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SOLVOTHERMAL SYNTHESIS OF TRUNCATED OCTAHEDRON Cu_2O AND THEIR CATALYTIC APPLICATIONS ON THE DEGRADATION OF METHYLENE BLUE

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ABSTRACT

Cu_2O photocatalyst is synthesized by solvothermal method. Morphology and structure of Cu_2O photocatalyst are analyzed by SEM, XRD and N_2 sorption technique. The catalytic performances and reaction kinetics of Cu_2O photocatalyst for the degradation of methylene blue (MB) are investigated. The toxicity effect of Cu_2O photocatalyst on yeast *Saccharomyces cerevisiae* is also studied. The results show pure Cu_2O photocatalyst with truncated octahedron morphology is obtained and demonstrates good potential on degradation of MB. The degree of MB degradation is improved significantly in the presence of H_2O_2, and the optimum H_2O_2 concentration is 1.3 wt%. The degradation rate constant decreases as the initial MB concentration increases, and the degradation reaction can be represented by pseudo-first-order kinetics model. Cu_2O photocatalyst shows a good reusability and slight limited growth rate of *Saccharomyces cerevisiae*, suggesting it can serve as an effective and recyclable photocatalyst.

Keywords: Cu_2O; Catalysis; Degradation; Methylene blue

1. Introduction

Water pollution caused by organic dyes has accelerated dramatically in recent years and became a crucial issue all over the world due to rapid industrialization of human society (Ramesh *et al*., 2014). These organic dyes, coming from textile, cosmetic, paper, leather, pharmaceutical and nutrition industries, posed a significant threat to the environment and public health owing to their potential to form toxic aromatic products with carcinogenic and mutagenic properties (Kalsoom *et al*., 2012). Methylene blue (MB) is the most commonly employed basic dye, which can cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Rastogi *et al*., 2008). Various methods, such as adsorption, coagulation, biodegradation, membrane separation and advanced oxidation processes (AOPs) have been developed for the treatment of colored wastewater (Hwang *et al*., 2012). Among them, AOPs have received much attention on the removal of various types of dye wastewater because of the generation of oxidizing radical species such as ·OH in the presence of catalysts, which can degrade a broad range of organic pollutants quickly and non-selectively (Khataee *et al.*, 2009). Recently, many semiconductor metal oxides, such as TiO_2, ZnO, CeO_2, MnO_2, CuO and Cu_2O etc., have been adopted as photocatalyst to degrade dye wastewater owing to their unique

physical and chemical properties (Park *et al*., 2013; Fink *et al*., 2012).

Cu_2O, as an important p-type semiconductor metal oxide with a direct band gap of 2.17 eV, has demonstrated its potential applications on the degradation of organic pollutants owing to its high efficiency, low cost and non-toxicity (Liu *et al*., 2011). In recent years, numerous Cu_2O nanostructures have already been synthesized, including nanowires, nanospheres, nanocubes, nanomultipods, nanoboxes, nanocages and nanooctahedra etc. (Zhang *et al*., 2013a; Basu *et al*., 2012). Among the above structures, octahedral Cu_2O nanocrystals have attracted considerable attention because other more complex structures can be derived from the simple structural form, and the well-defined surfaces provide unique facet-dependent properties on photodegradation (Kuo and Huang, 2008). In the present research, truncated octahedron Cu_2O nanocrystals are synthesized by solvothermal method, and their catalytic degradation ability, reusability and toxicity are also investigated to evaluate their potential in removal of MB from wastewater.

2. Experimental

2.1 Synthesis of Cu_2O photocatalyst

0.25 g $CuCl_2$ (CAS No: 7447-39-4) was added into 50 ml of N,N-dimethylformamide (DMF) (CAS No: 68-12-2) under stirring and 1 ml of distilled water was added dropwise into the above solution under vigorous stirring for 10 min. The mixture was sealed in a Teflon-lined stainless steel autoclave of 100 ml capacity and heat at 160 °C for 16 h, and then cooled to room temperature naturally. The solid precipitate was washed with distilled water, and dried at 60 °C for 4 h.

2.2 Characterization

X-ray diffraction (XRD) patterns of Cu_2O nanocrystals was recorded using a D/Max-2400 diffractometer (Cu Kα radiation, λ =1.54055Å) in a range of diffraction angle 2θ from 0o to 5o to analyze the diffraction peaks of Cu_2O nanocrystals. The morphology of Cu_2O nanocrystals was observed by SEM (Philips XL30 FEG). The Brunauer–Emmett–Teller (BET) surface area of Cu_2O nanocrystals was characterized by nitrogen sorption technique (Quantachrome Autosorb-iQ).

2.3 Methylene blue degradation

0.02 g of Cu_2O nanocrystals was dispersed in 50 mL of MB (CAS No: 61-73-4) aqueous solution (5 mg/L, 10 mg l^{-1}, 15 mg l^{-1}, 20 mg l^{-1}). Then, 0.5-5 ml of aqueous H_2O_2 (CAS No: 7722-84-1) (30 wt%) was added into the reaction mixture. The catalytic reaction was performed with a 40 W tungsten lamp (>400 nm) placed 10 cm away as the visible-light source under magnetic stirring at 25 °C for 5 h. The mixture of catalyst and MB solution was centrifuged for a given time interval. Then, 2 ml of supernatant solution was analyzed immediately using an UV–visible spectrophotometer.

The degree of MB degradation (D) was estimated by the following equation:

$$D= \frac{C_0\text{-}C_t}{C_0}\times 100\% \quad (1)$$

where C_0 (mg l^{-1}) is the initial concentration of MB and C_t (mg l^{-1}) is the concentration of MB at time *t* during the catalytic reaction.

The pseudo-first-order kinetics was expressed in terms of Langmuir–Hinshelwood (L–H) model (Luo *et al*., 2013).

$$\ln(\frac{C}{C_0}) = kt \quad (2)$$

where k is the pseudo-first-order rate constant.

2.4 Toxicity testing

To test the toxicity of Cu_2O nanocrystals, yeast *Saccharomyces cerevisiae* BY4741 was used as a model organism. This yeast was grown in yeast extract-peptone-dextrose (YPD) medium (1% yeast extract(CAS No: 8013-01-2), 2% peptone(CAS No: 73049-73-7), and 2% glucose(CAS No: 50-99-7)) for 16 hours at 30 °C. An initial cell density of OD_{600} 0.01 was supplemented with 0, 400 mg l^{-1} of Cu_2O. The OD_{600} of the cells was measured by at a 2-hour interval for 24 h and in three independent repeats.

3. Results and discussion

3.1 Morphology and structure of Cu_2O photocatalyst

Fig. 1 shows the typical XRD pattern of the as-prepared sample.

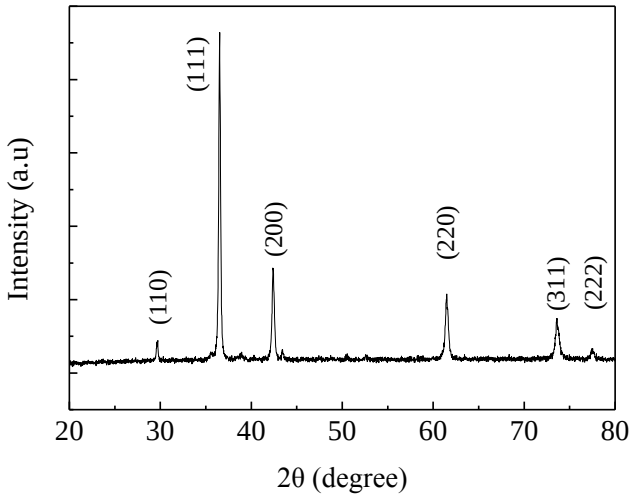

Figure 1. XRD patterns of Cu_2O nanocrystals

All the diffraction peaks are indexed to Cu_2O [JCPDS 05-0667] (Yang *et al*., 2010), and no other peaks are observed, suggesting pure Cu_2O is prepared.

The sharp and strong intensity of XRD peaks suggest that the samples have good crystallinity. The morphology of the Cu_2O samples is observed by SEM image (as shown in Fig. 2).

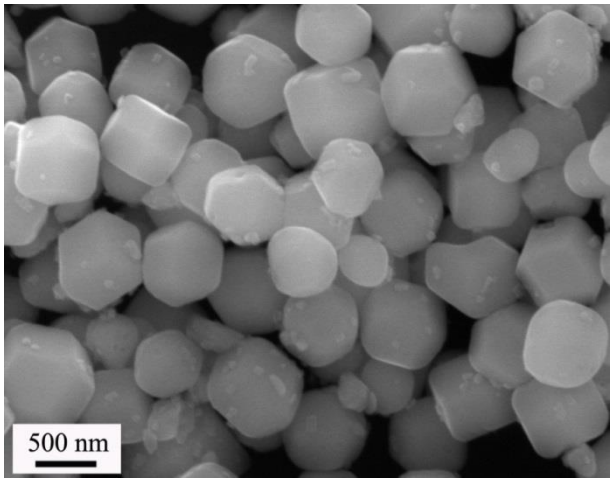

Figure 2. SEM image of Cu_2O nanocrystals

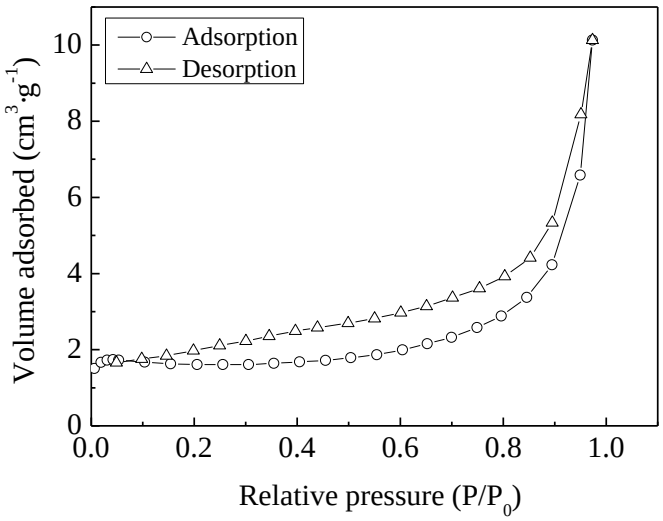

Figure 3. N_2 adsorption-desorption isotherms of Cu_2O nanocrystals

The Cu_2O products show the morphology of the truncated octahedron with edges ranging from 300 to 500 nm. N_2 adsorption isotherm of Cu_2O samples is presented in Fig. 3. The adsorption isotherm shows type-IV curve with the hysteresis loop, illustrating this material has typical mesoporous structure (Jiao *et al*., 2007). The Brunauer–Emmett–Teller (BET) surface areas of Cu_2O is found to be 8.94 $m^2 \cdot g^{-1}$, which may show a favorable influence toward the catalytic degradation of MB.

3.2 Effect of MB concentration on degradation efficiency

The influence of MB concentrations on the degree of MB degradation is shown in Fig. 4. It can be seen that the degree of MB degradation increases sharply in the initial stage and then gradually reaches equilibrium. With the increase of MB concentration from 5 mg l^{-1} to 20 mg l^{-1}, the degree of MB degradation decreases from 94.8% to 86.1%.

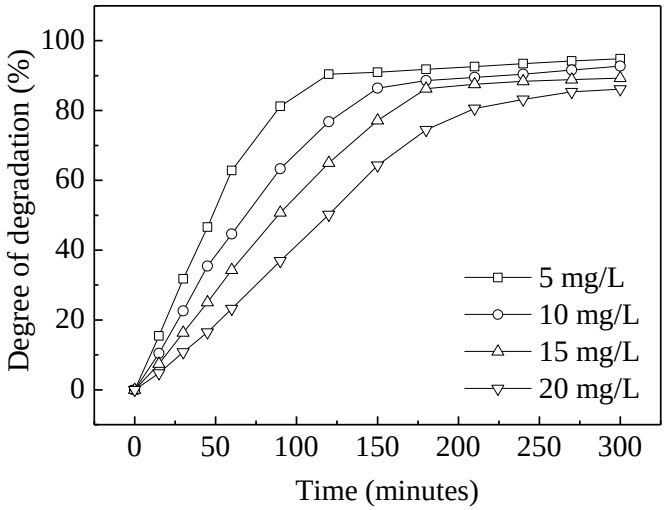

Figure 4. Effect of initial MB concentrations on degree of MB degradation

Moreover, the reaction time of reaching equilibrium is prolonged at high MB concentration. Fig. 5 shows the plots of $\ln(\frac{C_0}{C})$ versus *t* for MB degradation at different concentrations ranging from 5 mg l^{-1} to 20 mg l^{-1}, which indicates that the degradation process follows the pseudo-first-order kinetics model.

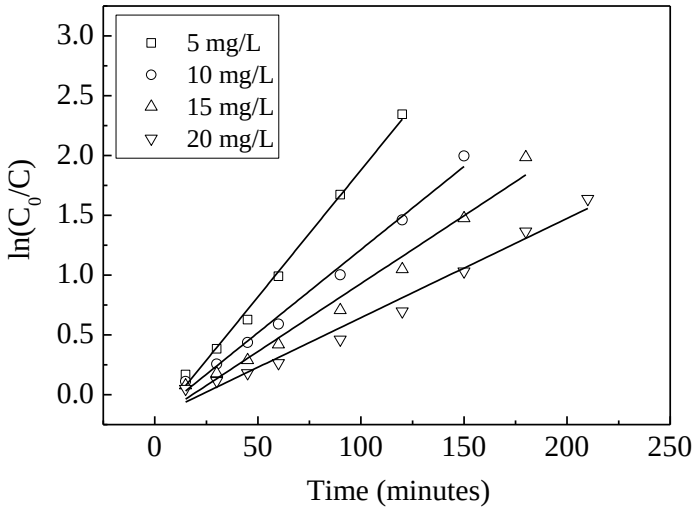

Figure 5. Pseudo-first-order kinetics model of MB degradation by Cu_2O nanocrystals

The degradation rate constants are found to be in the following order: 0.020 min^{-1} (5 mg l^{-1}) > 0.013 min^{-1} (10 mg l^{-1}) > 0.011 min^{-1} (15 mg l^{-1}) > 0.008 min^{-1} (20 mg l^{-1}), which is inversely in proportion to the MB concentration (as shown in Table 1).

Table 1. Kinetics parameters of MB degradation by Cu_2O nanocrystals

MB concentration (mg l^{-1})	The degradation rate constants (min^{-1})	R^2
5	0.020	0.9874
10	0.013	0.9889
15	0.011	0.9856
20	0.008	0.9799

The results may be attributed to that a relative lower concentration of ·OH produced in reaction system results in the decrease of the degree of MB degradation when higher concentration of MB is treated (Ji *et al.*, 2011). Another possible explanation for this result is the influence of light on MB degradation. At a high MB concentration, a significant amount of light can be absorbed by MB molecules rather than by Cu_2O nanocrystals, leading to the decrease in the degree of MB degradation (Dong *et al*., 2014).

3.3 Effect of H_2O_2 concentration on degradation efficiency

The influence of H_2O_2 on degradation degree of MB is shown in Fig. 6. When no H_2O_2 was added into the solution, only 6.5% of the MB is degraded in 300 min. Similarly, the degree of MB degradation is also very low using H_2O_2 in the absence of Cu_2O (only reaches 9.7% for 300 min), which indicates using Cu_2O or H_2O_2 alone is not effective in degrade the stable MB. When both Cu_2O and H_2O_2 are used to treat the MB solution, the synergistic effect on enhancing degradation capability of MB is great significant. The presence of 0.3 wt% H_2O_2 in the solution increases the degree of MB degradation to 84.6%. Further increasing H_2O_2 concentration to 1.3 wt%, the degree of MB degradation reaches 92.7%. Above this value, the degree of MB degradation only slightly improve to 93.3%, which suggests that the continuous increase in the amount of H_2O_2 is not beneficial to enhance the degradation. The reason may be due to that excess H_2O_2 will react with ·OH to form HO_2· that is less oxidizing power (Zhang et al., 2013b; Yang *et al*., 2014). Therefore, the optimum H_2O_2 concentration is 1.3 wt% for the degradation of 50 ml of 10 mg l^{-1} MB.

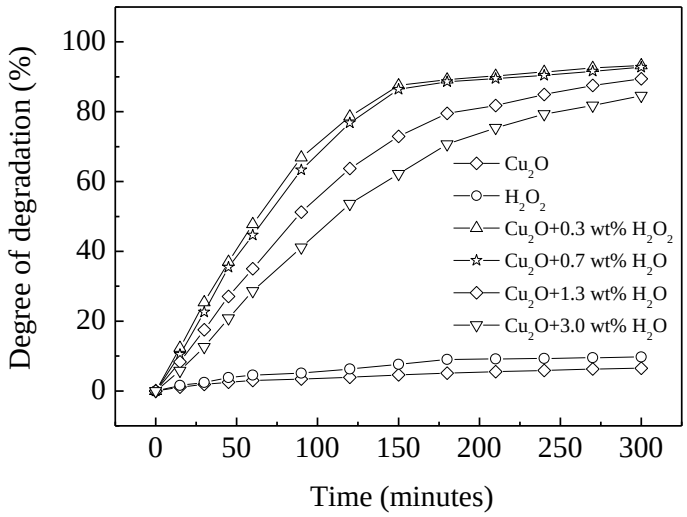

Figure 6. Effect of H_2O_2 concentration on degree of MB degradation

A possible photocatalysis reaction mechanism is proposed. When Cu_2O nanocrystals are irradiated by tungsten lamp, the electrons of the valence band are excited to the conduction band, and leave positive holes on the surfaces of Cu_2O nanocrystals (Eq. (3)). The photo-generated valence band holes can directly oxidized MB into degradation production (Eq. (4)). Additionally, H_2O_2 is a strong oxidant and it can also directly oxidize MB (Eq. (5)), so the degree of MB degradation was slightly higher than that in the presence of only Cu_2O nanocrystals (Dong *et al.*, 2014). As we know, H_2O_2, as a good electron acceptor, can be converted to ·OH radicals when accepting the electrons. The recombination of the electron-hole pairs is hindered, which enhances the degree of MB degradation (Eq. (6)). In addition, H_2O_2 is easy to be decomposed to O_2 (Eq. (7)). The resulting O_2 can scavenge the photo-generated electrons to produce O_2^-· (Eq. (8)), and then O_2^-· reacts with H_2O_2 to produce ·OH (Eq. (9)), enhancing MB degradation (Zhai *et al.*, 2013).

$$Cu_2O \xrightarrow{h\upsilon} Cu_2O\,(h^+) + Cu_2O\,(e^-) \quad (3)$$

$$h^+ + MB \xrightarrow{h\upsilon} \text{degradation production} \quad (4)$$

$$H_2O_2 + MB \xrightarrow{h\upsilon} \text{degradation production} \quad (5)$$

$$H_2O_2 + e^- \xrightarrow{h\upsilon} OH^- + \cdot OH \quad (6)$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (7)$$

$$e^- + O_2 \xrightarrow{h\upsilon} O_2^-\cdot \quad (8)$$

$$O_2^-\cdot + 2H_2O_2 \xrightarrow{h\upsilon} OH^- + O_2 \quad (9)$$

$$\cdot OH + MB \xrightarrow{h\upsilon} \text{degradation production} \quad (10)$$

3.4 Reusability and toxicity of Cu_2O photocatalyst

In order to check the reusability of Cu_2O nanocrystals, the degree of MB degradation is further studied during four consecutive cycles. As shown in Fig. 7, the Cu_2O nanocrystals do not exhibit a significant loss on photocatalytic activity after four consecutive runs, and the degree of MB degradation still can reach 79.3% for 50 ml of 10 mg l^{-1} MB solutions, demonstrating Cu_2O nanocrystals are effective and recyclable photocatalyst for degradation of dye wastewater. Compared to other catalysts reported in the literatures shown in Table 2, the degree of MB degradation using Cu_2O nanocrystals prepared in this work are higher than other catalysts (expect 97.2% degradation degree by CuO). These clearly indicate that Cu_2O nanocrystals prepared by solvothermal method in this paper is a promising catalyst for MB degradation.

The 24-hour growth curves of *Saccharomyces cerevisiae* were studied to determine its growth pattern in the absence of Cu_2O. As shown in Fig. 8, the growth rate of *Saccharomyces cerevisiae* treated with 400 mg l^{-1} of Cu_2O demonstrated slight decrease compared with that treated without Cu_2O. The toxic effects on *Saccharomyces cerevisiae* are attributed to nanoparticle toxicity and the dissolution of copper ions from Cu_2O (Kasemets *et al*., 2009).

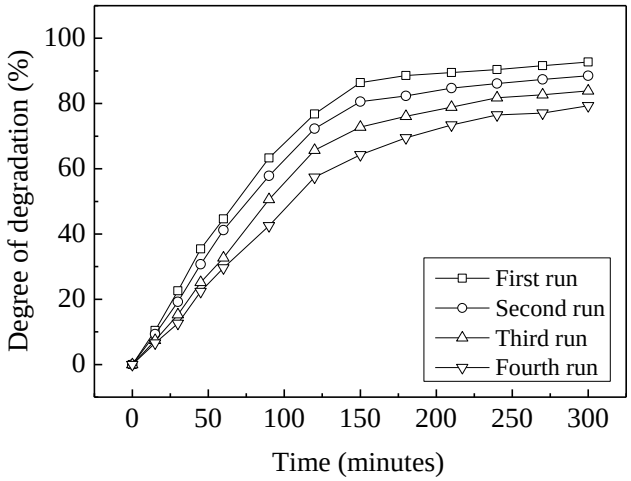

Figure 7. Degree of MB degradation by Cu_2O for four cycles

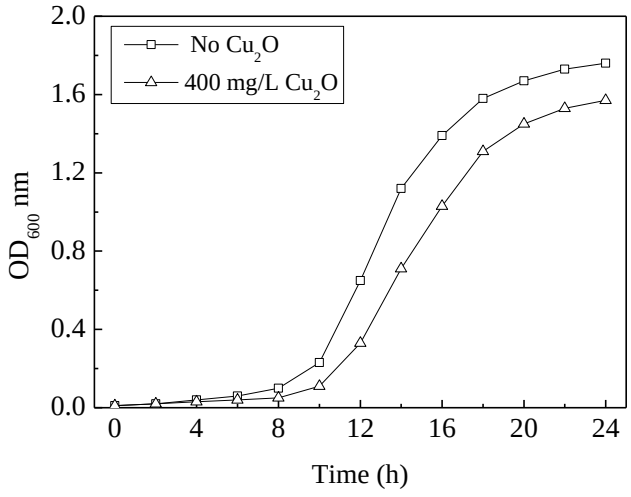

Figure 8. The growth curves of Saccharomyces cerevisiae

Table 2. Comparison of MB degradation degree of Cu_2O with that of other catalysts reported in the literatures

Catalysts	MB concentration (mg l^{-1})	The degree of degradation (%)	Reference
Cu_2O	10	92.7	In this work
Cu_2O	6.25	89	(Xu *et al*., 2012)
CuO	10	97.2	(Yang and He , 2011)
TiO_2	4	76	(Syoufian and Nakashima, 2008)
β-MnO_2	20	90.2	(Cheng *et al*., 2014)
CeO_2	20	90.6	(Pouretedal and Kadkhodaie, 2010)

4. Conclusions

In summary, truncated octahedron Cu_2O nanocrystals are prepared successfully by a facile solvothermal method. The investigation on catalytic activity of as-prepared Cu_2O nanocrystals demonstrates high degradation degree for MB can be obtained using Cu_2O nanocrystals as photocatalyst in the presence of H_2O_2. However, excess H_2O_2 does not favor the further improvement of degradation degree owing to the formation of HO_2·. The degradation degree of MB is dependent on its concentration. With the increase of MB concentration from 5 mg/L to 20 mg/L, the degradation degree of MB decreases from 94.8% to 86.1%. The degradation reactions follow the pseudo-first-order kinetics model. Reusability of Cu_2O photocatalyst is proved to be rather good after four consecutive runs. Compared to other catalysts reported in the literatures, the Cu_2O photocatalyst in this work still exhibits great competition. Yeast *Saccharomyces cerevisiae* is used as a model organism to study the toxicity of Cu_2O photocatalyst, and reveals slight limited growth rate of *Saccharomyces cerevisiae*. Future efforts would be directed to the development of photocatalytic reactor, in which nanosized Cu_2O photocatalyst is dispersed on substrates for the treatment of wastewater and waste activated sludge.

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