Microwave-Assisted Synthesis of Carbon-Based (N, Fe)-Codoped TiO$_2$ for the Photocatalytic Degradation of Formaldehyde

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Abstract

A microwave-assisted sol–gel method was used to synthesize (N, Fe)-codoped activated carbon (AC)/TiO$_2$ photocatalyst for enhanced optical absorption in the visible light region. The prepared samples were characterized via X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, Brunauer–Emmett–Teller analysis, ultraviolet–visible light spectroscopy, X-ray photoelectron spectroscopy, and photoluminescence spectroscopy. The results showed no significant difference in the surface area of AC/TiO$_2$ (approximately 500 m$^2$/g) after doping. TiO$_2$ was uniformly distributed on the surface of AC, which exhibited coexisting anatase and rutile structures with a mean crystallite diameter of approximately 20 nm. N and Fe monodoping on AC/TiO$_2$ reduced the energy band gap of TiO$_2$ to 2.81 and 2.79 eV, respectively, which mainly attributed to the impurity energy formed in the energy gap of TiO$_2$. In (N, Fe)-codoped AC/TiO$_2$, N and Fe are incorporated into the TiO$_2$ framework and narrow the band gap of TiO$_2$ to 2.58 eV, thereby causing a large redshift. Codoping of N and Fe enhanced the production of hydroxyl radicals (⋅OH) and improved the photocatalytic activity of the resultant AC/TiO$_2$ compared with those of undoped and N- or Fe-monodoped AC/TiO$_2$. N-Fe-AC/TiO$_2$ degraded 93 % of the formaldehyde under Xe-lamp irradiation. Moreover, the photocatalyst was easily recyclable. In summary, a novel and efficient method to mineralize low concentrations of HCHO in wastewater was discovered.

Keywords: Photocatalytic degradation; Microwave irradiation; Active carbon; Codoped AC/TiO$_2$; Formaldehyde

Background

Formaldehyde (HCHO) is a volatile organic compound that irritates the respiratory, cardiovascular, and nerve tissues of humans [1]. Thus, HCHO removal is essential for improving environmental quality. HCHO photodegradation in the presence of a titanium dioxide (TiO$_2$) photocatalyst completely degrades HCHO into CO$_2$ and H$_2$O [2]. Unfortunately, the photocatalytic activity of TiO$_2$ is limited by its low adsorption property and large band gap (3.2 eV) [3, 4].

Significant efforts have been made to overcome these two drawbacks. Preparation of TiO$_2$ photocatalysts loaded with porous materials and characterization of their photocatalytic performance have drawn great research attention [5]. Combination of the distinctive properties of mesoporous carbon materials and TiO$_2$ evidently improves optical absorption and has been adopted in the removal of organic contaminants [6]. Pastravanu et al. [7] reported that 92 % conversion of methyl orange is achieved after 170 min of ultraviolet (UV) irradiation with AC/TiO$_2$ composite, whereas only 42 % conversion is achieved with pure TiO$_2$. However, in our previous studies [8], the degradation efficiency of AC/TiO$_2$ (1 g) was only 36 % under UV irradiation for 420 min at a low concentration of HCHO (30 mg/L). Therefore, it is important to improve the photocatalytic performance of TiO$_2$ by improving its internal structure. Metal or nonmetal doping of TiO$_2$ could extend its optical absorption range into the visible light region and modify the generation rate of the electron–hole pairs [9–12]. TiO$_2$ doped with transition metals has recently been prepared, and studies on these materials have shown that the energy band gap of TiO$_2$ decreases with decreasing recombination rate of photogenerated electron–hole pairs [13–15]. Iron is considered one of the most appropriate transition metals for TiO$_2$.
doping because the atomic radius of Fe$^{3+}$ is close to that of Ti$^{4+}$, thus, the titanium positions in the TiO$_2$ lattice can be easily replaced by iron cations [16–18], remarkably improving photocatalytic efficiency. The results of Safari et al. [19] showed significant improvements in the photodegradation of Reactive Orange 16 by Fe-doped TiO$_2$ (nearly 93 %) compared with that by pure TiO$_2$ (approximately 71 %) under UV irradiation. Doping TiO$_2$ with nonmetallic anions, such as N, S, and C, has been proposed as a promising method for extending photore sponses from the UV to the visible light regions [20, 21]. Among them, N-doped TiO$_2$ has been demonstrated to be the most effective in narrowing the band gap and increasing photocatalytic activity in the visible light region [22]. Several papers have reported the effects of Fe and N modification of TiO$_2$ in enhancing photocatalytic activity [23, 24]. The photocatalytic activities of these powders are approximately two to four times higher than that of pure anatase TiO$_2$ under visible light irradiation. In addition, using microwave irradiation to synthesize TiO$_2$ nanoparticles is a recent innovation [25]. Compared with conventional methods, microwave irradiation presents several advantages in terms of cleanliness, short reaction times, and energy economy [26]. Because very few reports on the microwave synthesis of (N, Fe)-codoped TiO$_2$ photocatalysts coated on AC (N-Fe-AC/TiO$_2$) are available, the objective of the present work is to develop a rapid method to prepare N-Fe-AC/TiO$_2$ and investigate its photocatalytic effect on HCHO under visible light irradiation.

The present work focuses on the synthesis of N-Fe-AC/TiO$_2$ prepared using microwave irradiation and its structural characterization. The characteristics of the photocatalysts have been analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), Fourier transform infrared (FTIR), Brunauer–Emmett–Teller analysis (BET), ultraviolet and visible spectroscopy (UV–vis), X-ray photoelectron spectroscopy (XPS), and photoluminescence (PL). Studies on the use of catalysts for photodegradation of HCHO in aqueous solution under visible light irradiation are in progress.

**Experimental Methods**

**Catalyst Preparation**

AC was prepared based on the precious study [27]. A mixture of solid KOH (10 g) and dried coal at a ratio of 1:1 was placed in a quartzose tube in a microwave reactor and activated under vacuum atmosphere at 693 W for 10 min. The obtained AC samples were pretreated by adding into HNO$_3$ solution with 24 h. The mixture was filtered using distilled water until they became neutral. The pretreated AC was then dried and stored until use.

The TiO$_2$ gel/sol was obtained by conventional sol–gel method. All reagents were of analytical grade and used without further purification. In typical synthesis process, 30 mL of tetrabutyl orthotitanate (TBOT) was dissolved in anhydrous alcohol (EtOH) in proportion of 1:1 (volume ratio). This solution was thoroughly stirred for 40 min and named solution A. Solution B was prepared by mixing 14 mL of glacial acetic acid and 7 mL of distilled water in 35 mL of absolute alcohol. Solution B was added to solution A dropwise and continuously stirred for 1 h. Then, it was obtained pale yellow clear TiO$_2$ sol. Pretreated AC (10 g) was added into TiO$_2$ sol (100 g). The mixture was placed in an oven at 100 °C for 24 h. After solidification, AC/TiO$_2$ was prepared under microwave irradiation at 700 W for 15 min. To prepare Fe-doped AC/TiO$_2$, Fe(NO)$_3$·9H$_2$O was mixed with solution B, while for N-doped AC/TiO$_2$, urea was dissolved in solution B. The dosage of Fe iron was 0.008, 0.01, and 0.012 g, and the resulted samples were noted as 0.008 Fe-AC/TiO$_2$, 0.01 Fe-AC/TiO$_2$, and 0.012 Fe-AC/TiO$_2$, respectively. The dosage of N was 0.2, 0.4, and 0.6 g, and the resulted samples were noted as 0.2 N-AC/TiO$_2$, 0.4 N-AC/TiO$_2$, and 0.6 N-AC/TiO$_2$, respectively. Optimum concentrations of N and Fe were obtained by maximizing the photocatalytic activity for the mono doped (Fe or N) AC/TiO$_2$. These optimized concentrations were used for synthesizing (N, Fe)-codoped AC/TiO$_2$.

**Catalyst Characterization**

The crystal structures of the prepared samples were measured through XRD on a Rigaku D/Max-2500/PC powder diffractometer. Each sample powder was scanned using Cu-Kα radiation with an operating voltage of 40 kV and an operating current of 200 mA. The surface micromorphologies of photocatalysts were characterized through SEM (S4800, Hitachi LTD) at an accelerating voltage of 15 kV. TEM was performed on a Tecnai G2 F20 microscope at 100 kV. FTIR spectra were recorded with a Bruker Vertex FTIR spectrometer, resolution of 2 cm$^{-1}$, in the range of 4000–400 cm$^{-1}$ by KBr pellet technique. The UV–vis DRS were obtained with a powder UV–vis spectrophotometer (U-4100, Hitachi LTD). Specific surface area (SBET, m$^2$·g$^{-1}$) was calculated using the BET equation, and total pore volume ($V_p$, m$^3$·g$^{-1}$) was evaluated by converting the adsorption amount at $P/P_0=0.95$ to the volume of liquid adsorbate. XPS analysis of samples was conducted using a PHI5700 ESCA system equipped with a Mg Ka X-ray source (1253.6 eV) under a vacuum pressure <10$^{-6}$ Pa. The formation rate of -OH at photo-illuminated sample/water interface was detected by the PL technique using terephthalic acid (TA) as a probe molecule. PL spectroscopy of synthesized products was taken at room temperature on a Hitachi F2500 spectrofluorometer using a Xe lamp with an excitation wavelength of 325 nm.
Photocatalytic Activity
The photocatalytic activity of prepared photocatalyst was measured by degrading of the HCHO solution. In a typical test, 0.05 g of catalyst was added to 50 mL of HCHO solution (30 mg/L, pH = 6.8). The mixture was then irradiated under Xe lamp to degrade HCHO. The distance between the reactor and lamp housing is 8.5 cm. The removal efficiency of the photocatalyst can be calculated as follows:

$$\eta = \frac{C_o - C_t}{C_o} \times 100\%$$

where $C_o$ and $C_t$ are the concentrations of HCHO at initial and different irradiation times, respectively.

Discussion
To determine the optimal concentration of Fe and N for codoping, AC/TiO$_2$ was monodoped with Fe or N at three different concentrations. The XRD was used to investigate the composition of the crystalline phase and the average size of the catalysts. Anatase and rutile phase that are commonly existed in all samples can be seen in Fig. 1. The peaks observed at 25.3°, 38°, and 48° represent the anatase crystalline phase [14], whereas the peaks at 27.42°, 36.2°, 41.3°, 44.2°, 54.45°, and 56.82° represent the rutile crystalline phase. The diffraction peaks of anatase phase (101) widened, and their intensity strengthened with Fe and N doping, indicating lower crystallinity. As previously reported [16], both Fe and N influence crystallite growth, ratio of anatase phase to rutile phase, and mean crystallite sizes. The crystallite sizes of the samples were calculated using the Scherrer equation from the full widths at half maximum of the anatase (101) and rutile (110) peaks (Table 1). The results showed that the particle sizes of Fe-AC/TiO$_2$ are larger than those of AC/TiO$_2$ likely because Fe$^{3+}$ occupies the position of Ti$^{4+}$ in TiO$_2$ and distorts the crystal structure of the host compound owing to the difference in atomic size between Fe$^{3+}$ (0.079 nm) and Ti$^{4+}$ (0.075 nm). Although the crystallite size of N-doped samples was similar to that of undoped samples, their anatase content increased because of N doping (Table 1). The ionic radius of N$^3$− (0.171 nm) is much larger than that of O$^{2−}$ (0.144 nm). This difference in size induces the N atoms to lock the Ti–O species at the interface with the TiO$_2$ domains, thereby preventing anatase to rutile phase transformation when O$^{2−}$ is substituted by N$^3$− in the unit cell. In this study, however, no other peak besides that of TiO$_2$ was detected, which may be because the low concentration of Fe or N in the composition and sol–gel process allows uniform distribution of the dopants to form a solid solution.

According to earlier studies [26], the photocatalytic activity of the photocatalysts could be partially attributed to the amount of ⋅OH induced in the reaction system. The ⋅OH generated on the surface of different photocatalysts was determined using PL emission spectra. Figure 2 shows the of PL spectra from 5 × 10$^{-4}$ mol/L terephthalic acid solution in 2 × 10$^{-3}$ mol/L NaOH under Xe lamp irradiation in the presence of AC/TiO$_2$, Fe-AC/TiO$_2$, and N-AC/TiO$_2$ photocatalysts. It is clear that the PL spectra of the photocatalysts have a strong emission peak at around 450 nm. The rate of ⋅OH radical generation on the AC/

### Table 1 Powders with different dopant concentrations

| Samples          | Anatase size (nm) | Rutile size (nm) | Ratio of A and R % |
|------------------|-------------------|------------------|--------------------|
| AC/TiO$_2$       | 17.9              | 22.9             | 47/53              |
| 0.008 Fe-AC/TiO$_2$ | 19.6              | 24.1             | 49/51              |
| 0.01 Fe-AC/TiO$_2$ | 21.6              | 25.8             | 59/41              |
| 0.012 Fe-AC/TiO$_2$ | 32.4              | 39.3             | 33/67              |
| 0.2 N-AC/TiO$_2$  | 15.4              | 11.5             | 72/28              |
| 0.4 N-AC/TiO$_2$  | 17.2              | 18.6             | 62/38              |
| 0.6 N-AC/TiO$_2$  | 18.8              | 16.3             | 69/31              |
TiO$_2$ surface was lower than that on the other photocatalysts, which indicates that Fe doping changes the crystal structure and optical properties of the photocatalysts. The anatase/rutile ratio is an important factor determining the photocatalytic activity of a photocatalyst through $\cdot$OH formation [28, 29]. The rate of $\cdot$OH formation by Fe-AC/TiO$_2$ is enhanced by the increase in anatase/rutile ratio with increasing amount of Fe. The highest rate of $\cdot$OH formation was observed when the amount of Fe was 0.01 g (Fig. 2). Further increases in the amount of Fe to 0.012 g retained the composite structure of the sample with an anatase/rutile ratio of 33:67 but decreased the formation rate of $\cdot$OH. With N-AC/TiO$_2$, the anatase content significantly increased because of nitrogen introduction, and 0.4 N-AC/TiO$_2$ showed the highest $\cdot$OH formation rate. It can be seen that the photocatalyst showed higher $\cdot$OH formation rate when the anatase/rutile ratio was about 60:40.

HCHO degradation was examined in the presence of undoped and doped AC/TiO$_2$ powders under Xe-lamp irradiation to determine the resulting photocatalytic responses. Regardless of the doping concentration, N- and Fe-doped AC/TiO$_2$ showed higher photocatalytic activities than undoped AC/TiO$_2$ (Fig. 3). Moreover, Fe-doped TiO$_2$ exhibited considerably better activity than N-doped TiO$_2$. This finding is consistent with the results of Li et al. [24] reported that the rate of degradation of methyl orange by Fe/TiO$_2$ is higher than that of N/TiO$_2$ under natural light exposure for 60 min. At low Fe content ($\leq$0.01 g), the photocatalytic activity of Fe-AC/TiO$_2$ gradually increased with increasing Fe content; the best performance was observed when the Fe content was 0.01 g. However, when the Fe content was increased to 0.012 g, the photocatalytic activities of the products decreased. The photodegradation performance of N-AC/TiO$_2$ was similar to that of Fe-AC/TiO$_2$, and 0.4 N-AC/TiO$_2$ showed the highest photocatalytic activity. These results are in accordance with the PL intensities observed (Fig. 2). On the basis of these results, dopant concentrations...
of 0.01 g for Fe and 0.4 g for N were selected for codoping for further studies. Henceforth, the codoped sample is designated as 0.4 N-0.01 Fe-AC/TiO$_2$.

Figure 4 shows the X-ray diffraction (XRD) patterns of the codoped AC/TiO$_2$ catalysts, revealing that the bulk of the 0.4 N-0.01 Fe-AC/TiO$_2$ powder contains both anatase and rutile phases. The width of the (101) plane diffraction peak of anatase became narrower than that of monodoped AC/TiO$_2$. In codoped TiO$_2$, Fe$^{3+}$ replaces Ti$^{4+}$, and the size difference produces strain energy by lattice distortion. N$_3^-$ also replaces O$_2^-$ ions, thereby creating oxygen deficiencies in the TiO$_2$ lattice. These changes allow the rearrangement of Ti$^{4+}$ and O$_2^-$ ions in the lattice to favor anatase to rutile phase transformation [14]. Surface area measurements...
obtained by the single-point Brunauer–Emmett–Teller method using N₂ absorption are shown in Fig. 5. According to the IUPAC classification, the N₂ adsorption isotherms of the samples are of type IV, with a type-H₄ hysteresis loop. Degradation of organic pollutants generally occurs on the surface of AC in the AC/TiO₂ system; thus, the specific surface area of the catalyst plays an important role in this process. In this study, the specific surface area and pore size of AC (Fig. 5, inset) did not significantly change after the ions were codoped in AC/TiO₂ (Table 2).

Figure 6 presents SEM micrograph of the updoped AC/TiO₂, 0.4 N-AC/TiO₂, 0.01 Fe-AC/TiO₂, and 0.4 N-0.01 Fe-AC/TiO₂ photocatalyst. It has been observed that nano-TiO₂ particles were obtained rapidly via microwave heating method and are uniformly dispersed on the AC surface in all samples. Especially, the TiO₂ particles in the codoped samples exhibit uniform, dense, and compact morphologies. The morphology and microstructure of the samples were further analyzed using TEM (Fig. 7). Undoped AC/TiO₂ exhibited a spherical morphology, with average particle sizes of ~23 nm. 0.4 N-AC/TiO₂ also presented a spherical morphology but had a smaller particle size (~18 nm) than undoped AC/TiO₂. Conversely, large crystallites of 26 nm were observed for 0.01 Fe-AC/TiO₂. The TiO₂ particles of 0.4 N-0.01 Fe-AC/TiO₂ were spherical with particle sizes of ~20 nm. The particle sizes obtained through TEM analysis were in good agreement with the result calculated by XRD in Table 1.

Figure 8 shows FTIR spectra of AC/TiO₂, 0.4 N-AC/TiO₂, 0.01 Fe-AC/TiO₂, and 0.4 N-0.01 Fe-AC/TiO₂. The strong peak observed at 3445 cm⁻¹ can be assigned to the bending vibration of -OH or H₂O on the photocatalyst [24], and the vibrations of the hydroxyl moiety were enhanced upon AC/TiO₂ doping. Kim et al. [17] reported that photoinduced holes can attack surface hydroxyl groups and yield surface ⋅OH with high oxidation capability. Thus, the doped AC/TiO₂ may have better photocatalytic activity than undoped AC/TiO₂. The absorption peak at 1630 cm⁻¹ corresponded to the Ti–O structure [30], and the absorption peak at 1385 cm⁻¹ was assigned to the C–H species. Compared with AC/TiO₂ and Fe-AC/TiO₂, N-AC/TiO₂ and N-Fe-AC/TiO₂ displayed additional peaks at approximately 1080 cm⁻¹, which can be assigned to the vibration of the N–Ti bond formed when N atoms are embedded in the TiO₂ network [20]. Fe-O-Ti at 570 cm⁻¹ was not observed, which may be ascribed to its low doping content and high

### Table 2 Physicochemical properties of undoped, mono-doped, and co-doped AC/TiO₂ powders

| Samples         | Anatase size (nm) | Rutile size (nm) | SBET (m²/g) | Band gap (eV) | Ratio of A and R % |
|-----------------|-------------------|------------------|-------------|---------------|-------------------|
| AC/TiO₂         | 17.9              | 22.9             | 532         | 2.86          | 47/53             |
| 0.4 N-AC/TiO₂   | 17.2              | 18.6             | 487         | 2.81          | 62/38             |
| 0.01 Fe-AC/TiO₂ | 21.6              | 25.8             | 562         | 2.79          | 59/41             |
| 0.4 N-0.01 Fe-AC/TiO₂ | 19.3        | 23.4             | 550         | 2.58          | 57/43             |

![Fig. 6 SEM images of undoped, 0.4 N-doped, 0.01 Fe-doped, and 0.4 N-0.01 Fe-codoped AC/TiO₂ powders](image)
dispersion. The peak from 750 to 400 cm\(^{-1}\) bands are related to the bend vibration of Ti-O-Ti bonds [2].

The XPS analysis (Fig. 9) was performed in order to characterize elemental chemical states in undoped AC/TiO\(_2\), 0.4 N-AC/TiO\(_2\), 0.01 Fe-AC/TiO\(_2\), and 0.4 N-0.01 Fe-AC/TiO\(_2\). The binding energies of all of the samples at approximately 459 and 464 eV may be assigned to 2p\(_{3/2}\) and 2p\(_{1/2}\) of Ti, respectively, which indicates that Ti ions are in an octahedral environment [23] and that their valence state (+4) is not influenced by a small amount of doping. However, the binding energy of Ti 2p\(_{3/2}\) of doped AC/TiO\(_2\) is larger than that of undoped AC/TiO\(_2\) because of the interaction of ions with TiO\(_2\), which suggests that the surface acidity of TiO\(_2\) is enhanced and that polar organic pollutants easily adsorb on the catalyst surface [30]. The peaks at approximately 530 eV in the O1s region correspond to the Ti–O bond in TiO\(_2\) and the surface hydroxyl groups of TiO\(_2\) [17]. Upon examination of the Fe2p core level, two peaks at 710 and 723 eV, corresponding to the binding energies of Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\), respectively, of Fe\(_2\)O\(_3\) for both 0.01 Fe-AC/TiO\(_2\) and 0.4 N-0.01 Fe-AC/TiO\(_2\) samples, may be observed.
XPS spectra of undoped, 0.4 N-doped, 0.01 Fe-doped, and et al. Nanoscale Research Letters (2015) 10:360 powders: (N1s : 399.1 binding, so the peaks at 399.1 and 399.6 eV can be attributed to the anionic N\(^-\) in the interstitial N form. Asahi et al. [32] pointed out that N2p states can mix with O2p states, and thus, N atoms can substitute O atoms in the TiO\(_2\) crystal lattice. The XPS results demonstrate that Fe and N were successfully codeposited into the TiO\(_2\) lattice of 0.4 N-0.01 Fe-AC/TiO\(_2\).

The UV–vis absorption spectra of prepared AC/TiO\(_2\), 0.4 N-AC/TiO\(_2\), 0.01 Fe-AC/TiO\(_2\), and 0.4 N-0.01 Fe-AC/TiO\(_2\) photocatalysts are shown in Fig. 10 inset. In general, the fundamental absorption edge of elemental doped TiO\(_2\) can redshift toward the visible light region. This phenomenon is more apparent in codoped AC/ TiO\(_2\) than in N- and Fe-doped AC/TiO\(_2\) in previous studies. TiO\(_2\) is known as an indirect semiconductor, for which the Kubelka–Munk function between the absorption coefficient (a) and the incident photon energy (h\(\nu\)) can be written as \(a = \frac{Bi(h\nu-E_2)}{h\nu}\), where Bi is the absorption constant for indirect transitions, h\(\nu\) is the photon energy, and E\(_2\) is the band gap energy. Plots of (ah\(\nu\))\(^{1/2}\) versus h\(\nu\) from the spectral data are presented in Fig. 10. After monodoping, the band gap value decreased from 2.86 eV (AC/TiO\(_2\)) to 2.81 and 2.79 eV for 0.4 N- and 0.01 Fe-AC/TiO\(_2\) powders, respectively. However, for the codoped powder (0.4 N-0.01 Fe-AC/ TiO\(_2\)), the absorption edge decreased continuously in the lower energy range (2.58 eV). This behavior, previously reported in different doped TiO\(_2\) nanostructures, is usually interpreted as the result of the introduction of new intra-gap energy levels [33]. For N-AC/TiO\(_2\), the N that enters into the TiO\(_2\) lattice provides a new occupied orbital between the valence band (VB) of the O2p orbital and the conduction band (CB) of the Ti3d orbital, forming new energy levels between the VB and the CB within the band gap of TiO\(_2\) [22]. Electrons from the original VB can migrate into the mid-band gap energy level, leaving a hole in the VB. Xing et al. [34] showed that N doping effectively reduces the band gap of TiO\(_2\) by generating an isolated N2p narrow band above the O2p valence, which is formed by incorporation of N atoms into the TiO\(_2\) lattice. When Fe\(^{3+}\) was doped into AC/ TiO\(_2\), a new energy level was formed below the CB of TiO\(_2\). The Fe\(^{3+}\) ion can become the trapping site of photoinduced electrons because of the reducibility of these electrons, thereby reducing Fe\(^{3+}\) to Fe\(^{2+}\). Fe\(^{2+}\) ions then become the trapping site of holes, as holes feature oxidizability [10]. These findings suggest that N and Fe codoping of AC/TiO\(_2\) exerts a synergistic effect on reducing the band gap. Band gaps in semiconductor materials are closely related to the wavelengths they absorb and decrease with increasing absorption wavelength. Therefore, compared with N- and Fe-doped AC/TiO\(_2\), codoped AC/TiO\(_2\) may be expected to be a more active photocatalyst.
The photocatalytic activity of 0.4 N-0.01 Fe-AC/TiO$_2$ was compared with the monodoped (0.4 N-AC/TiO$_2$ and 0.01 Fe-doped AC/TiO$_2$) and undoped-AC/TiO$_2$ for photodegradation of HCHO (Fig. 11). The codoped AC/TiO$_2$ samples showed higher photocatalytic efficiency than other photocatalysts surveyed during the degradation process. Approximately 93% of the available HCHO was degraded in 120 min. The most important factor influencing the observed enhanced catalytic activity is the ability of the doped AC/TiO$_2$ to absorb large amounts of visible light and produce $\cdot$OH. The PL spectra of 0.4 N-0.01 Fe-AC/TiO$_2$ were compared with those of the monodoped and undoped AC/TiO$_2$ photocatalysts (Fig. 12). The generation rate of $\cdot$OH radicals on the 0.4 N-0.01 Fe-AC/TiO$_2$ surface was higher than those of the other photocatalysts, consistent with the photocatalytic efficiency illustrated in Fig. 11.

Several factors may result in the high generation rate of $\cdot$OH radicals and photocatalytic activity. First, codoped AC/TiO$_2$ contains anatase (57%) and rutile (43%) phases, which reduce the recombination of photogenerated electrons and holes and enhance the formation rate of $\cdot$OH [28]. Electrons from the VB can be excited and moved to the CB of TiO$_2$ by photon absorption. In undoped AC/TiO$_2$, the band gap energy between the VB and CB of TiO$_2$ is 3.86 eV. Fe ion...
occupancy in the Ti sites of the TiO$_2$ lattice of Fe-AC/TiO$_2$ can be seen in the XPS results shown in Fig. 9. When the catalysts were subjected to solar irradiation, the 3d electrons of Fe$^{3+}$ were excited into the CB of TiO$_2$, which introduces a new energy level [31]. Electrons can be excited in two stages; the first stage involves electron excitation from lower new states to the CB photon adsorption and the second stage involves excitation from the VB to the lower Fe$^{3+}$ states. Thus, an interaction among the d electrons of Fe and the TiO$_2$ CB or VB occurs, eventually narrowing the energy gap of TiO$_2$ through the formation of new intermediate energy levels. In N-AC/TiO$_2$, the Ti–N linkage (Fig. 8) is believed to lead to the formation of the N1s peak (Fig. 9), which is due to substitutional N doping in the TiO$_2$ lattice. Doping of N into TiO$_2$ forms a new state on N1s just above the O2p VB, leading to the strong absorption of visible light and enhancing the separation efficiency of photoinduced electrons and holes. Fe$^{3+}$ and N doping can suppress the recombination rate of electron–hole pairs and improve the photocatalytic activity of the resultant catalysts. Therefore, the cooperation of Fe$^{3+}$ and N induces the formation of new energy levels close to the CB and VB, respectively, leading to a much narrower band gap and greatly improved photocatalytic activity.

To confirm the stability and durability, the photocatalytic performances of 0.4 N-AC/TiO$_2$, 0.01 Fe-AC/TiO$_2$, 0.4N-0.01 Fe-AC/TiO$_2$...
and 0.4 N-0.01 Fe-AC/TiO$_2$ under visible light for the degradation of HCHO were investigated in four cycles (Fig. 13). The photocatalysts exhibited no apparent decrease in photocatalytic degradation of HCHO after four cycles of reuse. Among the samples surveyed, 0.4 N-0.01 Fe-AC/TiO$_2$ showed the best photochemical stability, degrading 83% of the available HCHO within 120 min even after four recycles. These results indicate that the photocatalysts present excellent stability and durability for practical applications.

**Conclusion**

N-Fe-AC/TiO$_2$ photocatalyst was successfully synthesized through an efficient and rapid microwave-assisted sol–gel method. The sphere-like TiO$_2$ showed anatase and rutile phases with a particle size of 20 nm in codoped AC/TiO$_2$, which features a specific surface area of 550 m$^2$/g. N and Fe ions occupied the TiO$_2$ lattice, replacing some Ti$^{4+}$ and O$^{2-}$, respectively, and extending the absorption range of the catalyst to the visible light region. The N-Fe-AC/TiO$_2$ photocatalyst exhibited better photocatalytic activity than undoped and Fe/N-monodoped AC/TiO$_2$, which degraded 93% of HCHO within 120 min under Xe-lamp irradiation. N-Fe codoping may have induced the formation of new states between the VB and CB. Moreover, N-Fe codoping can promote the separation of photogenerated electrons and holes to accelerate the transmission of photocurrent carriers. The produced photocatalyst can be easily recycled, which reveals its enhanced stability. These results suggest that the prepared (N, Fe)-codoped AC/TiO$_2$ exhibits the characteristics of a highly effective photocatalyst under visible light irradiation.

**Competing interests**
The authors declare that they have no competing interests.

**Authors’ contribution**

FT was involved in the design, development of material and photoelectrochemical measurements, and manuscript writing; ZW (Zhansheng Wu) supervised the whole work and helped in manuscript writing; YT performed the optical characterizations; GC and ZW (Zhlin Wu) revised the manuscript. All authors read and approved the final manuscript.

**Acknowledgements**

This work was supported financially by the National Natural Science Foundation of China (51262025), International scientific and technological cooperation project of Xinjiang Bingtuan (2013BC002), and Graduate Research Innovation Project in Xinjiang (XJGR2014053).

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Received: 2 August 2015 Accepted: 28 August 2015 Published online: 16 September 2015

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