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

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In this paper, a core–shell N-TiO₂@CuOₓ 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@CuOₓ 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@CuOₓ 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.

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.⁸⁻¹¹ 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.¹²⁻¹⁵ 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.¹⁹⁻²¹ 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 CuOₓ was obviously lower than those of AgOₓ and AuOₓ due to the catalytic reaction on the surface of CuOₓ 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@CuOₓ catalyst was prepared by a precipitation method.
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@CuOₓ and N-TiO₂@CuOₓ catalysts in UV, all wavelengths, and visible light respectively. This shows that the adsorption performance decreased and the catalytic activity increased as the CuOₓ loading increased. Considering the above conditions, the total degradation performances of TiO₂@0.1CuOₓ and N-TiO₂@0.1CuOₓ showed maximum activities in the respective catalytic systems. Therefore, 0.1CuOₓ 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@CuOₓ (C) and N-TiO₂@CuOₓ (D) catalysts. The XRD patterns of the four catalysts all clearly show anatase TiO₂ diffraction peaks, while only in the XRD pattern of TiO₂@CuOₓ (C) and N-TiO₂@CuOₓ (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@CuOₓ (C) and N-TiO₂@CuOₓ (D) catalysts. The TEM images of the four catalysts all clearly show the core and shell structures in the TiO₂@CuOₓ (C) and N-TiO₂@CuOₓ (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@CuOₓ and N-TiO₂@CuOₓ catalysts. The Ti 2p XPS spectra of TiO₂ and N-TiO₂ can be nicely fitted with one component centring at 458.5 eV, which can be attributed to Ti⁴⁺ on the surface.²² 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@CuOX and N-TiO₂@CuOX fit with another component centring at 459.0 eV, the formation of the chemical bonds increases the binding energy of Ti, which can be attributed to the complex species on the surfaces of core–shell structures.

Fig. 4 shows the Cu 2p½ XPS patterns of the TiO₂@CuOₓ and N-TiO₂@CuOₓ catalysts. Table 1 shows the peak-fitting results of the Cu XPS spectra. We can observe that the TiO₂@CuOₓ and N-TiO₂@CuOₓ catalysts both show double peaks which are split in the Cu 2p½ 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-up is unique for Cu⁺ in XPS spectra, and
the binding energy of Cu$^{2+}$ increases, we can confirm that it is the Cu$^{2+}$ 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 TiO$_2$ and N-TiO$_2$, the content of Cu$^0$ and Cu$^+$ obtained on the surfaces of TiO$_2$ and N-TiO$_2$ 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, 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 N$_2$ adsorption–desorption isotherms and textural parameters of TiO$_2$, N-TiO$_2$, TiO$_2$@CuO$_x$ and N-TiO$_2$@CuO$_x$ catalysts. The N$_2$ adsorption–desorption isotherms of TiO$_2$ and N-TiO$_2$@CuO$_x$ are similar with H2 hysteresis loops according to IUPAC, which illustrate that the mesoporuous structure exists on the surface of the catalysts.$^{36}$ We attribute the difference in adsorption and desorption mechanisms to the “ink-bottle” pore.$^{37}$ The N$_2$ adsorption–desorption isotherms of N-TiO$_2$ show that the hysteresis loop is very wide with a high specific surface area and small size. The N$_2$ adsorption–desorption isotherm of TiO$_2$@CuO$_x$ shows that the 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 TiO$_2$, N-TiO$_2$, TiO$_2$@CuO$_x$ and N-TiO$_2$@CuO$_x$ catalysts in the UV light, all wavelengths and visible light. The degradation properties are composed of two parts, adsorption activity and photocatalytic activity, and

| 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%      |

Table 1 Peak-fitting results of Cu XPS spectra of the TiO$_2$@CuO$_x$ and N-TiO$_2$@CuO$_x$ catalysts

Table 2 Textural parameters of TiO$_2$, N-TiO$_2$, TiO$_2$@CuO$_x$ and N-TiO$_2$@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                |
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@CuO₂ has the worst, while N-TiO₂@CuO₂ 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 adsorption 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@CuOₓ and N-TiO₂@CuOₓ 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@CuO₂ and TiO₂@CuO₂. 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@CuOₓ. The N-TiO₂ and N-TiO₂@CuOₓ catalysts exhibit a pale yellow colour. The UV-vis diffuse reflection spectra of these two catalysts show a continuous and tailing absorption in the visible region. The band-gap energies of the N-TiO₂ and N-TiO₂@CuOₓ catalysts are 2.83 and 2.80 eV, respectively, which were determined by the plot of the modified Kubelka–Munk function \((a h n)^{1/2}\) versus photon energy assuming indirect transitions. 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@CuOₓ catalysts.

Fig. 10 shows the H₂-TPR spectra of the catalysts of TiO₂@CuOₓ and N-TiO₂@CuOₓ. The H₂-TPR of CuO supported on CeO₂ has been extensively investigated: 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.

Considering the results from H₂-TPR and the photo-degradation performance of TiO₂@CuOₓ and N-TiO₂@CuOₓ 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@CuOₓ being worse than N-TiO₂@CuOₓ 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
of TiO$_2$, N-TiO$_2$, TiO$_2$@CuO$_x$ and N-TiO$_2$@CuO$_x$ and their responses to different wavelengths of light are schematically illustrated in Fig. 11. These results demonstrate that the interfacial reaction mechanisms on the surfaces of TiO$_2$@CuO$_x$ and N-TiO$_2$@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 N-TiO$_2$@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 N-TiO$_2$@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 TiO$_2$@CuO$_x$ and N-TiO$_2$@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 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 Al K$_\alpha$ excitation source (hv = 1486.6 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 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 photocatalyst with a core–shell structure.

Conflicts of interest
There are no conflicts to declare.

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