# Preparation of Flower-like ZnO Architecture for Photodegradation of Caffeine in Aqueous Solution

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**Abstract**

*The flower-like ZnO architecture was prepared by hydrothermal method. As-synthesized samples were characterized by XRD, SEM, and $N_2$ adsorption/desorption isotherm. The composition of samples before and after calcination was analyzed by XRD, the precursor was completely transformed to ZnO at 400 °C. The catalytic performance of ZnO was evaluated by the degradation of caffeine in aqueous solution under different irradiation of lights. The degradation efficiency was 97.6% under UV light in 120 min and it was 100% under solar light in 60 min. The reaction kinetic of photodegradation of caffeine was studied by first-order kinetic model and the reusability of the ZnO sample was investigated through five cyclic tests.*

Keywords: ZnO, Caffeine, Photocatalyst, Flower-like structure, First-order kinetic

## 1.Introduction

Pharmaceutical and personal care products (PPCPs) are increasingly important to our lives. However, they are classified as the most serious pollutants when discharged into the environment. Their presence in surface water pollutes the water environment and adversely effects on human health. Therefore, the treatment of PPCPs before emitting into environment has attracted the attention of many scientific researchers in the Global [1,2].

Caffeine, $C_8H_{10}N_4O_2$, an alkaloid belonging to the methylzanthine family [3], is an example of PPCPs that often appears in surface water. Caffeine present in beverages such as coffees, teas, soft drinks, chocolate, some drugs, which makes it a widely consumed substance in the world. The World Bank reported that with its potential, Vietnam's market may consume 70,000 tons of coffees per year [4].

The presence of caffeine in surface water is due to sewage spills, leaky sewer pipes, poorly maintained septic systems, and other means of sanitary sewer flows. In addition, it may be due to attributable to storm water runoff containing wastewater influences, food waste or beverage containers from trash receptacles, recycled water over-irrigation, human waste at homeless encampments, or other anthropogenic activities [5]. Caffeine alone does not seem to be toxic to domestic organisms. However, the presence of too much of it in surface water, along with other organic pollutants such as pesticides, pharmaceuticals and other chemicals, has serious implications for organisms and humans [5]. Therefore, removal of caffeine from effluents is very necessary.

Photocatalysis is an environmentally friendly method for water and wastewater treatment. The main advantage of advance oxidation process by photocatalyst is the mineralization of organic pollutants into $CO_2$, $H_2O$ and simple inorganic acids [3,6]. There are many types of semiconductor oxides such as $TiO_2$, ZnO, $Bi_2O_3$, and $Nb_2O_5$ were used as photocatalysts for the decomposition of organic pollutants. $TiO_2$ has been widely used because of the large band gap (>3.2 eV). However, ZnO presented a relative lower cost, easier to synthesize, greater thermodynamic stability than $TiO_2$. In addition, ZnO exhibited the great interest because of its excellent performance in photocatalyst, solar cell, paint manufacture and food additives [7].

In relation to structure, ZnO could be prepared with different morphologies and it strongly affected to the catalytic ability [8]. The architecture structure with the large surface area and high pore volume will give advantage for the adsorption, diffusion, and reaction of organic compounds on the surface of ZnO. Therefore, the objective of this research was to preparation of flower-like ZnO architecture for photodegradation of caffeine in water.

## 2. Experimental

### *2.1. Materials*

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 99.5%) and urea ($(NH_2)_2CO$, 99.5%) were purchased from China, caffeine was obtained from Sigma-Aldrich (99.0%). All the chemicals were used without any purification and distilled water was used

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throughout the experiments.

### *2.2. Synthesis of flower-like ZnO*

The hierarchical ZnO was fabricated by a simple hydrothermal process. In a first stage, 30 mL of zinc nitrate hexahydrate 0.5M, 0.03 mole urea, and 70 mL of distilled water were put in a bearker 250 mL. The mixed solution was stirred at 240 prm for 30 min. Then, the mixed solution was transferred into teflon-lined autoclave and heated at 90 °C for 24 h. Subsequently, the autoclave was cooled to room temperature, the precipitation was detached by vacuum pumping filtration, washed with distilled water for 4-5 times and dried at 90 °C for 24 h. Finally, the flower-like hierarchical ZnO were obtained by calcining the precipitate at 400 °C for 2 h with a heating rate of 2 °C/min.

### *2.3. Characterization*

The crystalline phase of samples was investigated by X-ray power diffraction. XRD patterns were obtained by using Bruker D8 Ax XRD-diffractometer (Germany) with Cu Kα irradiation (40kV, 40 mA). The 2θ ranging from 10° to 80° was selected to analyse the crystal structure. The morphology of the samples was observed by field emission scanning electron microscopy (FE-SEM, JEOL-7600F). The textural properties were measured via $N_2$ adsorption/desorption isotherms using a Micromeritics (Gemini VII analyzer). The specific surface area, pore volume and pore diameter were obtained by using the Brunauer-Emmett-Teller (BET) method.

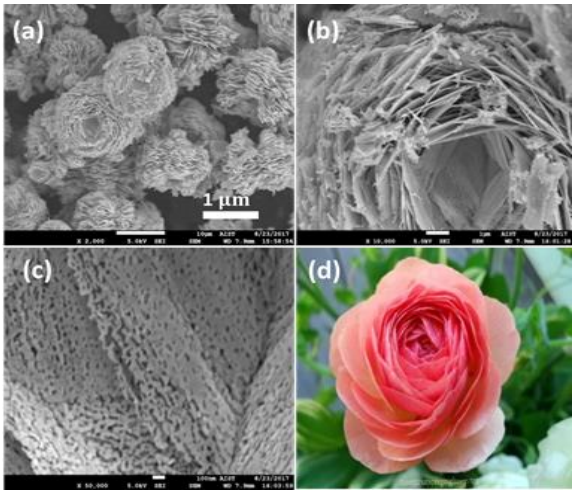


**Fig. 1.** (a-c) SEM images of hierarchical flower-like ZnO with different scale bars and (d) the digital photo of the Persian rose.

## 3. Results and discussion

### *3.1. SEM analysis*

The SEM images of as-synthesized ZnO are depicted in Fig. 1. ZnO was observed with uniformly hierarchical flower and 1 µm in size, as seen in Fig. 1(a). The micro flower-like ZnO was composed of many nano sheets formed by many zinc oxide nanoparticles, as seen in Fig.s 1(b) and (c). In addition, as-synthesized sample showed a beautiful rose-like ZnO, as seen in Fig. 1(d). Thus, exception of the ZnO particles are shaped like nanorods, nanoneedles, nanowires, nanobelts, nanosheet, etc., the flower-like shape is expected as a great morphology for photocatalytic application process.

### *3.2. XRD analysis*

The crystal phase of the samples was characterized by XRD analysis and the result is shown in Fig. 2. The diffraction peaks of precursor before calcination were in good agreement with with zinc hydroxide carbonate, $Zn_4(CO_3)(OH)_6.H_2O$ (JCPDS:11-0287). While, the diffraction peaks of precursor after calcination were attributed to zinc oxide, ZnO (JCPDS:19-1458) and no other characteristic peaks for impurities were detected, indicating precursor had completely transformed into the pure ZnO crystal at 400 °C in 2 h [9,10].

The ZnO formation mechanism was explained following: The mixing process was performed at room temperature. When urea was added to the $Zn^{2+}$ solution, the urea molecules hydrolysis in aqueous slolution to form amonniac and carbon dioxit, and then form $OH^-$ and $CO_3^{2-}$ anions:

$$(NH_2)_2CO+3H_2O\rightarrow 2NH_3.H_2O+CO_2 \quad (1)$$

$$NH_3.H_2O\rightarrow NH^{4+}+OH^- \quad (2)$$

$$CO_2 + OH^- \rightarrow CO_3^{2-} + H_2O \quad (3)$$

Then the $OH^-$ and $CO_3^{2-}$ was continue to react with $Zn^{2+}$ ion to generate zinc carbonate hydroxide

$$4Zn^{2+}+CO_3^{2-}+6OH^-+H_2O \rightarrow Zn_4(CO_3)(OH)_6.H_2O \quad (4)$$

The precipitate was filted, washed with distilled water several times, dried at 90 °C over night, and then calcined at 400 °C for 2 h with ramping rate 2 °C/min to obtain ZnO powder:

$$Zn_4(CO_3)(OH)_6.H_2O\rightarrow 4ZnO+CO_2+4H_2O \quad (5)$$

### *3.3. $N_2$ adsorption/desorption isotherm analysis*

The $N_2$ adsorption/desorption isotherm was conducted to investigate the porosity of the material, including its specific surface area and pore sizes. The isotherm and pore size distribution curves flower-like ZnO sample are presented in Fig. 3. The isotherm curve was identified as type IV. When the relative pressure ($P/P_o$) increased from 0.91 to 0.98, a sharp hysteresis loop was observed, indicating the presence of mesoporous material. In addition, when the

relative pressure was higher than 0.98, an abrupt increase in the amount of adsorbed nitrogen was observed. The pore size distribution was relatively wide and most of pores in range from 15 to 100 nm. As a result, ability to diffuse and efficiently transport hydroxyl radicals in photochemical reactions enhances the catalytic activity of the ZnO material [9,11]. The surface area and average pore size of as-prepared ZnO were 24.4 $m^2/g$ and 0.280 $cm^3/g$, respectively.

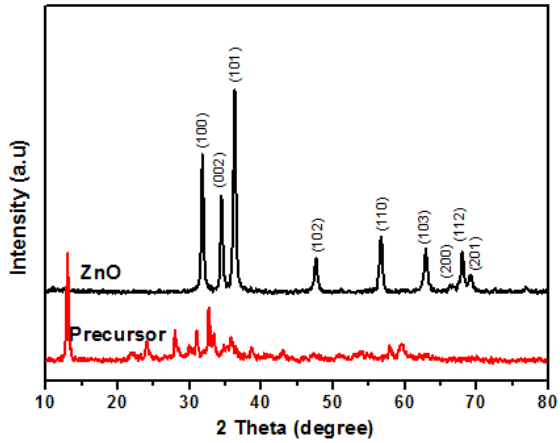


**Fig. 2.** XRD patterns of the precursor before calcination and as-synthesized ZnO

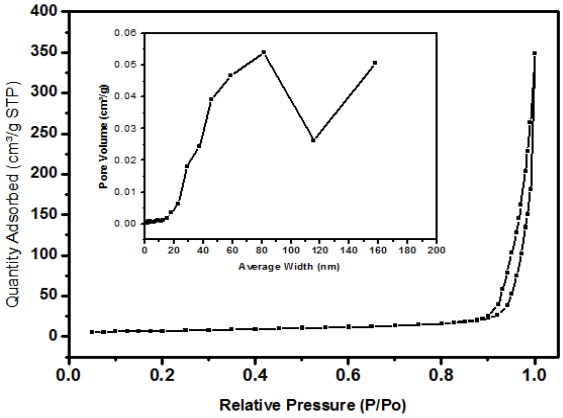


**Fig. 3.** $N_2$ adsorption/desorption isotherm (inset: pore size distribution) of as-synthesized ZnO.

### *3.4. Photocatalytic degradation mechanism of caffeine on ZnO*

The degradation of caffeine was conducted with 0.3 g ZnO, 100 mL caffeine solution with a concentration of 5 mg/L under subdued light, tungsten lamp (100 W), UV light (15 W) and solar light (at 11 h-13 h in summer). The results are shown in Fig. 4(a). It was clearly seen that the degradation efficiency of caffeine was strongly affected by light irradiation. Under subdued light, the degradation efficiency in 60 min was negligible. Under tungsten lamp, the degradation of caffeine was 18.8% in 120 min, whereas the degradation efficiencies of caffeine significantly increased under UV light and solar light, these values were 97.6 and 100%, respectively. Particularly, the caffeine was completely degraded in 60 min, it could be attributed to simultaneous existent of visible and UV in solar light, this was agreed with previous report [12].

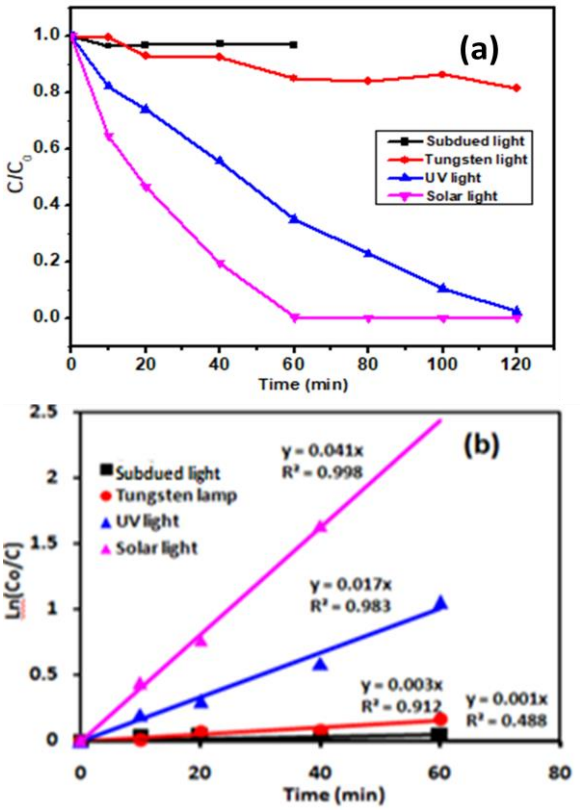


**Fig. 4.** (a) Effect of irradiation light on degradation of caffeine and (b) first-order curves.

The photodegradation rate of caffeine by flower-like ZnO can be evaluated by using the pseudo-first-order model called Langmuir–Hinshelwood model as follow:

$$\ln \frac{C_0}{C_t} = kt \qquad (6)$$

Where $C_0$ and $C_t$ are the concentration of caffeine at initial (t =0) and time t (min), respectively. k is the pseudo first-order rate constant. The k value was calculated from the slope of the ln ($C_0/C_t$) − t plots.

It is obviously seen that in Fig. 4(b), the degradation rate of caffeine under subdued light was low with a small rate constant 0.001 $min^{-1}$), the rate constant slightly increased to 0.003 $min^{-1}$ with irradiation of tungsten lamp. Howerer, it was strongly increased to 0.017 to 0.041 $min^{-1}$ for UV light and solar light, respectively.

The directed comparison as-prepared ZnO with

other samples in literature is a challenge since ZnO have been prepared by different methods for many applications such as cosmetic, paint, sensor, adsorption, and photocatalyst. However, it was clear showed that as-prepared ZnO had the hierarchical structure with the high reaction performance, the degradation efficiency was higher than that of other ZnO samples that had been reported, as seen in Fig. 1 and Table 1.

**Table 1.** Comparison as-prepared ZnO with other samples.

| ZnO samples | Particles Size | Applicati -on | Performance | Ref. |
|---|---|---|---|---|
| Flower | 1 µm | - | - | [13] |
| Flower | 1-2 µm | Bromop-enol dye removal | 96% within 120 min, concentration of 10 ppm | [14] |
| Rod | 80-100 nm | RhB removal | 97 % within 120 min, concentration of 10 ppm | [15] |
| Nano-spheres | 15-60 nm | RR141 removal | 78% within 240 min, concentration of 10 mg/L | [16] |
| Nano disks | ~ 200 nm | RhB removal | 90 % within 90 min, concentration of 10 ppm. | [17] |
| Flower | 1 µm | Caffeine | 100 %, within 60 min, concentration of 5 mg/L | This study |

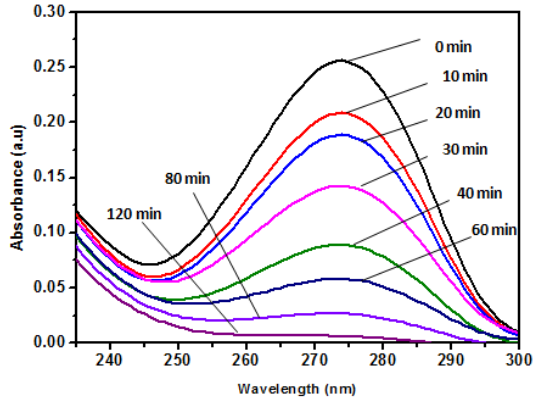


**Fig. 5.** UV-Vis spectra of caffeine aqueous solution as function of reaction time with ZnO as catalyst.

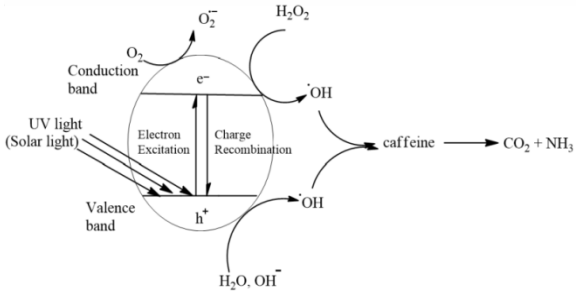


**Fig. 6.** Mechanism of caffeine photodegradation using flower-like ZnO under UV light and solar light.

Fig. 5 shows the absorption spectrum of the caffeine solution at the concentration of 5 mg/L with 0.3 g of ZnO under UV irradiation at different reaction times. The maximum absorption peak of the caffeine at 274 nm diminished gradually and even disappeared at 120 min. This result suggests that the caffeine molecules and intermediates are degraded almost completely by oxidation, hydroxylation and mineralization processes. It is therefore beneficial for water treatment to help protect the environment. The mechanism for photocatalyst activity of flower-like was proposed, as shown in Fig. 6.

Upon the UV or solar light irradiation, the electrons in the valence band of ZnO can be excited to the conduct band, leaving holes in the valence band. The electrons can active molecular oxygen to form superoxide ion ($O_2^-$) and the photogenerated holes react with either water ($H_2O$) or hydroxyl ions ($OH^-$). The formation of •OH, $•O_2^-$ radicals water have created hydroxylation, oxidation and mineralization processes, as described by equations 7-12 [1,18-20]. Which are able to degrade caffeine to intermediated products, $CO_2$ and $H_2O$.

Water is dissociated into ions

$$H_2O \rightarrow H^+ + OH^- \quad (7)$$

ZnO can absorb UV light (or solar light) and generate electron-hole pairs (Fig. 6)

$$ZnO + h\nu \rightarrow e^- + h^+ \quad (8)$$

The electrons move to the surface of the catalyst and adsorbed $O_2$ on the surface to form $•O_2^-$

$$e^- + O_2 \rightarrow •O_2^- \quad (9)$$

The $•O_2^-$ can react with surface adsorbed $H_2O$ to form $H_2O_2$:

$$•O_2^- + H_2O \rightarrow H_2O_2 \quad (10)$$

Photoconversion of $H_2O_2$ gives OH radicals:

$$H_2O_2 + h\nu \rightarrow 2•OH \quad (11)$$

The holes react with $OH^-$ ions in the water form OH radicals:

$$h^+ + OH^- \rightarrow •OH \quad (12)$$

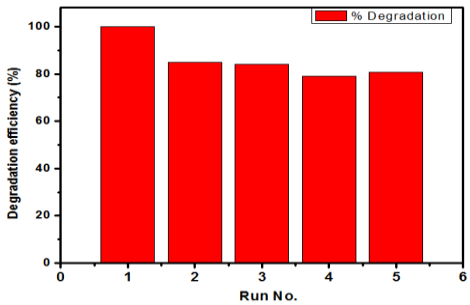


**Fig. 7.** Cycling stability of ZnO catalyst

### *3.5. Reusability of the catalyst*

In the practical application, the reusability of the catalyst is also the critical parameter. In this study, as-synthesized ZnO was reused for four times at the

same condition, caffeine concentration of 5 mg/L and ZnO 0.3 g under UV light. Fig. 7 shows the degradation efficiency caffeine of ZnO at each cycle. The performance of catalyst only presented a little drop. At the first run, the degradation efficiency was 97.6%, and this value was remained over 80.0% after four cycles. This revealed that flower-like ZnO architecture had a good cycling stability and potential application in industry.

## 4. Conclusion

In summary, flower-like ZnO architecture was successfully prepared by hydrothermal method. As-synthesized ZnO was mesoporous structure and composed from many nanosheets, it showed the large surface area (24.4 $m^2$/g) and high pore volume (0.280 $cm^3$/g). The degradation of caffeine on ZnO was fast and archived 97.6% under UV light at 120 min, particularly it was higher (100%) under solar light at 60 min. In addition, the flower-like ZnO exhibited a good cycling stability. Therefore, as-prepared sample was expected that could be potential material for cleaning industrial wastewater.

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