

Synthesis and Photocatalytic Activity Investigation of CuO Nanorod Functionalized with Porphyrin

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Abstract

In this work, a simple wet-chemical method was used for preparing of CuO nanorods in the presence of a nonionic surfactant, polyethylene glycol. Furthermore, CuO functionalized with porphyrin was synthesized for first time. The synthesized photocatalysts were characterized by IR, XRD, and SEM analysis. The photocatalytic activity of the synthesized catalysts were investigated in degradation of methylene blue under visible light irradiation.

Keywords: Porphyrin, Synthesis, CuO nanorods, Photodegradation

1. Introduction

About 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. The release of those colored waste waters in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbations in the aquatic life. As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants, such as dyes have been recently developed. Among them, physical methods, such as adsorption, biological methods (biodegradation) and chemical methods (chlorination, ozonation) are the most frequently used [1]. There is a growing interest in the field of nanostructured materials in recent years due to their enormous applications in opto-electronic devices, solar cells, catalysis, sensors, drug design etc. Nanostructured materials are also employed in water treatment, such as removal of hazardous dyes and other toxic organic compounds and metals from water. Various biomass and waste materials are used to remove hazardous dyes, metals and other toxic contaminants from water. These

processes are further improved by the introduction of nanostructured materials instead of waste products and biomass [2].

Dye sensitization is considered to be an efficient method to modify the photoresponse properties of CuO nanorod. Metal porphyrin may be an appropriate candidate because of its high absorption coefficient within the solar spectrum and its good chemical stability in comparison to that of other dyes [3].

In the past few years, CuO has attracted increasing interest for both fundamental and practical reasons. It has been shown that CuO is an important industrial material that can be widely used in applications such as gas sensors, magnetic storage media, solar-energy transformation, electronics, semiconductors, and catalysis. CuO is a *p*-type semiconductor. The direct band gap energy of CuO nanorods is evaluated to be 2.75 eV (450.85161nm). Recently, the synthesis of one-dimensional nanostructural materials such as nanorods or nanowires of various materials has received considerable attention, and the potential wide-ranging applications of these nanostructural materials have been predicted. For the preparation of nanorods or nanowires of desired materials, many methods have been developed including arc discharge laser ablation, templates, and other methods. However, high temperatures, special conditions, tedious procedures, or complex apparatus may be required for these methods. Here we report a simple wet-chemical method for preparing CuO nanorods in the presence of a nonionic surfactant, polyethylene glycol (PEG; *M*_w 20 000). This method requires neither complex apparatus nor long synthesis times. CuO nanorods can be prepared easily and effectively without complicated control of the reaction conditions [4].

The chemistry of porphyrin derivatives has played an important role especially during the past decade in particular branches of new materials science, and many researchers have undertaken projects on the synthesis of variously substituted compounds to obtain new functional materials. Porphyrin derivatives have been found to possess application for the construction of solar cells as light absorbents in organic dyes displaying notable stability and unique chemical, physical, and spectroscopic properties [5].

In our experiment, prepared CuO nanorods was photosensitized with TCPP to improving the visible spectral absorption and photoactivity under visible light irradiation. The photocatalytic properties of synthesized catalysts were investigated in photodegradation of methylene blue in the visible light irradiation. Moreover, the effect of porphyrin photosensitizer in improving of visible light photoactivity was discussed in details.

2. Experimental

2.1. Preparation of CuO nanorods

All of the chemical reagents used in this experiment were of analytical grade. CuO nanorods were synthesized as follows: in a typical synthesis, 200 mg of PEG (M_w 20000) and 178.48 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 200 ml H_2O , which was stirred with a magnetic stirrer. This solution was stirred for 15 min to ensure that the PEG and the CuCl_2 dissolved completely. Then, 2 ml of 6 M NaOH solution was added drop-wise into the CuCl_2 and PEG solution, under constant stirring. A blue precipitate of $\text{Cu}(\text{OH})_2$ was soon produced. After stirring for 15 min, the $\text{Cu}(\text{OH})_2$ precipitate was heated by putting on a steam tracing for 30 min to ensure that the $\text{Cu}(\text{OH})_2$ was turned into CuO completely. The black CuO precipitate was washed with distilled water several times and then with EtOH to remove the PEG completely, filtered, and dried in an oven at 80 °C for 5h.

2.2. Preparation of TCPP

Tetrakis (4-carboxyphenyl) porphyrin (TCPP) was prepared according literature [6, 7]. Briefly, 4-Carboxybenzaldehyde and pyrrole were refluxed in propionic acid for 180 min.

2.3. Photosensitization of CuO by TCPP

CuO and porphyrin were dissolved in DMF. The obtained solution refluxed at 150 °C. The product were separated by centerfiguration and washed with DMF.

3. Results and discussion

3.1. Characterization of TCPP

The FT-IR spectrum of TCPP is illustrated in Fig. 1. The FT-IR spectra were recorded on a FT-IR spectrometer ($4000 - 400 \text{ cm}^{-1}$) in KBr pellets; As shown in Fig. 1, FT-IR spectra of compound with the characteristic peak of C-H vibration of toluene in the range of 2920 cm^{-1} indicated that the relative schiff base porphyrin were successfully synthesized.

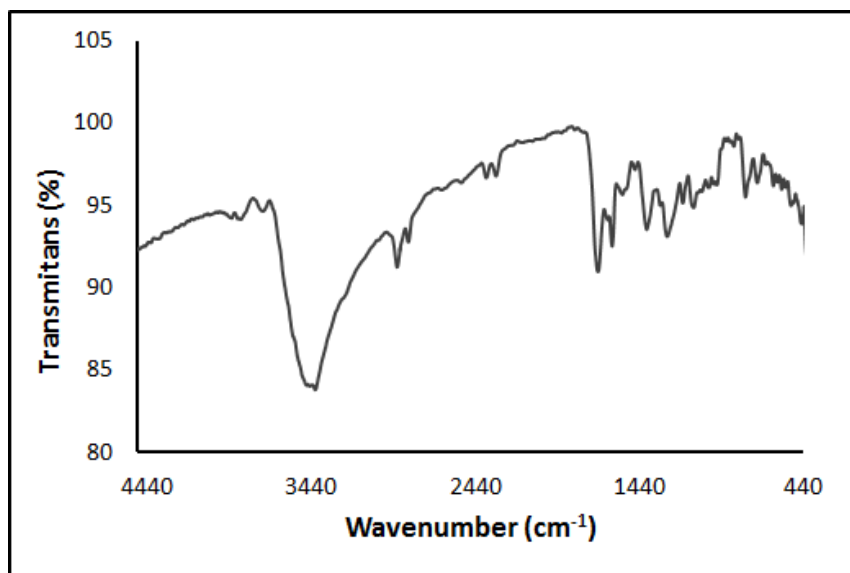


Fig. 1. FT-IR spectrum of TCPP

Fig. 2 shows UV-vis absorption spectrum of TCPP. As shown in this figure, the presence of characteristic peaks of porphyrin determines that TCPP was synthesized properly. TCPP spectrum exhibited a Soret band at 426 nm and four Q bands in the range of 500-700 nm.

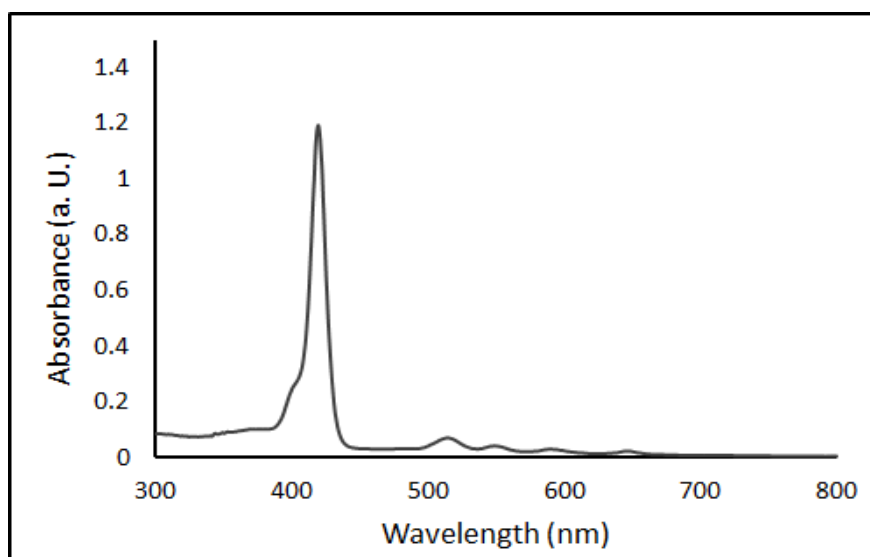


Fig. 2. UV-vis absorption spectrum of TCPP

3.2. X-ray powder diffraction

Fig. 3 shows the XRD pattern of CuO nanorods. It was compared with the data of the JCPDS file no. 5-661 and all peaks can be readily assigned to those of crystalline CuO, indicating the formation of single-phase CuO with a monoclinic structure. The CuO lattice constants calculated from the XRD data of the as-prepared nanorods are $a = 4.689\text{\AA}$, $b = 3.420\text{\AA}$, $c = 5.133\text{\AA}$, and $\beta = 99^\circ 24'$.

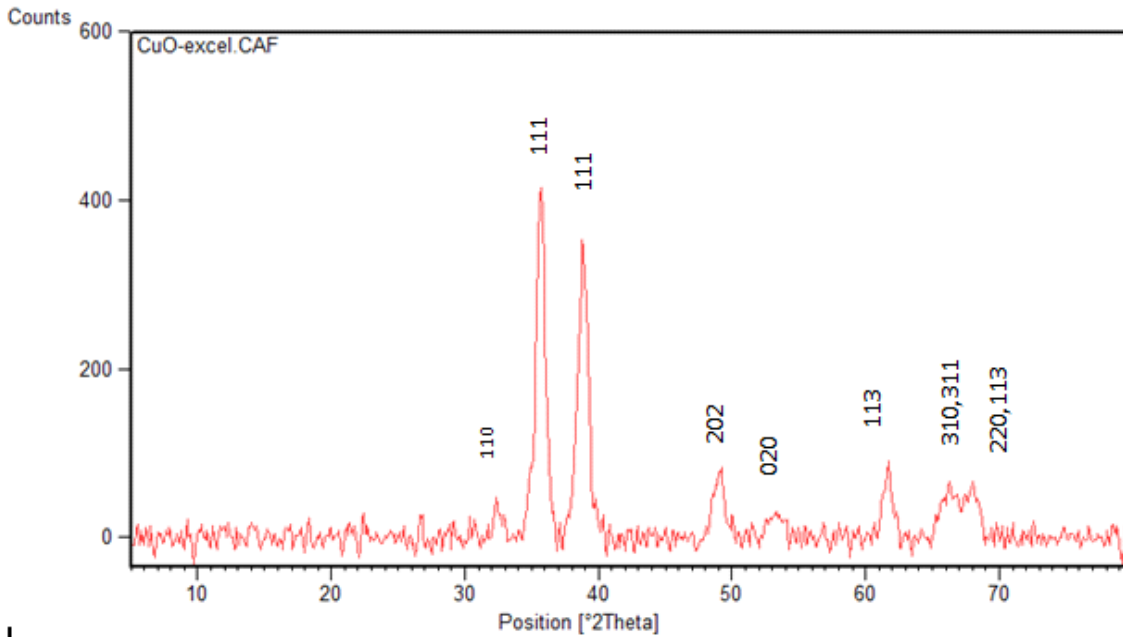


Fig. 3. The XRD pattern of CuO nanorod powders

3.2. Morphological characterizations

The SEM images of the CuO nanorods are shown in Fig. 4. Typical SEM images of the CuO nanorods revealed that these materials have a relatively straight rod-like shape and smooth surfaces. It can also be seen that the nanorods are of uniform lengths of up to 400 nm.

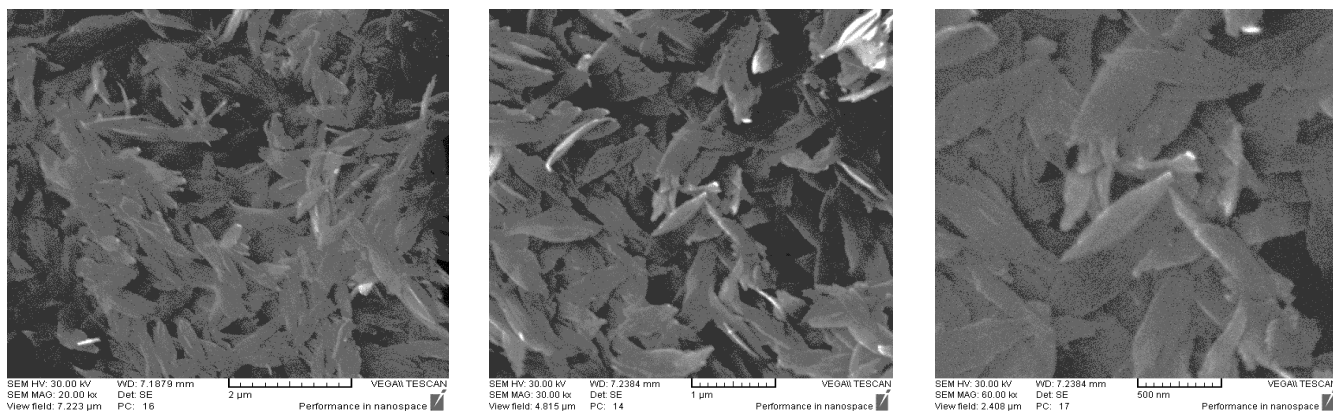


Fig 4 The SEM images of prepared CuO nanorod powders.

3.3. Photocatalytic activity investigation

The photocatalytic activity of CuO photosensitized with porphyrin were evaluated by the degradation of MB dye (10 ppm) solution under visible light illumination. 2 mg of photocatalyst was dispersed in 20 ml of MB aqueous solution by sonication. The solution was then exposed to visible LED irradiation for 3h. The degradation was monitored by measuring the absorbance amount using a double beam UV–vis spectrophotometer (Shimadzu UV-1700).

Fig.5 displays the changes in the UV-vis spectrum of MB aqueous solution during the photocatalytic degradation reaction in the presence of synthesized photocatalysts. Control experiments on the photodegradation of MB indicated that a negligible degradation of MB molecules could be observed in the absence of irradiation or photocatalyst. This suggests that the self-sensitized photodegradation of MB could hardly occur under the experimental conditions of this study.

Based on the photodegradation results, the photoactivity of TCPP-CuO was about 4 times higher than that of the pure CuO (Fig. 5). To the best of our knowledge, this result represents the porphyrin ability in absorbing of visible light. In this photocatalyst, porphyrin acts as a visible light harvesting agents. CuO is a wide band gap semiconductor. Thus it can not absorb visible light well. In CuO

photosensitized by TCPP, porphyrin can absorb wide range of visible light due to the high absorption coefficient in the UV-vis spectrum. Therefore, this photocatalyst are active in the visible light.

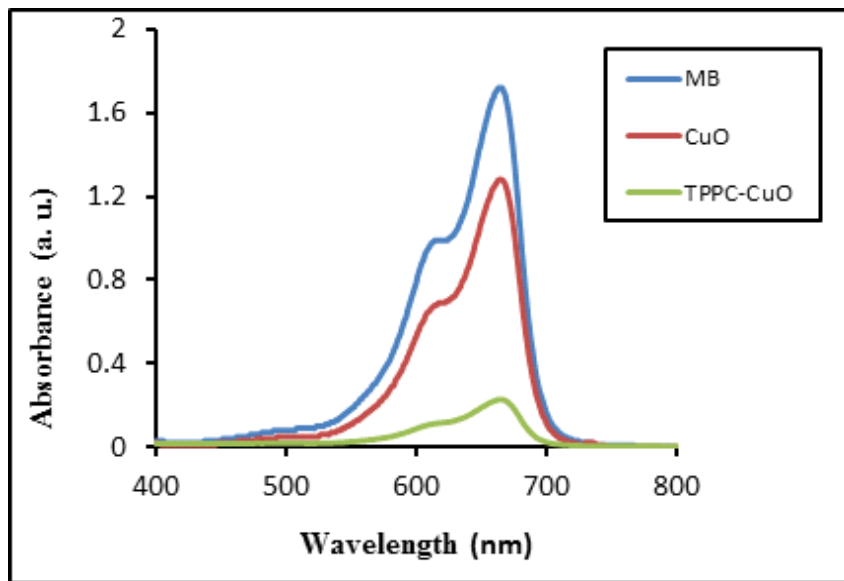


Fig. 5. absorption spectra of the MB solution (initial concentration: 10 mg/l) with CuO and CuO/TCPP under visible light irradiation after 180 min.

4. Conclusion

As a whole, in this work CuO nanorods were prepared using a simple wet-chemical method. The prepared CuO nanorods were photosensitized by porphyrin to improving visible light photoactivity. The TCPP-CuO photocatalyst showed high activity to degrade MB in aqueous solution under visible light irradiation. Furthermore TPPC-CuO can be precipitated without secondary pollution after reaction, and can be recovered or recycled after photocatalytic degradation.

This photocatalyst exhibited excellent visible light photocatalytic performance in degrading MB dye in water due to the porphyrin ability in absorption of visible light. A fourfold enhancement was observed in the photodegradation efficiency compared to the improved photocatalytic

performance of the TCPP-CuO photocatalyst with the pure CuO. In TCPP-CuO photocatalyst, TCPP can absorb visible light and acts as a visible light harvesting agents.

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