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Investigation of photodegradation of 2,4-Dichlorophenoxyacetic acid on $Cu_2O/g\text{-}C_3N_4$ catalysts

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ABSTRACT

The series x% (wt) $Cu_2O/g\text{-}C_3N_4$ composites were prepared by the conventional impregnation method. These compounds were characterized by different methods such as X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), UV–vis diffuse reflectance spectroscopy (UV-DRS), and Photoluminescence spectroscopy (PL). The results clearly showed the existence of Cu_2O and $g\text{-}C_3N_4$ phases. The photocatalytic activity was estimated by the degradation of 2,4-Dichlorophenoxyacetic acid (2,4-D). The 5% $Cu_2O/g\text{-}C_3N_4$ catalyst showed the highest activity, with the photodegradation yield reached 7,3%. The addition of H_2O_2 remarkably improved the yield, with 98,5% attained after 1 hour of irradiation.

Introduction

Along with the rapidely development of agriculture, different types of pesticides have been used widely. They are normally organochlorine insecticides such as polychorinated biphenyl (PCBs), pholychlorinated dibenzodioxin (PCDDs). Using an excessive amount of these pesticides in this field leads to soil poisoning and surface water pollution. These compounds are very stable and difficult to degrade in the natural environment. Therefore, their accumulation in the environment causes a threat to the ecosystem and human health [1-3].

There are different physical, chemical, or biological methods to decompose and mineralize these persistent organic pollutants. Among the mentioned methods above, chemical way, concretely photocatalytic decomposition exhibit a high potential. Oxide TiO_2 is the most popular photocatalyst due to its low cost, availability, chemical stability, and non-toxicity [4-7]. However, its bandgap energy is 3.2eV, and that means the TiO_2 is only activated under ultraviolet light. If sunlight, the most economical energy source, serves to activate catalyst, then this catalytic process is not efficient because the UV intensity in the solar spectrum is relatively low, only ~5%. That is why a lot of research focuses on finding new photocatalysts that can be activated in visible light. Recently, graphitic carbon nitride $g\text{-}C_3N_4$ has been attracted in the field of photocatalysis due to its good stability and visible light absorption properties (E_g = 2.7 eV) [8].

However, the photocatalytic efficiency of $g\text{-}C_3N_4$ is still relatively low due to the rapid recombination of produced photoelectron and hole pairs. To overcome this drawback, many composites of $g\text{-}C_3N_4$ with another oxide, metal, to form Z-scheme photocatalyst type, are investigated [9-11]. In this study, we have synthesized a Z-scheme $Cu_2O/g\text{-}C_3N_4$ catalyst. Its

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photocatalytic activity was estimated through the photodegradation of 2, 4-D.

Experimental

Catalyst preparation

The used chemicals were of analytical purity: Melamine $C_3H_6N_6$ (Merck), Ethanol 99% C_2H_5OH (China), $Cu(CH_3COO)_2.H_2O$ (China), $C_6H_{12}O_6$ (China),

The carbon graphitic nitride, g-C_3N_4, was formed when calcining melamine under N_2 flux at 550°C for 3 hours. The x% (wt) Cu_2O/g-C_3N_4 catalysts were synthesized by the following procedure: dissolving the adequate amounts of $Cu(CH_3COO)_2$. H_2O and g-C_3N_4 salts into a 100ml beaker then covered by paraffin paper. After that, the mixture was stirred at 60°C for one hour, then the paraffin paper was removed and the mixture continuously dried at 60°C to obtain powder; after that, adding a suitable amount of powder A in glucose 0.2M solution adjusted at pH equal to12 by NaOH 0.1M solution; the final mixture was filtered, washed and dried in oven at 70°C.

Characterization

The catalysts were characterized by different methods. The X-ray diffraction (XRD) pattern was measured on X-Ray Diffraction, D8 Bruckner. The Infrared (IR) spectra were determined on FT-IR 6300 type A, JASCO. UV-DRS spectra were collected by a Perkin-Elmer Lamda 365 spectrometer equipped with a reflectance sphere using pure calcium sulfate ($CaSO_4$) powder as a white reflection standard. The photoluminescence (PL) spectra were measured on the HORIBA Jobin Yvon-Fluoromax-4.

Photocatalytic procedure

The photocatalytic activity of the catalysts was evaluated through the photodegradation of 2,4-D, a popular pesticide. The different steps of the test were carried out as follows:

An amount of 0.1g of catalyst was added into 100mlsolution of 20ppm of 2,4-D. The mixture was stirred and maintained at room temperature during the experiment. Firstly, the system was left in the dark for 1h to reach adsorption equilibrium. After that, irradiation was carried out with a 500W halogen lamp (at a distance of 30 cm far from the solution's surface). 5ml of the solution was taken every hour to analyze the 2,4-D concentration by HPLC (Agilent) equipped C18 column. The photodegradation yield was calculated by the formula: $H(\%) = (C_0-C)/C_0 \times 100\%$.

Result and discussion

Characterization of the catalysts

Figure 1 presents the XRD pattern of x% (wt) Cu_2O/g-C_3N_4 (x= 1; 2.5; 5; 10):

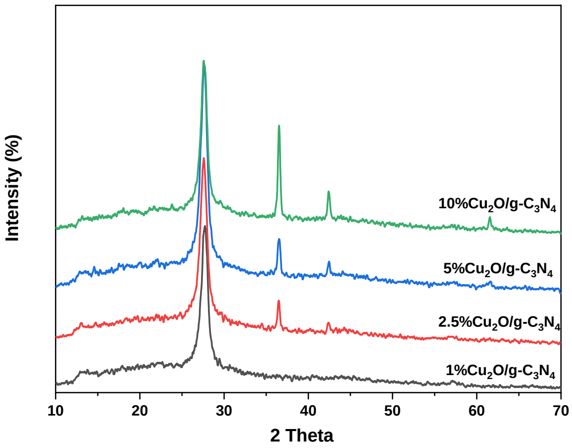

Figure1: XRD pattern of x%(wt) Cu_2O/g-C_3N_4 (x= 1; 2.5; 5; 10)

From Figure 1, it is evident that the g-C_3N_4 phase was not destroyed during the synthesis process. The diffraction peaks of the g-C_3N_4 phase appear at an angle of $2\theta = 27.5°$, corresponding to the d_{002} surface, which is a characteristic peak for the layered structure of g-C_3N_4. The typical peaks of the Cu_2O phase were observed in all samples of x% (wt) Cu_2O, except 1% (wt) Cu_2O. The characteristics of 2θ peaks for Cu_2O are of 35.6°, 42.5°, 62°, corresponding to the crystal faces of d_{111}, d_{200}, d_{220}, d_{311}, respectively. For the 1%Cu_2O catalyst, the presence of Cu_2O was not detected, probably because of the low content of Cu_2O.

Infrared spectra of catalysts

To determine the different functional groups and bonds in the synthesized catalysts, the IR spectra measurements were carried out and presented in figure 2 below.

From the IR spectra, it is noted that the catalysts showed a similar peak group in the range from 1200 to 1800 cm^{-1} corresponding to the vibrations of the CN, C=N bonds in the hydrazine ring structure of g-C_3N_4. For all samples, the broad absorption band centered at about 3500 cm^{-1} corresponds to the vibrations of the –

OH group of physically absorbed water on the catalyst surface. In addition, the results of IR spectroscopy show a small peak of at 620cm^{-1} corresponding to the vibration of the Cu-O bond in the Cu_2O phase [11].

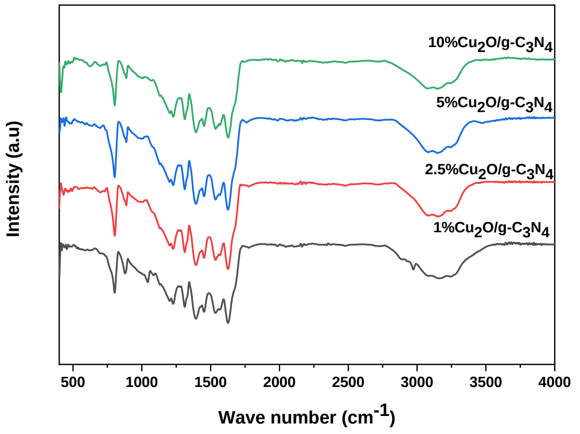

Figure 2: IR spectra of x% (wt) Cu_2O/g-C_3N_4catalyst (x= 1; 2.5; 5; 10)

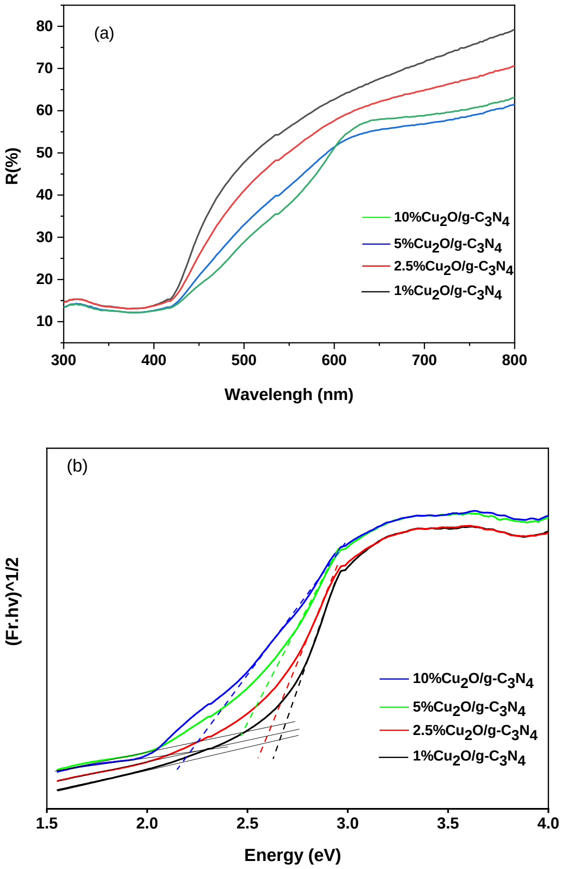

Figure 3: UV-DRS spectrum (3a) and of its calculated Kubelka-Munk *function (b)* of catalyst Cu_2O/g-C_3N_4

To determine the light wavelength activating photocatalytic reaction, the UV-DRS spectra of the catalysts were measured (figure 3a). The plot of Kubelka-Munk function calculated from UV-DRS spectrum results is presented in figure 3b. Based on this result, the bandgap energy was determined and resumed in table 1.

Table 1: Band-gap energy of catalysts Cu_2O/g-C_3N_4

N^0	Catalyst	E_g (eV)
1	1%Cu_2O/g-C_3N_4	2.66
2	2.5%Cu_2O/g-C_3N_4	2.60
3	5%Cu_2O/g-C_3N_4	2.47
4	10%Cu_2O/g-C_3N_4	2.25

As expected, the combination of two phases, Cu_2O and g-C_3N_4, decreased the band-gap energy of the catalysts compared with g-C_3N_4, from E_g = 2,7 eV of g-C_3N_4 to 2.25 eV for 10% (wt) Cu_2O/g-C_3N_4. More content of Cu_2O presented in composite, more E_g reduced. This result confirmed that all catalysts could be activated in the visible light range.

Figure 4 presents Photoluminescence spectra of g-C_3N_4 and 5%(wt) Cu_2O/g-C_3N_4. The intensity of 5%(wt) Cu_2O/g-C_3N_4 is remarkably lower than that of g-C_3N_4. This result is probably due to preventing the recombination of photogenerated electron-hole pairs in the presence of the Cu_2O phase. This synergistic property could favor the photooxidation of 2,4-D.

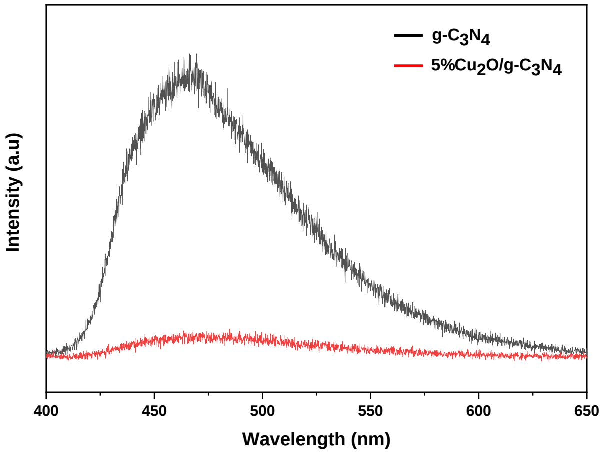

Figure 4: PL spectra of g-C_3N_4 and 5%Cu_2O/g-C_3N_4

Photodegradation of 2,4-D on the catalysts

Figure 5 showed a relatively low activity of g-C_3N_4 and x% (wt) Cu_2O/g-C_3N_4. The obtained result indicated that the catalyst 5% (wt) Cu_2O/g-C_3N_4 exhibited the highest activity, reaching 7,3% (wt). The order activity is following: 5% (wt) Cu_2O/g-C_3N_4> 10% (wt) Cu_2O/g-C_3N_4> 2,5% (wt) Cu_2O/g-C_3N_4> 1%(wt) Cu_2O/g-C_3N_4.

Although the yield was quite low, the result showed an improvement in photocatalytic activity when combining g-C_3N_4 with Cu_2O to form a Z-scheme type catalyst [12].

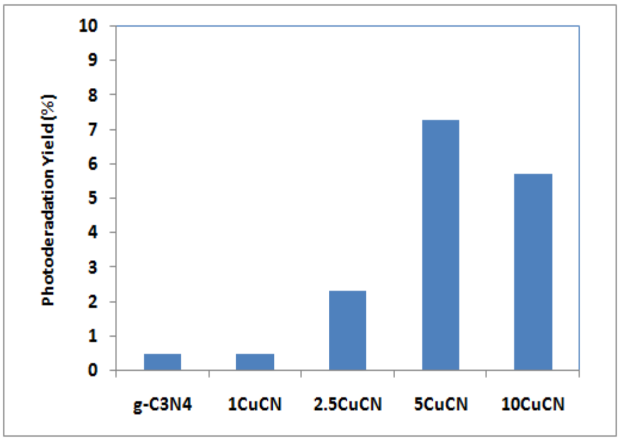

Figure 5: Photodegradation yield of x% (wt) Cu_2O/g-C_3N_4 versus 2,4D after 4 hour of irradiation

This one is probably due to the transfer of photogenerated electrons on the Cu_2O phase onto the conduction band of g-C_3N_4 and, inversely, photogenerated holes onto the Cu_2O valence band as manifested in figure 6. The PL spectra above are according to this hypothesis. The 5% of Cu_2O seems to be the most suitable amount for combining with g-C_3N_4 to reach better photoactivity. This positive synergetic combination was already observed in the researches [13, 14].

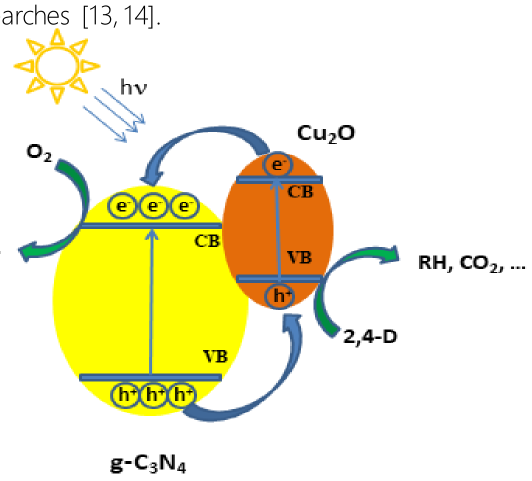

Figure 6: Proposed mechanism of photodegradation 2,4-D on the catalyst Cu_2O/g-C_3N_4

Although the catalyst 5%Cu_2O/g-C_3N_4 showed the highest activity however the yield was relatively low, only 7,3%. A stronger oxidant seems to be necessary to better degrades 2,4-D. Hence, 1 ml H_2O_2 , an well-known strong oxidant was added in the test. The result is exhibited in figure 7.

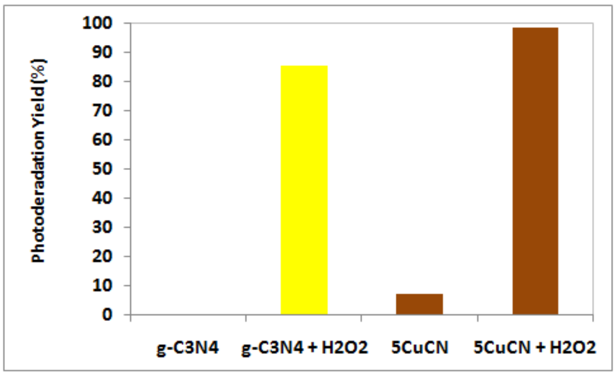

Figure 7:Photodegradation of g-C_3N_4 and 5% (wt) Cu_2O/g-C_3N_4 in the absence and presence of H_2O_2

From the results in figure 7, after 1 hour of illumination, the photodegradation reaction achieved a yield of 98.5% in the presence of H_2O_2. This result is better than that of g-C_3N_4, which is 85.6%. The photo-Fenton process that many studies have mentioned showed a remarkable improvement of photoactivity. The obtained result is likely high potential to treat the 2,4-D pollutant thoroughly in water.

Conclusion

The catalysts x% (wt) Cu_2O/g-C_3N_4 were synthesized by the conventional impregnation method. The XRD and IR characterization results showed the clear presence of the Cu_2O and g-C_3N_4 phases. The catalytic activity was evaluated by the 2,4-D photodegradation reaction. The improvement of photocatalytic activity was observed over all the composite catalysts. This confirmed a positive synergetic combination of two phases, Cu_2O and g-C_3N_4. The highest photodegradation of 2,4-D attained 7.3% on the catalyst 5% (wt) Cu_2O/g-C_3N_4 after 5 hours of illumination. This is explained by the lower bandgap energy (E_g=2.2 eV) of Cu_2O and the transfer of electron and hole pairs between the two phases, leading to more existence of photogenerated electron-hole pairs. Especially in the presence of 1ml H_2O_2, 98.5% of 2,4-D was oxidized after 1 hour of irradiation. It is a remarkable result from the point of application view. Optimizing photodegradation of 2,4-D is needed in further studies.

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