

# Photocatalytic and physicochemical properties of pure and variously CeO<sub>2</sub>-doped CuO-Fe<sub>2</sub>O<sub>3</sub>/cordierite system

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## ABSTRACT (ARIAL, BOLD, 11 FONT, LEFT ALIGNED, CAPS)

A Mixture of 10wt% CuO-10wt% Fe<sub>2</sub>O<sub>3</sub> supported on cordierite and CeO<sub>2</sub>-doped (0.75-3 mol%) with different temperatures (500, 700 and 900°C) were prepared by wet impregnation. The effects of calcination temperatures and doping ratio on the crystalline phase, morphology, surface area were investigated by XRD, HR-TEM, N<sub>2</sub>-adsorption-desorption. Moreover, their photocatalytic activities of samples calcined at 700°C on the degradation of a mixture of phenol, 4-chloro-phenol and cresol were evaluated under UV irradiation. CeO<sub>2</sub>-doping led to a progressive increase in S<sub>BET</sub>. Sample treated with 0.75 mol% CeO<sub>2</sub> and calcined at 700°C had the best photocatalytic activity. This might be attributed to the presence of un-reacted oxides (CuO and Fe<sub>2</sub>O<sub>3</sub>) which have low redox potentials.

*Keywords:* Cordierite, COD, Photocatalysis, Copper ferrite, CeO<sub>2</sub>-doping

## 1. INTRODUCTION (ARIAL, BOLD, 11 FONT, LEFT ALIGNED, CAPS)

Numerous applications utilized Fe<sub>2</sub>O<sub>3</sub> because of its non-harmfulness, accessibility, high imperviousness to oxidative change and low preparing cost[1,2]. Adjustment of iron oxide by blending it with different oxides because of its low warm strength, surface

territory diminishment and fast deactivation in reactant examinations [1,2]. CuO/Fe<sub>2</sub>O<sub>3</sub> was chosen as potential unstable natural mixes, (VOCs) oxidation catalyst [3].

Cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>) is a crystalline magnesium aluminosilicate MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [4]. Cordierite utilized as a conceivably accessible material in electronic industry and heterogeneous catalysis because of its minimal effort, low weight drop in the fumes framework, great warm resistance and little warm development coefficient [5]. Cordierite has been effectively utilized as an impetus support for Co<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, CuO, Fe<sub>2</sub>O<sub>3</sub> and NiO [6-8]. Cerium doping attracted more interest, might be due to the following reasons: (1) the redox couple Ce<sup>3+</sup>/Ce<sup>4+</sup> makes cerium oxide shift between CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> under oxidizing and reducing conditions; (2) the different electronic structures between Ce<sup>3+</sup> (4f<sup>1</sup> 5d<sup>0</sup>) and Ce<sup>4+</sup> (4f<sup>0</sup>5d<sup>0</sup>) could result in different optical properties and catalytic properties[9].

The evacuation of compound contaminants has advanced a broad inquiry managing combination and portrayal of nano organized impetuses [4-7]. The destructive of fragrant toxins, which are generally present in various waste water from pharmaceuticals and other industries. O<sub>2</sub>-based photocatalytic response can be acknowledged in evacuation harmful poisons in water [8,10,11]. Phenolic mixes found in mechanical effluents. Nitrophenolic mixes, for instance, are discharged into the earth through their wide use as colors, pesticides, plasticizers, and solvents. It is accounted for that some monitrophenol can be framed as corruption result of herbicide nitrofen when it is presented to daylight [12]. One of the water quality method is concoction oxygen request (COD). COD is viewed as a method of portrayed natural toxins present in wastewater. Measure of natural contaminants and water clean degree can be recognized by COD substance [13].

The present work talked about surface and photocatalytic properties of CuO-Fe<sub>2</sub>O<sub>3</sub>/cordierite. The concentration of CeO<sub>2</sub>-doping (0.75-3 mol%) and calcinations temperature (500,700 and 900 °C) on

photocatalytic successes of the prepared solids were explored regarding COD evacuation.

## 2. MATERIAL AND METHODS

### 2.1. Materials and catalyst preparation

Calculated amounts of a mixture of equal amounts of copper nitrate  $[\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  and ferric nitrate  $[\text{Fe}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$  was impregnated in a given mass of a finely powdered cordierite  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  (commercial grade supplied by Baikowski Inc. company) by dissolving the mixture in the least amount of distilled water sufficient to make paste. The pastes were dried at 100 °C then calcined at 500, 700 and 900 °C for 4 h. The amounts of copper and ferric nitrates were calculated in a manner that the calcined prepared samples contained 10 wt.% CuO and 10 wt.%  $\text{Fe}_2\text{O}_3$ .  $\text{CeO}_2$ -doped solids (0.75- 3 mol%) were prepared by impregnating a known mass of finely powdered support material with different amounts of cerium nitrate solution prior to treating with copper and ferric nitrates followed by drying and calcination at 500, 700 and 900 °C for 4 h. The employed chemicals were of analytical grade and supplied by Fluka company.

### 2.2 Techniques

X-ray powder diffractograms of variously supported solids calcined at 400 – 700 °C were determined using a Bruker diffractometer (Bruker D 8 advance target). The patterns were run with copper  $K_\alpha$  with secondly monochromator ( $\lambda = 1.5405 \text{ \AA}$ ) at 40 kV and 40 mA. The scanning rate was 8° and 0.8° in 0.2° in  $2\theta$ .  $\text{min}^{-1}$  for phase identification and line broadening profile analysis, respectively. The crystallite size of the phases present in pure and variously supported solids was determined using the Scherrer equation [14]

$$d = K \lambda / \beta_{1/2} \cos \theta$$

where d is the mean crystalline diameter,  $\lambda$  is the X – ray wave length, K is the Scherrer constant (0.89),  $\beta_{1/2}$  is the full width at half maximum

(FWHM) of the main diffraction peaks of the crystalline phase present and  $\theta$  is the diffraction angle.

The structure and the surface morphology of the resulted nano-composites were examined using JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of about 80 kV and JEOL-SEM scanning electron microscope (SEM) respectively. The wastewater effluents were characterized and analyzed for Chemical oxygen demand (COD) according to the procedures described in Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, 1995) [15]. Chemical oxygen demand (COD) was carried out via a Hach-2000 spectrophotometer using a dichromate solution as the oxidant in strong acid media using closed reflux, colorimetric method according to APHA, 1995 section 5220-D.

The amount of catalyst is one of the main parameters for the degradation studies. In order to avoid the use of excess catalyst it is necessary to find out the optimum catalyst loading for efficient removal of COD of the wastewater. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic oxidation process [11, 12].

### 3. RESULTS AND DISCUSSION

#### 3.1. XRD investigation of different solids

X-ray diffraction pattern of pure and variously doped solids being calcined at 500, 700 and 900°C were determined. The diffractograms of pure and variously doped solids are given in Figs. (1-3). Examination of Figs.(1-3) showed that: (i) treatment of cordierite solid sample with a mixture of 10 wt% CuO and 10 wt% Fe<sub>2</sub>O<sub>3</sub> followed by calcination at 500, 700 and 900 °C decreases slightly the relative intensity of all diffraction peaks of the cordierite phase. This decrease might reflect a limited structure collapse as been evidenced by the observed decrease in the degree of crystallinity of the treated cordierite. (ii) The appearance of some diffraction peaks of un-reacted CuO phase having poorly

crystalline state. (iii) There is no diffraction peaks of  $\text{Fe}_2\text{O}_3$  phase have been detectable. This disappearance of  $\text{Fe}_2\text{O}_3$  might be attributed to possible dissolution of  $\text{Fe}_2\text{O}_3$  in cordierite lattice and/or found in small portion that could not be detectable by x-ray diffractometer. (iv) Doping the investigated samples with (1.5 mol% and 3 mol%  $\text{CeO}_2$ ) and being calcined at 500 and 700 °C led to the appearance of new diffraction line (copper ferrite ( $\text{CuFe}_2\text{O}_4$ ) (34-0425 JCPDS-ICD, copyright 2001). This finding reveals that ceria enhanced the ferrite formation in low temperature. Opposite trend observed at high temperature (900 °C) as there is no diffraction line of copper ferrite could be detectable.

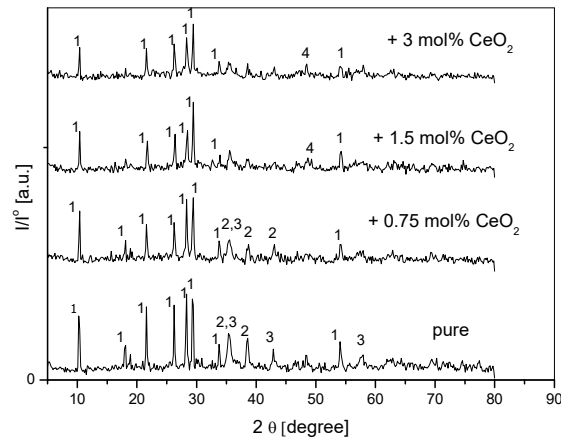


Fig.1: XRD diffractograms of  $\text{CuO-Fe}_2\text{O}_3/\text{cordierite}$  calcined at 500°C  
(1.Cordierite, 2. CuO, 3.  $\text{Fe}_2\text{O}_3$ , 4.  $\text{CuFe}_2\text{O}_4$ )

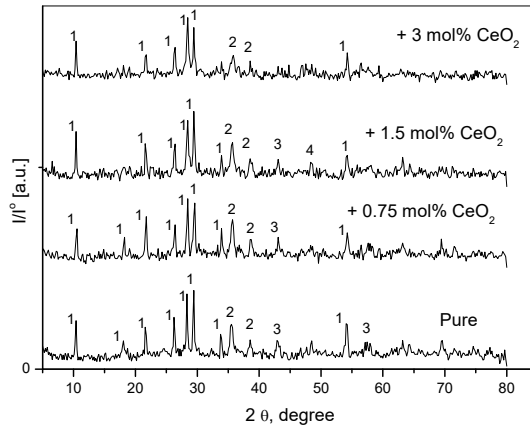


Fig.2: XRD diffractograms of  $\text{CuO-Fe}_2\text{O}_3/\text{cordierite}$  calcined at  $700^\circ\text{C}$   
(1.Cordierite, 2. CuO, 3.  $\text{Fe}_2\text{O}_3$ , 4.  $\text{CuFe}_2\text{O}_4$ )

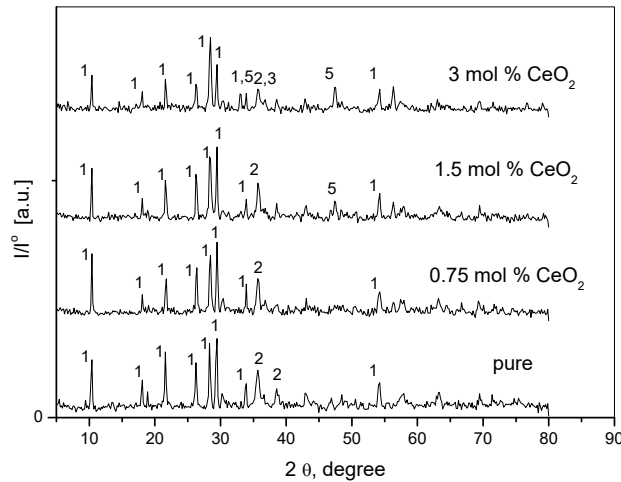
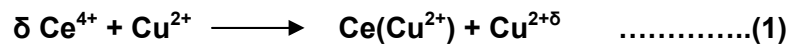


Fig.3: XRD diffractograms of  $\text{CuO-Fe}_2\text{O}_3/\text{cordierite}$  calcined at  $900^\circ\text{C}$   
(1.Cordierite, 2. CuO, 3.  $\text{Fe}_2\text{O}_3$ , 4.  $\text{CuFe}_2\text{O}_4$ , 5.  $\text{CeO}_2$ )

The role of  $\text{CeO}_2$ -doping on  $\text{CuFe}_2\text{O}_4$  formation could be discussed as follows: a portion of ceria might dissolve in the matrix of copper oxide. The dissolution process could be simplified adopting Kröger notations as follows [17]:





where  $\text{Ce}(\text{Cu}^{2+})$  is cerium ion located in the position of  $\text{Cu}^{2+}$  and "A.V." is created anionic vacancies. " $\delta$ " is a small fraction the amount of which increases by increasing the degree of substitution and the electrical neutrality is kept by creation of a small fraction of divalent copper cation to a valence state slightly bigger than 2 i.e. some of both copper cations shared an extra positive charge.

The substitution process might occur readily because of the similarity between ionic radii of  $\text{Ce}^{4+}$  and  $\text{Cu}^{2+}$ . In fact,  $\text{Ce}^{4+}$  and  $\text{Cu}^{2+}$  measured an ionic radius of 1.034 and 0.93 Å, respectively [18].

So, dissolution of cerium cation in copper oxide lattice according to reaction (1) decreased slightly the concentration of  $\text{Cu}^{2+}$  cation via conversion into  $\text{Cu}^{2+\delta}$  ions. While incorporation of tetravalent cerium in CuO lattice according to reaction (2) created some anionic vacancies.

The role of ceria in opposing copper ferrite formation for solids calcined at 900°C might be tentatively attributed to the possible decrease in the concentration of divalent copper cation ( $\text{Cu}^{2+}$ ) via conversion into  $\text{Cu}^{2+\delta}$ . This process might decrease the concentration of divalent copper cation involved in copper ferrite formation.

The stimulation effect of ceria in  $\text{CuFe}_2\text{O}_4$  formation for solids calcined at 500 and 700 °C might be attributed to dissolution of the dopant cation in CuO lattice according to reaction (2) via increasing the concentration of anionic vacancies. These vacancies facilitate migration of reacting cations i.e. increasing the mobility of divalent copper cations taking part in copper ferrite formation.

### 3.2. HRTEM of various solids

Fig. 4 shows congregates of nano-particles of spherical morphology and relatively uniform with diameter range from 35.21nm to 101nm. These results were in a good agreement with the results obtained by XRD investigation.

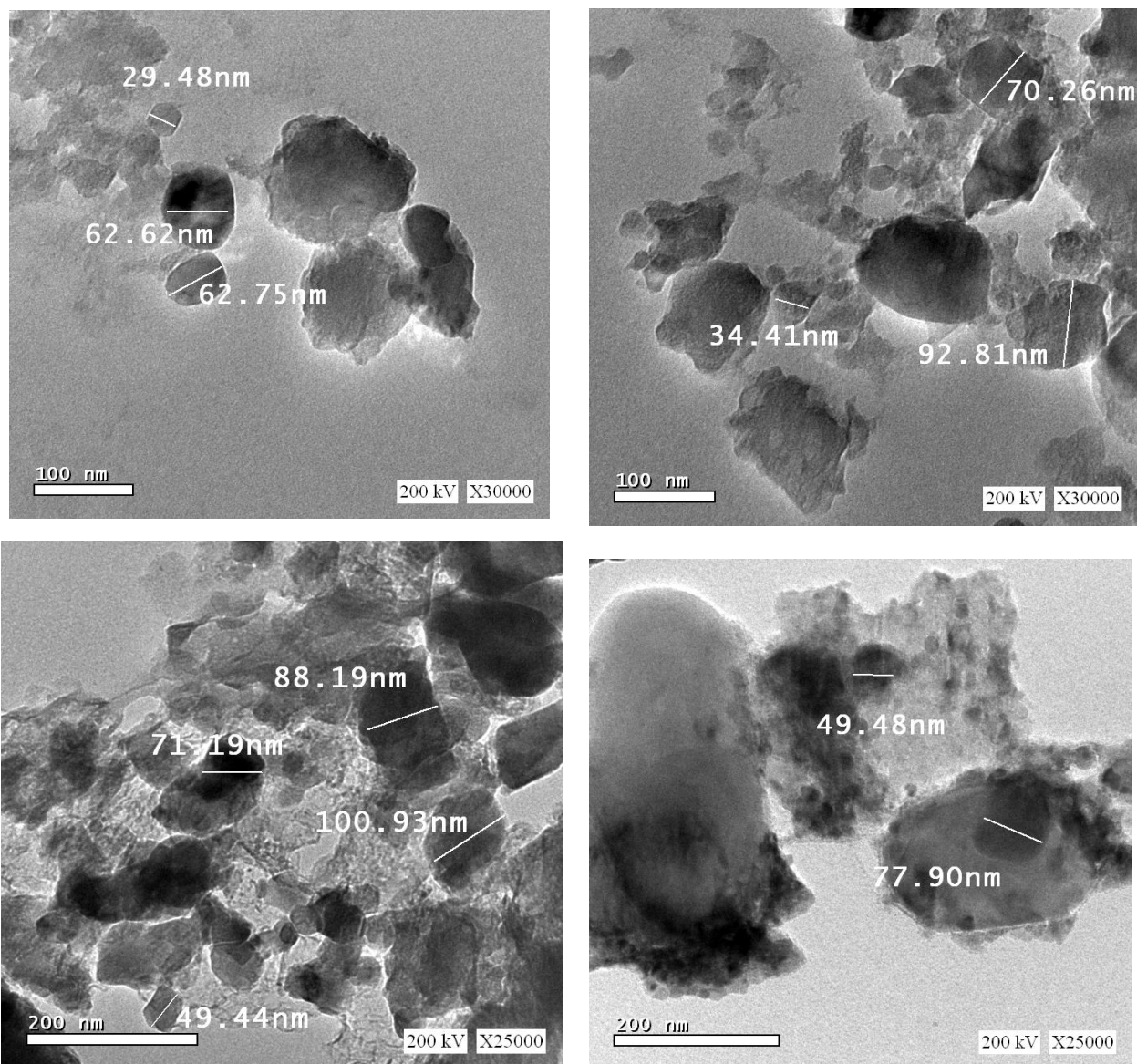


Fig.4: TEM photographs of pure and variously doped solids calcined at 700°C

### 3.3. Surface characteristics of different solids

The surface characteristics including BET surface areas, total pore volume ( $V_p$ ) and average pore radius ( $r$ ). The results obtained are given in Table 1. Inspection of Table 1 shows: (i) The  $S_{BET}$  of cordierite support material calcined at 500°C increased by the coexistence of CuO and  $Fe_2O_3$ . (ii)  $CeO_2$ -doping led a progressive increase in the  $S_{BET}$  value. The maximum increase due to  $CeO_2$ -doping (3 mol%) attained 60%, 40% and

**40% for samples calcined at 500, 700 and 900°C, respectively. (iii) The pore structure figures (not given) exhibit tri-modal mesoporous.**

Table 1: specific surface areas( $S_{\text{BET}}$ ) of different investigated solids calcined at 500, 700 and 900 °C

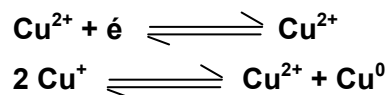
| Solid catalyst                                                                     | Calcination temperature (°C ) | $S_{\text{BET}}$ |
|------------------------------------------------------------------------------------|-------------------------------|------------------|
| Cordierite                                                                         | 500                           | 5                |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite                            | 500                           | 6.2              |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite + 0.75 mol% $\text{CeO}_2$ | 500                           | 11.8             |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite + 1.5 mol% $\text{CeO}_2$  | 500                           | 14               |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite + 3 mol% $\text{CeO}_2$    | 500                           | 15.4             |
| Cordierite                                                                         | 700                           | 4                |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite                            | 700                           | 9.4              |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite + 0.75 mol% $\text{CeO}_2$ | 700                           | 11.6             |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite + 3 mol% $\text{CeO}_2$    | 700                           | 10.2             |
| Cordierite                                                                         | 900                           | 4                |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite                            | 900                           | 6.2              |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite + 0.75 mol% $\text{CeO}_2$ | 900                           | 8.6              |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite + 1.5 mol% $\text{CeO}_2$  | 900                           | 8.9              |
| 10 wt% CuO – 10 wt% $\text{Fe}_2\text{O}_3$ /cordierite + 3 mol% $\text{CeO}_2$    | 900                           | 9.6              |

### 3.4. Photocatalytic degradation

Photocatalytic activity of pure and variously doped solids calcined at 700°C were investigated by the method was discussed in the previous paper of one of the author [14].

The results obtained are given in Fig. 5. Examination of Fig. 5 showed that: (i) The maximum percentage of COD removal for 120 min. reaction were 80%, 56%, 53% and 84.5% for pure , 0.75 mol% CeO<sub>2</sub>, 1.5 mol% CeO<sub>2</sub> and 3 mol% CeO<sub>2</sub>, respectively. This finding might due to the presence of portion of un-reacted individual oxides (CuO and Fe<sub>2</sub>O<sub>3</sub>). It is known that [19] metal cation might increase the oxidation rate. This catching of photogenerated electrons by oxidant species (Cu<sup>2+</sup> or Fe<sup>3+</sup>) is conceivable due to the values of redox potentials of these couples (+0.34 and +0.77 V ,respectively).

The reliance of the current on [Cu<sup>2+</sup>]<sup>1/2</sup> recommended on electron decrease to Cu<sup>+</sup>, trailed by fast disproportionation, rather than an immediate two-electron venture to metallic copper:



The more prominent proficiency of Fe<sup>3+</sup> might because of the capacity of Fe<sup>2+</sup> to move far from the molecule into arrangement, keeping the pernicious back-response.

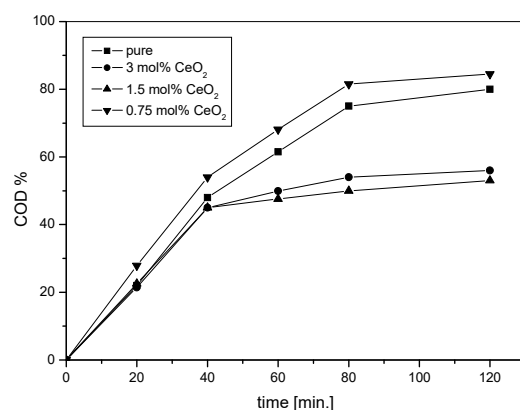


Fig.5: The percent of COD removal during wastewater treatment by different oxidation process

#### 4. CONCLUSION

Cuo-Fe<sub>2</sub>O<sub>3</sub> mixed oxides supported on cordierite were prepared by wet impregnation and doped with (0.75- 3 mol% CeO<sub>2</sub>). It was discovered that doping ratio and calcination temperature lead to the change in the crystalline phase, morphology, surface area and playing important roles in photocatalytic activity. The results revealed that sample treated with 0.75 mol%CeO<sub>2</sub> has the best activity. This high activity might be attributed to the presence of un-reacted oxides (CuO and Fe<sub>2</sub>O<sub>3</sub>) which have low redox potentials.

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