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CO oxidation over the Cu₂O deposited on 2D continuous lamellar g-C₃N₄

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Abstract

Cu₂O deposited on 2D continuous lamellar g-C₃N₄ (Cu₂O/g-C₃N₄) was prepared via a facile impregnation-chemical reduction procedure. The composition, structure and morphology of as-prepared Cu₂O/g-C₃N₄ were characterized by XRD, SEM, TEM, CO-TPR, FT-IR and nitrogen adsorption, respectively. The influence of Cu₂O loading on the performances of Cu₂O/g-C₃N₄, e.g. adsorption ability for methyl orange (MO) and the stability as well as catalytic activity for CO oxidation, was investigated. The changing trend of adsorption ability and the catalytic activity of Cu₂O/g-C₃N₄ moved in the same direction. When the mass ratio of Cu₂O to g-C₃N₄ was 4:10, the as-prepared composite exhibited the strongest adsorption ability and the highest catalytic activity; it also showed excellent stability in CO oxidation and over it the 100 % conversion of CO was kept for more than 12 h under reaction condition. The strong adsorption ability and good catalytic performance of the Cu₂O/g-C₃N₄ were ascribed to the synergetic effects between g-C₃N₄ and Cu₂O as well as the improved dispersibility and the decreased particle size of Cu₂O.

Keyword: Cu₂O, g-C₃N₄, CO oxidation, adsorption ability

Introduction

The catalytic oxidation of CO is an important reaction from the point of view of environment protection and many other potential applications, such as automotive exhaust controls and the operation of fuel cells.^{1,2} For a long time, precious metals, e.g. Au,³⁻⁵ Pt⁶ and Pd⁷ have been used for this reaction. However, the high cost and sensitivity to sulfur poisoning of precious metals prohibit their widespread exploitation in this reaction.⁸ People make a great effort to develop low-cost, high-activity modified and non-noble metal-based catalysts.⁹ Copper-based catalyst is one of non-noble metal-based catalysts, being widely investigated for CO oxidation.¹⁰⁻¹² The Cu-Cu₂O-CuO system has been known to facilitate oxidation reactions in the bulk, suggesting it has potential as a cost-effective substitute for noble metals in CO oxidation catalytic systems.¹³ The CO oxidation rates over polycrystalline Cu, Cu₂O, and CuO, respectively, were investigated and the results showed that the reaction rate over Cu₂O was the highest,¹⁴⁻¹⁵ which means that Cu₂O or supported Cu₂O for CO oxidation should be paid close attention and investigated in detail.

Generally, the supported catalysts for CO oxidation are alumina,¹⁶⁻¹⁷ silica,¹⁸ ceria,^{1, 8, 19} and titania oxide^{3, 5, 20-22} supported ones. It has been extensively reported that the nature of the support affects enormously the catalytic activity of catalysts.²³⁻²⁴ Catalysts are usually desired to finely disperse active species on a support with high surface area for the efficient use of catalytically active components, which enhances active area relative to the volume of catalysts and reduces the consumption and cost.²⁵ Therefore, many efforts have been made to develop new supports that are capable

of developing suitable interactions with the loaded metal.²⁶⁻²⁸

Graphitic carbon nitride (g-C₃N₄), a superior catalyst support with high surface area, superior chemistry stability, amenability to chemical modification and many other fascinating properties, has been recently focused on heterogeneous catalysis.²⁹⁻³¹ As the s-triazine ring (C₃N₄) is aromatic, it is expected that a conjugated, two-dimensional polymer of s-triazine would tend to form a delocalized conjugated π structure like that of graphite.³² Wang et al.³³ have reported that the delocalized conjugated π structure can interact with the various metals, double- and triple-bond reactants, e.g. CO and so on, which should be favorable for reactions related to CO, e.g. CO oxidation. The delocalized conjugated π structure of g-C₃N₄ is also beneficial to improving electron transfer in the supported catalyst, which can play an important role in improving the stability of the highly dispersed metal particles. In particular, g-C₃N₄ with high number of nitrogen atoms in the networks can stabilize metal particles by the tight coordination. In the present contribution, we present a comprehensive study on CO oxidation over Cu₂O/g-C₃N₄ prepared via a facile impregnation-chemical reduction procedure and explore the relation between adsorption ability and the catalytic activity of Cu₂O/g-C₃N₄.

Experimental

Materials

All the reagents were analytical grade and used without any further purification.

Preparations

g-C₃N₄

The g-C₃N₄ was synthesized from urea by a facile template-free method.³⁴ In detail, 20.0 g of urea powder was put into a crucible with a cover, then the crucible was heated to 550 °C at a heating rate of 10 °C min⁻¹ and kept for 2 h in a muffle furnace. The yellow powder resultant was collected for use without further treatment.

Cu₂O

The calculated amounts of cupric nitrate were dissolved in distilled water (50 mL) to form a solution. Then, NaOH aqueous solution (0.2 mol L⁻¹) and ascorbic acid aqueous solution (0.1 mol L⁻¹) were dropwise added, while vigorously stirred, into the cupric nitrate solution, respectively. After addition, the mixture was continually stirred for another 4 h at 50 °C to form a claybank precipitation. The precipitate of Cu₂O was filtered, and washed several times with distilled water and ethanol, and dried at 40 °C in vacuum for 12 h.

Cu₂O/g-C₃N₄

Cu₂O/g-C₃N₄ was synthesized via the following typical procedure. The calculated amounts of cupric nitrate were dissolved in distilled water (50 mL) to form a solution, and g-C₃N₄ (0.5 g) was added to the solution, and the mixture was vigorously stirred for 1 h. After low-energy sonication for 0.5 h, the NaOH aqueous solution (0.2 mol L⁻¹) and ascorbic acid aqueous solution (0.1 mol L⁻¹) were dropwise added, while vigorously stirred, into the mixture, respectively. After addition, the mixture was continually stirred for another 4 h at 50 °C. Finally, the precipitate of Cu₂O/g-C₃N₄ was filtered, and washed to neutral with distilled water and ethanol, and dried at 40 °C in vacuum for 12 h. The samples with various mass ratio of Cu₂O to

g-C₃N₄, 2:10, 3:10, 4:10, 5:10 and 6:10, were marked as Cu₂O/g-C₃N₄-2, Cu₂O/g-C₃N₄-3, Cu₂O/g-C₃N₄-4, Cu₂O/g-C₃N₄-5 and Cu₂O/g-C₃N₄-6, respectively.

Catalyst characterization

TEM images of Cu₂O and Cu₂O/g-C₃N₄ were obtained with a JEM-2100 TEM working at 200 kV. The surface morphologies of the Cu₂O and Cu₂O/g-C₃N₄ were observed using X-650 scanning electron microscope (SEM) operated at 25 kV. The powder XRD experiments were carried out at room temperature using a Rigaku D/Max-2500 X-ray diffractometer (*CuKα* $\lambda = 0.154$ nm) to identify the crystal phase of the samples. The FT-IR spectra were recorded on Fourier transform infrared spectroscopy (Bruker Vector 22). The specific surface areas (SSA) were measured by nitrogen adsorption (BET, JW-K, at liquid N₂ temperature).

Temperature-programmed reduction with CO (CO-TPR) experiment was carried out using a Micromeritics TPR 2910 instrument. The sample (0.05 g) was loaded in a quartz tube reactor and flushed with Ar at 120 °C for 60 min. Then CO-TPR was performed by heating the samples to 800 °C at a ramp rate of 10 °C/min in a flow of 10% CO/Ar mixture with a rate of 30 mL/min. TCD was used to detect new gas formed in the determination process.

Catalytic tests

The absorption abilities of as-prepared Cu₂O, g-C₃N₄ and Cu₂O/g-C₃N₄ were measured by their decoloration activities for MO solution in the dark. Typically, catalyst (0.05 g) and 60 mL of MO aqueous solution (20 mg L⁻¹, neutral) were put into a 60 mL quartz test tube. The tube was placed in a dark box with magnetically

stirring. At regular time intervals, a sample of mixture was withdrawn and centrifuged, and the MO concentration of clear solution was measured using a TU-1901 UV-vis spectrometer at 463.8 nm, which is the maximum absorption wavelength of MO.

The evaluation of catalytic activities of Cu₂O and Cu₂O/g-C₃N₄ for CO oxidation was carried out in a fixed-bed flow microreactor under atmospheric pressure using 200 mg Cu₂O or Cu₂O/g-C₃N₄ samples containing 200 mg Cu₂O. A stainless steel tube with an inner diameter of 8 mm was chosen as the reactor tube. The catalyst was diluted with chemically inert quartz sand. Reaction gas mixture consisting of 10 % CO balanced with air was passed through the catalyst bed at a total flow rate of 36.3 mL min⁻¹. The temperature dependence of the sample catalytic activity was recorded in the range of 100-220 °C at a ramping rate of 10 °C min⁻¹. After holding at the reaction temperature for 30 min, effluent gases were analyzed on-line by GC-508A gas chromatography. The activity was expressed by the degree of conversion of CO.

Results and discussion

Structure and morphology

The morphology of the g-C₃N₄ was clearly visualized using transmission electron microscopy (TEM), as shown in Fig. 1a. The synthesized g-C₃N₄ shows obvious two-dimensional (2D) continuous lamellar structure, which is consistent with that reported in the previous report.³² The enlarged view in Fig. 1a indicates that the edges of the layers tend to bend in order to reduce surface energy.³⁴ The XRD pattern showed in Fig. 1b displays two pronounced diffraction peaks of (100) and (002) planes at $2\theta = 13.1^\circ$ and 27.1° , which can be ascribed to the characteristic inter-layer

structural packing and the interplanar stacking peaks of the aromatic systems, respectively. Fig. 1c depicts the FTIR spectra of the g-C₃N₄. A broad band centered at 3188 cm⁻¹ corresponds to the stretching modes of terminal NH groups at the defect sites of the aromatic ring. The absorption band at 1641 cm⁻¹ can be ascribed to the C-N stretching vibration modes, while the four strong peaks at 1253, 1329, 1417 and 1572 cm⁻¹ to the CN heterocycle stretching of g-C₃N₄. The absorption band at 808 cm⁻¹ can be assigned to breathing mode of heptazine ring system. These are consistent with the reported values. These results indicate that the g-C₃N₄ has been synthesized.

Fig. 2 shows the XRD patterns of Cu₂O and Cu₂O/g-C₃N₄ with different mass ratio. As can be seen, all samples show the diffraction peaks at 29.6°, 36.4°, 42.3°, 61.5°, 73.6° and 77.5°, which can be attributed to the (110), (111), (200), (220), (311) and (222) planes of cubic Cu₂O, corresponding to JCPDS card no. 65-3288. No obvious peaks corresponding to CuO or Cu are observed in the patterns. Compared with that of Cu₂O, the patterns of Cu₂O/g-C₃N₄ samples have no obvious difference, indicating that the existence of g-C₃N₄ do not change the crystal form of Cu₂O. It is noteworthy that for Cu₂O and Cu₂O/g-C₃N₄ samples, the (111) diffraction peaks of Cu₂O are all the strongest, which implies that {111} facets are dominated in samples. In the XRD patterns of Cu₂O/g-C₃N₄, the weak peak related to g-C₃N₄ (002) appears at 27.1°, indicating that g-C₃N₄ and cubic Cu₂O phase coexist in the composite.

The SSA of Cu₂O, g-C₃N₄ and Cu₂O/g-C₃N₄ with different mass ratio are listed in Table 1. The SSA of primary Cu₂O and g-C₃N₄ are 0.9 and 293 m²/g, respectively; the latter is consistent with the relevant literature of g-C₃N₄.³⁴ The SSA of all

Cu₂O/g-C₃N₄ samples are lower than that of pure g-C₃N₄, and decrease with the increase of Cu₂O content. It can be envisioned that the high surface area of g-C₃N₄ should be able to improve the dispersibility and decrease particle size of Cu₂O.

The morphologies and detailed microstructure of as-prepared Cu₂O particles and Cu₂O/g-C₃N₄-4 were investigated by SEM and HRSEM analyses. It can be seen from Fig. 3a that most particles of as-prepared Cu₂O are octahedral and their size is about 400-700 nm, which is in accordance with the relevant results of literature.³⁵⁻³⁶ The SEM images of Cu₂O/g-C₃N₄-4 shown in Fig. 3(b, c) clearly display that the sample is composited with Cu₂O particles and g-C₃N₄, in which the size of Cu₂O particle is smaller than that of prime Cu₂O (Fig. 3a) and there is a close interface between the Cu₂O and g-C₃N₄, which obviously demonstrates that the smaller Cu₂O particles can be separated from each other by g-C₃N₄ efficiently. It is understandable that the two-dimensional (2D) continuous lamellar structure of g-C₃N₄ with delocalized conjugated π -bonds can offer plentiful of nucleation sites and N-donor ligands, preventing Cu₂O particles from aggregation leading to the formation of discrete Cu₂O particles³⁷, which should be beneficial for enhancing the catalytic activity for CO oxidation.

Fig. 4 shows the TEM images of the Cu₂O/g-C₃N₄-4. As shown in Fig. 4a, the Cu₂O/g-C₃N₄-4 with particle-on-sheet morphology is obtained; all Cu₂O particles are deposited or attached to the surface of the g-C₃N₄ substrate and the size of Cu₂O particles is 100-200 nm, which is smaller than that of pure Cu₂O. The HRTEM image of the as-prepared Cu₂O/g-C₃N₄-4 also clearly reveals a close interface between the

Cu₂O and g-C₃N₄ in the as-prepared composite, which is significant for electrons transfer between the Cu₂O and g-C₃N₄ layer.³⁸

CO-TPR analysis

The oxidisability and stability of Cu₂O/g-C₃N₄ composite in CO was studied by means of CO-TPR, and the results are shown in Fig. 5. For g-C₃N₄, its CO-TPR is actually a temperature programmed decomposition because g-C₃N₄ is not reducible with CO + Ar. As shown in Fig. 5, g-C₃N₄ shows a distinguished peak at around 700 °C, which is ascribed to the thermal vaporization and decomposition of g-C₃N₄. Wang et al.³³ have reported that the sublimation of g-C₃N₄ increased massively at 650°C and complete decomposition occurred at 750 °C. Compared with g-C₃N₄, Cu₂O/g-C₃N₄-4 shows two CO reduction peaks centered at 420 and 630 °C, corresponding to the reduction of various Cu₂O crystals on g-C₃N₄. Fig. 5 clearly reveals that Cu₂O/g-C₃N₄ is stable and cannot be reduced by CO + Ar at temperature below 350 °C.

Adsorption ability

In order to explore the synergistic effect between the g-C₃N₄ and Cu₂O in the as-prepared Cu₂O/g-C₃N₄ composite, the decoloration activities of samples for MO solution in the dark were characterized and the results are shown in Fig. 6. MO is a sulfonic acid sodium salt, which can clearly indicate the adsorption ability of sample for negatively charged species in neutral solution. The g-C₃N₄ has hardly any adsorption ability for MO within 1.5 h. However, the Cu₂O particles and Cu₂O/g-C₃N₄ show strong adsorption for MO under the same conditions. Moreover,

Cu₂O/g-C₃N₄-3, -4 show stronger adsorption ability than pure Cu₂O. This result strongly suggests that the intimate junctions between g-C₃N₄ and Cu₂O bring some synergistic effects to enhance the decoloration activity, or adsorption ability, of the g-C₃N₄/Cu₂O composite. As the result of XRD, the {111} facets in Cu₂O particles are dominated, which is responsible for the strong adsorption ability of the Cu₂O particles. It is well known that the Cu₂O crystals bounded by the {111} facets contain positively charged copper atoms on the surfaces,³⁹ which can interact more strongly with MO anions. This phenomenon should be noteworthy, because it suggests the as-prepared Cu₂O/g-C₃N₄ may strongly interact between the g-C₃N₄ and Cu₂O to enhance the catalytic activity of Cu₂O/g-C₃N₄ for CO oxidation. In additionally, Cu₂O content can obviously affect the decoloration activity, the Cu₂O/g-C₃N₄-4 displays the highest decoloration activity. It could be predicted that the Cu₂O/g-C₃N₄-4 should also have the highest catalytic activity for CO oxidation.

CO oxidation activity

The catalytic activities of Cu₂O and Cu₂O/g-C₃N₄ with different mass ratio for CO oxidation are shown in the Fig. 7. It can be seen from the figure that no significant CO conversion over the pure Cu₂O is found until 180 °C, and $T_{100\%}$ appears at about 220 °C. However, the Cu₂O/g-C₃N₄ shows extremely attractive catalytic activity and the activity increases from Cu₂O/g-C₃N₄-2 to Cu₂O/g-C₃N₄-4; when mass ratio of Cu₂O to g-C₃N₄ increases any further, the activity decreases (Cu₂O/g-C₃N₄-5). The high activities of the Cu₂O/g-C₃N₄ samples should come from synergetic effects of g-C₃N₄ and Cu₂O. Additionally, the improved dispersibility and the decreased particle

size of Cu_2O of the as-prepared composites also play important roles in enhancing CO oxidation activity. Xu et al.⁴⁰ have reported that the {111} facets of Cu_2O have high surface atomic density of Cu atoms, which can provide more adsorbed and reactive sites; the two-dimensional (2D) continuous lamellar structure of g- C_3N_4 with high SSA can disperse Cu_2O particles so efficiently that more small Cu_2O particles form and increase in turn active sites for the oxidation reaction. It is obvious that $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4\text{-4}$ exhibits the best catalytic performance, over which the CO oxidation starts at $\sim 140^\circ\text{C}$ and 100 % CO conversion can be achieved at $\sim 200^\circ\text{C}$ with a T_{50} of $\sim 180^\circ\text{C}$. In comparison with $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4\text{-4}$, the catalytic performance of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4\text{-5}$ decreases sharply. The result may be attributed to the fact that the high content of Cu_2O is not benefit for dispersion of Cu_2O particles, which decreases the synergistic effects, e.g. the transfer of electrons between coordination unsaturated Cu of Cu_2O and g- C_3N_4 .

The long-term stability of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ catalysts in the catalytic reaction is an important parameter to consider when evaluating catalytic performance. Stability of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4\text{-4}$ was examined by running for 12 h and the results are presented in Fig. 8. After continuous operation for 12 h, the conversion of CO remains at 100 % and no deactivation is found at 200°C , indicating that the as-prepared $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ catalysts have high stability for CO oxidation. In order to further confirm the stability of the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ catalysts, the $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4\text{-4}$ used for the 12 h was collected and analyzed by XRD, which is shown in Fig. 9. It can be seen from Fig. 9 that the diffraction peaks assigned to Cu_2O match very well with JCPDS card no. 65-3288 and

no peaks related to Cu or CuO are observed, which is in good agreement with the results of CO-TPR, indicating that no new species generated in the process of CO oxidation. It can be concluded that the Cu₂O/g-C₃N₄ catalysts in the present contribution are highly stable based on the all results above.

Mechanism of CO oxidation

The interactions between Cu₂O and g-C₃N₄ are responsible for the results discussed above. Zhang et al. have reported the interactions between Pd atoms and g-C₃N₄.³⁸ The g-C₃N₄ has a lot of π orbitals, which can adjust electron density of Cu₂O through the $P\pi$ - $d\pi$ bonding between the π -orbitals of g-C₃N₄ and d -orbitals of coordination unsaturated Cu of Cu₂O. With the help of delocalization of electrons in whole of Cu₂O/g-C₃N₄, the coordination unsaturated Cu of Cu₂O could accept the donation of CO + O₂ more effectively and enhance the catalytic activity of catalysts.

The reaction mechanism of CO oxidation over metal oxides catalyst has been well established.⁸ It has been reported that Cu₂O has extremely high activation energy of 600 kJ mol⁻¹, which could be due to the extra energy needed to dissociate O₂ on the Cu₂O surface. Thus, the usual MVK mechanism is not suitable for CO oxidation on Cu₂O (111). Based on the relevant literatures^{9, 41-42} and the results above, the mechanism of Cu₂O/g-C₃N₄ catalysts for CO oxidation reaction is proposed and shown in **Scheme 1**. The reaction could take place via two paths. Path I is that CO attacks the O₂ binding to Cu₂O to directly produce CO₂, which leaves behind an oxygen atom bounding to Cu₂O surface, namely, $\text{CO}_{(\text{gas})} + \text{O}_{2(\text{ads})} \rightarrow \text{CO}_{2(\text{gas})} + \text{O}_{(\text{ads})}$. Path II is of Langmuir-Hinshelwood type where adsorbed CO reacts with

adsorbed oxygen. The peroxo-type (OOCO) complex generated from the co-adsorption of CO and O₂ decomposes into product CO₂, and an oxygen atom bounding to Cu₂O surface is left behind, namely, $\text{CO}_{(\text{ads})} + \text{O}_{2(\text{ads})} \rightarrow \text{OOCO}_{(\text{ads})} \rightarrow \text{CO}_{2(\text{gas})} + \text{O}_{(\text{ads})}$.

Conclusions

In this paper, the Cu₂O deposited on 2D continuous lamellar g-C₃N₄ catalysts with different mass ratio were prepared via impregnation-facile chemical reduction method. Cu₂O particles were highly dispersed on the surface and interspace of g-C₃N₄. The mass ratio of Cu₂O to g-C₃N₄ showed a significant influence on the adsorption ability and catalytic performance for CO oxidation. The Cu₂O deposited on g-C₃N₄ with the mass ratio of 4:10 exhibited the strongest adsorption ability for methyl orange and highest catalytic activity. The strong adsorption ability was ascribed to the dominant exposure of {111} facets in Cu₂O particles, which have the dangling bonds from the surface copper atoms interacting well with negative charged methyl orange. The enhancement of catalytic performance could be attributed to the synergetic effects between g-C₃N₄ and Cu₂O and the improved dispersibility of Cu₂O particles.

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Captions of Tables and Figures

Table 1 SSA of Cu₂O, g-C₃N₄ and Cu₂O/g-C₃N₄ with different mass ratios

Fig. 1 TEM images (a), XRD pattern (b) and FT-IR pattern (c) of g-C₃N₄.

Fig. 2 XRD patterns of Cu₂O and Cu₂O/g-C₃N₄ with different mass ratios.

Fig. 3 SEM images of Cu₂O (a) and Cu₂O/g-C₃N₄-4 (b, c).

Fig. 4 TEM images of Cu₂O/g-C₃N₄-4.

Fig. 5 CO-TPR profiles of g-C₃N₄ and Cu₂O/g-C₃N₄-4

Fig. 6 Adsorption abilities of as-prepared g-C₃N₄, Cu₂O and Cu₂O/g-C₃N₄ for
MO in the dark.

Fig. 7 Catalytic activities of Cu₂O and Cu₂O/g-C₃N₄ with different mass ratios.

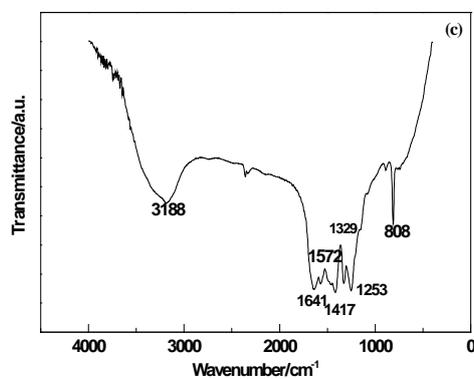
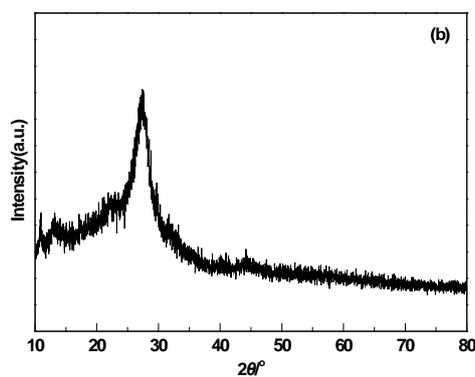
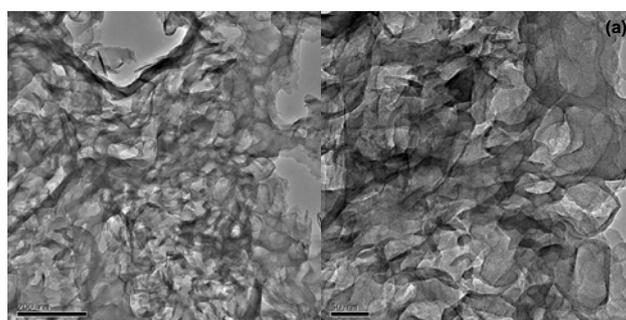
Fig. 8 Stability of Cu₂O/g-C₃N₄-4, reaction temperature: 200 °C.

Fig. 9 XRD patterns of fresh Cu₂O/g-C₃N₄-4, used Cu₂O/g-C₃N₄-4 and SiO₂.

Scheme 1. The possible mechanism of Cu₂O/g-C₃N₄ catalysts for CO oxidation
reaction.

Table 1 SSA of Cu₂O, g-C₃N₄ and Cu₂O/g-C₃N₄ with different mass ratios

Samples	Cu ₂ O	g-C ₃ N ₄	Cu ₂ O/g-C ₃ N ₄ -2	Cu ₂ O/g-C ₃ N ₄ -3	Cu ₂ O/g-C ₃ N ₄ -4	Cu ₂ O/g-C ₃ N ₄ -5
S _{BET} (m ² /g)	0.9	293	76	71	65	37

**Fig. 1**

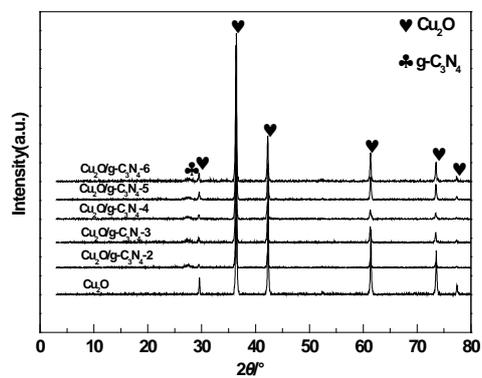


Fig. 2

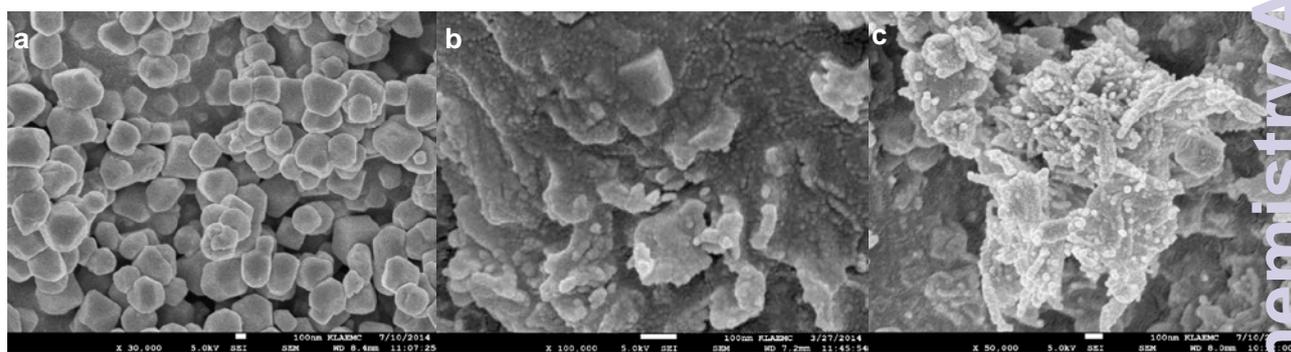
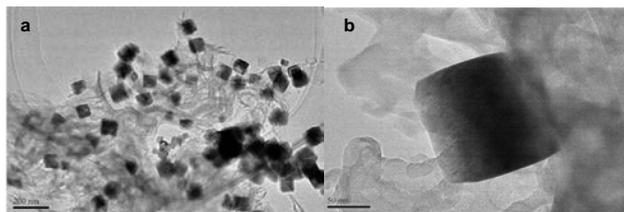
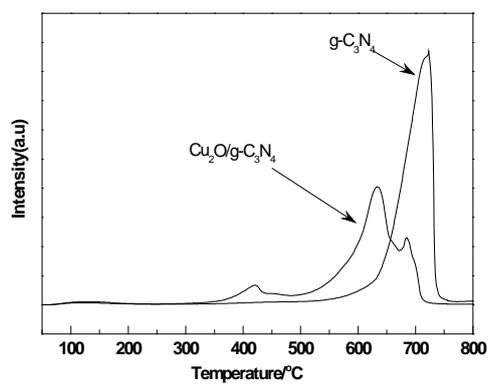


Fig. 3

**Fig. 4****Fig.5**

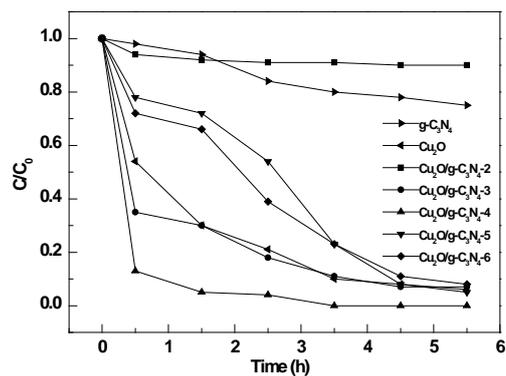


Fig. 6

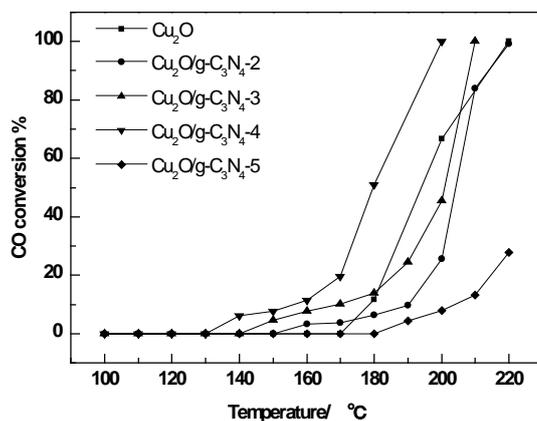


Fig. 7

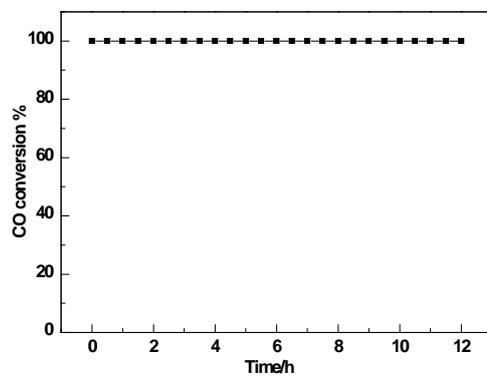


Fig. 8

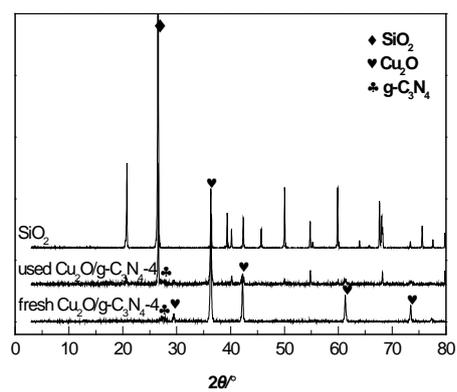
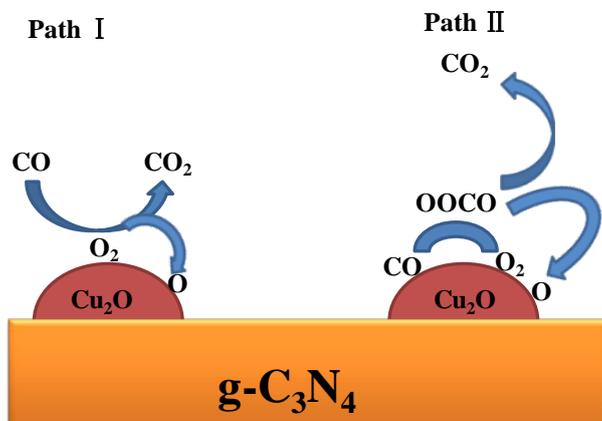


Fig. 9



Scheme 1.