

Degradation of Methylene Blue Using Synthesized Nanostructured CuO with High Specific Surface Area through Catalytic Oxidation

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Nanostructured CuO (CuO Nst) with specific surface area of 144.473 m²/g has been successfully synthesized via a facile solution-phase method at room temperature. As prepared CuO was characterized using x-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and transmission

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electron microscopy (TEM). The synthesized CuO was demonstrated as efficient and re-used catalyst in degradation of methylene blue in the presence of sodium hypochlorite through catalytic oxidation. More than 95% of the methylene blue was degraded after 30 min. After 5 successive catalytic cycles, the as-prepared CuO still remained its original catalytic activity, exhibiting good reusability and durability.

Keywords: Methylene blue; degradation; nanocrystalline copper (II) oxide; current efficiency; reusability.

1. INTRODUCTION

Colored wastewater from different industries affects the ecosystem in many ways. With the environmental regulations which become more and more stringent in recent years, how to eliminate hazardous materials (especially those highly toxic and carcinogenic contaminants) from wastewater and prevent them from entering environmental system is a focus of international concern [1].

A variety of physical, chemical, and biological methods have been applied for the treatment of wastewater, which contains dyes and heavy metals. Some methods such as catalytic reduction [2], photocatalysis [3], electrochemical oxidation [4], adsorption [5], and advanced oxidation [6], have been proven as practical methods for removing methylene blue (MB) from solutions. Therefore, in the course of this last decade, considerable interest has been paid to the oxidation processes, in which the highly reactive hydroxyl radicals ($\cdot\text{OH}$) are generated and cause the oxidative degradation of organics [7]. Among these, copper oxide (CuO) has gained increasing attention because of its low cost, non-toxic nature and high efficiency. It has been studied as a p-type semiconductor material (band gap = 1.2 eV) with distinctive properties, which makes it suitable for applications in many important fields of science and technology. However, for these applications, the size, morphology and specific surface area of the CuO particles are very important and sometimes, are strongly dependent on the preparation methods. Hence, powdery nanocatalysts are very likely to aggregate during the catalytic reaction owing to their high surface energy, which will significantly decrease their catalytic activity and reduce their lifetime. A lots of well-defined CuO nanostructure have been prepared, such as nanoparticles [8], nanosheets [9], nanorings [10], nanowhiskers [11], nanotubes [12], nanoleaves [13] and nanoflowers [14]. They have been made by a variety of synthetic routes, including thermal decomposition [15], sol-gel

[16], sonochemical [17], microwave irradiation [18], hydrothermal [19], precipitation [20], pyrolysis [21], electrochemical approaches [22] and mechanical milling methods [23]. All these methods require high temperature, inert atmosphere and long reaction time.

The current work is devoted to the synthesis of nanostructured CuO (CuO Nst) with high specific surface area using a fast, facile and inexpensive solution method which should be suitable for large-scale production. The synthesis was realized at room temperature from commercially available copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sodium dodecyl sulfate (SDS) as surfactant agent. Oxidative degradation of MB is applied as a model reaction to test the catalytic performance of the as-prepared CuO nanostructures.

2. MATERIALS AND METHODS

2.1 Materials

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, methylene blue (MB), sodium dodecyl sulfate (SDS), aqueous NaOCl solution (12%), NaOH and ethanol were purchased from Sigma-Aldrich. All of those reagents were of analytic grade and used as received without further purification. Distilled water was used throughout the experiments.

2.2 Preparation of the CuO Nanostructures

The typical reaction process for the synthesis of nanostructured CuO was as follows. Firstly, 1g (4,01 mmol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0,2 g (0,62 mmol) of SDS were dissolved in 30 mL of distilled water. To the obtained blue suspension, 20 mL of aqueous NaOCl solution (12%) was added and the solution was stirred vigorously at room temperature for 5 minutes. The mixture turns immediately to a black suspension with addition of 20 mL of aqueous NaOH solution (0,3 M) and stirring was continued for 10 min.

The final black suspension was filtered and washed several times with water and finally with ethanol. The product was dried in air at 100°C for 24 h. This process can be simply scaled up for mass production.

2.3 Characterizations

The crystallographic information and chemical composition of the synthesized nanostructured CuO were established by X-ray diffraction patterns (XRD) using a Philips X'Pert MPD diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). Transmission Electron Microscopy (TEM) observations were carried out at 100 kV (JEOL 1200 EXII). Samples for TEM measurements were prepared by embedding the hybrid material in AGAR 100 resin, followed by ultramicrotomy techniques and deposition on copper grids. The specific surface area was obtained by BET on a Micromeritics Tristar 3000 after one night vacuum (10⁻² mbar) at 120°C. The average pore diameter and pore volume were calculated by the barrett-Joyner-Halenda (BJH) method.

2.4 Methylene Blue Degradation

Commercial Methylene blue (C₁₆H₁₈ClN₃S, MW = 319.852 g/mol), was chosen as the model pollutants to evaluate the catalytic activity of the as-synthesized catalyst (Fig. 1). During the degradation process, 10 mg of the catalyst was suspended in 50 mL of the MB (10 mg/L) aqueous solution. The MB color removal was evaluated by measuring the absorbance decrease at 664 nm by using an UV-visibe spectrometer apparatus (2300-Techcomp). The suspension was initially stirred for 10 min to disperse the catalyst; 10 mL of aqueous NaOCl (12%) was added to the reaction mixture and allowed to react at room temperature. Each analysis point reported in this study was an average of at least three independent parallel sample solutions. The standard deviation of the results was $\pm 3\%$.

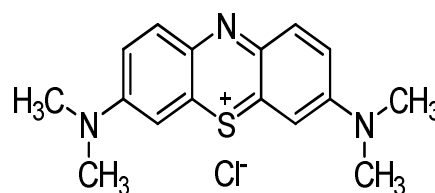


Fig. 1. Molecular structure of methylene blue

3. RESULTS AND DISCUSSION

3.1 Structure and Morphology

The X-ray diffraction pattern of the CuO samples prepared in the presence of SDS and ClO⁻/OH⁻ combination is depicted in Fig. 2. It can be clearly seen that all diffraction peaks can be indexed in the CuO monoclinic phase [24]. The obtained parameters were ($a = 4.653$ Å, $b = 3.410$ Å and $c = 5.108$ Å with volume cell of 79.94 Å³) consistent with the standard values for bulk CuO (JCPDS 05-0661). No peak from impurities can be observed in the XRD spectrum of the obtained sample, indicating high purity of CuO products. The broadening of the peaks indicates the small size of the product. The crystallite size (Table 1) was also calculated by X-ray line broadening analysis using the Debye–Scherrer formula [25]. We found that the average CuO crystallite size was 22.3 nm. After the five cycle of the CuO catalyst (Fig. 2b), we observed a slight decrease of the average crystallite size to ~19 nm (Table 1).

Fig. 3 shows the nitrogen adsorption–desorption isotherm of the prepared CuO, which was type II according to BDDT classification [26,27]. The pore volume and pore size distribution were obtained using the Barrett, Joyner and Halenda (BJH) method from desorption branch of the isotherms [28]. It was found that structured CuO possessed 144.473 m²/g of BET surface area, 0.092 cc/g pore volume and 5.619 nm Pore Diameter.

Table 1. Average crystallite size of CuO Nst calculated by the Scherrer's formula for the intense peak

(hkl)	2 θ of the intense peak (deg)	HWFM of intense peak β (°) before/after	Size of the particle D(nm) before/after
(-111)	35,60	0.6298 / 0.3936	23.61 / 21
(111)	39,02	0.3936 / 0.4723	21 / 17.48

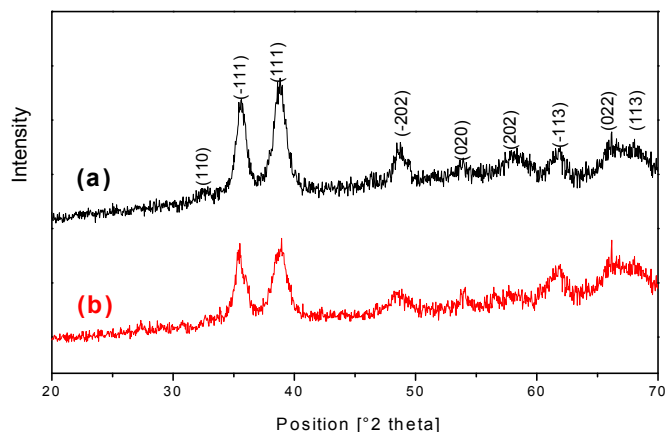


Fig. 2. XRD patterns of polycrystalline CuO (a) before and (b) after recycling.

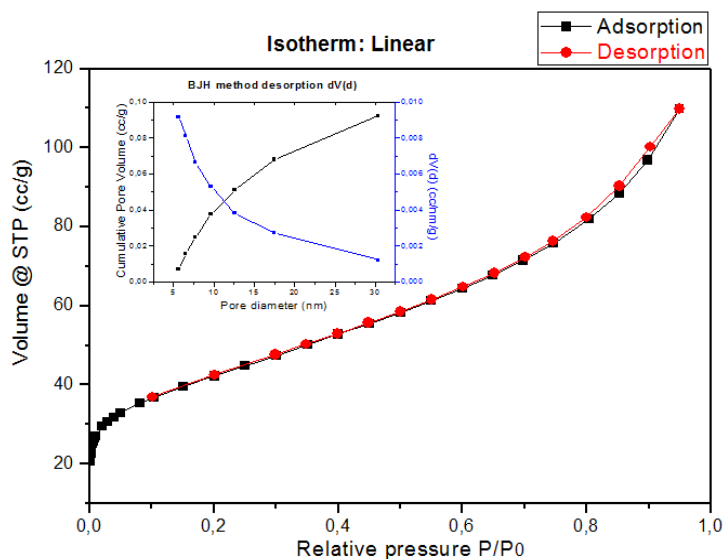


Fig. 3. N₂ adsorption isotherm of the prepared CuO

The morphology of the as-prepared CuO nanostructures is presented with TEM panoramic image in Fig. 4. Interestingly, the product consisted of ultrafine crystallites. Closer observation revealed that these ultrafine nanostructure materials were composed of nanowires. Most of the nanowires are densely to form compact nanowire arrays (Fig. 4a). Careful scaling of CuO nanowires reveals that they are 3-7 nm in diameter and about 8-30 nm in length. In order to provide further insight into the atomic structure of the prepared CuO nanowires, we have performed HR-TEM measurements. Fig. 4(b) reveals that the synthesized CuO product consists of highly ordered nanowires.

Concerning the synthetic mechanism of CuO, we can show an indirect evidence that the NaOCl had an important effect in this synthesis by the transformation of Cu(OH)₂ to CuO. It's noteworthy that at room temperature and without NaOCl, the reaction leads to the formation of Cu(OH)₂. In the same conditions, the preparation of CuO needs high temperature [8,13,15,19]. Hence the presence of NaOCl facilitates the synthesis of CuO at room temperature. The same results are obtained by Viñals et al. [29] who reported that leaching of enargite (Cu₃AsS₄) in the presence of ClO⁻/OH⁻ gave crystalline CuO.

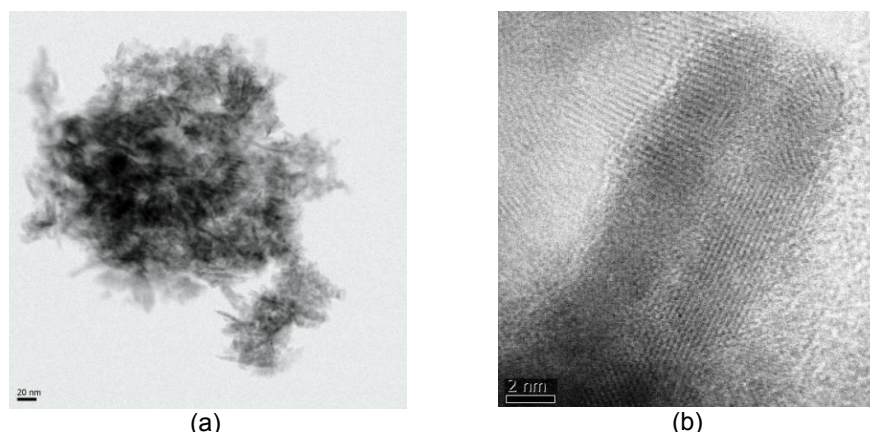


Fig. 4. (a) TEM image showing a cluster of CuO nanowire, (b) TEM image showing a highly oriented crystalline CuO nanowire

3.2 Evaluation of the Catalyst in the Oxidative Degradation of Methylene Blue

To explore the potential capability of the obtained CuO Nst to remove contaminants from wastewater, the catalytic activity was evaluated in the oxidation of MB in the presence of NaOCl. Experiments were carried out both in the presence and in the absence of catalyst. In the absence of NaOCl, no considerable degradation of MB took place after 60 min.

During the course of the degradation, the color of MB solution became less intense, and the characteristic absorption of MB decreased gradually with the evolution of the reaction, due to the oxidation of MB in the presence of CuO. Fig. 5 shows UV-vis absorption spectra of aqueous solution of MB in the presence of CuO and NaOCl at different reaction times. The intensity of the band at 664 nm decreases with the time during the catalytic oxidation without occurrence of new absorbance maxima. After 30min, 93% of MB removal was occurred. In addition, the shift of the absorbance maximum to shorter wavelengths (hypsochromic effect) is not observed, which shows that N-demethylation of MB auxochromic groups does not take place during the catalytic oxidation. A similar effect was observed by other authors studying the photocatalytic oxidation of MB [30].

Therefore, for the evaluation of the reaction rate, pseudo-first order kinetics with respect to MB is a reasonable assumption. Because the ratio of the absorbance A_t of MB at time= t to its initial

value A_0 measured at $t=0$ equals the concentration ratio C_t/C_0 of MB, the reaction rate constant (k) for the first order reaction is $\ln(A_t/A_0) = kt$.

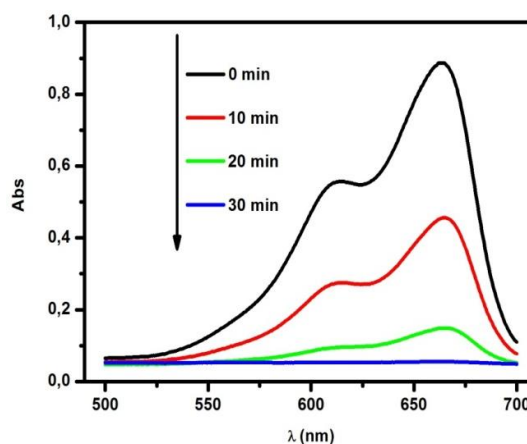


Fig. 5. UV-visible spectra obtained during the MB oxidative degradation in the presence of CuO Nst

As depicted in Fig. 6, the evolution of $\ln(C_0/C_t)$ versus time shows a linear relationship ($R^2 = 0.99$), indicating clearly that the oxidative degradation of the dye follows a pseudo first order kinetics. The rate constant k was calculated from the slope of the line and a value of 0.10643 min^{-1} was obtained.

In order to study the effect of the catalyst on the degradation of MB, discoloration experiments were carried out at different amounts of catalyst (5, 8, 10, 15 mg), and the corresponding results are given in Table 2. The discoloration rate

increased with increasing the catalyst amount to 8-10 mg. However, exceeding the optimum amount of catalyst amount (8-10 mg), have a negative effect on the degradation efficiency (Table 2, entries 1, 2, 3 and 6). It can be concluded that the higher loading of the catalyst may not be useful in view of the aggregation [31,32].

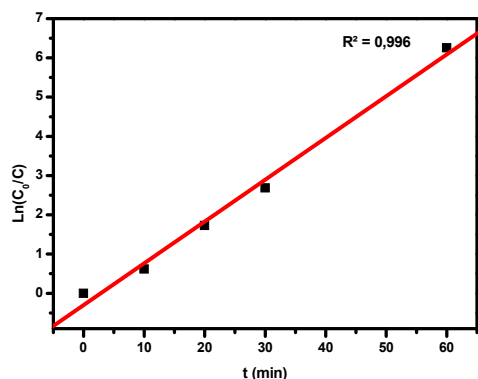


Fig. 6. Plot of $\ln(C_t/C_0)$ versus time for the oxidation of MB by CuO Nst

The effect of initial concentration of MB on catalytic activity of CuO Nst was studied by varying the initial dye concentration from 10 to 30 mg/L (Table 2). It seems that the degradation efficiency is not significantly dependent on the initial dye concentration. The results in Table 2 show that dye degradation efficiency decreases slowly as the concentration of MB increased (Table 2, entries 3, 4 and 5). The decrease of catalytic activity can be explained by the saturation of the catalyst surface by dye molecules reducing the contact with NaOCl molecules.

In the other hand, increasing volume of NaOCl solution lead to decrease of the degradation efficiency when exceeding the volume of 10 mL (Table 2, entries 3, 7, 8 and 9). The results regrouped in Table 2 showed that 10 mL of NaOCl solution (12%) was the optimum volume.

3.3 Recycling Catalyst

After demonstrating the high catalytic activity of the prepared CuO Nst and in order to delineate the scope and limitation of the procedure described above, the reusability of the catalyst was checked. Hence, the catalyst was recovered for successive degradation of MB showing good catalytic activity (Table 3). The catalyst was separated by filtration, washed with water, ethanol and acetone and dried at 100°C overnight before reuse. As it can be seen in Table 3, the yields of MB degradation after 60 min were still very good after five run.

These results showed that the catalyst can be reused more than five cycles without any decrease in activity. The high catalytic activity of reused CuO Nst is visualized by the nearly unalterable crystallite size of CuO (Nst) during the five cycles (Fig. 2, Table 1) and no agglomeration of nanowires in the reaction medium, acting positively on the substrate–catalyst contact surface. Furthermore, X-ray fluorescence study of aqueous reaction mixture after filtration shows that there is no trace of copper found in the solution. All these results conclude that as-prepared CuO Nst could work as an effective and reusable heterogeneous catalyst and the reaction occurs in the surface of nanowire without any leaching of metal species.

Table 2. Effect of the amount of CuO, volume of NaOCl solution and concentration of MB on the degradation of MB catalyzed by CuO Nst

Entries	CuO (mg)	MB (mg/L)	NaOCl (mL)	% MB degradation	
				30 min	60 min
1	5	10	10	83.9	100
2	8	10	10	93.69	100
3	10	10	10	93.67	100
4	10	20	10	92.56	99.79
5	10	30	10	91.61	99.36
6	15	10	10	86.23	98.83
7	10	10	05	91.37	99.08
8	10	10	15	88.15	98.39
9	10	10	20	74.11	98.27

Table 3. Degradation of MB catalyzed by CuO Nst: catalyst recyclability

N° of cycle	1	2	3	4	5
% MB degradation	95.08	96.17	96.37	95.32	96.16

Conditions: reaction time: 60 min, CuO (10 mg), [MB] = 10 mg/L, 10 mL of 12% NaOCl solution

4. CONCLUSION

Nanostructured CuO with high surface area and uniform pore size distribution has been prepared by simple and inexpensive room temperature solution method. The synthesized CuO product consists of highly ordered nanowires with 3–7 nm in diameter and about 8-30 nm in length. It is a promising candidate for potential application in catalysis. We have shown that it can be used as efficient catalyst for the degradation of methylene blue in the presence of commercially available sodium hypochlorite. Moreover, the CuO Nst could be re-used at least five times maintaining an excellent activity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Akrouf H, Jellali S, Bousselmi L. Enhancement of methylene blue removal by anodic oxidation using BDD electrode combined with adsorption onto sawdust. *C R Chimie*. 2015;18:110–120.
- Junejo Y, Sirajuddin, Baykal A, Ssfadar M, Balouch A. A novel green synthesis and characterization of Ag NPs with its ultra-rapid catalytic reduction of methyl green dye. *Appl Surf Sci*, 2014;290:499-503.
- Sohrabnezhad SH. Study of catalytic reduction and photodegradation of methylene blue by heterogeneous catalyst. *Spectrochim Acta Part A*. 2011;81:228-235.
- Lin SH, Peng CF. Treatment of textile wastewater by electrochemical method. *Water Research*. 1994;28:277-282.
- Cooper P, Removing color from dye house waste waters, a critical review of technology available. *J Soc Dyers Colourists*. 1993;109:97-100.
- Chan PY, Gamal EDM, Bolton JR. A solar-driven UV/chlorine advanced oxidation process, *Water Res*. 2012;46:5672-5682.
- Liao J, Li H, Zhang X, Xiao D, Qiang N. Facile fabrication of Ti supported CuO film composed of bamboo-leaf-like nanosheets and their high catalytic performance in the oxidative degradation of methylene blue with hydrogen peroxide. *Applied Catalysis A: General*. 2015;491:94–99.
- Zhong Z, Ng V, Luo J, Teh Sp, Teo J, Gedanken A. Manipulating the Self-assembling process to obtain control over the morphologies of copper oxide in hydrothermal synthesis and creating pores in the oxide architecture. *Langmuir*. 2007; 23(11):5971–77.
- Faisal M, Khan Sb, Rahman Mm, Jamal A, Umar A. Ethanol chemi-sensor: Evaluation of structural, optical and sensing properties of CuO nanosheets. *Mater. Lett*. 2011;65(9):1400-03.
- Liu Y, Liao L, Li J, Pan C. From copper nanocrystalline to cuo nanoneedle array: Synthesis, growth mechanism, and properties. *J. Phys. Chem. C*. 2007; 111(13):5050-56.
- Zhang W, Wen X, Yang S. Controlled reactions on a copper surface: Synthesis and characterization of nanostructured copper compound films. *Inorg Chem*. 2003;42(16):5005-14.
- Cao M, Hu C, Wang Y, Guo Y, Guo C, Wang E. A controllable synthetic route to Cu, Cu₂O and CuO nanotubes and nanorods. *Chem Commun*. 2003;15:1884-85.
- Liang ZH, Zhu YJ. Microwave-assisted synthesis of single-crystalline CuO nanoleaves. *Chem. Lett*. 2004;33(10): 1314-15.
- Yu Y, Zhang J. Solution phase synthesis of rose like CuO. *Mater. Lett*. 2009;63: 1840-43.
- Yuvaraj H, Jae-Jin S. Facile synthesis of CuO nanospindles from a 3D coordination complex and its application to nanofluids. *Materials Letters*. 2014;116:5–8. b) Xiling L, Wenfeng G, Hui H, Tingfang C, Moyu Z, Yinshu W. Synthesis and photocatalytic properties of CuO nanostructures. *Journal of Nanoscience and Nanotechnology*. 2014;14:3428-32.
- Su Y, Shen C, Yang H, Li H, Gao H. Controlled synthesis of highly ordered CuO nanowire arrays by template-based

- sol-gel route. *Trans Nonferrous Met Soc China*. 2007;17:783-86.
17. Pendashteh A, Rahmanifar MS, Mousavi M. Morphologically controlled preparation of CuO nanostructures under ultrasound irradiation and their evaluation as pseudocapacitor materials. *Ultrasonics Sonochemistry*. 2014;21:643-652
 18. Chao Y, Feng X, Jide W, Xintai S. Synthesis and microwave modification of CuO nanoparticles: Crystallinity and morphological variations, catalysis, and gas sensing. *Journal of Colloid and Interface Science*. 2014;435:34-42.
 19. Tingting J, Yongqian W, Dawei M, Xiuling W, Junxia W, Jieyu C. Controllable fabrication of CuO nanostructure by hydrothermal method and its properties. *Applied Surface Science*. 2014;311:602-608
 20. Dan R. Clary, G. Mills. Preparation and thermal properties of CuO particles. *Journal of Physical chemistry*. 2011;115: 1767-1775.
 21. Chiang C, Aroh K, Ehrman H. Copper oxide nanoparticle made by flame spray pyrolysis for photoelectrochemical water splitting Part I. CuO nanoparticle preparation, *Int. J Hydrogen Energ*. 2012; 37(6):4871-79.
 22. Borgohain K, Singh J, Rama M, Shripathi T, Mahamuni S. Quantum size effects in CuO nanoparticles. *Phys. Rev. B*. 2000; 61:11093-96.
 23. Zheng X, Xu C, Nishikubo K, Nishiyama K, Higemoto W, Moon W, Tanaka E, Otabe E. *Phy Rev B*. 2006;72:14464-68.
 24. Hanawalt JD, Rinn WH, Frevel KL. Chemical analysis by X-ray diffraction Classification and use of x-ray diffraction patterns. *Anal Chem*. 1938;10:475-512.
 25. Scherrer P. Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen, *Göttinger Nachrichten. Gesell*. 1918;2:98-100.
 26. Zhang H, Zhang Y, Li C. Enantioselective epoxidation of olefins catalyzed by the Mn(salen) catalysts immobilized in the nanopores of mesoporous materials. *J Catal*. 2006;238(2):369-81.
 27. Blin JL, Flamant R, Su B. Synthesis of nanostructured mesoporous zirconia using CTMABr-ZrOCl₂.8H₂O systems: a kinetic study of synthesis mechanism. *Inter J Inorg Mater*. 2001;3(7):959-72.
 28. Brunauer S, Deming L, Deming W, Teller E. On a theory of the van der Waals adsorption of gases. *J Am Chem Soc*. 1940;62(7):1723-32.
 29. Vin˘alsa J, Rocaa A, Herna˘ndezb MC, Benaventea O. Topochemical transformation of enargite into copper oxide by hypochlorite leaching. *Hydrometallurgy*. 2003;68:183-193.
 30. Zhang T, Oyama T, Aoshima A, Hidaka H, Zhao J, Serpone N. Photooxidative N-demethylation of methylene blue in aqueous TiO₂ dispersions under UV irradiation. *J Photochem. Photobiol. A: Chem*. 2001;140(2):163-72.
 31. Nezamzadeh-Ejhieh A, Zabihi-Mobarakeh H, Heterogeneous photodecolorization of mixture of methylene blue and bromophenol blue using CuO-nanoclinoptilolite. *J Ind Eng Chem*. 2014;20: 1421-1431.
 32. Nezamzadeh-Eghieh A, Khorsandi M. A comparison between the heterogeneous photodecolorization of anazo dye using Ni/P zeolite and NiS/P zeolite catalysts. *Iranian J Catal*. 2011;2:99-104.

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