

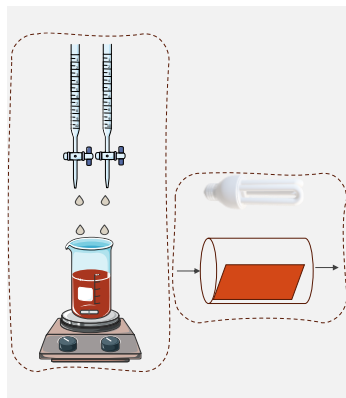
Ag-Cu₂O Photocatalyst: Synthesis and Its Application in Ethylene Degradation

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Ethylene, a plant hormone essential for various physiological processes, notably fruit ripening, plays a pivotal role in the maturation of climacteric fruits. Then, controlling ethylene concentration during fruit transportation and storage is fundamental to improve the shelf-life of some fruits. Various technologies to eliminate the ethylene presence including chemical or photocatalytic oxidation, and removal by adsorption, for example, can be used. In this study, Cu₂O particles with varying Ag content (0%, 4%, and 8% w/w) were synthesized and investigated for their efficacy in ethylene photodegradation under both UV-A and visible light. Our findings revealed a notable enhancement in photocatalytic activity with the inclusion of 4% Ag, indicating promising prospects for the photocatalytic removal of ethylene in the gas phase.

Introduction

One third of all fruits and vegetables productions are losses during storage and transportation, that indicated a global problem. Fruits and vegetables accounting for up to 45% of losses, due to the rapid perishability of these products [1,2]. A way to extend shelf life during the transportation and storage of climacteric fruits and vegetables is by ethylene removal in the storage chambers through adsorptive or reactive processes, since this gas is the hormone responsible to trigger their ripening [3].

Much has been studied in terms of developing photocatalysts to degrade ethylene in the gas phase. However, the key aspect that affect the efficient ethylene removal is the photocatalyst active both under UV and visible light. In this context, incorporating silver into photocatalysts can enhance the activation mechanism by reducing electron-hole recombination [4]. In this study, the doping of silver particles into Cu₂O particles is carried out using simultaneous dripping of NaBH₄ and different amounts of AgNO₃. The photocatalysts containing 0, 4 and 8% (w/w) of silver were synthesized and characterized (XRD and FTIR), and the photocatalytic activity was investigated under UV-A and visible light in the degradation of ethylene.

Material and Methods

All of the chemical reagents used in this experiment were of analytical grade and used without further purification. The following chemicals were used: polyvinylpyrrolidone (M_w 30.000), copper chloride dihydrate, sodium hydroxide, ascorbic acid, sodium borohydride (NaBH₄), silver nitrate (AgNO₃), ethanol, and ethylene 1.0% (%mol, synthetic air).

The Cu₂O particles were synthesized according to the method suggested by Zhang *et al.* [4], and the solids were collected by centrifugation (7500 rpm, 5 min), washed three times with deionized water and twice with ethanol, and dried at 60 °C overnight. For the synthesis of Ag/Cu₂O, before centrifugation of Cu₂O particles, NaBH₄ solution (20 mL) and AgNO₃ solution (20 mL) were dripped concomitantly into the particle solution and kept under magnetic stirring for 3 h. Particles with 4 and 8% Ag (w/w) were synthesized, designated 4Ag/Cu₂O and 8Ag/Cu₂O, respectively. The solids particles were characterized by XRD and FTIR.

The photocatalytic activity of the materials was investigated in a continuous flow reactor as previously described [5]. The composition of the gas phase was continuously monitored by gas chromatography, using a GC-2014 (Shimadzu) with TCD/FID detectors, and a methanizer MTN-1 (Shimadzu). A gas aliquot of 0.1 mL (20 min each injection) is injected into a CarboxenTM 1000 60/80 packed column (SUPELCO) under a carrier gas flow rate of 30 mL.min⁻¹ of argon (99.999%). The GC was previously calibrated using standard gas mixtures. The photocatalytic ethylene oxidation was accomplished by the formation of carbon dioxide.

Results and Discussion

XRD analysis (Figure 1) indicated the formation of crystalline structure with characteristic octahedral Cu₂O peaks at approximately 29.6, 36.4, 42.3, 61.3, 73.5 and 77.3°, attributed to the cubic facets (1 1 0), (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2), respectively (JCPDS no. 05-0667). Additionally, it was possible to identify the presence of Ag with the characteristic

peaks at approximately 38 and 44°, attributed to the (1 1 1) and (2 0 0) facets of the cubic phase of the silver particles (JCPDS no. 04-0783), indicating the formation of the particles of interest.

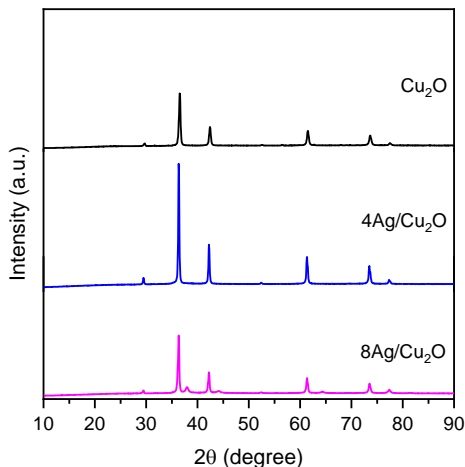


Figure 1. XRD pattern of Cu₂O (black), 4Ag/Cu₂O (blue), and 8Ag/Cu₂O (magenta) particles.

The FTIR spectrum of the synthesized particles revealed the presence of a band in 619 cm⁻¹, which was attributed to the symmetric and asymmetric stretching of Cu(I)-O bond [6,7]. The absence of any cupric oxide (CuO) impurity can also be observed since the characteristic vibration of Cu(II)-O bond around 588 cm⁻¹ was not identified [7].

The photocatalytic assays were performed under visible light and UV-A irradiation, with a flow rate of 50 mL.min⁻¹. The CO₂ formation rate (Table 1) was calculated in the steady state assuming differential reactor behavior [8].

Table 1. Carbon dioxide production rate, under visible light and UV-A irradiation (ethylene concentration: 1.0%, gas flow rate: 50 mL.min⁻¹).

Photocatalyst	Rate (μmol.min ⁻¹ .g _{cat} ⁻¹)	
	Visible light	UV-A
Cu ₂ O	~zero	0.11 ± 0.05
4Ag/Cu ₂ O	0.13 ± 0.05	0.27 ± 0.05
8Ag/Cu ₂ O	0.12 ± 0.09	0.16 ± 0.02

Under similar conditions, using Ag₂MoO₄/C₃N₄ and UV-A irradiation, our research group obtained similar results (0.070 μmol.min⁻¹.g_{cat}⁻¹) [5], indicating that the hybrid samples prepared in this work are promising as a photocatalyst. As shown in Table 1, the presence of Ag increases significantly the photocatalytic activity, mainly under visible light.

This can be attributed to the Ag particles acting as a co-catalyst, capturing photoelectrons and forming a barrier at the Ag-Cu₂O interface, reducing the recombination of photogenerated charges [9]. The sample 4Ag/Cu₂O resulted in the highest photocatalytic activity under UV-A irradiation (0.27 μmol.min⁻¹.g_{cat}⁻¹). However, with an increase in the amount of Ag loading, the formation rate of CO₂ product over 8Ag/Cu₂O photocatalysts decreases to 0.16 μmol.min⁻¹.g_{cat}⁻¹, which can be attributed to the decrease in the surface density of photoinduced electrons in the presence of a high amount of Ag, as observed by Tang *et al.* [9]. Thus, the presence of Ag in Cu₂O photocatalyst improves the activity for the degradation of ethylene, indicating prospects for its application in photocatalytic processes.

Conclusions

The XRD results indicated Cu₂O formation and the presence of Ag on the composition. The oxidation of gaseous ethylene under UV-A irradiation or visible light increased due to presence of Ag. The sample with 4% Ag showed the highest ethylene degradation activity. These results indicate the promising use of Ag/Cu₂O compounds as a photocatalyst for gaseous reactions.

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