Synthesis of copper oxide nano-rice structures for enhancement of photocatalytic activity under natural sunlight

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Abstract
In this work, copper oxide (CuO) nano-rice structure was prepared by hydrothermal method. The prepared samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), and UV-visible spectrophotometer. CuO nano-rice structure showed high photocatalytic activity towards degradation of methylene blue (MB). Hydrothermally growth of CuO provided uniformly distributed nano-rice structures with high degradation efficiency (90.41%) and rate constant (k_t) 16.6×10^{-2} min^{-1} for methylene blue degradation**.**

Keywords: Copper Oxide, Nano-rice structures, hydrothermal, photocatalyst.

تكوين اوكسيد النحاس ذات التركيب النانو–أرز لتحسين فعالية التحفيز الضوئي تحت اشعة الشمس الطبيعية

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الخلاصـــة:

في هذا العمل ، تم تحضير اوكسيد النحاس ذات التركيب النانو– أرز بأستخدام طريقة الهايدروثيرمال. تم دراسة خواص العينات المتكونة باستخدام حيود الاشعة السينية (XRD)، مسح المجهر الانبعاث الالكتروني (FESEM) و الفحوصات البصرية. ان تركيب النانو – أرز لأوكسيد النحاس اظهرت فعالية عالية للتحفيز الضوئي اتجاه صبغة المثيلين الازرق. ان جزيئات اوكسيد النحاس المحضرة بطريقة الهايدروثيرمال توزعت بأنتظام لتكوين تركيب النانو – أرز مع كفاءة

انحلال يصل الى 90.41 % و النسبة الثابتة (k_t) تساوي $16.6\times 10^{-2}\ min^{-1}$ لانحلال المثيلين الأزرق.

Introduction

In the past few years, the rate growth of pollution will be significantly increased with the advent of technology [1, 2]. From many problems in environment, the pollution in the water is responsible for 80% of all deaths and illnesses in the whole world [3, 4]. Using a solar energy driven photocatalysis has been attracting high attention to removing organic pollutants from the water [5, 6].

Recently, the metal oxide based photocatalyst has emerged as effective technique for wide range of waste water treatment [7]. Among various metal oxides, copper oxide (CuO) is a best visible light photocatalysts due to its high optical absorption, narrow band gap (1.2-1.5 eV), low toxicity, and low preparation cost [8, 9]. There are many methods to prepare copper oxide (CuO) nanostructures such as electrochemical method [10], hydrothermal [11], and thermal oxidation [12]. A low-cost and well-known method for fabricating copper oxide (CuO) nanostructures with high purity is the hydrothermal process.

Important operators that affect the photocatalytic activities of copper oxide (CuO) based photocatalyst are the recombination of photogenerated electron-hole pairs and the surface active sites of the prepared structures.

In this work, CuO nano-rice structures will be prepare by hydrothermal method. X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), UV-visible is measured. The photocatalytic performance of prepared CuO nano-rice structures were investigated by following the degradation of methylene blue (MB) under natural sunlight.

Chemicals

Copper carbonate dihydrate ($CuCO_3$. Cu (OH).$2H_2O$), polyethylene glycol (MW=400), sodium hydroxide (NaOH), and distilled water was used throughout the experiments.

2. Experimental part

0.13 g of copper carbonate dihydrate and 0.1 g polyethylene glycol (PEG) was dissolved in 100 ml distilled water. Then, the mixed solution stirred for 1 hour by magnetic stirrer. 0.22 g of NaOH was dissolved in 5 ml distilled water and added to above solution. 80 ml of the prepared solution transferred to glass autoclave and place in an oven at 120 °C for 3 hours. The prepared copper oxide (CuO) was annealing at 500 °C for 1 hour.

Photocatalytic activity

The photocatalytic activity of fabricated CuO nano-rice structures were studied using degradation of methylene blue (MB) under natural sunlight. The photodegradation process were carried out by following conditions: 0.03 g of CuO nano-rice structures as the photocatalyst were added into 100ml methylene blue (MB) aqueous solution with concentration of 10mg/L at room temperatures. The suspension was stirred for 60 min in the dark using magnetic stirrer to establish an adsorption-desorption equilibrium. The methylene blue (MB) and CuO nano-rice structures suspension was then irradiated under natural sunlight for 70 min. The small amount of suspension was removed with set interval time. Then, centrifuged and determined with UV-visible spectrophotometer. The absorbance maxima for methylene blue (MB) were determined at 664 nm. The rate constant of reaction calculated by using following formula:

$$\ln(C_0 - C) = k_t \quad (1)$$

Where C_o is the concentrations of methylene blue (MB) before illuminated to natural sunlight, C is the concentration at time t, and k_t is the rate constant at time t.

The degradation efficiency of methylene blue (MB) was calculated using following formula:

$$degradation\ efficiency\ (\%) = \frac{C_o - C}{C_O} \times 100\% \quad (2)$$

Results and discussions

Figure (1) shows the XRD patterns of prepared CuO nano-rice structures by hydrothermal method. The peaks shown in the XRD patterns at 2θ values of 35.5°, 38.7°, 48.8°, 53.4°, 58°, 61.4°, 66.9°, 67.8°, 72.3°, and 74.85° match the respective (002), (111), (-202), (020), (202), (-113), (-311), (220), (311), and (-222) Miller indices, reveal the formation of monoclinic copper oxide (CuO) phase (JCPDS 05-0661). Crystallite size was calculated from Scherrer's formula:

$$D = k\lambda / (\beta\cos\theta)$$

where, k a constant, λ is the X-ray wavelength 0.15406 nm, θ is the Bragg diffraction angle and β is the full width at half maximum. The average crystallite size for CuO nano-rice structure found to be 11.4 nm.

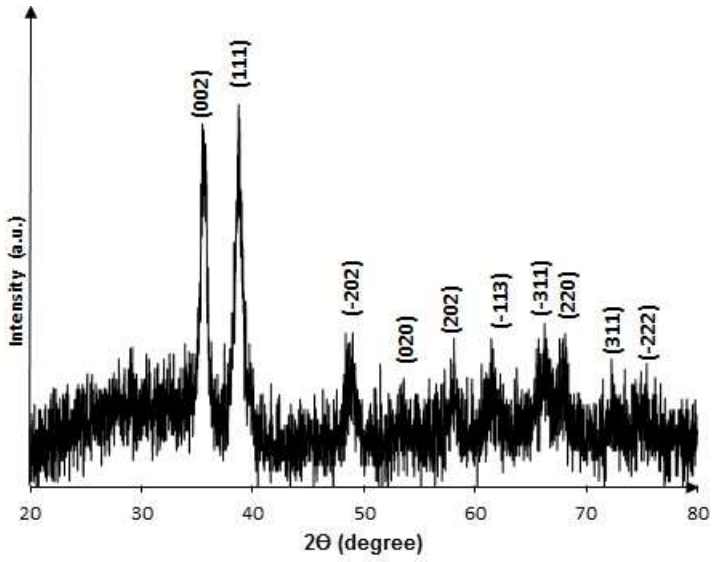

Fig.(1) XRD spectra of CuO nano-rice structures prepared by hydrothermal method.

The morphology of CuO nano-rice structure is shown in figure (2). From the figure, the image indicates the formation of CuO nano-rice structures having uniform distribution with average diameter in the range 29.86 nm. Each nano-rice connected with each other forming homogeneous sheet like structures.

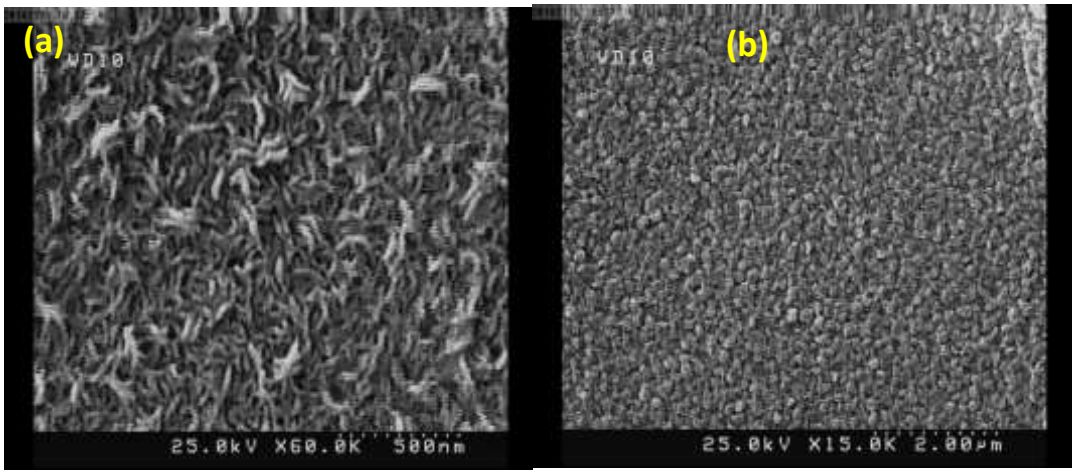

Fig.(2) FESEM images of: (a) CuO nano-rice structures, and (b) magnification of CuO nano-rice structures.

Figure (3)(a) shows the optical absorbance spectra of the CuO nano-rice structures. The CuO nano-rice structure depicts the adsorption edge around 635 nm corresponds to band gap of 1.95 eV, significantly larger than (1.2-1.5 eV) for the bulk CuO. This increasing in band gap is due to confinement of material to nanometer scale. Also, this band gap is helpful for sunlight driven photodegradation process.

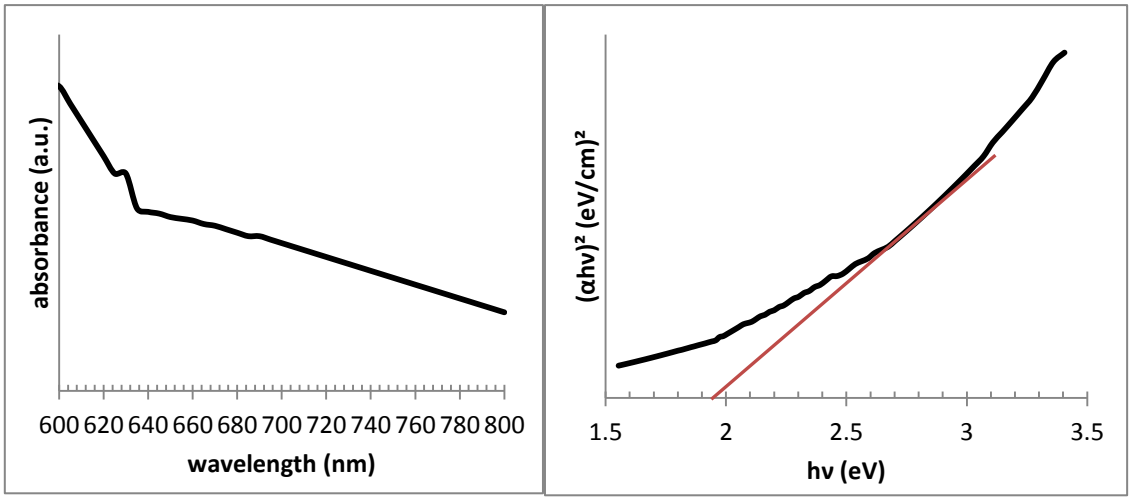

Fig. (3). (a) absorbance curve for CuO nano-rice structures and (b) $(\alpha h\nu)^2$ vs. photon energy for CuO nano-rice structures.

The photocatalytic activity was determined using methylene blue (MB), which is one of the major ingredients in the textile waste. The photocatalytic study was performed in sunny days during the month of September between 11 am to 1 pm under natural sunlight. The UV-visible absorbance of methylene blue (MB) with time is showed in figure (4). From the figure it's clear that the absorbance decreased gradually with sunlight exposure time. Figure (5) showed that the color of methylene blue (MB) faded within 70 min of natural sunlight irradiation in presence of CuO nano-rice structures.

The chemical kinetics of blue methylene degradation reactions is studied. The pseudo first-order rate constant k_t (min^{-1}) can be calculated using the slope between lnC_o/C Vs. irradiation time of the line as showed in figure (6a). CuO nano-rice structure showed apparent rate constant (k_t) 16.6 $\times$ 10^{-2} min^{-1} for methylene blue degradation. Methylene blue dye was removed from the aqueous solution during the photocatalytic process after 70 min of sunlight irradiation. The photodegradation efficiency for CuO nano-rice structures was estimated by equation (2) and is shown in figure (6b). The efficiency after 70 min is 90.41% when CuO nano-rice structures concentration is 0.03 g to 100 ml of methylene blue aqueous solution. The responsible of good photocatalytic activity of CuO nano-rice structures is due to structure of CuO which is uniformly distributed and having small size about 29.86 nm.

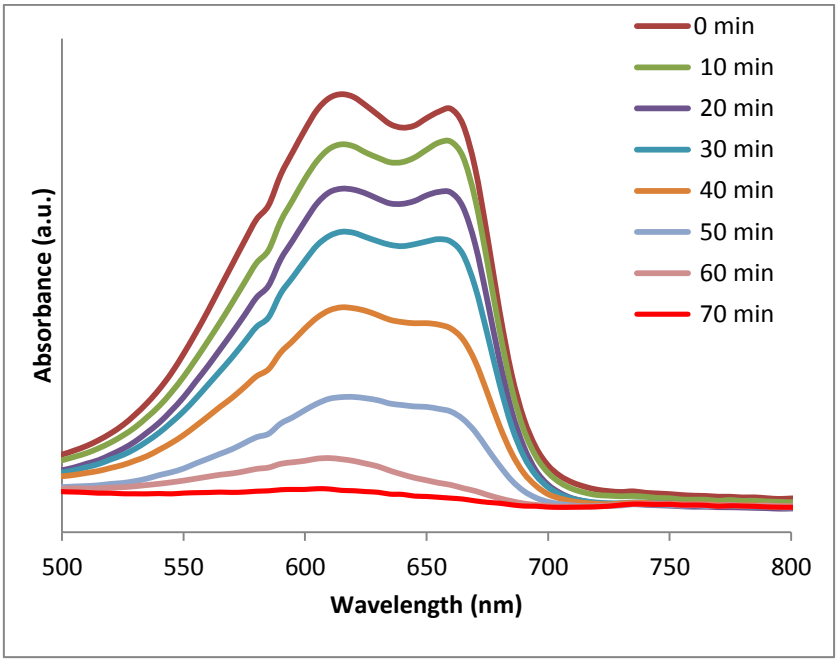

Fig.(4) UV-visible absorbance of methylene blue (MB) for CuO nano-rice structures.

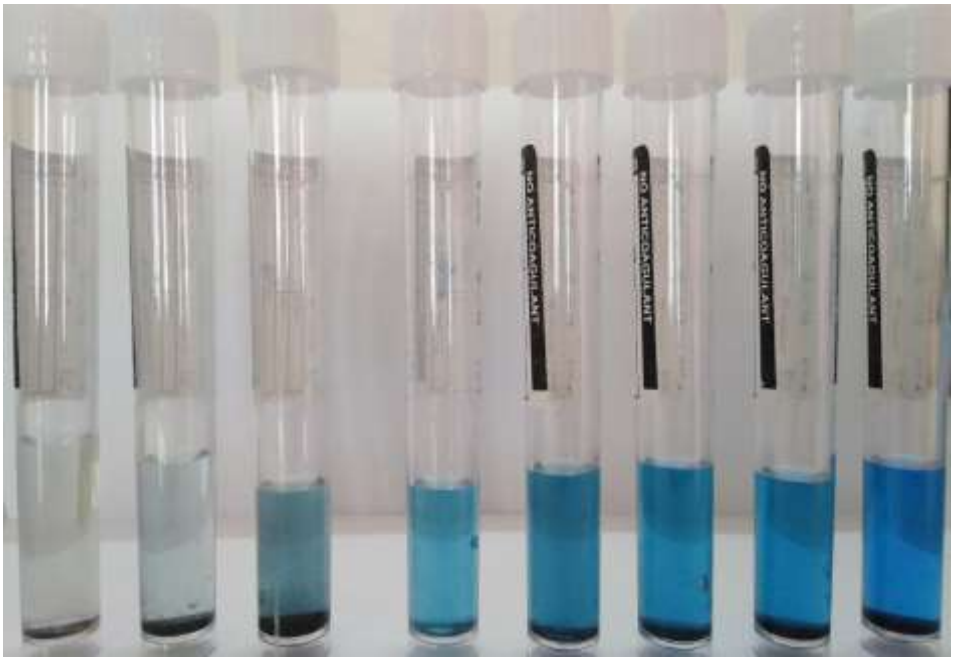

Fig.(5) Color of methylene blue (MB)/CuO nano-rice structures within 70 min of natural sunlight irradiation.

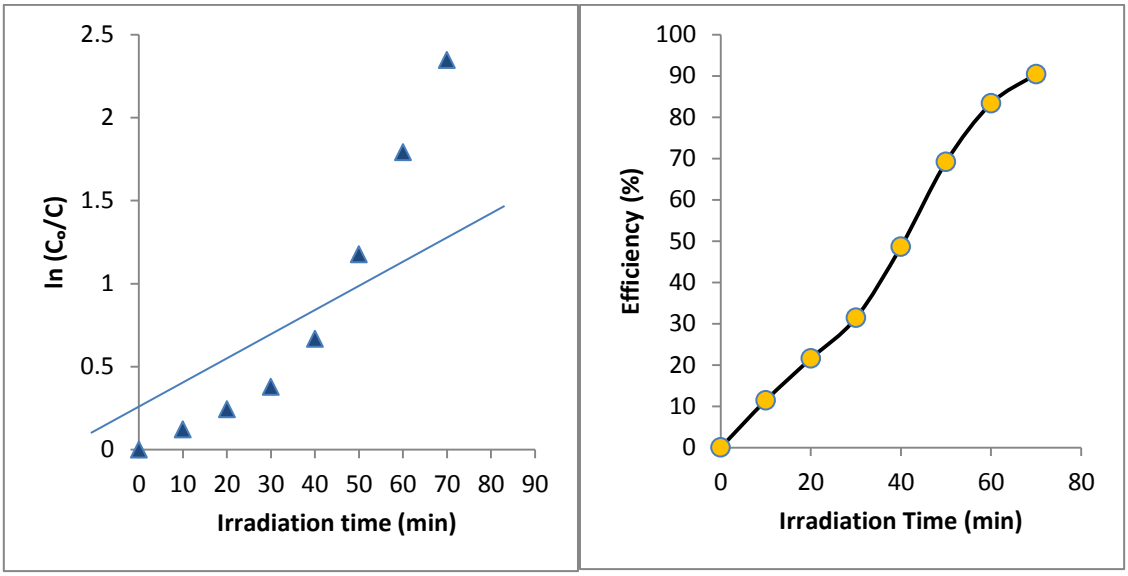

fig.(6) (a)kinetic study for methylene blue (MB) degradation, and (b) Degradation efficiency of methylene blue (MB) of CuO nano-rice structures.

Conclusion:

In summary, CuO nano-rice structures have successfully prepared by hydrothermal method. The XRD pattern of the specimen shows that the CuO is monoclinic structure and the copper carbonate dihydrate completely transformed to CuO. The morphological characteristics indicate the formation of nano-rice structures of CuO including uniform nanoparticles with an average diameter in the range 29.86 nm. Also, the optical study show that the energy band gap of CuO is 1.95 eV. The CuO nano-rice structure prepared was apt to break down the coloured pollutants of blue methylene dye as a result of a redox process during sun illumination. The photocatalytic study determined the best performance of CuO nano-rice structures and it can be used as a photocatalyst for removal of organic contaminants present in water.

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