore size distribution curves of T-750-5.

Table 1 BET surface area and pore volume

Sample	BET surface area ^a / (m ² ·g ⁻¹)	Pore volume ^b / (cm ³ ·g ⁻¹)
T-750-0	92.0968	0.352194
T-750-5	124.1995	0.444217
T-750-10	121.2822	0.357775
T-750-15	119.3035	0.354761
T-450-5	62.4815	0.343618
T-600-5	84.8480	0.343541
T-900-5	94.8775	0.419434

^a BET surface area is calculated basing on the linear part ($P/P_0 = 0.3$).

^b Pore volume is N₂ adsorption volume at $P/P_0 = 0.995$.

Selective adsorption ability

Two cation (BV and MB) and two anion (TY and CR) dyes were selected as model pollutants to elucidate the adsorption abilities of the as-prepared samples. The results are displayed in Tables 2 and 3. It can be seen that all of the samples at 450 and 600 °C exhibited selective adsorption for cation dyes (MB and BV); about 70%–80% of the cation dyes were absorbed within 90 min, whereas there was negligible absorption for the anion dyes (TY and CR). As revealed in Table 2, there were no significant difference among the adsorption abilities of the samples for the two cation dyes, which indicated that the carbon content had little effect on the adsorption abilities of the samples that were calcined at 450 and 600 °C.

Table 2 Adsorption rates for four dyes (samples at 450 and 600 °C)

Sample	TY	CR	MB	BV
T-450-0	2.0%	1.0%	74.5%	75.8%
T-450-5	3.5%	1.2%	80.8%	74.1%
T-450-10	1.8%	5.3%	76.9%	72.2%
T-450-15	0.9%	5.2%	70.2%	69.2%
T-600-0	1.8%	2.4%	78.2%	76.8%
T-600-5	2.0%	1.1%	80.5%	77.8%
T-600-10	0.5%	0.6%	77.6%	76.4%
T-600-15	0.3%	1.0%	75.1%	74.2%

Table 3 Adsorption rates for four dyes (samples at 750 and 900 °C)

Sample	TY	CR	BV	MB
T-750-0	1.9%	3.9%	73.4%	71.1%
T-750-5	2.8%	1.6%	92.5%	88.5%
T-750-10	39.6%	32.8%	88.1%	75.4%
T-750-15	25.1%	13.5%	90.3%	82.2%
T-900-0	45.2%	20.8%	74.6%	73.0%
T-900-5	51.5%	23.6%	76.2%	74.0%
T-900-10	70.5%	36.1%	86.7%	83.3%
T-900-15	79.7%	47.1%	91.1%	88.0%
P25	4.0%	5.2%	3.1%	9.2%

However, when the calcination temperature was increased to 750 °C, the T-750-0 and T-750-5 samples still exhibited selective adsorption for cation dyes; whereas for T-750-10 and T-750-15, their selective adsorption abilities appeared to have been lost, although the adsorption rates for anion dyes were still low. When the temperature was increased to 900 °C, all of the samples lost their selective adsorption abilities. Simultaneously, the adsorption rates for TY and CR increased in contrast to the samples at 750 °C.

For comparison, the adsorption tests of P25 for the four dyes were carried out (Table 3 and Figure 6). It can be seen that P25 had negligible adsorption abilities for both cation and anion dyes. Among all samples, T-750-5 exhibited the highest adsorption ability for cation dyes, with adsorption rates of 92.5% and 88.5% for BV and MB, respectively, which were 1.26 and 1.24 times than those of T-750-0.

To investigate why some samples had selective adsorption while others did not, Zeta potential tests were carried out. The Zeta potentials for T-600-5 and T-750-5 were -43.2 and -42.6

eV, respectively, whereas for T-750-10 and T-900-5, they were -38.7 and -37.0 eV. The samples with selective adsorption abilities showed more negative Zeta potentials compared to those that did not. A conclusion could likely be drawn that the capacity for selective adsorption was caused by charge attractions between cation dyes and negative charges that resided on the surface of the samples.^[41,48] Selective adsorption could only be obtained when the surface of the sample possessed sufficient negative potentials.

Figure 6 Adsorption abilities of T-750-5 and P25 for four dyes.

Photocatalytic activities

Ciprofloxacin (CIP) was selected as model pollutant to test the photocatalytic activities of the samples under simulated sunlight (Figure 7). It may be seen that the CIP could hardly be degraded without a catalyst under simulated sunlight. The effects of the calcination temperature on the photocatalytic activities of the samples were investigated. The results indicated that the calcination temperature played a significant role (Figure 7a). For the samples with 5 mg glucose addition, the photocatalytic activity increased along with higher temperatures, with T-750-5 exhibiting the highest photocatalytic activity. However, the photocatalytic activity decreased when the temperature was increased to 900 °C. Moreover, all of the samples had higher photocatalytic efficiencies compared to P25. The degradation data were analyzed using the pseudo-first-order model and the kinetic constants were 0.01091, 0.02275, 0.035 and 0.01194 min⁻¹ for T-450-5, T-600-5, T-750-5 and T-900-5, respectively. As for P25, the kinetic constant was 0.00537 min⁻¹. The effects of carbon content on the photocatalytic activity were presented in Figure 7b. It can be seen that all carbon-containing samples exhibited higher adsorption and photocatalytic abilities in contrast to T-750-0. Specifically, the further introduction of carbon may improve not only the adsorption abilities, but also photocatalytic activities of non-carbon containing TiO₂. Furthermore, the carbon content influenced the photocatalytic activities as well. Among all carbon-containing samples, T-750-5 exhibited the highest photocatalytic activity. The first order kinetic constants were 0.009, 0.035, 0.01813 and 0.02672 min⁻¹ for T-750-0, T-750-5, T-750-10 and T-750-15, respectively. The kinetic constant for

T-750-5 was almost 4 times that of T-750-0. We learned from the XRD and BET results that T-750-5 showed the best crystallinity and the highest surface area, which were likely the drivers behind its excellent photocatalytic activity.

Figure 7 (a) CIP degradation under simulated sunlight with samples of 5 mg glucose addition. (b) with samples calcined at 750 °C. Conditions: 200 W xenon lamp, CIP concentration $\sim 10 \text{ mg} \cdot \text{L}^{-1}$.

Conclusions

Carbon was successfully introduced into N, Zr/TiO₂ using glucose as carbon precursor. XPS analysis revealed that the carbon did not enter into TiO₂ phase and it connected with the TiO₂ via a Ti-O-C link, which facilitated charge transfer and the inhibition of the recombination of photo-induced electrons and holes. The introduction of carbon had a negligible effect on the crystalline structure of TiO₂, whereas it played a role in the BET surface area and degree of crystallinity. Therefore, it influenced the adsorption and photocatalytic activities. The adsorption of four dyes and the degradation of CIP revealed that the introduction of appropriate amounts of carbon improved adsorption abilities and photocatalytic activities under simulated sunlight irradiation. In addition, several samples demonstrated the ability to adsorb cation dyes selectively due to sufficient negative charges on their surfaces. This warrants further study toward the selective removal of co-existing pollutants.

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