RESEARCH PAPER

H$_2$O$_2$-based Green Corrosion Route to ZnO Microrods Photocatalysts on Zn Plate

Xu Liu [1], Yan Yang [1], Yunfei Han [1], Lihong Wang [1], Gang Chen [1], Xuechun Xiao [1], Yude Wang [1,2] *

[1] *School of Materials Science and Engineering, Yunnan University, 650091 Kunming, People's Republic of China*

[2] *Key Lab of Micro-Nano Materials and Technology of Yunnan Province, Yunnan University, 650091 Kunming, People's Republic of China*

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ABSTRACT

Single crystal ZnO microrods are deposited on the surface of Zn plate through corrosion of Zn plate by H$_2$O$_2$ which is a green neutral reagent and easy to transform to H$_2$O and O$_2$. The structure and morphology of the obtained ZnO microrods were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and electron diffraction. A thermodynamics mechanism was brought up. It was found that the transformation from Zn to ZnO is mainly attributed to that H$_2$O$_2$ possessing enough redox potential oxidizes the Zn. At the same time, the photodegradation properties of the obtained ZnO microrods array were also evaluated. The obtained wurtize-type ZnO microrods show an effective degradation for methyl orange under ultraviolet, and it keeps a good efficiency during the ten repeated photocatalytic tests. The results demonstrate a potential of obtained ZnO/Zn in real application of water pollutant photodegradation, making them promising candidates for the wastewater treatment.

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INTRODUCTION

Water pollutants including organic dyes [1]., inorganic heavy metal ions [2]. and so on are critical issues for worry our human beings. The photocatalysis process based on the generation of active radical like photogenerated holes (h$^+$), hydroxyl free radicals (•OH) and superoxide anion radicals (• O$_2^-$) that can break down the pollutants quickly and non-selectively has gained considerable attentions [3]. Owing to the heterocatalysis nature of the photocatalysis process, decreasing the size of the catalysts to micro even nanoscale is a general way to enhance the degradation activity through increasing the contact between pollutant and catalysts, which favors both the absorption and catalysis processes. However, the centrifugation process with thousands even more than ten thousands revolutions per minutes are needed to realize a disjunction of the powder-like photocatalysts with small size from the water after the degradation process, which obviously hinders the practical applications of the catalysts [4-6]. Directly preparing the catalysts with micro size on some hard substrates could be an effective solution to this problem and attract numerous attentions. For example, Chen et al. directly deposited Cu$_2$O nanowires on the surface of Cu foam through a novel oxidation/reduction process, and the Cu$_2$O@Cu foam photocatalysts exhibited effective visible-light activity in the degradation of methylene blue [7]. And Lai et al. reported that the W, N co-doped TiO$_2$ nanobelt thin film on

* *Corresponding Author Email: ydwang@ynu.edu.cn*

the surface of Ti plate showed advanced cycling performance. Its efficiency kept stable even after 10 times photodegradation of rhodamine B aqueous solution under Xe-lamp [8].

With a wide band gap (3.37 eV) and proper band structure, wurtize-type ZnO has strong photoredox ability and is considered as one promising photocatalyst. Especially, the rod-like ZnO, its built-in electronic field caused from the ionic crystal trait results in a separation of photogenerated carries, which is helpful for a better photocatalytic activity [9]. More importantly, Zn is one active metal and easy to transform to ZnO. In 2006, Yang's group reported that a layer of ZnO nanofibers which are no thicker than 10 nm and 500 nm in length was deposited on the Zn plate through corrosion of Zn plate by ammonia aqueous solution under hydrothermal condition [10], after which some other bases like LiOH [11]. and NaOH [12,13]. were used to replace the ammonia in order to study their influence on the morphology of ZnO grown on Zn plate. In our previous works, the influence of base, its concentration, and reaction temperature on the morphology and photodegradation properties of ZnO have been carefully studied [14,15]. The ZnO rods prepared under optimal conditions possess high degradation activity under ultraviolet and visible light irradiation, even in dark. Unfortunately, for all these studies, the strong base solution is involved. The residual needs further dispose which is uneconomic and ungreen, so the synthesis method should be further explored.

From the previous works, one can find that the zinc element is oxidized in the reaction from metallic zinc to zinc oxide. Hence, there must be some reduction action in the system. But the elements making up the base which is the parameter explored most during the past research cannot join any reduction reaction. Lu et al. reported that the ultralong ZnO nanowire and nanobelt arrays can be fabricated by hydrothermal corrosion of zinc foil in aqueous alkaline $(NH_4)_2S_2O_8$ solutions, which follows the Eqn. (1) [16].

$$Zn + 4NaOH + (NH_4)_2S_2O_8 \rightarrow$$
$$ZnO + 2Na_2SO_4 + 2NH_3 + 3H_2O \tag{1}$$
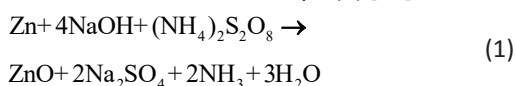
In this reaction, it is obvious to know that the added $(NH_4)_2S_2O_8$ acts as the oxidizing agent and the role of base is only providing the OH$^-$ to react with generated Zn^{2+} to form Zn(OH)$_2$ and final ZnO. From this point, if the oxidizing agent used to oxidize zinc can produce OH$^-$ during its reduction, it is possible to avoid the use of strong base, like ammonia, LiOH, and NaOH. And H$_2$O$_2$ is such an ideally neutral oxidizing agent. Moreover, the excessive H$_2$O$_2$ is easy to transform to H$_2$O and O$_2$.

Hence, in this work, the authors try to use the H$_2$O$_2$ as the corrosion agent to grow ZnO microrods on Zn plate. With the help of X-ray diffraction, scanning electron microscopy and transmission electron microscopy, it is found that single crystal ZnO microrods are deposited on the surface of Zn plate through the designed synthesis route. Further step, the obtained ZnO/Zn was directly used as the photocatalysts to evaluate its activity, and a good degradation performance toward methyl orange (MO) is observed, especially for its remarkable stability.

MATERIALS AND METHODS

A piece of Zn plate with a size of 2.5×2.5 cm^2 was washed by ethanol and deionized water for 10 and 30 min with ultrasound, respectively. Then it was placed into a Teflon autoclave with a content of 30 mL. Later 24 mL deionized water with addition of 0.6 mL H$_2$O$_2$ solution (30 wt.%) was poured into the autoclave. The autoclave was sealed with stainless steel and reacted at 120 °C for 24 h. When the autoclave was cooled down to room temperature, ZnO microrods/Zn was obtained.

The crystal structure of ZnO/Zn was characterized by X-ray diffraction (XRD, Rigaku, TTRIII) with an incident X-ray wavelength of 1.54056 Å. Scanning electron microscopy (SEM) analysis was taken on FEI QUANTA200 with a microscope operating at 30 kV. Transmission electron microscopy (TEM) was obtained with a Zeiss EM 912Ω instrument at an acceleration voltage of 120 kV.

MO is chosen as the model pollutant. Light source is provided by 8 W UV lamp (Spectroline EA-180/FE). In a typical degradation test, 2 pieces of the ZnO/Zn was placed in a quartz baker with addition of 40 mL MO solution (5×10^{-6} M). The distance between the lamp and the solution surface was 6 cm. 4 mL solution was extracted at different intervals. Due to the strong combination of the ZnO and Zn substrate, the clear solution is directly used for the further test of absorbance and UV-vis spectra through UV-1800 spectrophotometer.

RESULTS AND DISCUSSION

The crystal structural of the as-prepared ZnO/Zn was characterized through XRD, and the results
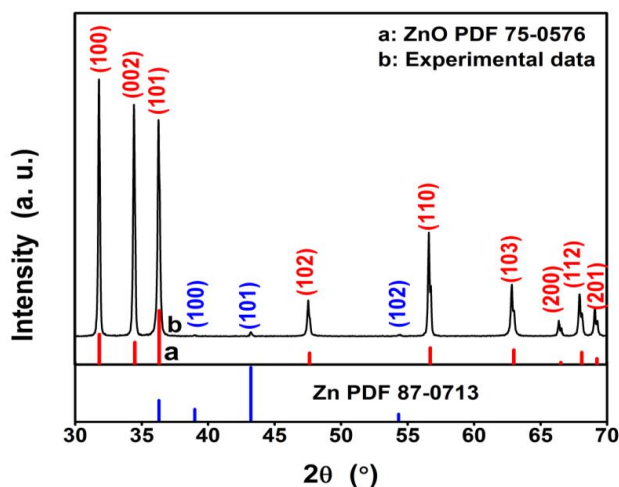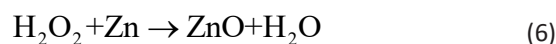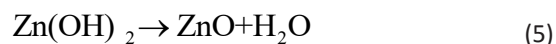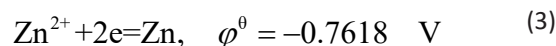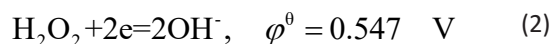
Fig. 1. XRD pattern of as-prepared ZnO/Zn.

are shown in Fig. 1. The small peaks located at 39.02º and 43.24º are originated from the (100) and (101) peaks of Zn substrate, respectively. The series of peaks indexed with red are associated to the peaks of wurtize ZnO (PDF 75-0576). Through the corrosion of Zn plate by H$_2$O$_2$ solution with assistance of hydrothermal condition, the transformation from Zn to wurtize-type ZnO was realized. And the sharp peaks of ZnO demonstrate a high crystalline of the formed ZnO. Comparing the experimental ZnO peaks with the stander pattern, one can observe that the intensity of (100) and (002) is obviously increased, indicating the existence of orientation of the ZnO crystals. The orientation means anisotropy sharp of the crystal.

To evaluate the morphology of the obtained ZnO, SEM characterization was carried out and shown in Fig. 2. Fig. 2(a) shows the cross-section morphology of the ZnO modified Zn plate. Obviously, it consists of three layers, including the compact Zn substrate, transition and rod-like ZnO layers. Such the transitional structure makes the deposited ZnO to attach on the Zn substrate tightly, which is good for its reborn and high stability in practical application. The top layer is further magnified and shown in Fig. 2(b). It is found that this layer is made up of tens thousands of standing ZnO rods whose length reaches tens micrometers. Fig. 2(c) displays the morphology of the transition ZnO layer. Through the magnified figure, it is observed that this layer also consists of rod-like ZnO. Its length is much smaller than that of the previous rods. Such the difference could be

attributed to that the rods on the top have enough space for growth. In order to understand the finer characters of the deposited ZnO microrods, TEM characterization was carried out and shown in Fig. 2(d). Through the TEM imagine, one can ascertain that the wideness of the obtained rod falls in the sub-micro scale. The inset is the selected-area electron-diffraction (SAED) pattern of the ZnO microrod, the diffraction spots demonstrate the single crystal nature of the microrod. Through calculation, the pattern belongs to the 122. electron diffraction pattern of wurtize-type ZnO, which further verifies the rod belongs to ZnO.

Based on the aforementioned characterizations, it is proved that a ZnO microrod layer can be deposited on the surface of Zn substrate through the corrosion of Zn plate by H$_2$O$_2$. And the core of this process is the transformation from Zn to ZnO with H$_2$O$_2$. The thermodynamics mechanism of this reaction can be described as following equations:

$$H_2O_2 + 2e = 2OH^-, \quad \varphi^\theta = 0.547 \quad V \quad (2)$$

$$Zn^{2+} + 2e = Zn, \quad \varphi^\theta = -0.7618 \quad V \quad (3)$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (5)$$

$$H_2O_2 + Zn \rightarrow ZnO + H_2O \quad (6)$$

Due to the higher potential, H$_2$O$_2$ can oxidize Zn with the production of Zn^{2+} and OH$^-$. The ion product can reach the solubility product of indissoluble Zn(OH)$_2$ as description of Eqn. (4).
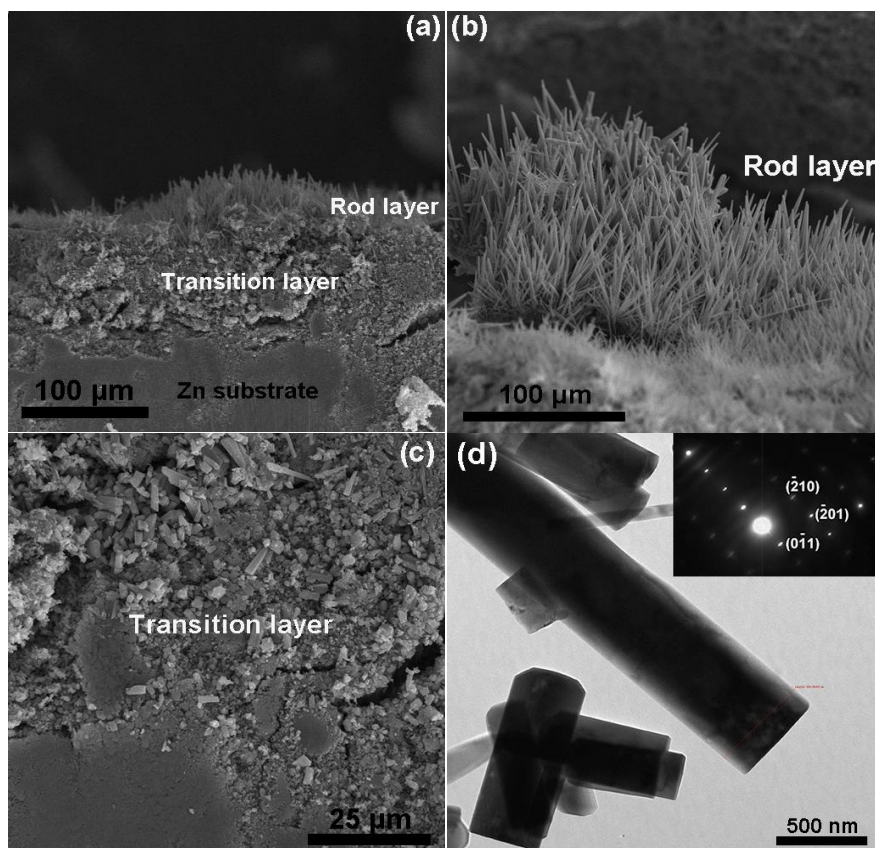
Fig. 2. SEM imagines of the cross-section of (a) ZnO/Zn, (b) rod layer, (c) transition layer, (d) TEM imagine of the ZnO single microrod. Inset is the SAED pattern.

With the hydrothermal condition, the formed Zn(OH)$_2$ further transfers to ZnO rod, which has been detailed discussed in our previous work 14,15.. In general, the formation of the ZnO rods through the corrosion of Zn by H$_2$O$_2$ is generally attributed to the Eqn. (2) and (3). And the general reaction is summarized as Eqn. (6). The schematic diagram of the forming mechanism of ZnO microrods on Zn plate is presented in Fig.3.

The photocatalytic activity of the obtained photocatalysts was evaluated. The concentration evolution of the MO solution is displayed in Fig. 4(a). To eliminate the portion of absorption, 45-minutes dark treatment was carried out. It is observed that the concentration of MO is decreased with the irradiation of UV light, indicating the obtained ZnO rods on Zn possesses the photodegradation ability of the pollutant. After 8 h, only 9.24% of the dye was residual, and it further decreases to 5.88% at 11 h. It means the ZnO rods on Zn plate shows strong degradation ability. Fig. 4(b) displays the UV-vis spectra of the centrifuged solutions. One

can find that the intensities of the peaks at 463 and 271 nm decrease along the time without any peak shifts, but a new peak around 246 nm arises after irradiation with UV light. These phenomena demonstrate some new smaller molecules are generated during the degradation of MO, and this processes occur only with the UV irradiation, which further verifies the decreased concentration of MO is caused by photocatalytic degradation of ZnO rods.

As it has been introduced that the powder-form photocatalysts are hard to realize a disjunction, and the loss of the catalysts also will decrease its efficiency in degradation of same amount of pollutant. In this work, the ZnO rods possessing photocatalytic activity are directly deposited on the Zn plate. The good combination made the disjunction is easy to be realized, and it also could decrease the loss of the catalysts as well as a consequently good catalytic stability. To this term, the catalytic reactions were carried out for ten times toward same amount of the pollutant,
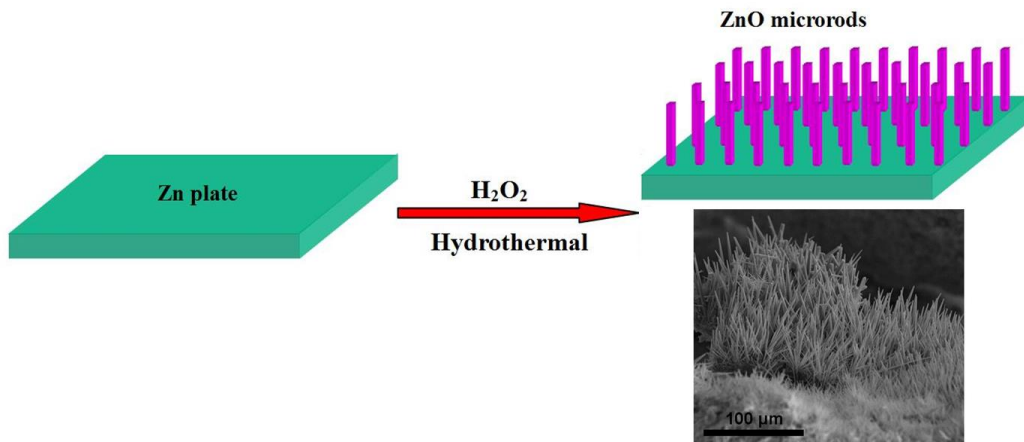
Fig. 3. Schematic illustration of the possible formation mechanism for the ZnO microrods on Zn plate.
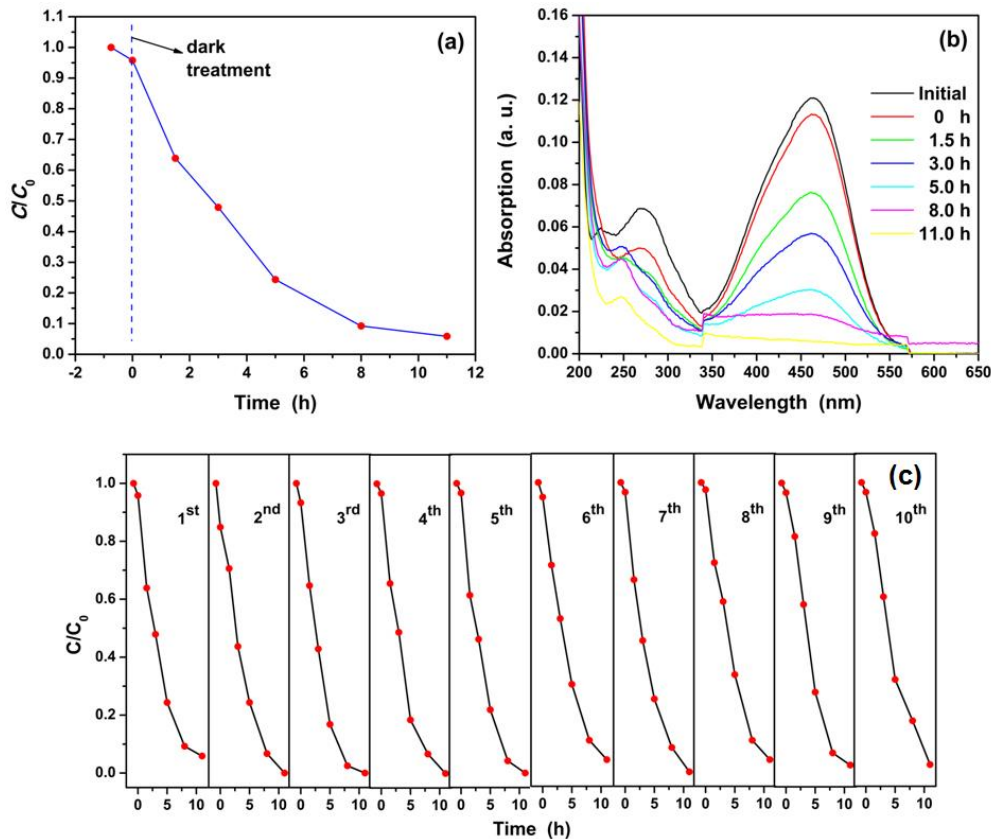

Fig. 4 (a) The degradation rate of MO, (b) the UV-vis absorption spectra of the centrifuged solutions at different intervals during the photodegradation test, and (c) the concentration evolution of ten repeated photocatalytic experiments of the as-prepared ZnO/Zn.

and the results are shown in Fig. 4(c). At 11 h, more than 95% of the MO is removed for all the tests, which is identical to the prediction that the obtained ZnO microrods surely have an excellent stability.

CONCLUSION

Through the green corrosion of Zn plate by H$_2$O$_2$ with the assistant hydrothermal condition, wurtize ZnO microrods are deposited on the surface of the Zn plate. The transformation from Zn to ZnO is

mainly attributed to that H_2O_2 possessing enough redox potential oxidizes the Zn. The obtained ZnO microrods show degradation ability toward the methyl orange under ultraviolet. Owing the strategy that directly depositing the ZnO rods photocatalysts on the hard substrate, Zn plate, the good combination of ZnO and Zn benefits for reborn and endows it excellent photocatalytic ability, demonstrating a potential for its real application in photodegradation of water pollutant.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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