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Synthesis of core–shell N-TiO₂@CuO_x with enhanced visible light photocatalytic performance†

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In this paper, a core–shell N-TiO₂@CuO_x nanomaterial with increased visible light photocatalytic activity was successfully synthesized using a simple method. By synthesizing ammonium titanyl oxalate as a precursor, N-doped TiO₂ can be prepared, then the core–shell structure of N-TiO₂@CuO_x with a catalyst loading of Cu on its surface was prepared using a precipitation method. It was characterized in detail using XRD, TEM, BET, XPS and H₂-TPR, while its photocatalytic activity was evaluated using the probe reaction of the degradation of methyl orange. We found that the core–shell N-TiO₂@CuO_x nanomaterial can lessen the TiO₂ energy band-gap width due to the N-doping, as well as remarkably improving the photo-degradation activity due to a certain loading of Cu on the surfaces of N-TiO₂ supports. Therefore, a preparation method for a novel N, Cu co-doped TiO₂ photocatalyst with a core–shell structure and efficient photocatalytic performance has been provided.

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Introduction

Metallic oxides are important and widely used in catalysis, environmental science, ceramics, electronic devices and materials chemistry.^{1–4} However, there are some disadvantages to single metallic oxides.^{5–7} For example, anatase TiO₂ as a photocatalyst has many advantages, such as: cheapness, nontoxicity, stable chemical properties, degradation of organic matter and so on.^{8–13} In the past twenty years, it has received wide attention. However, the band gap of 3.2 eV can only respond to UV light with a wavelength less than 387 nm.^{14–17} The energy of ultraviolet light in sunlight only accounts for about 5%, so this seriously restricts the application of this photocatalyst to solar energy. If the scope of TiO₂ light absorption can be effectively expanded to visible light, its application will be greatly expanded, so this photocatalyst can make full use of solar energy, and the two major problems facing humanity, the energy crisis and environmental pollution, will be effectively solved.

Since Asahi¹⁸ reported the semiconductor TiO₂ photocatalytic degradation of organic pollutants, crucial progress has been made by the doping of the element N, which causes the decrease of the band-gap of TiO₂ because of the element N. The amount of research on TiO₂ doped with N has been increasing.^{19–23} In the process of the preparation of TiO₂, a variety of physical and chemical methods are needed to prepare N-doped TiO₂. These methods, without exception,

require nitrogen sources. On this basis, Fang²⁴ found that a N-doped TiO₂ photocatalyst could be obtained using ammonium titanyl oxalate as the precursor, and the efficiency of the process was greatly improved.

At the same time, the precious metals that have been reported with TiO₂ to improve the photocatalytic performance include precious metals such as Pt, Ag, Ir, Au, Ru, Pd, Rh and so on, among which there are the most reports about Pt, followed by Pd and Au.^{25–28} The photocatalytic performance after Pt modification is the best, but comes with a higher cost. Ag modification leads to relatively less toxicity and has a lower cost. Therefore, the preparation of highly active noble metal doped photocatalysts by Ag deposition and modification is considered to be one of the important directions to improve photocatalytic activity in the future. Cu, Ag and Au elements belong to the same group of the periodic table IB, which means they may have a similar catalytic activity in the oxidation colour-fading reaction. However, the catalytic activity of CuO_x was obviously lower than those of AgO_x and AuO_x due to the catalytic reaction on the surface of CuO_x which has been shown to have a higher activation energy in previous research.^{29–31}

In this paper, from the perspective of energy utilization and catalytic activity, we composed a new TiO₂ compound with N and Cu co-doped by a two-step method. When TiO₂ was synthesized, N doping was completed simultaneously using a suitable synthesis in the first step, which is different to the traditional method. There are many benefits to employing the new synthetic method of N-doped TiO₂, such as: excellent reproducibility of sample synthesis, a better N-doped effect, and outstanding stability of catalytic activity based on “zero” loss of the N element. In the second step, the core–shell structure N-TiO₂@CuO_x catalyst was prepared by a precipitation method.

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The light energy which was absorbed by N doped TiO₂ could be translated into the internal energy which was employed across the high energy barrier mentioned above. Then, their structures were examined with XRD, TEM, BET, and XPS. Lastly, we compared their catalytic activities using methyl orange degradation experiments. Therefore, an N, Cu co-doped TiO₂ photocatalyst has been synthesized using a simple and low-cost process, and its core-shell structure and efficient photocatalytic performance have been studied.

Results and discussion

Fig. S1† displays the concentration of methyl orange as a function of the reaction time over the different amounts of copper oxide in the catalytic system of TiO₂@CuO_x and N-TiO₂@CuO_x catalysts in UV, all wavelengths, and visible light respectively. This shows that the adsorption performance decreased and the catalytic activity increased as the CuO_x loading increased. Considering the above conditions, the total degradation performances of TiO₂@0.1CuO_x and N-TiO₂@0.1CuO_x showed maximum activities in the respective catalytic systems. Therefore, 0.1CuO_x was chosen in the later text and we do not specifically point out “0.1”.

Fig. 1 displays the XRD patterns of the TiO₂ (A), N-TiO₂ (B), TiO₂@CuO_x (C) and N-TiO₂@CuO_x (D) catalysts. The XRD patterns of the four catalysts all clearly show anatase TiO₂ diffraction peaks, while only in the XRD pattern of TiO₂@CuO_x (C) and N-TiO₂@CuO_x (D) catalysts can we find Cu₂O diffraction peaks. These indicate the amount of Cu₂O nanoparticles formed when the copper nitrate was deposited on the surface of TiO₂ and N-TiO₂.

Fig. 2 shows representative transmission electron microscopy (TEM) images of TiO₂ (A), N-TiO₂ (B), TiO₂@CuO_x (C) and N-TiO₂@CuO_x (D) catalysts. The TEM images of the four catalysts all clearly show the core and shell structures in the TiO₂@CuO_x (C) and N-TiO₂@CuO_x (D) catalysts, but not in the TiO₂ (A) and N-TiO₂ (B) catalysts.

Fig. 3 displays Ti 2p XPS patterns of the TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x catalysts. The Ti 2p XPS spectra of TiO₂ and N-TiO₂ can be nicely fitted with one component

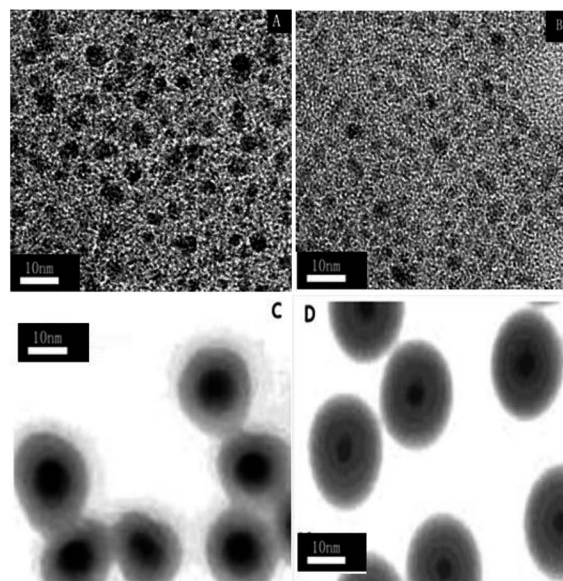


Fig. 2 Transmission electron microscopy (TEM) images of the TiO₂ (A), N-TiO₂ (B), TiO₂@CuO_x (C) and N-TiO₂@CuO_x (D) catalysts.

centring at 458.5 eV, which can be attributed to Ti⁴⁺ on the surface.³² With the Cu loading on TiO₂ and N-TiO₂, the Ti 2p peak shifts from 458.5 eV to 459.0 eV. Therefore, we hypothesize that the interaction between Ti and Cu on the interface contributes to this shift. While the Ti 2p XPS spectra of TiO₂@CuO_x and N-TiO₂@CuO_x fit with another component centring at 459.0 eV, the formation of the chemical bonds increases the binding energy of Ti,¹⁷ which can be attributed to the complex species on the surfaces of core-shell structures.

Fig. 4 shows the Cu 2p_{3/2} XPS patterns of the TiO₂@CuO_x and N-TiO₂@CuO_x catalysts. Table 1 shows the peak-fitting results of the Cu XPS spectra. We can observe that the TiO₂@CuO_x and N-TiO₂@CuO_x catalysts both show double peaks which are split in the Cu 2p_{3/2} XPS patterns. As the binding energy is almost the same for Cu⁰ and Cu⁺ in XPS,³³ we cannot differentiate between the two peaks at low binding energies in the XPS spectra. As the 941–944 eV shake-up³⁴ is unique for Cu²⁺ in XPS spectra, and

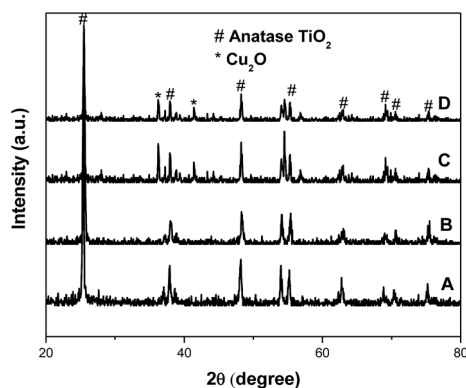


Fig. 1 XRD patterns of the TiO₂ (A), N-TiO₂ (B), TiO₂@CuO_x (C) and N-TiO₂@CuO_x (D) catalysts.

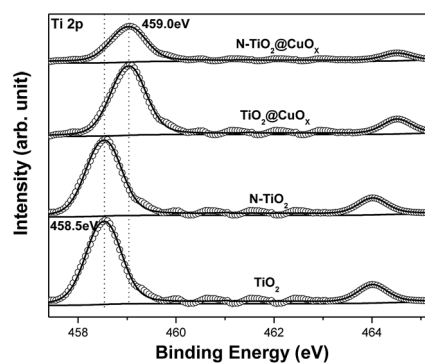


Fig. 3 Ti 2p XPS patterns of the TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x catalysts. Scattered circles and solid lines indicate the experimental data and fitting spectra, respectively.



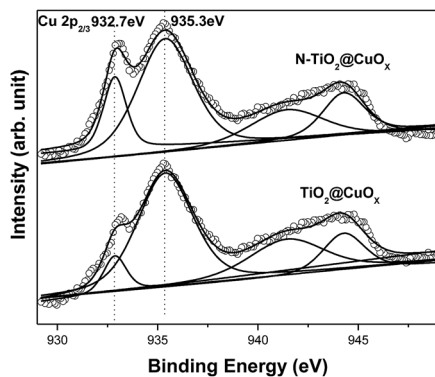


Fig. 4 Cu 2p_{3/2} XPS patterns of the TiO₂@CuO_x and N-TiO₂@CuO_x catalysts. Scattered circles and solid lines indicate the experimental data and fitting spectra, respectively.

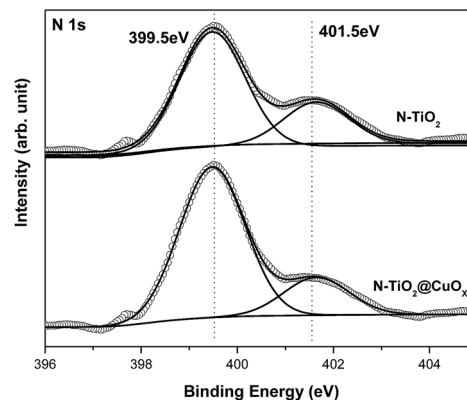


Fig. 5 N 1s XPS patterns of the N-TiO₂ and N-TiO₂@CuO_x catalysts. Scattered circles and solid lines indicate the experimental data and fitting spectra, respectively.

Table 1 Peak-fitting results of Cu XPS spectra of the TiO₂@CuO_x and N-TiO₂@CuO_x catalysts

Catalyst	Component 1		Component 2	
	BE (eV)	Fraction	BE (eV)	Fraction
TiO ₂ @CuO _x	932.7	9%	935.3	91%
N-TiO ₂ @CuO _x	932.7	25%	935.3	75%

the binding energy of Cu²⁺ increases, we can confirm that it is the Cu²⁺ that caused the peak at 935.3 eV. The difference between the Cu 2p_{3/2} XPS spectra of the two samples is great, which indicates the different speciation which exists on their surfaces.

The following conclusions can be reached by analyzing the above results. When the copper nitrate was separately deposited on the surfaces of TiO₂ and N-TiO₂, the content of Cu⁰ and Cu⁺ obtained on the surfaces of TiO₂ and N-TiO₂ was consistent with previous XRD results. Furthermore, we cannot find a peak due to CuO in the XRD patterns, but it is obvious in the XPS patterns. Therefore it can be hypothesized that the CuO on the surface of the catalysts was amorphous.

The N 1s XPS peak could be adequately fitted by two components with the N 1s binding energies at 399.5 and 401.5 eV in Fig. 5. We attribute the binding energy at 401.5 eV to the substitution with N in O-Ti-N,³⁵ while we attribute the binding energy at 399.5 eV to doped N in interstitial lattice sites, which can decrease the band gap from 3.2 eV to 2.4 eV.²²

Fig. 6 and Table 2 show the N₂ adsorption-desorption isotherms and textural parameters of TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x respectively. The N₂ adsorption-desorption isotherms of TiO₂ and N-TiO₂@CuO_x are similar with H2 hysteresis loops according to IUPAC, which illustrate that the mesoporous structure exists on the surface of the catalysts.³⁶ We attribute the difference in absorption and desorption mechanisms to the “ink-bottle” pore.³⁷ The N₂ adsorption-desorption isotherms of N-TiO₂ show that the hysteresis loop is very wide with a high specific surface area and small size. The N₂ adsorption-desorption isotherm of TiO₂@CuO_x shows that the

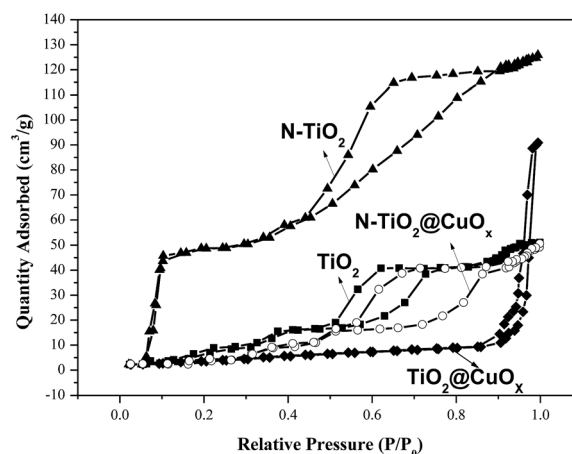


Fig. 6 The N₂ adsorption-desorption isotherms for TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x.

hysteresis loop shifts to the higher relative pressure ($P/P_0 = 0.9$) between the H2 and H3 hysteresis loops according to the BDDT classification, which illustrates that the macro-pore structure exists on the surface of the support with a low specific surface area and big size.

Fig. S2† shows the concentration of methyl orange as a function of the reaction time over the TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x catalysts in UV light, all wavelengths and visible light. The degradation properties are composed of two parts, adsorption activity and photocatalytic activity, and

Table 2 Textural parameters of TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x

Support	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
TiO ₂	38.2	0.195	22.4
N-TiO ₂	174	0.294	15.4
TiO ₂ @CuO _x	16.5	0.115	62.7
N-TiO ₂ @CuO _x	29.4	0.181	48.7



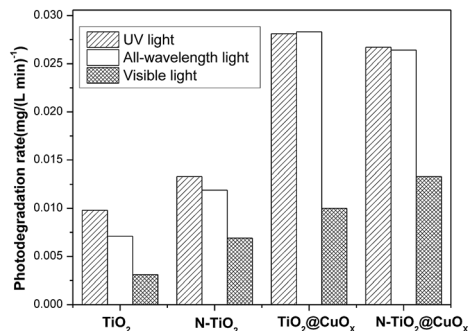


Fig. 7 Photo-degradation rate of the TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x catalysts in UV light, all wavelengths and visible light.

the degradation of methyl orange as the probe reaction was employed to respond to these two parts of the activity under different conditions. The results before the light illumination were characterized as adsorption activity, and after the light illumination as photocatalytic activity. Considering the results of BET and the adsorption and activity performance, we find that the adsorption performance is closely correlated to the specific surface area and size. Among the catalysts, N-TiO₂ has the best adsorption and TiO₂@CuO_x has the worst, while N-TiO₂@CuO_x is close to TiO₂ which is in the middle. We can conclude from the results of XPS, TEM and the absorption data that N-doping can effectively improve the absorption by the catalyst, but the core-shell structure may have an adverse effect.

Fig. 7 and 8 display the photo-degradation rate and total degradation rate of the TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x catalysts in UV light, all wavelengths and visible light. The catalytic activity of N-TiO₂ is much better than that of TiO₂ in visible light, and also of N-TiO₂@CuO_x and TiO₂@CuO_x. We can make a conclusion that N-doping can effectively reduce the band gap of energy of TiO₂ and improve the use of visible light.

Fig. 9 shows the UV-vis diffuse reflection spectra of N-TiO₂ and N-TiO₂@CuO_x. The N-TiO₂ and N-TiO₂@CuO_x catalysts exhibit a pale yellow colour. The UV-vis diffuse reflection spectra of these two catalysts show a continuous and tailing

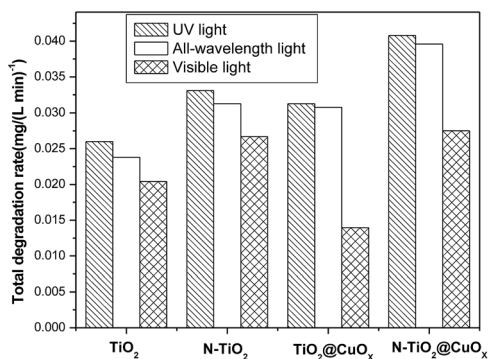


Fig. 8 Total degradation rate of TiO₂, N-TiO₂, TiO₂@CuO_x and N-TiO₂@CuO_x catalysts in UV light, all wavelengths and visible light respectively.

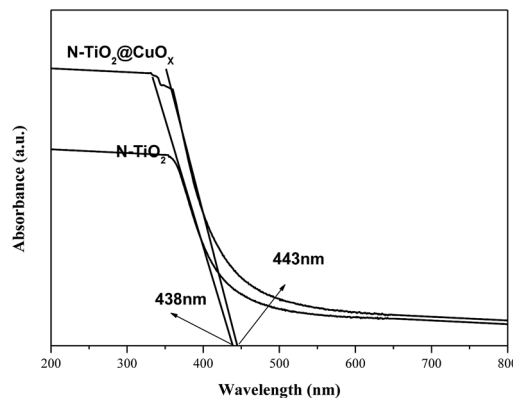


Fig. 9 UV-vis diffuse reflection spectra for the catalysts N-TiO₂ and N-TiO₂@CuO_x.

absorption in the visible region. The band-gap energies of the N-TiO₂ and N-TiO₂@CuO_x catalysts are 2.83 and 2.80 eV, respectively, which were determined by the plot of the modified Kubelka-Munk function $(\alpha h\nu)^{1/2}$ versus photon energy assuming indirect transitions.³⁸ Based on the above data, we can make a conclusion that N-doping can effectively reduce the band gap of energy of TiO₂ in N-TiO₂ and N-TiO₂@CuO_x catalysts.

Fig. 10 shows the H₂-TPR spectra of the catalysts of TiO₂@CuO_x and N-TiO₂@CuO_x. The H₂-TPR of CuO supported on CeO₂ has been extensively investigated.^{39–42} CuO is reduced below 300 °C and the reduction temperature of different CuO species on CeO₂ follows the order: finely dispersed CuO < large CuO crystallites < bulk CuO. Therefore, the reduction peak at 221 °C is assigned to the reduction of finely dispersed CuO, and that at 258 °C to the reduction of large CuO crystallites and bulk CuO.⁴³

Considering the results from H₂-TPR and the photo-degradation performance of TiO₂@CuO_x and N-TiO₂@CuO_x catalysts in UV and all-wavelength light, the activity increases as the size of CuO decreases on the surface. However, the reason for the activity of TiO₂@CuO_x being worse than N-TiO₂@CuO_x in visible light can be attributed to the decrease in efficiency for visible light.

On the basis of TEM, BET, H₂-TPR, XPS, the catalytic activity performance and the stability results, the interfacial structures

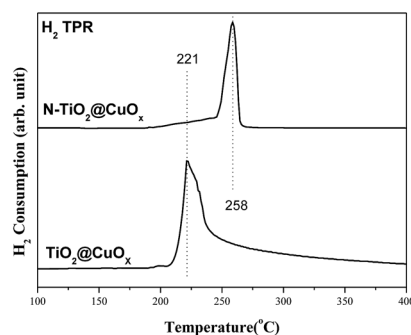


Fig. 10 H₂-TPR spectra of the catalysts TiO₂@CuO_x and N-TiO₂@CuO_x.



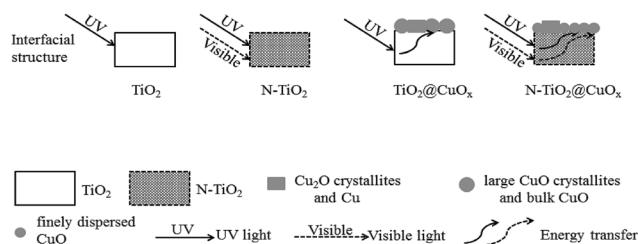


Fig. 11 Schematic illustration of the interfacial structures of TiO_2 , N-TiO_2 , $\text{TiO}_2@\text{CuO}_x$ and $\text{N-TiO}_2@\text{CuO}_x$ and their responses to different wavelengths of light.

of TiO_2 , N-TiO_2 , $\text{TiO}_2@\text{CuO}_x$ and $\text{N-TiO}_2@\text{CuO}_x$ and their responses to different wavelengths of light are schematically illustrated in Fig. 11. These results demonstrate that the

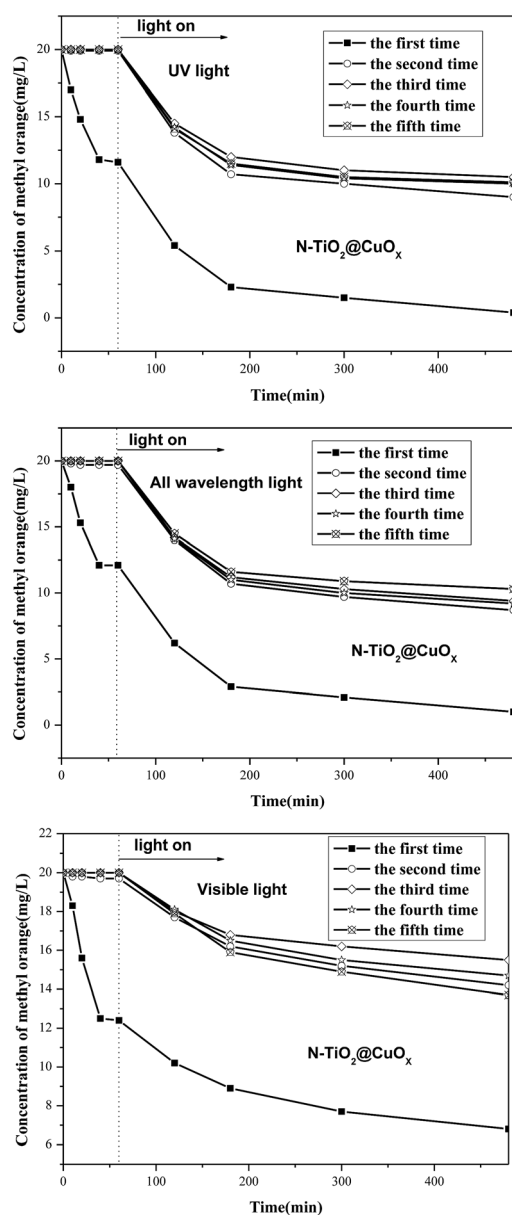


Fig. 12 Stability of the $\text{N-TiO}_2@0.1\text{CuO}_x$ in UV light, all wavelengths, and visible light.

interfacial reaction mechanisms on the surfaces of $\text{TiO}_2@\text{CuO}_x$ and $\text{N-TiO}_2@\text{CuO}_x$ are the same. The light energy which was absorbed by TiO_2 and N-doped TiO_2 is translated into the internal energy which was employed to overcome the energy barrier of the reaction on the CuO_x surface. The difference is simply the wavelengths of light which are responded to by TiO_2 and N-doped TiO_2 .

Fig. 12 shows the stability of $\text{N-TiO}_2@\text{CuO}_x$ in UV light, all wavelengths, and visible light, and obviously shows that there is hardly any absorption performance, although the activity performances are almost unchanged during the 40 hours. We consider that the $\text{N-TiO}_2@\text{CuO}_x$ catalyst is a kind of reusable material to degrade the methyl orange.

Experimental

Catalyst preparation

We prepared two solutions by adding 20.0 g oxalic acid to 200 mL distilled water for both, then dripped 10 mL titanium tetrachloride into both of them dropwise, and stirred them evenly. After the drops were added, we added sodium hydroxide and ammonia solution respectively to adjust the pH values of the solutions to 8–9. We continuously stirred the above solutions for 8 h, after which white precipitates were produced. After the agitation, we aged them for 8 h, and then filtered out these white precipitates. These white precipitates were washed with distilled water and ethanol several times until there was no chloride in the filtrate, then dried at 70 °C and calcined for 2 h at 400 °C in sequence. These two obtained products were recorded as TiO_2 and N-TiO_2 , respectively.

The above TiO_2 (5 g) and N-TiO_2 (5 g) were ground to powders and each was put into a three-neck bottle. Then we added 5 mL copper nitrate solution (1.06 mol L^{-1}) and distilled water to both of them and stirred them at 70 °C for 30 min. Then we added sodium hydroxide and ammonia solution respectively to adjust the pH values of the solutions to 8–9 separately, and stirred them at 70 °C for 24 h. Then we filtered these solids, washed them with distilled water and ethanol several times, dried them at 70 °C for 12 h, and calcined them in air at 400 °C for 4 h. These two obtained products were recorded as $\text{TiO}_2@\text{CuO}_x$ and $\text{N-TiO}_2@\text{CuO}_x$ respectively.

Catalyst characterization

Powder X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert PRO SUPER X-ray diffractometer with a Ni-filtered $\text{Cu K}\alpha$ X-ray source operating at 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 electron spectrometer using a monochromatized $\text{Al K}\alpha$ excitation source ($h\nu = 1486.6 \text{ eV}$). Transmission electron microscopy (TEM) measurements were carried out on a JEOL-2100F transmission electron microscope at an accelerating voltage of 200 kV. N_2 adsorption-desorption isotherms (BET) were acquired on a Beckman Coulter SA3100 surface area analyzer, in which the sample was degassed at 300 °C for 30 min under a nitrogen atmosphere prior to the measurements. The reduction behaviors of the catalysts were



measured using H₂ temperature-programmed reduction (H₂-TPR) techniques. UV-vis absorption spectra were recorded using a SolidSpec-DUV-3700 DUV-vis-NIR spectrometer.

Degradation property measurements

The degradation property is composed of two parts, the adsorption activity and the photocatalytic activity. We employed the degradation of methyl orange as the probe reaction. We added 0.12 g catalyst to 20 mg L⁻¹ methyl orange aqueous solution (40 mL), and stirred it for 1 h whilst avoiding light. We subjected the catalyst to the different wavelengths of irradiation, and took the supernatant to measure the concentration of methyl orange at different time points. The results before the light illumination were characterized as adsorption activity, and after the light illumination as photocatalytic activity.

Conclusions

A novel N, Cu co-doped TiO₂ photocatalyst with a core-shell structure has been prepared using a simple method and the structure-adsorption-photo-degradation activity relationships of TiO₂ base catalysts were examined using the probe reaction of the degradation of methyl orange. The results suggested that the N-TiO₂@CuO_x nanomaterial can reduce the band gap width of TiO₂ by N-doping. Meanwhile, we found the photo-degradation rate of catalysts clearly improved with a certain loading of Cu on the surfaces of N-TiO₂. Consequently, we synthesized an efficient N-doped TiO₂@CuO_x photocatalyst with a core-shell structure.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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