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Photodegradation of p-nitrophenol using octahedral Cu_2O particles immobilized on a solid support under a tungsten halogen lamp

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ABSTRACT

Octahedral Cu_2O particles were prepared on an indium-tin oxide glass via electrodeposition and were employed in the catalytic degradation of p-nitrophenol in the presence of H_2O_2. Under irradiation of a warm visible-light source, tungsten halogen lamp, Cu_2O particles not only acted as a photocatalyst, but might also act as a thermal-catalyst to induce the decomposition of H_2O_2 and produce O_2 at higher temperatures. The photogenerated electrons and holes could react with H_2O_2, O_2, and H_2O to produce abundant $^{\bullet}OH$ radicals, resulting in the effective oxidation of p-nitrophenol. High-performance liquid chromatography measurements of degradation intermediates showed that p-nitrophenol was first decomposed into hydroquinone and benzoquinone and then mineralized. The degradation efficiency was dependent on electrodeposition time, light intensity, H_2O_2 amount, and solution temperature. This catalyst could be easily recycled and used in the efficient degradation of other phenolic compounds.

1. Introduction

p-Nitrophenol (PNP) is one of the most hazardous refractory pollutants with high stability and solubility in water. It can be found in industrial and agricultural wastewaters, posing a significant environmental and public risk. Generally, these PNP molecules can be effectively decomposed by several advanced oxidation processes (AOPs), for example, microwave-assisted oxidation [1], electrocatalytic oxidation [2], radiation-induced catalytic oxidation [3], and photoelectrocatalytic oxidation [4]. However, the requirements of various devices, the complex designs of oxidation systems, or low degradation efficiency limit the practical applications of these methods. Photo-induced oxidation, which is also an AOP, is economical, environmentally friendly, and promising in treating contaminated water. In addition to the homogenous catalyst systems of UV/H_2O_2 photo-oxidation [5] and photo-Fenton oxidation [6], several TiO_2-based heterogeneous photocatalysts, such as nanosized TiO_2 or TiO_2/SiO_2 composite particles [7,8], organic acid-modified TiO_2 particles [9], and Fe-doped TiO_2 particles [10], have been used in the photocatalytic degradation of PNP, but they are activated only under UV-light irradiation. Moreover, in all reports, the catalyst particles have to be dispersed in solution and are difficult to be recycled. The preparation or the construction of a recyclable photocatalyst or photocatalytic system for PNP photodegradation under the irradiation of a low-cost, harmless, and easily operated lamp remains a challenge.

Recently, Cu_2O, as a new type of photocatalyst, has attracted much attention because it has low toxicity, is environmentally friendly, and has a narrow direct band gap (2.17 eV) that can be easily activated by visible light. In many studies, Cu_2O can be efficiently used in the photocatalytic degradation of various dyes and in the decomposition of water into H_2 and O_2 [11,12]. In photodegradation of PNP and other organic pollutants, only Cu_2O/TiO_2 [13] heterojunction network, $Cu_2O@TiO_2$ core–shell particles [14] and Cu_2O/Ag composite nanoparticles [15] have ever been reported exhibiting high efficiency; when Cu_2O particles alone were used directly [16], the degradation process took longer to obtain a low efficiency. In addition, Cu_2O particles cannot be immobilized and have to be directly dispersed in solutions, which inevitably results in the aggregation of different particles, a decrease in the activities, and make the particles difficult to recycle.

In this study, we introduce for the first time the application of octahedral Cu_2O particles on an indium-tin oxide (ITO) glass for PNP photodegradation in the presence of H_2O_2. The particles obtained

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via electrodeposition directly grew on the substrate and were isolated from each other. A Cu_2O crystal with octahedral shape was hypothesized to possess the highest stability and the best activities [17]. A warm visible-light source, tungsten halogen lamp, was employed. The lamp provides the visible light required in the photochemical reactions and increases the temperature of the solution. The increase in the temperature could excite the thermal-catalytic activity of Cu_2O to induce the catalytic decomposition of H_2O_2 and produce O_2 [18]. The combined effects of both oxidants, H_2O_2 and O_2 [19], caused the production of more $^{\bullet}OH$ radicals [20], thereby oxidizing PNP more efficiently. The method required no protection measure, stirring apparatus, cooling system, and aeration device. These requirements are commonly found in a general photocatalytic system. The catalyst could also be used in the degradation of many other pollutants and could be easily recycled.

2. Materials and methods

2.1. Materials

Analytical-grade reagents including copper sulfate ($CuSO_4{\cdot}5H_2O$), hydrogen peroxide (H_2O_2), poly(vinyl pyrrolidone) (PVP), PNP, phenol, and *p*-chlorophenol were all purchased from the Aladdin Reagent Company and were used without further purification. ITO-glass substrates were employed as the conducting substrates and carriers for the preparation of the Cu_2O particles. These substrates were ultrasonically and sequentially cleaned in acetone, ethanol, and distilled water prior to use.

2.2. Electrodeposition of the Cu_2O particles

Octahedral Cu_2O particles on the ITO substrates were galvanostatically electrodeposited at an ambient temperature in an electrolyte solution composed of copper sulfate (0.02 M) and PVP (8.0×10^{-4} M). ITO substrates ($4.0 \times 1.5\ cm^2$) immersed in the electrolyte were used as the working electrode, and a graphite plate was used as the auxiliary electrode. The distance between the two electrodes was maintained at 10 cm. Electrodeposition was carried out at a current density of $0.18\ mA\ cm^{-2}$ for a specific period. Subsequently, the samples were obtained and rinsed with abundant distilled water to remove impurities. The samples were labeled as "sample-15," "sample-30," "sample-45," "sample-60," and "sample-90" according to different electrodeposition times (min). The electrodeposition area for each sample was maintained at 3.0 cm × 1.5 cm.

2.3. Photodegradation experiments

In a typical experiment, one piece of ITO glass covered with octahedral Cu_2O particles was immersed in 50 mL of $20\ mg\ L^{-1}$ PNP solution in a beaker. 1 mL of 3 vol% H_2O_2 was added into the solution using a pipette. After the beaker was covered with a polyethylene film, it was directly placed beside a 150 W tungsten halogen lamp while maintaining a 15 cm distance. Agitation in the solution or any protection measure was not necessary. When the sample was illuminated, approximately 3.0 mL of the reactive pollutant solution was taken from the beaker to analyze the variations in the concentration of the degraded solution every 20 min. The analyzed solution was poured back into the beaker to keep the total volume of the solution constant.

2.4. Characterization and analytical methods

The morphologies of the Cu_2O particles on the ITO glass were directly investigated via field emission scanning electron microscopy (JSM-6630F). The phase identification of the sample was characterized via X-ray powder diffraction [XRD, Bruker D8 Advance X-ray diffractometer, with Cu Kα radiation ($\lambda = 1.54178$ Å)]. A UV–vis spectrophotometer (UV-2500PC) was used to measure the diffuse reflectance spectrum of the octahedral Cu_2O particles formed on the ITO substrates. During the degradation reactions, the photolyzed solutions were analyzed using a UV–vis spectrophotometer (UV-752), and the absorbance was measured at a wavelength of 320 nm, corresponding to the maximum absorption wavelength of PNP. The total organic carbon (TOC) of the PNP solutions was analyzed using a Shimadzu TOC-V_{CPH} analyzer to evaluate the mineralization degree of the organic material.

3. Results and discussion

3.1. Morphologies of the particles

The morphologies and compositions of the Cu_2O particles growing on the ITO glass through electrodeposition are shown in Fig. 1. When the electrodeposition time was increased from 15 min to 90 min, the morphologies of all Cu_2O particles became consistent and exhibited octahedron shapes. However, the sizes had a tendency to increase (from ~3 μm to ~6 μm). According to the crystallographic character of Cu_2O particles, the surfaces of such particles should be only composed of the {1 1 1} crystalline faces. The formation of the octahedron particles was closely related to the addition of PVP in the electrolyte. Similar to other previously reported surfactants [21], PVP would be preferably adsorbed onto the {1 1 1} facets once the crystal nuclei were formed to slow down the corresponding growth rate. A suitable amount of PVP (e.g., $1\ g\ 100\ mL^{-1}$ electrolyte) caused the {1 1 1} facets to have the slowest growth rate, resulting in the formation of octahedral particles with naked {1 1 1} crystalline faces. Using a lower current density ($0.18\ mA\ cm^{-2}$), the nuclei could preferably form on certain sites of the polycrystalline ITO glass, which had higher conductivity in the micro-scale. Thus, most particles adhered to the substrate alone without coming into contact with each other in a large area over a short deposition time (e.g., 15 and 30 min; Fig. 1A and B). Every crystalline face could be exposed except the one in contact with the substrate. When the time was increased, the particles gradually grew and the distances between the particles decreased. At the same time, some newly formed particles were observed among the enlarged particles. Therefore, more particles began to come into contact with each other (Fig. 1C–E), which reduced the exposure of the crystalline faces. We speculate that an increasing number of particles would come into contact with each other as the electrodeposition time is increased. Thus, a closed film with slightly exposed crystalline faces could be formed.

The XRD patterns of sample-30 (Fig. 1B) are shown in Fig. 1F. Four characteristic peaks appeared at 29.87°, 36.27°, 42.30°, 61.37°, and 73.26°, which correspond to the (1 1 0), (1 1 1), (2 0 0), (2 2 0), and (3 1 1) crystal faces of Cu_2O (JCPDS No. 782076), respectively. The peaks of the ITO substrate were also determined. The other samples showed the same test results.

3.2. Abilities of Cu_2O particles in the photodegradation of PNP

The kinetics of PNP degradation with different samples in 3 h is shown in Fig. 2. In the dark, no degradation was observed in the presence of both Cu_2O particles and H_2O_2, suggesting that lamp irradiation was essential for PNP degradation by Cu_2O. Even under irradiation, PNP was still difficult to degrade in the H_2O_2-only solution. This result suggests that the auto-degradation of PNP was a rather slow process under the irradiation of the tungsten halogen lamp. Moreover, the bare ITO glass support lacked active sites for H_2O_2 activation. All samples shown in Fig. 1 had high

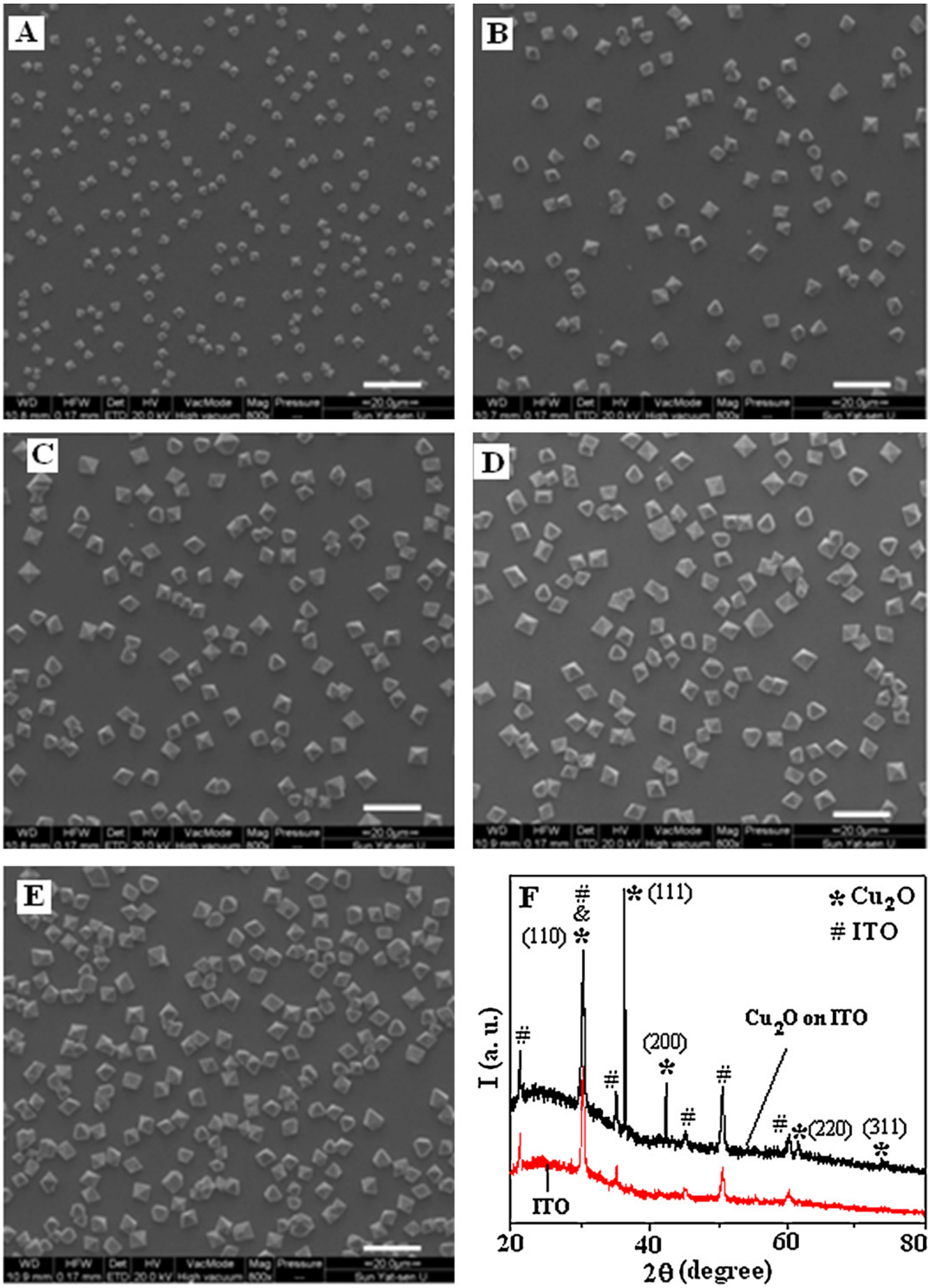


Fig. 1. SEM images of the Cu_2O particles on the ITO glass obtained using different electrodeposition times: (A) 15, (B) 30, (C) 45, (D) 60, and (E) 90 min. (F) XRD spectra of B and ITO glass (scale bar = 20.0 μm).

activities in PNP degradation in the presence of H_2O_2. However, the total weight of the octahedral Cu_2O particles in the deposited area (3.0 cm × 1.5 cm) for each sample was only approximately 1.0 mg. When the time was increased, the concentration of PNP gradually decreased because of the decomposition processes. About 180 min later, nearly all (more than 98%) PNP was completely decomposed in a solution containing any of the aforementioned Cu_2O samples. However, a slight difference was observed in the degradation rates among the different samples obtained at different electrodeposition times. The sample with an electrodeposition time of 30 min (sample-30) had the best activity, which resulted in the highest degradation rate of PNP. Compared with the other four samples, the complete degradation time was shortened by approximately 40 min in sample-30. Regardless of the decrease or increase in the electrodeposition time, the obtained samples (samples-15, 45, 60, and 90) all had reduced activities, which resulted in lower degradation rate of PNP. The variations in the activities might be dependent on the sizes and distributions of the electrodeposited Cu_2O particles. When the electrodeposition time was too short (e.g., 15 min), the obtained particles had smaller sizes, and the total surface area of all particles in the electrodeposition area was also smaller than those of others. As a result, the activities decreased. By contrast, a

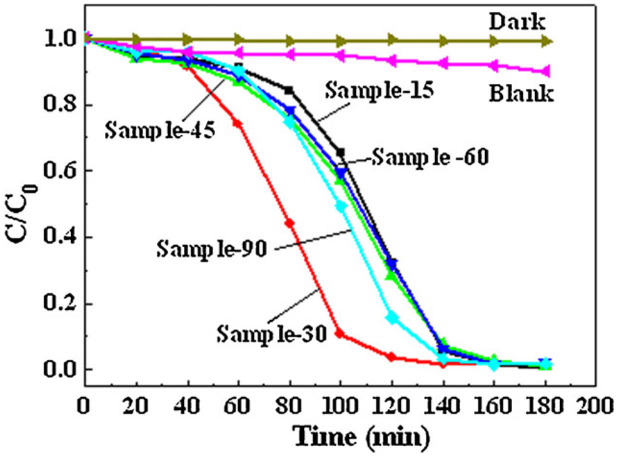


Fig. 2. Degradation of 50 mL 20 mg L^{-1} PNP solution by different Cu_2O particle samples obtained using different electrodeposition times.

long electrodeposition time would cause more particles to come into contact with each other. Thus, the exposed part of the active crystalline faces would be suppressed, reducing the total activities of all particles in the sample (e.g., samples-45, 60, and 90).

The Cu_2O particles on the ITO glass exhibited strong abilities in the catalytic degradation of PNP. A piece of glass covered with the particles led to the complete degradation of more than 1000 mL of PNP solution in a reasonable time. The kinetics of the degradations of PNP solutions with different volumes by sample-30 is shown in Fig. 3A. The concentrations of PNP and H_2O_2 were kept constant, and the volumes of the solutions were changed from 25 mL to 1000 mL. All solutions could be fully degraded; however, the consumed time increased when the volume was increased. When 20 mg L^{-1} PNP was degraded, the degradation processes of 25, 50, 100, 200, and 1000 mL of PNP solution took 100, 140, 180, 220, and 400 min, respectively. According to this trend, a higher volume of the PNP solution would be efficiently degraded. Moreover, compared with the powder catalysts, the Cu_2O particles growing on the ITO glass could be recycled easier. After the photocatalytic reaction was finished, the support covered with particles was simply taken out with a pair of tweezers and was then flushed with deionized water. The support could be then directly placed into a new solution that contains pollutants. The catalyst (sample-30) could be repeatedly used at least 7 times. In addition, it did not exhibit a significant loss of activity in the degradation of 25 mL of 20 mg L^{-1} PNP solutions (Fig. 3B). The Cu_2O particles were stable and could not be oxidized after recycled 7 times (Fig. S1 in the supporting data).

The use of sample-30 in the degradation of 50 mL of PNP solution was taken as an example to discuss further the degradation process, the influencing factors, and the corresponding mechanism.

3.3. Decolorization and mineralization of PNP

The absorption spectrum of the PNP solution in the presence of sample-30 under irradiation of the 150 W halogen tungsten lamp at various durations is shown in Fig. 4A. The absorption peak at 320 nm, which corresponds to the maximum absorption peak of the PNP molecule, gradually weakened as the exposure time was increased. This peak disappeared after 180 min. At this time, the degradation efficiency reached 98.57% (curve of sample-30, Fig. 2). The mineralization degree of PNP was examined by measuring the decrease in the TOC during the degradation process (Fig. 4B). During the irradiation, the TOC removal ratio gradually increased as the irradiation time was prolonged. The maximum TOC removal of PNP reached 79.19% after 180 min when no PNP molecules were detected (Figs. 2 and 4A). The fast mineralization of PNP indicated that the Cu_2O particles irradiated by the halogen tungsten lamp could effectively remove PNP and organic intermediates in the presence of H_2O_2.

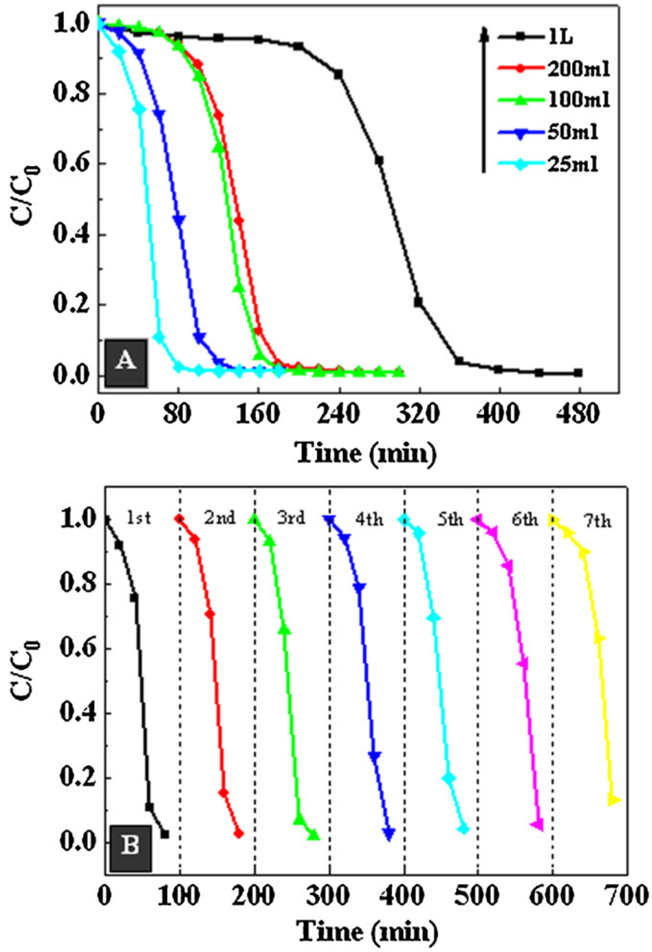


Fig. 3. Degradation of different volumes of PNP by sample-30 (A) and catalyst recycling in 25 mL solution during degradation (B). Concentrations of PNP and H_2O_2 were kept at 20 mg L^{-1} and 0.06 vol%, respectively.

3.4. Influencing factors in PNP degradation

Further experiments revealed that the degradation of PNP was strongly dependent on light intensity, H_2O_2 addition, and solution temperature. To describe the influencing factors easily, other factors were kept constant when a particular influencing factor is discussed.

3.4.1. Effect of light intensity

Most of the light from the halogen tungsten lamp was in the visible region, while some was in the UV region. The intensity of the 254 nm UV light ranged from 11.4 μW cm^{-2} to 112.0 μW cm^{-2} and was related to the distance of the samples from the lamp, which was equivalent to that of sunlight. The Cu_2O particles on the ITO glass had high absorption values in visible light and showed a direct bandgap of 2.1 eV (Fig. 5A). These results indicate that the Cu_2O particles could be activated by the light from the lamp to induce a series of photochemical reactions in the PNP solution. Light intensity had an important function in the photodegradation reactions. In this study, the light intensity was tuned by changing the distance

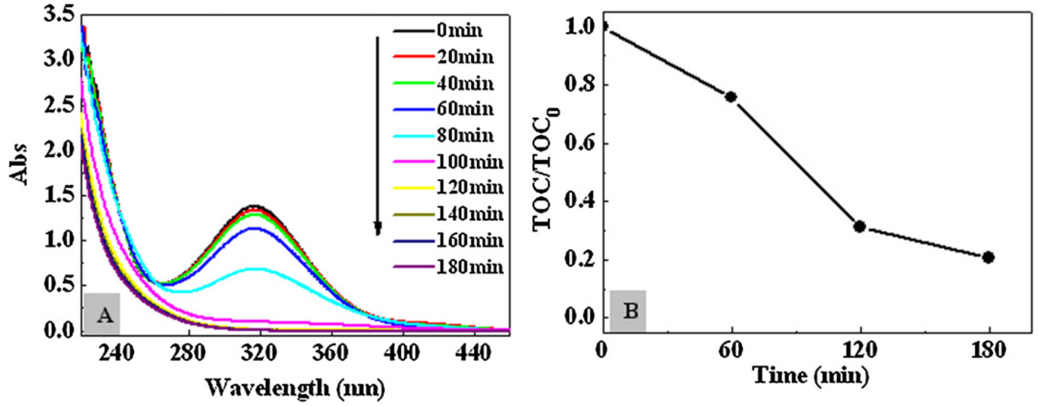


Fig. 4. (A) UV–vis spectra of PNP at different intervals, and (B) changes in TOC during PNP degradation.

between the lamp and the beaker containing the PNP solution. At the same time, when the light intensity was increased, the solution temperature also increased. A glass cold trap refrigerator with a continuous flow of water was used to maintain the temperature at 41 °C and avoid the effect of temperature. The distances were changed from 20 cm to 15 and 8 cm, which gradually increased light intensity and further increased degradation efficiency. Although all cases showed lower degradation rates with lower temperatures, the changes in the samples placed at different locations could still be determined (Fig. 5B). When the distance was decreased from 20 cm to 8 cm, the final degradation ratio increased from 8.47% to 18.39% in 3 h (inset in Fig. 5B). These results indicate that light alone could lead to PNP degradation without the assistance of temperature.

3.4.2. Effect of H_2O_2 amount

The kinetics of PNP degradation by the octahedral Cu_2O particles on the substrates (sample-30) containing different amounts of 3 vol% H_2O_2 is shown in Fig. 5C. When no H_2O_2 was added into the solution, only 7.58% of the PNP was degraded in 3 h. Although the degradation rate was very low, the results proved that the octahedral Cu_2O particles on the substrates could be activated by

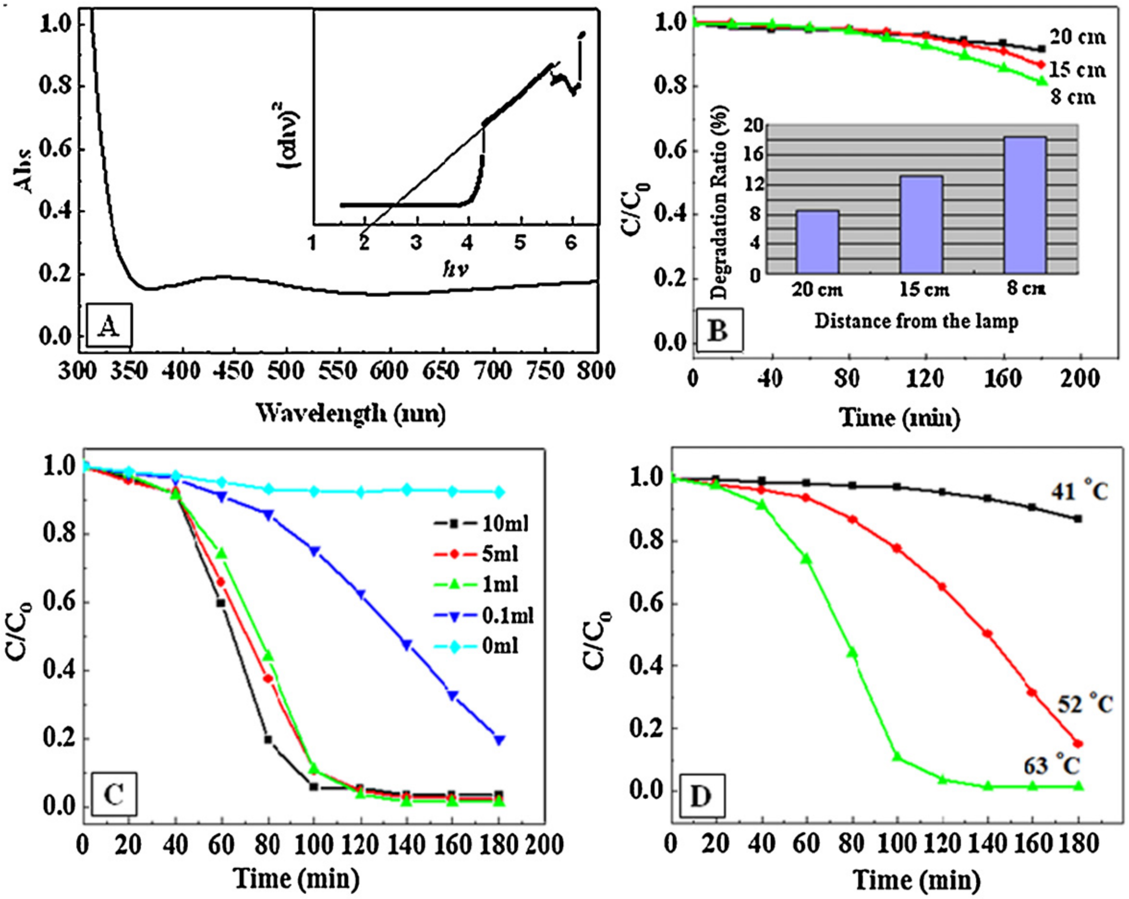


Fig. 5. UV–vis diffuse reflectance spectra of sample-30 (A) and different effects on PNP degradation by different factors. (B) Effect of light intensity, (C) effect of H_2O_2 amount, (D) effect of solution temperature. The inset of A shows the variation of $(\alpha h\nu)^2$ as a function of photo energy ($h\nu$); the inset of B shows the final degradation ratios of the PNP solutions with different distances from the lamp.

light from the halogen tungsten lamp and that PNP degradation was a photo-initiated reaction. The addition of H_2O_2 significantly enhanced the degradation reactions. The presence of 0.1 mL H_2O_2 in the solution increased the degradation ratio to 80.13%. The addition of more H_2O_2 (e.g., 1, 5, and 10 mL) significantly increased the degradation rates of all the samples. Further increasing the amount of H_2O_2 slightly increased the degradation. In all cases, the samples nearly had the same degradation ratio after 2 h. This result suggested that the continuous increase in the amount of H_2O_2 alone did not enhance the degradation, and 1 mL of H_2O_2 was sufficient for the degradation of 50 mL of 20 mg L^{-1} PNP.

3.4.3. Effect of solution temperature

The increase in the solution temperature caused by the irradiation of the halogen tungsten lamp could significantly affect PNP degradation. The solution temperature was kept at 63 °C when no cooling system was employed and the distance between the beaker containing the PNP solution and the lamp was set at 15 cm. By changing the immersion depth of the glass cold trap refrigerator, the temperature could be maintained within the range of 41 °C to 63 °C, and the degradation efficiency of PNP could be changed accordingly. As shown in Fig. 5D, the degradation rate at 41 °C was significantly lower than that at higher temperatures. The final degradation ratio was only 13.15% in 3 h. When the temperature was increased to 52 °C, the rate significantly improved, and the degradation ratio reached 86.37%. At 63 °C, the corresponding data reached the maximum (98.57%).

3.5. Degradation mechanism and pathway

Based on the experimental results, the degradation mechanism of PNP in the presence of Cu_2O particles and H_2O_2 was determined.

Once the Cu_2O microcrystals were irradiated by UV and visible light (from the lamp), the electrons of the valence band could be excited to the conduction band, which would leave positive holes on the {1 1 1} surfaces (Eq. (1)), regardless if the temperature in the PNP solution was increased or not. The photo-generated valence band holes could directly oxidize the pollutants into inorganic or nontoxic materials (Eq. (2)). However, the electrons and holes easily recombined to reduce the number of holes and the corresponding activities of the Cu_2O particles, which resulted in the low degradation ratio (7.58%) of PNP when the Cu_2O particles alone were used (Fig. 5C). H_2O_2 has been used as a green additive in numerous studies to enhance catalytic activities. The enhancements were generally attributed to two reasons. First, H_2O_2 is a good electron acceptor and can be converted to $^{\bullet}OH$ radicals after accepting the electrons [18] (Eq. (3)). The recombination of electron–hole pairs is therefore hindered, promoting the applications of holes. Second, H_2O_2 might be directly photolytically split to produce $^{\bullet}OH$ under UV radiation of up to ~370 nm [22] (Eq. (4)). The light from the halogen tungsten lamp contained a small amount of UV light, which facilitated the occurrence of the reaction in Eq. (4). All the formed $^{\bullet}OH$ radicals could directly oxidize PNP (Eq. (5)). Thus, the degradation rate was enhanced compared with the solution without H_2O_2 (Fig. 5B and C). However, the enhancement was still very limited at lower temperatures (≤41 °C).

The temperature induced by the lamp was mainly responsible for the high increase in the degradation rate of PNP. On one hand, increasing the temperature might accelerate the aforementioned reactions [23]. On the other hand, several new reactions might occur. Based on the composition of the catalytic system, the decomposition of H_2O_2 was thought to have an important function in PNP degradation. H_2O_2 is not stable and can be decomposed to molecular O_2 (Eq. (6)) at elevated temperatures. The decomposition rate increases with increasing temperature and the addition of a certain catalyst [24,25]. A previous study reported that Cu_2O has a high activity in the catalytic decomposition of H_2O_2 and that a higher temperature could also enhance the decomposition [17]. Many bubbles were continuously produced around the Cu_2O particles when the temperature was increased to 63 °C. However, no such phenomenon was observed at 41 °C or in the solution without a Cu_2O sample at any temperature. This result indicates that O_2 could be produced at a higher temperature during the degradation reactions. In other studies, O_2 was externally introduced. In the present study, O_2 was directly produced on the surfaces of the Cu_2O particles. Thus, O_2 could easily scavenge the photo-generated electrons accumulated on the Cu_2O {1 1 1} facets to produce superoxide ions $O_2^{\bullet-}$ (Eq. (7)) [12]. $O_2^{\bullet-}$ then reacted with H_2O_2 to produce hydroxyl radicals ($^{\bullet}OH$) [26] (Eq. (8)) and further accelerate the oxidation of PNP. When the temperature was increased, the decomposition rate of H_2O_2 also increased, which resulted in a rapid decomposition of PNP. A radical scavenger (*t*-butanol) was added into the PNP solution in a control experiment to evaluate the effect of oxidation via hydroxyl radical (Fig. 6). The removal rate significantly decreased, and the degraded ratio was only 5.21% in 3 h. This value was much lower than that without *t*-butanol. Therefore, the hydroxyl radical had the most important function in the degradation process.

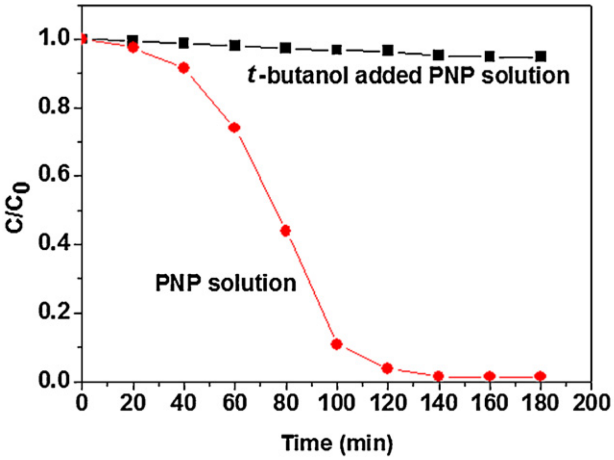


Fig. 6. A comparison of degradation dynamics of PNP added with and without *t*-butanol.

$$Cu_2O \xrightarrow{h\nu} Cu_2O(h^+) + Cu_2O(e^-) \quad (1)$$

$$h^+ + PNP \rightarrow \text{degraded product} \quad (2)$$

$$H_2O_2 + e^- \rightarrow OH^- + {}^{\bullet}OH \quad (3)$$

$$H_2O_2 \xrightarrow{h\nu} 2{}^{\bullet}OH \quad (4)$$

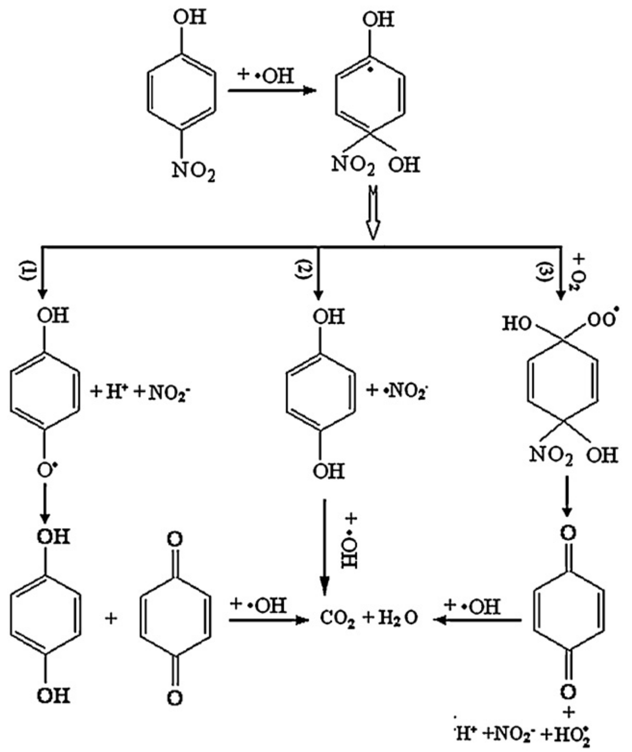
$${}^{\bullet}OH + PNP \rightarrow \text{degraded product} \quad (5)$$

$$2H_2O_2 \xrightarrow{\Delta, Cu_2O} 2H_2O + O_2 \uparrow \quad (6)$$

$$O_2 + e^- \rightarrow O_2^{\bullet-} \quad (7)$$

$$O_2^{\bullet-} + H_2O_2 \rightarrow OH^- + O_2 + {}^{\bullet}OH \quad (8)$$

The irradiated solutions were qualitatively analyzed via high-performance liquid chromatography (HPLC) to determine the reaction intermediates and reveal some details of the reaction process (Fig. S2 in the supporting data). During the irradiation, PNP could be degraded gradually into two intermediates: hydroquinone and 1,4-benzoquinone. After 3 h, PNP and 1,4-benzoquinone disappeared, and most of the hydroquinone was decomposed. Based on the variations in the intermediates, the degradation of PNP followed the hydroquinone pathway [3], as shown in Scheme 1. The phenolic hydroxyl group is an electron donor, which can increase the electron density at the *ortho*- and *para*-positions, whereas



Scheme 1. Degradation pathway of PNP in the presence of Cu_2O particles and H_2O_2 under the irradiation of the halogen tungsten lamp.

the —NO_2 group is an electron-withdrawing substituent and is a very good leaving group. In such molecular structure, electrophilic attack preferentially occurs in the *para*-positions with respect to the —OH group. When the PNP solution containing H_2O_2 and Cu_2O particles was irradiated by the lamp, abundant ·OH radicals were generated. These radicals could attack the *para*-positions to form a kind of unstable OH-adduct. Subsequently, the adduct could be immediately decomposed to release the nitro group and produce intermediates via three possible routes. First, the nitro group could be released in the form of nitrous acid, and 1,4-benzosemiquinone could be formed as an intermediate, which subsequently disproportionates into hydroquinone and 1,4-benzoquinone [27]. Second, the C—N bond might be directly broken, which could result in the formation of hydroquinone [28]. Last, under the assistance of O_2 from the decomposition of H_2O_2, 1,4-benzoquinone could also be formed. At the same time, 1,4-benzoquinone was unstable and might be converted into hydroquinone in a weak acid environment or might be quickly decomposed by further oxidization. Thus, hydroquinone was more easily detected than benzoquinone in the HPLC spectra. Finally, hydroquinone and 1,4-benzoquinone could be further oxidized by the •OH radical and oxygen, resulting in the aromatic ring cleavage and the mineralization into CO_2 and H_2O. The nitro group released from PNP was oxidized to nitric acid.

4. Conclusions

In summary, the octahedral Cu_2O particles that were isolated from each other on the ITO glass showed high catalytic abilities during PNP degradation in the presence of a small amount of H_2O_2 under a halogen tungsten lamp. During the degradation process, the photogenerated electrons and holes were first produced on the surfaces of the Cu_2O particles and then reacted with H_2O_2 and O_2 to produce an abundant amount of •OH radicals. Thus, PNP was decomposed into hydroquinone and benzoquinone, and was finally mineralized to CO_2 and H_2O. A TOC removal of ca. 80% was achieved. The degradation efficiency regularly varied with electrodeposition time, light intensity, H_2O_2 amount, and solution temperature. The particles were easily recycled and maintained their high activities. In addition to PNP, other phenolic and dye pollutants in wastewaters could be effectively degraded (Fig. S3 in the supporting data).

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.12.032.

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