Synthesis of Visible-Light-Responsive Cu and N-Codoped AC/TiO₂ Photocatalyst Through Microwave Irradiation

Fei Tian, Zhansheng Wu*, Yujun Yan, Bang-CE Ye and Dandan Liu

Abstract

N–Cu-activated carbon (AC)/TiO₂ nanoparticles were prepared by the sol-gel technique through microwave irradiation to modify the visible-light response of TiO₂. Their structure, surface chemical composition, and optical absorption properties were characterized. The results showed that the codoped particles had a higher surface area and smaller particle size than pure AC/TiO₂ and monodoped AC/TiO₂. X-ray photoelectron spectroscopy of N–Cu-AC/TiO₂ showed that Cu atoms replaced Ti atom sites, whereas N atoms occupied the O atom sites and interstitial sites in the TiO₂ lattice, which changed the electric and band-gap structures of the photocatalyst. N or Cu monodoping of AC/TiO₂ reduced the energy band gap of TiO₂ from 2.86 eV to 2.81 or 2.61 eV, respectively. In (N, Cu)-codoped AC/TiO₂, N and Cu were incorporated into the TiO₂ framework and narrowed the band gap of TiO₂ to 2.47 eV, causing a large red shift and enhancing visible-light utilization efficiency. Photocatalytic activities were further examined by formaldehyde degradation under visible-light irradiation. N–Cu-AC/TiO₂ was found to have the highest activity (ca. 94.4 % formaldehyde degradation efficiency) and to be easily recyclable. These results show an important and innovative method of improving AC/TiO₂ activity by modifying the nonmetallic and metallic species.

Keywords: N–Cu-codoped, TiO₂, Sol-gel, Microwave irradiation, Formaldehyde

Background

Nanocrystalline TiO₂ has potential for application to photocatalytic degradation of harmful pollutants dispersed in the environment because of its relatively low cost, nontoxicity, favorable optoelectronic properties, and excellent chemical stability [1, 2]. However, the photocatalytic activity and utilization efficiency of visible light are limited because of the small specific surface area and large band gap (3.2 eV) of pure TiO₂ [3–5]. Adsorption can be increased by preparing a porous material-loaded TiO₂ photocatalyst, and this has drawn much attention. Given that activated carbon (AC) has a large specific surface area, the reaction rate constant of AC/TiO₂ is high for the photocatalytic degradation of organic pollutants [6]. In the work of Pastravanu et al., 92 % methyl orange conversion was achieved after 170 min irradiation using AC/TiO₂ with a large surface area of 357 cm²/g [7].

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TiO$_2$ lattice to generate energy levels just above the top of the TiO$_2$ valence band [14–16]. In terms of performance, nitrogen doping is undoubtedly the most impressive solution for improving the visible-light response of TiO$_2$ [17–20]. Recently, the concept of second-generation TiO$_2$-based materials has been introduced, wherein codoping with two dopant elements produces a synergistic effect to enhance the visible-light absorption efficiency and reduce the recombination processes of the photogenerated charges [21–24]. A Ag/N-codoped TiO$_2$ system was prepared using a sonication-assisted sol-gel method by Mothi et al. [25] who found that the system was highly active for the photoconversion of 9-(N,N-dimethylaminomethyl) anthracene.

Microwave-assisted preparation of catalytic materials is gaining increased attention [26]. This method is an efficient alternative because it allows swift heating to the required temperature and extremely rapid rates of crystallization, leading to simplification of the preparation procedure [27–29]. However, codoping Cu and N to TiO$_2$ to reduce its band gap and load it onto the AC through a microwave-assisted method has rarely been reported. Thus, an important and innovative method has been attempted to enhance the photodegradation activity of AC/TiO$_2$ with visible-light response via modification with Cu and N through microwave irradiation.

In the present paper, AC/TiO$_2$, N, Cu-monodoped AC/TiO$_2$ and N/Cu-codoped AC/TiO$_2$ nanoparticles were synthesized by a sol-gel method under microwave assistance. The phase structure, morphology, specific surface area, and optical properties were investigated using a variety of techniques. Studies on the use of catalysts for photodegradation of HCHO in aqueous solution under visible-light irradiation are also in progress. The concept used in this research can be further applied to modify other materials for improved photocatalytic performance.

**Main Text**

**Experimental Methods**

**Catalyst Preparation**

AC was prepared by the means described in a previous study [30]. The obtained AC samples were pretreated by addition to HNO$_3$ solution, then being left for 24 h. The mixture was filtered using distilled water until it became neutral. The pretreated AC was then dried and stored until use. All reagents were of analytical grade. The TiO$_2$ gel/sol was obtained by the conventional sol-gel method [31]. 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. A clear, pale-yellow TiO$_2$ sol was then obtained. Pretreated AC (10 g) was added to TiO$_2$ sol (100 g). The mixture was placed in an air-dry 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 Cu-doped AC/TiO$_2$, 0.44 g of Cu(NO$_3$)$_2$ was mixed with solution B, while for N-doped AC/TiO$_2$, 1.71 g of urea was dissolved in solution B. The doped N and Cu in the samples of N-AC/TiO$_2$ and N–Cu-AC/TiO$_2$ were 0.04 g and 0.01 g, respectively. For N, Cu-codoped AC/TiO$_2$, the sample was noted as 0.04 N-0.01 Cu-AC/TiO$_2$.

**Catalyst Characterization**

The crystal structures of the prepared samples were measured by X-ray diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer. Each sample was scanned using Cu-Ka radiation with an operating voltage of 40 kV and an operating current of 200 mA. The surface micromorphology of the photocatalyst was characterized by scanning electron microscopy (SEM; S4800, Hitachi Ltd.) at an accelerating voltage of 15 kV. Transmission electron microscopy (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 4000–400-cm$^{-1}$ range by the KBr pellet technique. UV-vis diffuse reflectance spectra were obtained with a powder UV-vis spectrophotometer (U-4100, Hitachi Ltd.). The specific surface area (SBET, m$^2$/g) was calculated using the Brunauer–Emmett–Teller (BET) equation. X-ray photoelectron spectroscopy (XPS) analysis of the samples was conducted using a PHI5700 ESCA system equipped with an Mg Kα X-ray source (1253.6 eV) under a vacuum pressure <10$^{-6}$ Pa. The formation rate of ·OH at the photo-illuminated sample/water interface was detected by photoluminescence (PL) using terephthalic acid (TA) as a probe molecule. PL spectroscopy of the synthesized products was undertaken 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 the HCHO solution. In a typical test, 50 mg of catalyst was added to 50 mL of HCHO solution (30 mg/L, pH = 6.8). The mixture was then irradiated under a 500 W Xe lamp (any irradiation below 420 nm was removed by using a cut-off filter) to degrade HCHO. The distance between the reactor and lamp housing was 8.5 cm. The concentration of HCHO was measured using an ultraviolet visible spectrophotometer under the maximum absorption wavelength of 413 nm.
The removal efficiency, $\eta$, 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.

The rate of ·OH in the photocatalytic reactions was evaluated by adding 50 mL of terephthalic acid in a manner similar to the above photodegradation experiment. For terephthalic acid, to ensure solubility, solutions were prepared in dilute ($2 \times 10^{-3}$ mol/L) NaOH solution. Photocatalyst in the solution was magnetically stirred and illuminated under visible-light irradiation. The photocatalytic experiment was carried out in the presence of 2 mL (10.66 mol/L) t-BuOH, a radical scavenger [32].

**Discussion**

**XRD and BET Characterization**

The XRD patterns of the different samples are presented in Fig. 1. The peaks observed at 25.3°, 38°, and 48° represent the anatase crystalline phase, and the peaks at 27.42°, 36.2°, 41.3°, and 44.2° represent the rutile crystalline phase. These all agree with previously reported values [5]. It can be seen that the TiO$_2$ crystals obtained via the microwave radiation method with only 15 min, which is conducive to stabilize the AC structure and makes for a more energy-efficient process compared with the traditional heating method [7]. In addition, an additional peak at 43.3°, corresponding to a Cu species, was obtained when Cu was codoped, indicating the formation of Cu$^0$ [9]. The Cu$^0$ was formed according to the following chemical reaction [14]:

Cu$^{2+}$-$\text{TiO}_2$ + e$^-$ @Cu$^+$-$\text{TiO}_2$

Cu$^+$-$\text{TiO}_2$ + e$^-$@Cu$^0$-$\text{TiO}_2$

The XRD patterns show that both the monodoped and codoped AC/TiO$_2$ can prevent the phase transformation process from anatase TiO$_2$ to rutile from occurring, as shown in Table 1. This may be favorable with respect to degradation of the catalyst [33]. The average crystal sizes of the nanoparticles have been obtained from the Scherrer equation:

$$D = \frac{k \lambda}{\beta \cos \theta},$$

where $D$ is the average crystallite diameter (nm), $k$ is the X-ray wavelength, $\theta$ is the Bragg angle, and $\beta$ is the line broadening at half the maximum intensity. The mean crystallite sizes of the doped-TiO$_2$ are slightly smaller than that of its precursor (Table 1). In the codoped AC/TiO$_2$, the entrance of Cu$^{2+}$ (0.72 Å) into the TiO$_2$ crystal lattice to substitute Ti$^{4+}$ (0.68 Å) produces strain through lattice distortions [4], whereas when N$^-$ replaces O$^{2-}$ ions, it creates oxygen deficiencies in the TiO$_2$ lattice. These features allow the rearrangement of Ti$^{4+}$ and O$^{2-}$ ions in the lattice to interfere with the crystallite growth mechanism and phase transformation [14]. The specific surface area of the catalyst also has an important effect on the degradation of organic compounds because of the synergistic effect of AC and TiO$_2$ [31]. The BET surface areas of the AC/TiO$_2$ before and after doping were measured by N$_2$ adsorption/desorption (Fig. 2) at a liquid N$_2$ temperature of 78 K, as shown in Table 1. The doping of ions has little effect on the surface area of activated carbon, and...
the N–Cu-AC/TiO₂ maintained a large surface area of 548 m²/g.

**Morphology of Photocatalysts**

The surface structure, particle morphology, and crystal-lite sizes of the photocatalysts before and after doping were investigated by SEM and TEM. SEM images of various photocatalyst powders are presented in Fig. 3a. Undoped AC/TiO₂ exhibited smooth surfaces with a TiO₂-particle-like morphology with irregular spherical shapes. Rough surfaces of AC/TiO₂ spheres with obvious granular features were produced through N or Cu doping. In the case of the N–Cu-AC/TiO₂ sample, the TiO₂ particle sizes are quite uniform in a nearly spherical morphology and are well-distributed on the AC surface, as shown in the SEM images. Yi et al. [14] also reported that nonmetal and metal-codoped TiO₂ present homogeneous morphologies, and this may be beneficial to enhanced catalytic efficiency. The TEM image (Fig. 3b) shows the presence of 10–40 nm powders, consistent with those calculated by XRD (Table 1). However, Cu cannot be observed in the TEM image, suggesting that Cu and N are doped into the TiO₂ framework. XPS would confirm this.

**FTIR Spectra**

The FTIR spectra of various photocatalysts are shown in Fig. 4. All samples show similar FTIR spectra, indicating that the TiO₂ structure did not change after doping with N and Cu. The absorption peak at 3445 cm⁻¹ is attributed to the stretching vibration of surface hydroxyl groups—this could yield surface -OH with a high oxidation capability [7]. The vibrations of the hydroxyl moiety were enhanced after AC/TiO₂ doping (Fig. 4). Thus, doped AC/TiO₂ may improve photocatalytic activity relative to undoped AC/TiO₂. A band at around 1630 cm⁻¹ is attributed to the bending vibration of the Ti-O bond. Compared with Cu-AC/TiO₂, N-AC/TiO₂ and N–Cu-AC/TiO₂ display an additional peak at approximately 1080 cm⁻¹ that can be assigned to the

| 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               |
| N-AC/TiO₂   | 17.2              | 18.6             | 487         | 2.81          | 62/38               |
| Cu-AC/TiO₂  | 16.5              | 20.6             | 508         | 2.61          | 54/47               |
| N–Cu-AC/TiO₂| 17.8              | 19.7             | 548         | 2.47          | 57/43               |
vibration of the N–Ti bond formed when N atoms are embedded in the TiO₂ network [15].

**UV-vis Diffuse Reflectance Spectroscopy**

UV-vis diffuse reflectance spectroscopy permits the study of the optical properties and the TiO₂ framework of the samples. Figure 5 (inset) shows the diffuse reflectance spectra of the prepared photocatalyst samples in the range 200–700 nm. The spectrum for pure AC/TiO₂ shows an absorption edge of approximately 412 nm, whereas the N, Cu-monodoped samples show a red shift in the absorption edge and a strong absorption in the visible-light region. The absorption wavelengths of N, Cu-codoped AC/TiO₂ increased to 450 nm.

Application of the Kubelka–Munk [8] conversion can explain the red shift:

\[
\alpha h\nu = A (h\nu - E_g)^{1/2},
\]

where \( \alpha, h\nu, E_g, \) and \( A \) are the absorption coefficient, photon energy, band-gap energy, and a constant, respectively. In accordance with the above equation, a modified plot of the Kubelka–Munk function versus the energy of the exciting light was used to determine the band gap of the samples. A band-gap value of 2.86 eV was obtained for AC/TiO₂. According to data reported in literature, it is well-known that bulk anatase and rutile have the direct band-gap energy of 3.2 and 3.0 eV.
respectively [3, 5]. This means that the radiation wavelength used for electron excitation of the titania should be smaller at about 387 nm (UV region). The band gap of TiO$_2$-coated on AC samples decreased to 2.86 eV, indicating an influence of the AC support on the optical properties of TiO$_2$ photocatalyst. Coromelci-Pastravanu et al. [7] also reported that the optical band gap of TiO$_2$-coated mesoporous carbon samples decreases slightly comprised with pure TiO$_2$. The carbon-based composites were found to be able to promote a rapid photoinduced charge separation and a slow charge recombination, by accepting photogenerated electrons from the photocatalytic TiO$_2$ nanoparticles. After N doping, the band gap of TiO$_2$ decreased to 2.81 eV and the band gap of Cu-AC/TiO$_2$ was about 2.61 eV. Meanwhile, significant narrowing of the band gap to approximately 2.47 eV was observed after N, Cu codoping. This significant band-gap reduction is associated with charge-transfer, corresponding to the electronic excitation from the valence band (VB) to the conduction band (CB). Reduction in the band gaps correspondingly reduced the energy required for electron transition from the VB to the CB, thus shifting the optical absorption to a lower energy. This large decrease in band gap for the codoped catalyst may be attributed to the formation of mixed energy levels between the VB and CB. Thus, Cu and N doping promotes the visible absorption of the catalyst and plays a significant role in enhancing the photocatalytic activity of the catalysts.

XPS Characterization

XPS analysis of different photocatalysts was performed to examine the chemical states of each element (shown in Fig. 6). From the XPS spectra, all samples display peaks at about 458 and 464 eV, and these can be assigned to the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ of Ti$^{4+}$ states, respectively, in the Ti2p core level [10]. Thus, the Ti is found as Ti$^{4+}$ in the samples and this was not significantly affected by the incorporation of Cu and N. When investigating the Cu2p core level of Cu-AC/TiO$_2$ and N–Cu-AC/TiO$_2$, Cu was found to be present only in the oxidation state of Cu(II), with corresponding peaks at 932.8 (Cu-AC) and 933.2 (N–Cu-AC) [9]. This finding signifies that Cu is incorporated into the TiO$_2$ lattice, in agreement with the XRD results. The peak at approximately 400 eV can be attributed to the interstitial N atoms in N–O bonds or Ti–(N–O) bonds in the case of N-AC/TiO$_2$ and Cu–N-AC/TiO$_2$, indicating that some nitrogen groups are adsorbed on the TiO$_2$ as the interstitial N-doping [19]. An isolated level is formed above the VB because of the Cu-3d orbital in the case of Cu-doped AC/TiO$_2$ [10], and this decreased the energy required for electronic excitation from the VB to CB, in accordance with the UV-vis results. Lin et al. [2] also reported that Cu doping makes the absorption edge of TiO$_2$ red shift because of the transition of the excited 3d electrons from the Cu$^{2+}$ ions to the CB of TiO$_2$.

PL Spectra

The ·OH radicals in the reaction systems were detected by PL (Fig. 7). The radicals were generated on the four samples after illumination. The formation rate of the ·OH radicals on the AC/TiO$_2$ powders increased after Cu, N doping on TiO$_2$, and the generation rate of the ·OH radicals on the N–Cu-AC/TiO$_2$ surface was higher than that of the other photocatalysts. A previous study reported that ·OH is the major reactive species for photocatalytic oxidation [33]. Sin et al. [34] also found that ·OH was the main active species during the Eu/ZnO degradation of phenol. The production rate of ·OH follows the order N–Cu-AC/TiO$_2$ > Cu-AC/TiO$_2$ > N-AC/TiO$_2$ > AC/TiO$_2$. 

![Fig. 4 FTIR spectra of AC/TiO$_2$, N-AC/TiO$_2$, Cu-AC/TiO$_2$, and N–Cu-AC/TiO$_2$.](image)

![Fig. 5 Band-gap energies and UV-vis diffuse reflectance spectra (inset) of different photocatalysts.](image)
Photocatalytic Activity of Photocatalysts
The photocatalytic activity of these photocatalysts was evaluated by degradation of HCHO, as shown in Fig. 8. Under identical experimental conditions, N–Cu–AC/TiO₂ showed much higher activities (94.38 % degradation efficiency) than those of pure AC/TiO₂ (31.4 % degradation efficiency), N-AC/TiO₂ (59.9 % degradation efficiency), and Cu-AC/TiO₂ (83.6 % degradation efficiency), while the removing efficiency of HCHO without photocatalyst under irradiation and with N–Cu-AC/TiO₂ in the dark for 150 min was about 2.74 and 8.67 %, respectively. First, the photocatalytic activity of the products corresponds to the generation rate of the ⋅OH radicals. Photocatalysis of HCHO in the presence of radical scavengers reduced reaction efficiency from 94.38 to 49.89 %, indicating that the hydroxyl radical initiated degradation is the dominant route over degradation by reactive electron-hole pairs on the catalyst surface and photolytic cleavage. The anatase/rutile ratio is an important factor in determining the photocatalytic activity of the samples through the formation of ⋅OH. The ratio of anatase/rutile (54/47) in Cu-AC/TiO₂ is greater than that of pure AC/TiO₂ (47/53). This resulted in more ⋅OH on the Cu-AC/TiO₂ surface under irradiation. In N, Cu-codoped AC/TiO₂, the ratio of anatase/rutile increased to 57/43, which led to the highest ⋅OH formation rate of the reaction systems studied. Commonly, the composite of two phases of the same semiconductor is beneficial for reducing the combination of photogenerated electrons and holes [1], thereby enhancing the ⋅OH.

![Fig. 6 XPS spectra of Ti2p, Cu2p, and N1s levels of various photocatalysts](image-url)
formation rate. In N-AC/TiO\(_2\), the formation rate of \(\cdot \text{OH}\) decreased with the increase in anatase/rutile ratio to 62/38, implying that the optimal anatase to rutile ratio is likely approximately 57/43.

The most important factor for the enhancement of photocatalytic activity of doped AC/TiO\(_2\) is that Cu substitution of the partial Ti leads to an isolated energy band formation between the VB and CB in the band structure of TiO\(_2\). The formation of \(\cdot \text{OH}\) is attributed to the transition of electrons between the VB and CB.

When doped with Cu, a two-step optical transition will occur because of the formation of the newly isolated energy band and the decrease in band-gap energy between the VB and the CB of TiO\(_2\), as shown in Fig. 5. This increased the optical response of Cu-doped AC/TiO\(_2\).

In N-AC/TiO\(_2\), the Ti–N linkage may lead to formation of an N1s peak because of substitutional N doping in the TiO\(_2\) lattice [23]. Doping of N into TiO\(_2\) forms a new state on N1s, just above the VB, leading to strong absorption of visible light and enhancement in the separation efficiency of the photoinduced electrons and holes. The significant enhancement of photocatalytic activity of N, Cu-codoped AC/TiO\(_2\) in this study can be attributed to the synergistic effect of N, Cu codoping. Doping of the TiO\(_2\) lattice with Cu can lead to O vacancy production, which in turn facilitates N doping. Both Cu and N doped on TiO\(_2\) decreases the electronic transition energy and improve the photocatalytic activity of N–Cu-AC/TiO\(_2\).

**Mechanism of N, Cu-Codoped AC/TiO\(_2\)**

Figure 9 illustrates the band structures of the N, Cu-codoped AC/TiO\(_2\) materials. Possible mechanisms responsible for the observed improvement in photocatalytic activity of the new material under visible-light irradiation are proposed. When nitrogen is incorporated into the TiO\(_2\) lattice, the N2p states are positioned above the TiO\(_2\) CB, which increases the CB energy by 0.46 eV [35]. TiO\(_2\) band-gap narrowing also takes place, as shown in procedure 1 and compared with 1\* in Fig. 9. Thus, the response light of N-AC/TiO\(_2\) is increased to 425 nm compared with 415 nm for pure AC/TiO\(_2\) (Fig. 5). For the Cu co-modified N-AC/TiO\(_2\), the light response increased to 465 nm (Fig. 5) because the band energy of TiO\(_2\) decreased to 2.47 eV (Table 1). In N–Cu-AC/TiO\(_2\), the Cu d-states lie deep in the band gap that lies below the CB of TiO\(_2\) [10]. In the case of visible-light irradiation, TiO\(_2\) can be excited at a wavelength <465 nm (procedure 1). Thereafter, the excited electron may be transferred from the TiO\(_2\) CB to the Cu CB (procedure 2), thereby improving the charge separation and allowing oxidation/reduction processes to occur on the TiO\(_2\) VB/Cu CB. Yang et al. [36]
also reported that Cu species have smaller band gaps and higher work functions than does bare TiO$_2$, so the electron can transfer from the CB of TiO$_2$ to a metallic copper ion. The excited electrons can be further scavened by surface-adsorbed H$_2$O on the TiO$_2$ to generate -OH and other active species. Moreover, the electron from the Cu VB may also be transferred to the TiO$_2$ CB (procedure 3), creating a hole in the Cu VB. The additional charge separation significantly improves the photocatalytic performance. In addition, the mixed phases of anatase and rutile in TiO$_2$ may inhibit the electron-hole recombination of TiO$_2$ and thus enhance the photocatalytic ability [37, 38]. Thus, the photocatalytic performance enhancement of TiO$_2$ may be attributed to the synergistic effect of Cu and N co-implantation, which resulted in a change in the electronic and band-gap structures.

Reusability of the Catalyst
The stability and recyclability of a photocatalyst are important for its potential application. To evaluate the stability of the N–Cu-AC/TiO$_2$ catalysts, the nanoparticles were collected after the photocatalytic reaction, and then the nanoparticles were put in ethanol solution with ultrasonic treatment for 2 h, dried at 120 °C for 4 h. The photocatalytic test was repeated up to seven times while keeping all other parameters constant. Figure 10 shows that, after the seven recycling experiments, the N–Cu-AC/TiO$_2$ particles retained their high photocatalytic activity, and 80.2 % of the HCHO was degraded. This result indicated that the N, Cu-codoped AC/TiO$_2$ prepared in the present study had good photocatalytic stability and allowed for possible repeat utilization.

Conclusion
A novel and simple technique for incorporating N and Cu on TiO$_2$ nanoparticles loaded on AC was presented. The nanoscale TiO$_2$ showed anatase and rutile phases with a particle size of 18 nm, an appropriate proportion in codoped AC/TiO$_2$, and a specific surface area of 548 m$^2$/g. Nitrogen and Cu may occupy the internal TiO$_2$ crystal framework, replacing some Ti$^{4+}$ and O$^{2-}$, respectively, and extending the band-gap excitation to the visible region. The obtained N–Cu-AC/TiO$_2$ shows a distinctive absorption band in the visible region and presents the lowest band-gap value among all of the samples studied. The N–Cu-AC/TiO$_2$ photocatalyst exhibited good photocatalytic activity for the degradation of HCHO under visible-light irradiation. The incorporation of Cu and N may decrease the required energy for electronic transitions, thereby improving the photocatalytic activity. Furthermore, the produced photocatalyst can be
easily recycled and exhibits enhanced stability. Therefore, using N, Cu-doped AC/TiO₂ for pollutant photodegradation is a practical method for purifying water under visible light.

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

Authors’ contributions
FT and ZSW provided the idea and drafted the manuscript. FT, BCY, and XQC designed and carried out the experiment. Both authors read and approved the final manuscript.

Authors’ information
Master FT is a student of Shihezi University. His major research area is in material science.

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