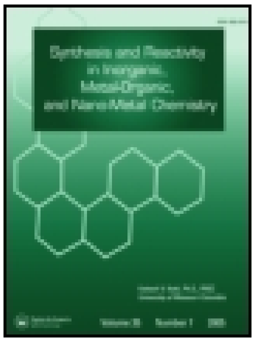

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Comparison N-Cu co-doped nanotitania and N doped nanotitania in photocatalytic reduction of CO_2 under UV light

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Abstract

Nitrogen-copper co-doped nanotitania and nitrogen doped nanotitania for CO_2 photoreduction by water in liquid phase were prepared by sol-gel method. The catalysts were characterized by XRD, HRTEM, DRS, FTIR, and XPS. N doped TiO_2 have remarkably better photocatalytic activity than N and Cu co-doped TiO_2 for the CO_2 photoreduction to acetone under ultraviolet illumination. The acetone yield of N_3/TiO_2 could reach 52.6 μmol/g·h and the acetone yield of $Cu_{0.6}N_4/TiO_2$ could reach 33.2μmol/g·h under UV conditions. The mechanism of CO_2 photoreduction on N doped nanotitania and N -Cu co-doped TiO_2 was proposed.

keywords

Nano-TiO_2; Nitrogen and copper codoping; Sol-gel;CO_2 photoreduction; Acetone.

1. Introduction

Global warming caused by the emission of greenhouse gases, primarily carbon dioxide (CO_2), is attracting increasing attention all over the world [1].It is highly desired to convert atmospheric CO_2 into useful substances. Previous work demonstrated that CO_2 could be photocatalytically reduced to carbon monoxide and hydrocarbons including methane, ethane, formaldehyde, methanol, and formic acid [2-5] in both liquid phase and gas phase. Most of the investigations of photoreduction of CO_2 have focused on TiO_2.From the view point of practical application, TiO_2 is reasonably cheap, photo-stable, and non-toxic, making it a perfect candidate for photocatalytic processes. Yet carbon dioxide conversion rates still low despite using ultraviolet illumination for band gap excitations. [6].

Numerous studies have been reported on how to increase the photoreduction activity of TiO_2 using metal-doped modified TiO_2 [7-9]. For example, the optimal Cu-loaded titania was a highly efficient, photocatalyst for CO_2 reduction since copper are an effective electron trapper [10-11]. Besides, nonmetal-doped TiO_2 have been used as visible light-responsive photocatalysts for CO_2 photoreduction. Significant enhancement of CO_2 photoreduction to CO have been reported for I-doped TiO_2 due to the extension of TiO_2 absorption spectra to the visible light region by I doping [12].There have been literature reports that suggest that co-doping of metal and nonmetal species on TiO_2 leads to enhanced photoreduction activity as compared with single N-doped TiO_2.For example, Ni and N co-doped TiO_2 for enhanced CO_2 photoreduction as compared to N/TiO_2

because of a smaller crystal size and higher surface area[13]. The V-N co-doped TiO2 nanotube arrays co-doped TiO2 photocatalysts show remarkably enhanced photocatalytic activity for the CO2 photoreduction to methane under ultraviolet illumination[14].

Among the current research of Cu and N doping into anatase TiO_2, the photocatalytic activity of some Cu-N co-doped TiO_2 was considerably greater than that of the sample N doped TiO_2 and commercially available TiO_2 which is attributed to the synergistic effect of Cu-N co-doped[15-16].

But in Kuvarega’s particle, the Cu-N co-doped TiO_2 showed least photoactivity than N doped TiO_2[17] due to the lowest adsorption capacity of Cu-N co-doped TiO_2. In other words, the photocatalytic activity of N and Cu co-doped TiO_2 in photocatalytic was not absolutely better than N doped TiO_2. At present, Cu-N co-modified TiO_2 for photocatalytic CO_2 reduction has been reported only once in the literature. Varghese et al [18] synthesized N-doped TiO_2 nanotube arrays sputtered with Cu nanoparticles as a co-catalyst and tested the catalytic activity for CO_2 reduction with water under sunlight. The raw materials used in the work of Varghese were expensive and the fabrication process was relatively complicated. In this work, we used a much simpler method and cheaper raw materials to synthesize Cu and N co-modified TiO_2 nanoparticles. The catalytic activities for the photocatalytic reduction of CO_2 with water under ultraviolet illumination and the mechanism of photocatalytic reduction CO_2 on Cu-N co-doped

TiO_2 catalyst. In order to comparion, photocatalytic reduction CO_2 on N doped TiO_2 were proposed.

2. Experiment

2.1 Catalyst preparation

The synthesis of N and Cu co-doped TiO_2 (N-Cu/TiO_2) nanoparticles involved the following steps:First, tetrabutyl titanate and ethanol were mixed and stirred for 30 min at room temperature(solution A).A appropriate amount of acetic acid, copper nitrate($Cu(NO_3)_2{\cdot}6H_2O$),urea, H_2O, dissolved in ethanol(solution B). Then, solution B was dropped into solution A and kept the solution stirring for 2 h. Thereafter, the solution was aged until the gel formed. The gel was dried at 80℃ and calcined in a muffle at 500℃ for 2h. Then, the N and Cu co-doped TiO_2 samples can be obtained. The doping amount of N varied from 1 to 6 wt%(N:TiO_2 = 1wt%,2wt%,3wt%,4wt%, 5wt%,6wt% respectively)and the amount of Cu^{2+} was 0.6wt%(Cu:TiO_2 = 0.6wt%). (For short, hereafter, $Cu_{0.6}N_X/TiO_2$ denotes the sample containing X wt% of N and 0.6wt% of Cu^{2+}).

2.2 Characterization

The phase compositions of samples were identified by X-Ray Powder Diffraction (Cu Kα radiation). The UV-vis diffuse reflectance spectra (DRS) were recorded at room temperature on a Shimadzu UV-3600 UV-vis spectrometer with barium sulfate as the reference sample. FT-IR spectra of the samples were collected on a Nicolet 6700 FT-IR spectrophotometer at room temperature by KBr method. Morphologies of samples were characterized using a high resolution transmission electron microscope (JEM-2100F). The XPS measurement was performed using a PHI1600 Analyzer.

2.3 Photocatalytic reduction of CO_2

The photocatalytic reaction system was illuminated by a 365W Hg lamp in the center, and it was shielded by a black box during the reaction to prevent interference from outside light. The catalyst was suspended in 40 ml of 0.2mol/L NaOH aqueous solution. Ultra pure CO_2 was bubbled through the reactor for at least 30 min to eliminate the dissolved oxygen and saturate the solution. The catalyst suspended solution was agitated by a magnetic stirrer. A needle-type probe was inserted into the reactor to withdraw a small liquid sample, and after the catalyst powder were filtered, the liquid sample was analyzed using gas chromatography (Agilent 6890N-05973). Analysis indicated that acetone was the major hydrocarbon. Blank reactions were also conducted, one without catalyst, and one without illumination; no hydrocarbon was detected in the blank tests. Then the N and Cu co-doped TiO_2 ($Cu_{0.6}N_1/TiO_2$,$Cu_{0.6}N_2/TiO_2$,$Cu_{0.6}N_3/TiO_2$,$Cu_{0.6}N_4/TiO_2$, $Cu_{0.6}N_5/TiO_2$,$Cu_{0.6}N_6/TiO_2$) samples turned on to start the reaction. For the sake of comparison, pure $Cu_{0.6}TiO_2$ and N doped TiO_2 (N_1/TiO_2, N_2/TiO_2, N_3/TiO_2, N_4/TiO_2, N_5/TiO_2, N_6/TiO_2)samples, also prepared by the similar procedure.

3. Results and Discussion

3.1 Characterization

3.1.1 XRD

Characteristics of samples the XRD of the catalysts in Fig.1 shows all samples were ascribed to pure anatase TiO2 .The grain sizes of the catalyst were calculated from the Scherrer equation. The particle sizes of sol-gel derived N-Cu co-doped TiO_2 and N doped TiO_2 are uniform and the diameter is between 10-15nm, The particle sizes of $Cu_{0.6}N_2/TiO_2$, $Cu_{0.6}N_4/TiO_2$, $Cu_{0.6}N_6/TiO_2$ are 15.2nm, 9.6nm, 13.7 nm respectively; N_2/TiO_2, N_4/TiO_2, N_6/TiO_2 are 11.0 nm, 9.1nm, 12.6 nm respectively. From above the result, the particle sizes of Cu-N co-doped TiO_2 are larger than N doped TiO_2.A detail analysis of XRD patterns was performed by enlarging the anatase (101) plane of the samples as shown in the inset of Figure.1.(a) and (b), Figure.1.(a) indicated that the peak position of the Cu-N co-doped TiO_2 samples gradually shifted toward a higher diffraction angle. It suggested that Cu, N might be incorporated into the crystal lattice of anatase[14]. Figure.1.(b) indicated that the peak position of the N doped TiO_2 samples gradually shifted toward a higher diffraction angle too. However, peak position change of N_4/TiO_2 was not obvious, indicating that the doped N might be excessive then inhibit the incorporation of N into crystal lattice.

3.1.2 FT-IR

Fig.2 shows the FTIR spectrum of $TiO_{2,}$ $Cu_{0.6}/TiO_{2,}$ $Nx/TiO_{2,}$ and $Cu_{0.6}N_X/TiO_2$. All of the samples show similar FT-IR spectra, indicating the structure of TiO_2 did not change after copper and nitrogen-doping. The absorption bands at about 3406 cm^{-1} and 1663 $cm^{-1}$are assigned to the surface adsorbed water and hydroxyl groups. The absorption band corresponds to Ti-O-N was not observed for the nitrogen-doped samples, probably because the amount of doped N was very small. The peak at 500 cm^{-1} is due to stretching vibration of Ti-O[19,20]. The peak at 1380 cm^{-1} was ascribed to the symmetric stretching vibration of bidentate carbonate b-CO_3^{2-} bonded with Ti^{4+}-O^{2-}[21].The peaks were seen at 2330 cm^{-1} and 2360 cm^{-1}, which can be assigned to the stretching vibration of C-O, maybe due to the oxidation of existing C element when the products exposed to air.[22]

3.1.3 TEM

The morphologies of the particles measured by transmission electron microscopy (TEM) are given in Figure.3.(a)(b)(c).Figure.3.(a) shows the $Cu_{0.6}N_4/TiO_2$ particles with uniform spheroidal shape, and an average agglomerate size are about 9-12nm for $Cu_{0.6}N_4/TiO_2$. The difference of the particle size by TEM with that estimated by XRD results is attributed to the particle agglomeration. The diffraction pattern of the $Cu_{0.6}N_4/TiO_2$ shown in Figure.3.(b) indicates the presence of TiO_2 anatase with the typical (101) direction [23]. Fig.3.(c) shows the EDX spectrum of $Cu_{0.6}N_4/TiO_2$, which indicates the presence of Cu and N in the nanocomposite.

3.1.4 Optical property

Fig.4.(a) displays the UV-vis diffuse reflectance spectra of serial copper and nitrogen co-doped TiO_2.The $Cu_{0.6}N_4/TiO_2$ and $Cu_{0.6}N_2/TiO_2$ shows absorption in the UV region, However $Cu_{0.6}N_6$-TiO_2 shows absorption in the visible region. Fig.4.(b) presents the spectra of nitrogen doped TiO_2 and non-doped TiO_2 samples. The N_4/TiO_2 and N_2/TiO_2 shows absorption in the UV

region. However, N_6/TiO_2 shows absorption in the visible region. Kubelka-Munk function was used to estimate the band-gap energy of all samples [24]. The calculated results of band gap energies for the $Cu_{0.6}$-TiO_2, $Cu_{0.6}N_2$-TiO_2, $Cu_{0.6}N_4$-TiO_2 and $Cu_{0.6}N_6$-TiO_2 are 2.76eV, 2.98eV, 3.02eV and 2.86eV ；TiO_2, N_2-TiO_2, N_4-TiO_2 and N_6-TiO_2 are 3.03eV, 3.1eV, 3.06eV and 2.95 eV respectively. It shows that the Cu-N co-doped TiO2 have a narrower band gap than that of N doped TiO2 samples. And with the increase of N doping amount, an obvious red shift of the N-Cu/TiO_2 and N/TiO_2.The N_6/TiO_2 and $Cu_{0.6}N_6/TiO_2$ absorption in the visible-light range was related to impurity energy levels of N doping in the gap[25]-[26]. The reason of $Cu_{0.6}N_2$-TiO_2, $Cu_{0.6}N_4/TiO_2$, N_2/TiO_2 and N_4/TiO_2 absorption in the UV-light range may be the small amount of N.

3.1.5 XPS

To explore the states of the copper and nitrogen doped species, the samples were subjected to X-ray photoelectron spectroscopy (XPS) analysis. Fig.5.(a) shows the XPS survey spectrum of the representative $Cu_{0.6}N_4/TiO_2$ sample and TiO_2. Obviously, Ti, O, N and C elements exist at the surface of the sample. Fig. 5.(b) depicts the N 1s XPS spectra of $Cu_{0.6}N_4/TiO_2$, showing the peaks at the binding energy positions of ca.395-405 eV. After background subtraction and curve fitting, the N1s peak could be decomposed to one component peaks centered at ca.400.23. These peak were attributed to the signals of the molecularly chemisorbed nitrogen species (N_2) or nitroxide species (e.g., NO and NO_2) [27].The peak related to the signal of Ti-N bonding (at ca.

396--397eV) was not observed [28].There were approximately 0.7% of lattice O atoms substituted by N atoms for the $Cu_{0.6}N_4/TiO_2$ sample.

3.2 Activity evaluation

3.2.1 The effect of N in photoreduction of CO_2

The aqueous phase was analysed for the reduction products of CO_2. Photoreduction of products were determined by gas chromatography on a Hp-innowax column using a flame ionization detector. During the research acetone is the only one hydrocarbon product to be detected in the aqueous phase over all the samples.

From Fig.6, one can see that the unloaded TiO_2 sample shows poor activity and there was trace amount of acetone detected. The loading of Cu^{2+} and N generally promoted the formation of acetone. The optimum loading amounts for N is 4 wt%. The acetone yield is two times that achieved over the unloaded TiO_2 sample. Fig.7 shows the loading of N sample promoted the formation of acetone, too. The optimum loading amounts for N is 3 wt%; The acetone yield is three times that achieved over the unloaded TiO_2 sample. N doping can greatly enhance the activity of light absorption. But when the doping amount of N is excess, N species may be piled together on the crystal surface of TiO_2.

The acetone yield of N_3/TiO_2 could reach 52.6μmol/g·h and the acetone yield of $Cu_{0.6}N_4/TiO_2$ could reach 33.2μmol/g·h under UV conditions(λ = 365nm). In this article, N doped TiO_2 have better property than Cu-N co-doped TiO_2 on photoreduction of CO_2, the one reason is maybe the particle sizes of N-doped TiO_2 smaller than Cu-N co-doped TiO_2 on the basis of XRD result; the other reason is the band gap of N doped TiO_2 (N_2/TiO_2-3.1eV;N_4/TiO_2-3.06eV) are little higher than Cu-N co-doped TiO_2 ($Cu_{0.6}N_2/TiO_2$-2.98eV ；$Cu_{0.6}N_4/TiO_2$-3.02eV), meaning the better absorption of ultraviolet light.

3.3 Mechanism of photoreduction of CO_2

In liquid system of photoreduction of CO_2, CH_3OH, HCOOH often detected as photoreduction production. At present, acetone as photoreduction product is scarce. $TiO_2/Pd/Al_2O_3$ system is quite noteworthy in relation to other semiconductor based systems ($TiO_2/Pd/SiO_2$,etc) which generate abroad distribution of C_1--C_3 product (CH_3OH, C_2H_5OH, C_3H_6O),and the C_3H_6O yield notebalely higher than the yield of CH_3OH and C_2H_5OH[29].C_3H_6O may be producted by CH_3OH and C_2H_5OH.Other based sample of derived from the urea graphitic carbon nitride (u-g-C_3N_4) result in the formation of a mixture containing CH_3OH and C_2H_5OH,too[30]. Cu-N co-doped TiO_2 and N doped TiO_2 regard as the based sample due to the N doping, so generate C_3 product(C_3H_6O).

Therefore, we propose the following scheme. When illuminated by UV light, photo generated electron and holes,photon-generated electrons(e^-) and holes (h^+) are created on the surface of the TiO_2 catalysts(Eq.(1)). The holes first react with water adsorbed on the catalyst, producing oxygen and H^+ (Eq.(2)).The interaction of H^+ ions with the excited electrons leads to the formation of ·H radicals (Eq. (3)). At the same time,·CO_2 radicals are formed by CO_2(Eq.(4)).·H radicals react with ·CO_2 radicals leading to formation methyl alcohol and formaldehyde[30](Eq.(5)

and Eq.(6)).Then the $\cdot CH_3$ and H-·C(OH) radicals are formed from methyl alcohol and formaldehyde respectively(Eq.(7) and Eq.(8)) [29].The H-·C(OH) radicals fixation via $\cdot CH_3$ radicals lead to form ethyl alcohol(Eq. (9)). So methyl alcohol and ethyl alcohol possiblely produce acetone(Eq. (10)).

$$TiO_2 \longrightarrow e^- + h^+ \tag{1}$$

$$4h^+ + 2H_2O \longrightarrow O_2 + 4H^+ \tag{2}$$

$$H^+ + e^- \longrightarrow \cdot H \tag{3}$$

$$CO_2 + e^- \longrightarrow \cdot CO_2^- \tag{4}$$

$$\cdot CO_2^- + 6 \cdot H \longrightarrow CH_3OH + 2H_2O \tag{5}$$

$$\cdot CO_2^- + 4 \cdot H \longrightarrow HCOH + H_2O \tag{6}$$

$$CH_3OH + \cdot H \longrightarrow \cdot CH_3 + H_2O \tag{7}$$

$$HCOH + \cdot H \longrightarrow H \cdot C(OH) - H \tag{8}$$

$$\cdot CH_3 + H - \cdot C(OH) - H \longrightarrow C_2H_5OH \tag{9}$$

$$CH_3OH + C_2H_5OH \longrightarrow CH_3COCH_3 + 2H_2O \tag{10}$$

4. Conclusion

In this study, Cu-N co-doped TiO_2 and N doped TiO_2 photocatalysts were prepared by sol-gel method for CO_2 photoreduction by water in liquid phase. All of the TiO_2 samples were crystallized basically in anatase phase. The TEM image revealed that the $Cu_{0.6}N_4/TiO_2$ were uniform spheroidal shape with agglomerate size of 9-12nm.The $Cu_{0.6}N_4/TiO_2$ and N_3/TiO_2 catalyst showed the maximum activity in photoreduction of CO_2. When the N amount was 2wt% and 4wt%, the N doped and Cu-N co-doped TiO_2 showed absorption in the UV region, However, when the N amount was 6wt% the N doped and Cu-N co-doped TiO_2 had good visible light absorption. XPS analysis indicated that the doped nitrogen was in the state of molecularly chemisorbed nitrogen. Acetone is the only hydrocarbon product in CO_2 photoreduction over the TiO_2 samples. The acetone yield of N doped TiO_2 higher than TiO_2 and the optimum loading amount of N was

3wt%. However, the acetone yield of Cu-N co-doped TiO_2 was lower than that of N doped TiO_2 due to the bigger particle size and narrower band gap.

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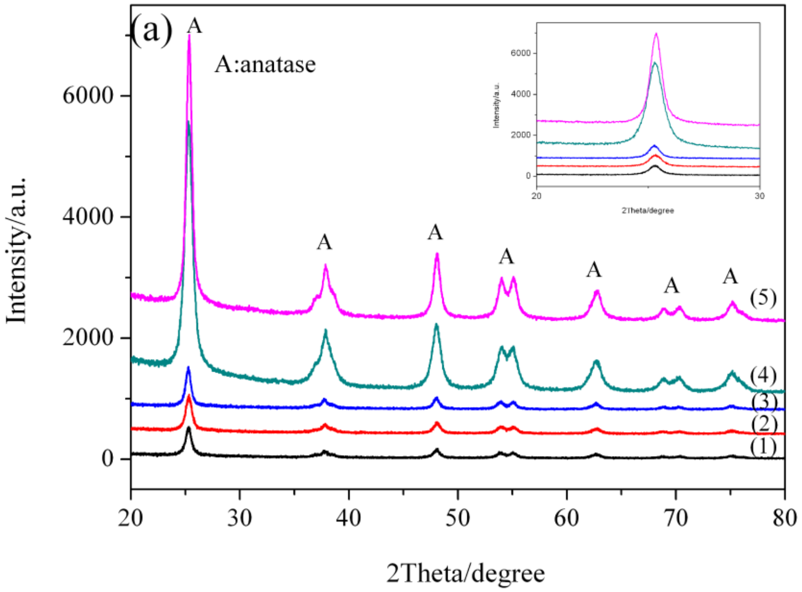

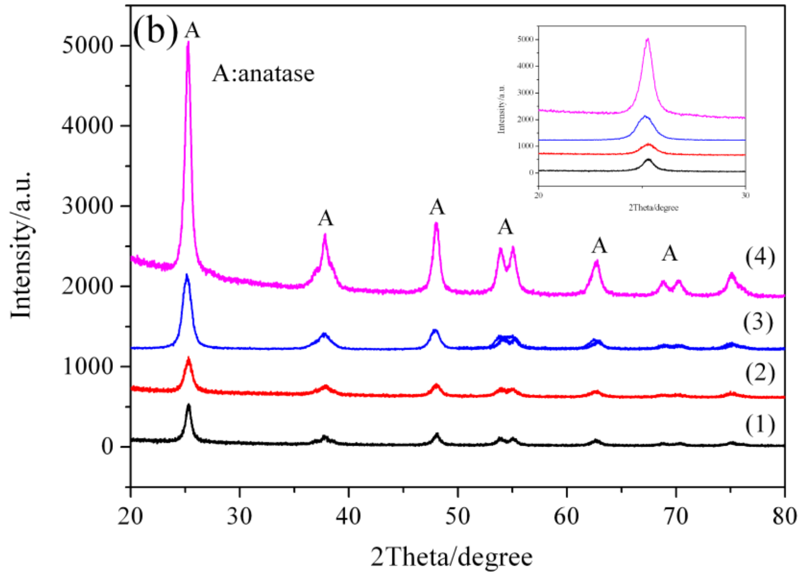

Fig.1. XRD pattern of (a) Cu and N co-doped TiO_2 -(1)TiO_2 (2)$Cu_{0.6}/TiO_2$ (3)$Cu_{0.6}N_2/TiO_2$ (4)$Cu_{0.6}N_4/TiO_2$ (5)$Cu_{0.6}N_6/TiO_2$ (b) N doped TiO_2- (1)TiO_2 (2)N_2/TiO_2 (3)N_4/TiO_2 (4) N_6/TiO_2

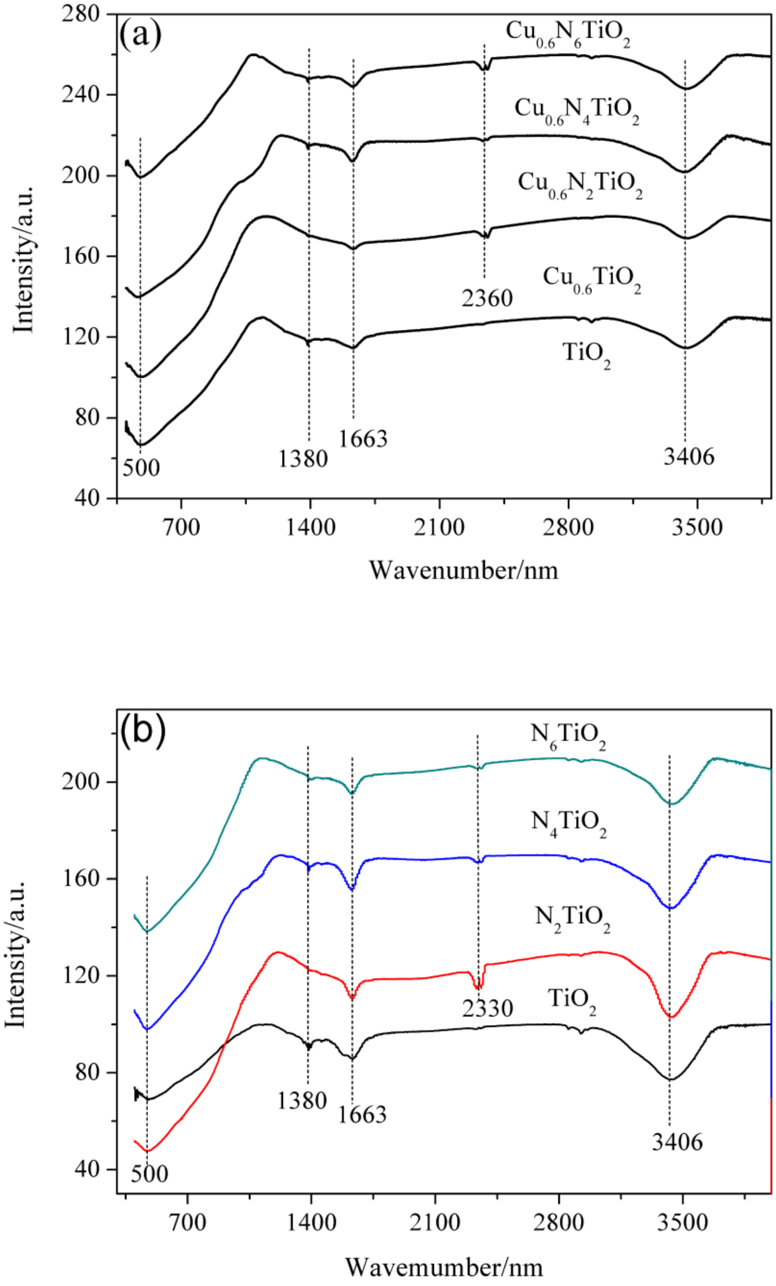

Fig.2. FTIR pattern of (a) Cu and N co-doped TiO_2 (b) N doped TiO_2

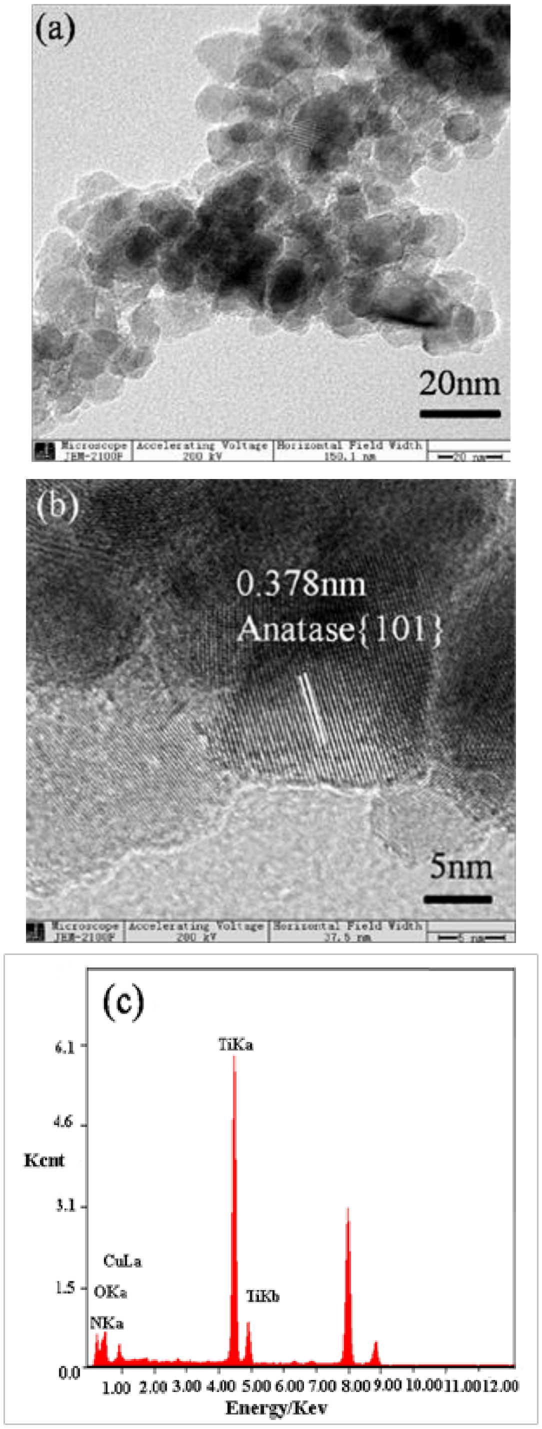

Fig.3. (a) TEM of $Cu_{0.6}N_4/TiO_2$ (b) HRTEM image of $Cu_{0.6}N_4/TiO_2$ with labeled lattice spacings and surface facet for anatase (101) (c) EDX of $Cu_{0.6}N_4/TiO_2$

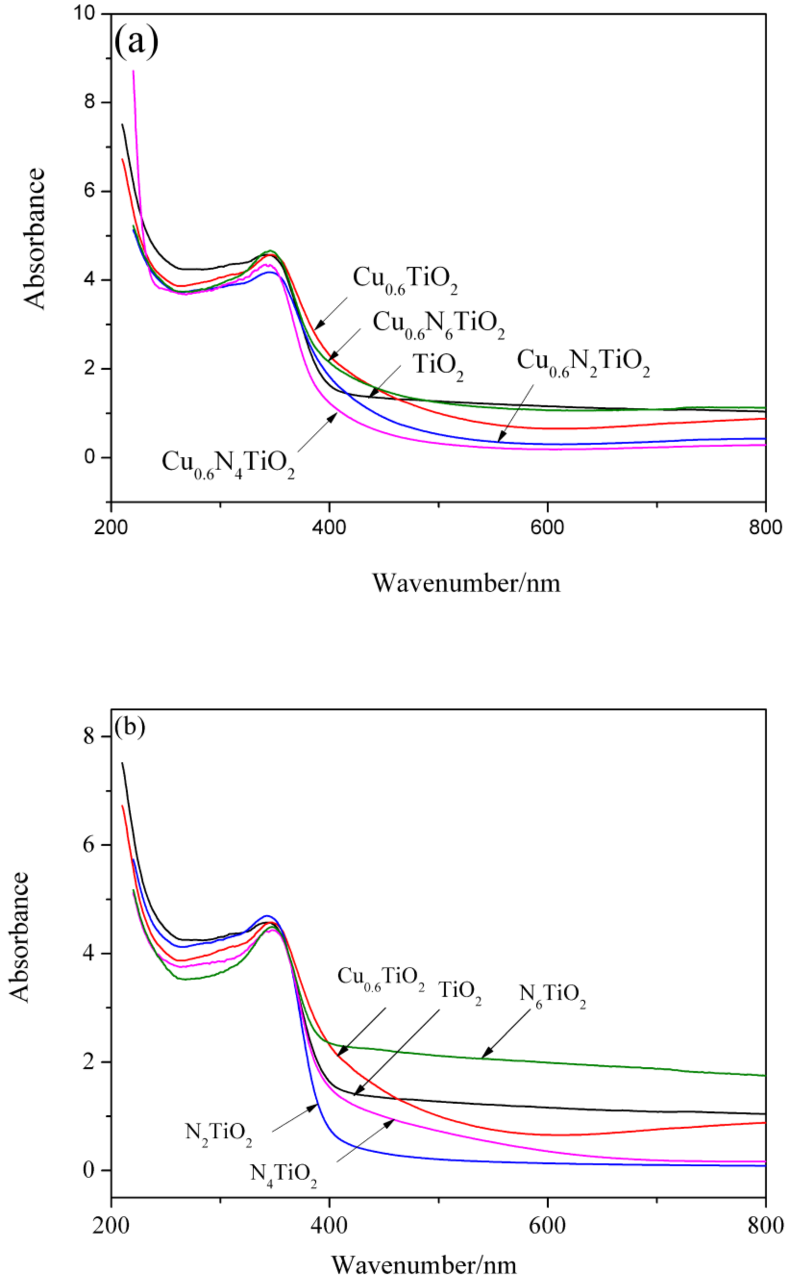

Fig.4. UV-vis of (a) Cu and N co-doped TiO_2 (b) N-doped TiO_2

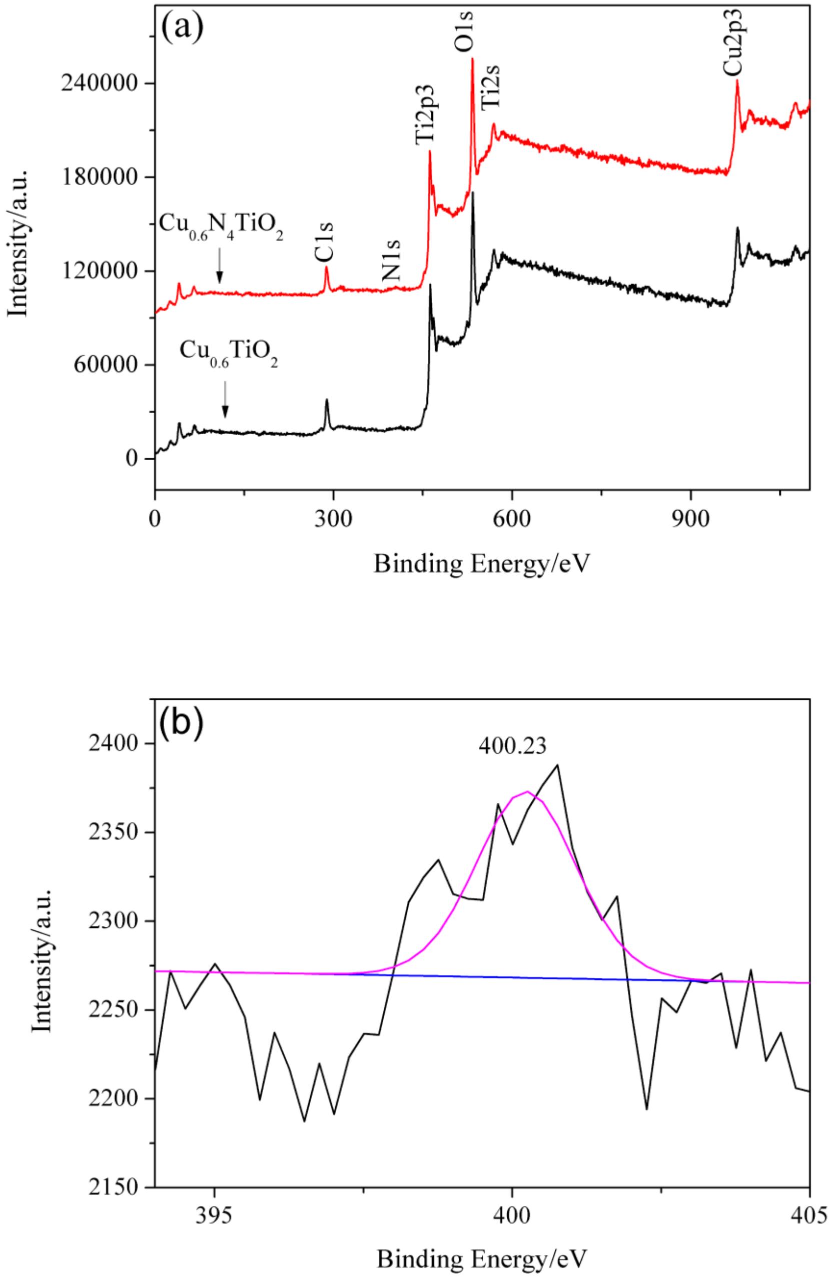

Fig.5. XPS spectra of $Cu_{0.6}N_4/TiO_2$ and TiO_2 (a) Survey spectrum and (b) peak fitting of N 1s spectrum of $Cu_{0.6}N_4/TiO_2$.

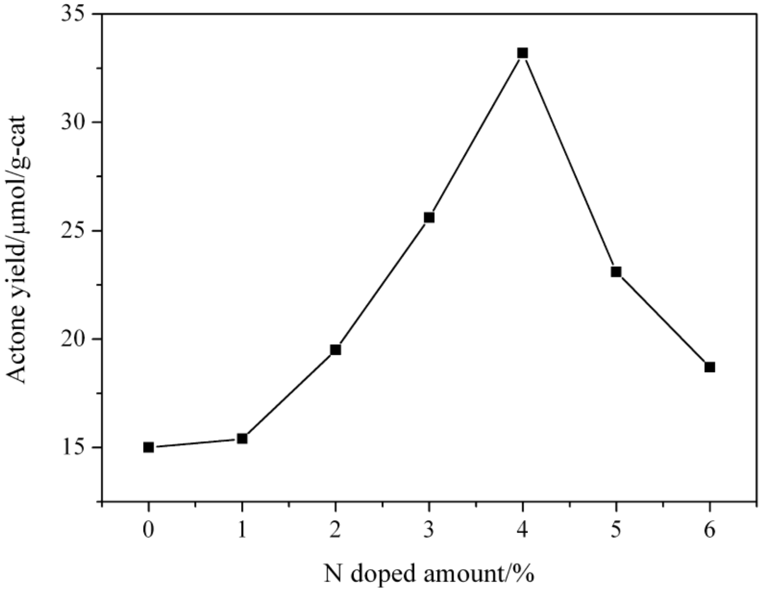

Fig.6. Effect of N doping amount on acetone yield of Cu-N co-doped TiO_2

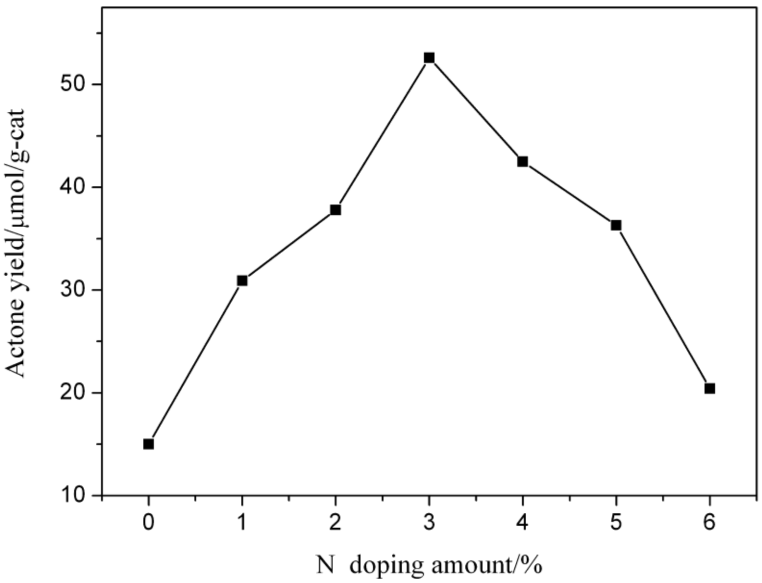

Fig.7. Effect of N doping amount on acetone yield of N doped TiO_2