Polyacrylamide Synthesis of Nanostructured Copper Aluminate for Photocatalytic Application

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ABSTRACT

This paper reports the synthesis of nanostructured copper aluminate powders and their efficient application as a potential photocatalysts for photodegradation of organic dyes. The synthesized nanocomposite powders were characterized by XRD, TEM, DTA-TG analyses and UV-vis spectroscopy. The XRD results showed that pure and single phase copper aluminate was obtained after calcination at 700 °C. The obtained powders had a layered structure and each layer was composed of many interconnected nanoparticles. The average particle size of the samples calcined at 700 °C was about 26 nm. The photocatalytic activity of the prepared nanocatalysts was investigated via photodegradation of methyl orange under the UV light. The band gap energy values of $CuAl_2O_4$ calcined at 700 and 900 °C were 1.79 and 1.72 eV, respectively. The results showed that the samples calcined at 700 °C showed the highest activity with 95 % photodegradation efficiency for degradation of methyl orange dye.

1-Introduction

The residues of toxic chemicals from different industries are major pollutants. They are toxic for the human life [1, 2]. The organic dyes are an important part of these chemicals which are mostly stable in nature, creating lots of problems in ecosystems [3]. In this relation, different techniques have been proposed to remove the organic pollutants from wastewater [4]. The photocatalytic degradation is an effective and easy method for decomposition of these organic dyes [5]. The development of new active photocatalysts with a high efficiency for application in water and air purification is a hot debate in the world. In recent years, many new ceramic photocatalysts have been used [6-8]. These ceramics are semiconductors like TiO_2, ZnO, WO_3 and some spinel structures. Among many types of spinel structured catalysts, copper aluminate ($CuAl_2O_4$) shows a relatively high performance. $CuAl_2O_4$ spinel also has a high thermal stability and low surface acidity [7, 9, 10].

However, these spinels are typically synthesized using a high calcination temperature above 1000 °C. It can cause grain growth and agglomeration in the final product. Therefore, new synthesis methods demand solutions to overcome these disadvantages. Copper aluminate has been recently prepared by different methods such as co-precipitation [7], soft chemical synthesis [11] and the sol–gel method [12].

The use of the polyacrylamide gel method for preparation of nanomaterials is an interesting way because of the fact that this method isa fast, time saving, reproducible, and easily scaled method [13, 14]. It is believed that this approach will be a better method for the preparation of

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$CuAl_2O_4$ nanostructures. Therefore, in the present study the preparation of nanostructured $CuAl_2O_4$ has been carried out using the polyacrylamide gel method. In addition, the photocatalytic properties of the synthesized powders were investigated.

2- Experimental procedure

2-1- Materials and methods

The raw materials for the synthesis of nanostructured $CuAl_2O_4$ were aluminum nitrate nonahydrate ($Al(NO_3).9H_2O$, Merck Co., Germany) and copper nitrate hexahydrate ($Cu(NO_3)_2.6H_2O$, Merck Co., Germany). Also, methyl orange (Merck Co., Germany) was used as a model compound for water-soluble azo dye. Acrylamide ($C_2H_3CONH_2$) and N,N′-methylene bis acrylamide ($(C_2H_3CONH_2)_2CH_2$) were used as monomer and a cross-linker monomer, respectively. Ammonium persulfate ($(NH_4)_2S_2O_8$) and N,N,N′,N′-tetramethyl ethylenediamide ($C_6H_{16}N_2$) were used as an initiator and an accelerator, respectively. Aluminum nitrate and copper nitrate (Al:Cu = 2:1) were dissolved in water. Synthesis of $CuAl_2O_4$ was performed by dissolving acrylamide and N,N′-methylene bis acrylamide monomers with a molar ratio of 22:1. Then 10% (w/v) ammonium persulfate and 1% (v/v) N,N,N′,N′-tetramethyl ethylenediamide were added to the solution. A transparent gel was rapidly obtained. The gel was dried at 100 °C for 3 h. The gel was calcined in air at different temperatures for 3 h.

2-2- Characterization

The morphology and particle size of $CuAl_2O_4$ powders were determined by a JEM-100CX transmission electron microscope (TEM). The X-ray diffraction (XRD) patterns were obtained using a Philips Xpert model with Cu-Kα radiation. UV–Vis spectroscopy was performed on a Shimadzu spectrophotometer (model UV-1601 PC). Fourier-transform infrared (FTIR) spectroscopy of the powder was carried out by a Nicolet Nexus 6700 to study the chemical bonds of the powders. Differential thermal (DTA) and thermogravimetric (TG) analyses were used in the range of 25–1000 ºC at a rate of 10 ºC/min using the STA equipment (PL Thermal Sciences 1640)

2-3- Adsorption measurements

Photocatalytic activities of the $CuAl_2O_4$ samples were evaluated by degradation of methyl orange (MO) in water under UV irradiation of a 100W UV light. In all of the photocatalytic experiments, 0.05 g of the product was added to 10 ml of the aqueous solution of MO. At specific time intervals, 5 mL of the samples was separated and centrifuged. The quantitative determinations of MO were performed by measuring its absorbance using a UV–Vis spectrophotometer. The degradation rate of MO was calculated according to the following equation:

$$E_t = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration at time=0 and C_t is the concentrations of methyl orange at time=t.

3- Results and discussion

The XRD pattern of the samples calcined at 500, 700 and 900 °C is shown in Fig. 1. The XRD pattern of the sample calcined at 500 °C consists of the peaks related to the CuO phase (JCPDS No. 45-0937) and the peaks of $CuAl_2O_4$ (JCPDS No. 01-078-1605). After increasing the calcination temperature to 700 °C, the peaks related to the CuO disappeared , the intensity of $CuAl_2O_4$ peaks increased and only spinel peaks of $CuAl_2O_4$ crystals were observed. As the calcination temperature increased to 900 °C, the intensity of the peaks increased and the full width at half maximum of the peaks decreased which showed an increase in crystallinity and crystallite size of the powders. As can be seen, the temperature for the synthesis of single phase of $CuAl_2O_4$ is about 700 °C which is lower than that of the traditional method. This effect can be due to the molecular mixing of the raw materials in the wet chemical methods [7, 15].

Fig. 2 shows the DTA and TG curves of the powders. The DTA curve represents two exothermic peaks at 240 and 540 °C. As it is known, the elimination of organic components via oxidation is an exothermic reaction, and the two exothermic peaks can be attributed to the decomposition of the organic materials [16]. The TG curve shows a total weight loss of about 80%, which occurs at two stages. At the first stage (100–300 °C), the weight loss is about 22% which is due to the dehydration of the

powders and elimination of the organic matter [17]. The second stage of weight loss occurring at the temperature between 300 to 550 °C is about 58% and is due to decomposition of polyacrylamide and other residues [12].

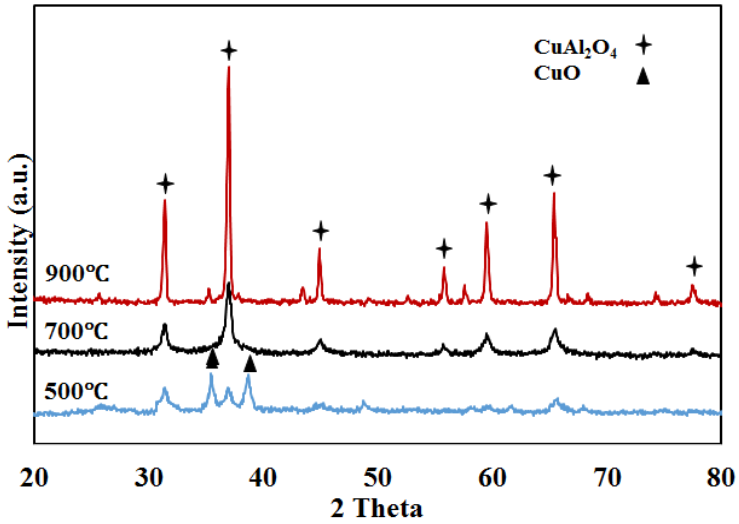

Fig 1. X-ray diffraction patterns of the samples calcined at different temperatures

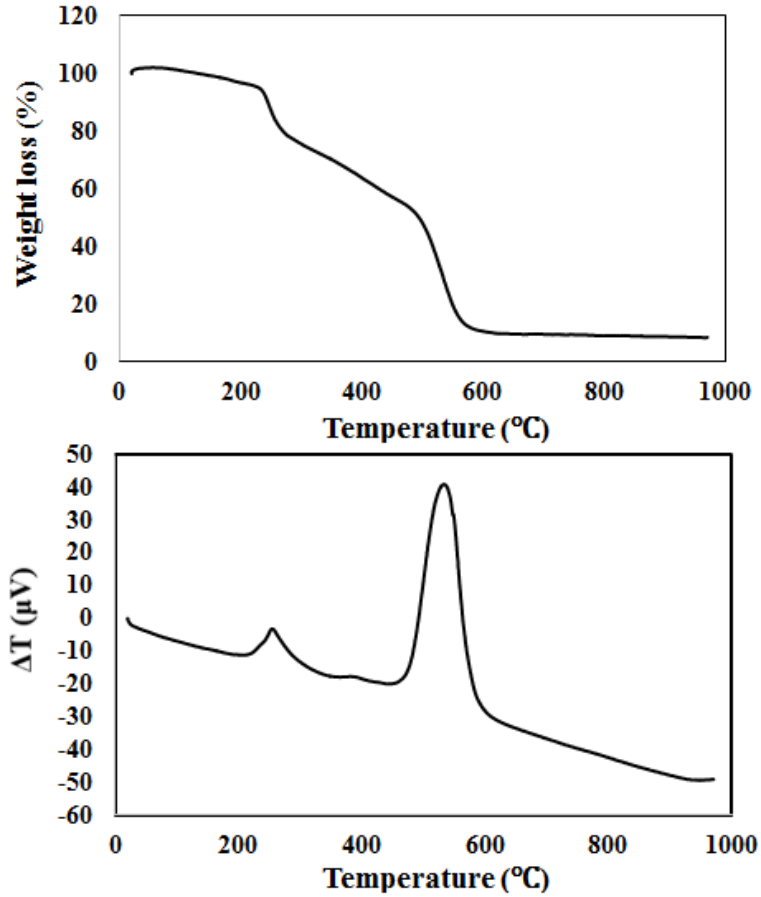

Fig. 2. DTA and TG curves of the dried powders

The FTIR analysis (Fig. 3) was used to characterize the chemical bands of the samples calcined at different temperatures. The bands at 1660 and 3430cm^{-1} are assigned to the vibrating mode of the OH groups in the dried sample [10, 11]. The absorption band at 2935 cm^{-1} and between 1042 and 1460 cm^{-1} is related to the stretching vibration of organic compounds [18, 19]. Upon calcination, these bands disappeared which confirms the removal of the organic components and dehydration of the powders. These results are in good agreement with the DTA–TG analysis (Fig. 2). The stretching vibrations appeared in the range of 450–800 cm^{-1} correspond to the vibrations of Cu–O, Al–O, and Cu–O–Al bands [10, 11]. These results indicate that the obtained crystal was copper aluminate spinel. TEM micrographs of the samples calcined at 700 and 900 °C are shown in Fig. 4. As can be seen, a layered structure can be found in both samples. Each layer is composed of nanoparticles which are attached together. The formation of the layered structure in these samples can be attributed to the polymerization of acrylamide. In this method of synthesis, a polymeric network can be formed which acts as a temporary template [14, 16]. In the polyacrylamide gel method, the polymerization of acrylamide happens, which is started by free radicals afforded by ammonium persulfate. Meanwhile, the polyacrylamide chains are linked by two functional groups of N,N′-methylene bis acrylamide monomer which leads to the formation of a three dimensional (3D) polymeric network. This 3D web of interconnected branches can trap the metal ions within itself. The TEM image of the sample calcined at 700 °C shows an irregular morphology with the average diameter of about 26 nm. As the calcination temperature increases to 900 °C, the particle size increases to 38 nm. UV-Vis spectrophotometer was used to study the effect of calcination temperature on the optical properties of $CuAl_2O_4$. The band gap of $CuAl_2O_4$ can be calculated using Tauc's formula. This formula represents the relationship between the absorption coefficient (α) and photon energy (hυ) which is shown in Eq. (2) [20, 21]:

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \quad (2)$$

where E_g is the optical band gap energy of the sample and A is an energy dependent constant. in order to calculate the band gap energy, an extrapolation of the linear part of $(\alpha h\upsilon)^2$ versus hυ plot should be made as shown in Fig. 5. It is observed that the band gap energy values of $CuAl_2O_4$ calcined at 700 and 900 °C are 1.79 and 1.72 eV, respectively. It was also noted that by increasing the calcination temperature, the particle size increases which leads to a reduction in E_g [20].

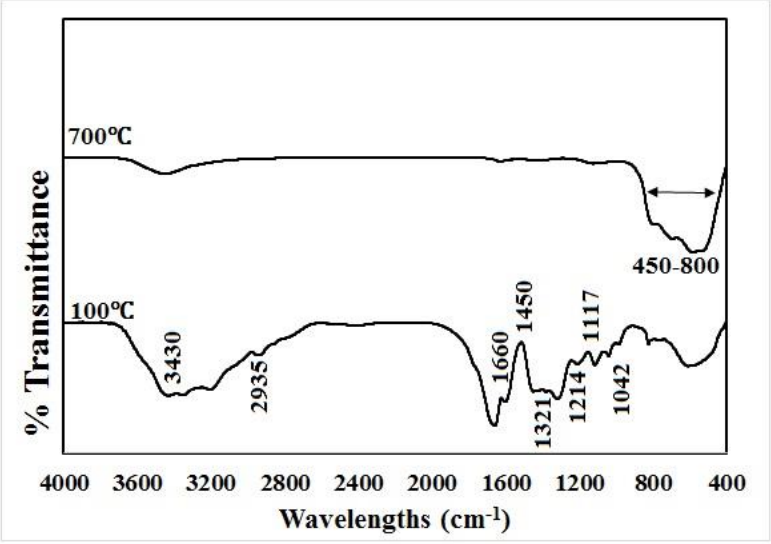

Fig. 3. FTIR analysis of the powders calcined at different temperatures

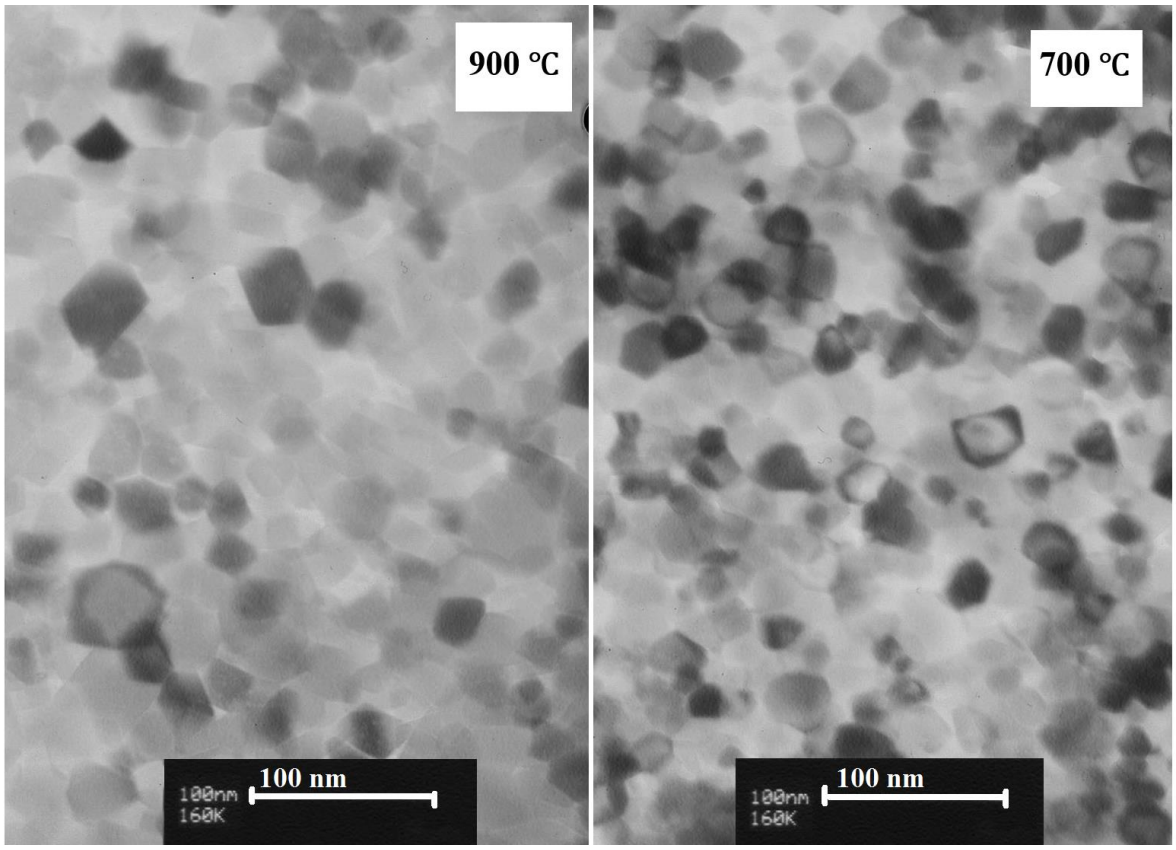

Fig. 4. TEM images of the samples calcined at different temperatures

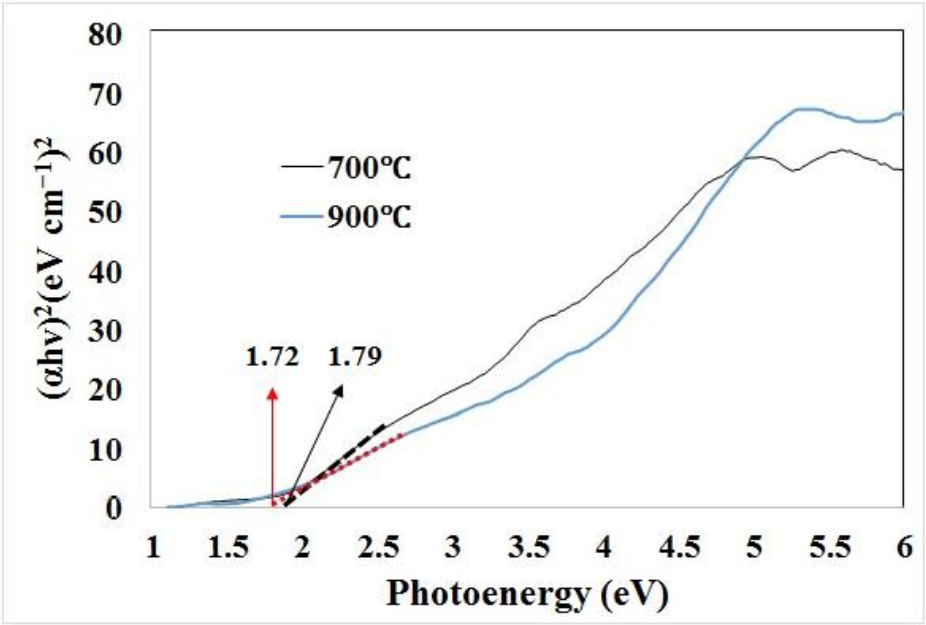

Fig. 5. The plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of the samples calcined at different temperatures

The results of photocatalytic activity of the samples calcined at 700 and 900 ˚C for the photodegradation of MO are shown in Fig. 6. At first, the photodegradation of MO was performed without photocatalyst under UV light. As can be seen, there is no degradation. It was reported that MO dye is stable under the UV light [22]. In addition, the photodegradation of MO was investigated in a dark chamber in the presence of photocatalyst to evaluate the amount of dye adsorption on the surface of photocatalyst. The amounts of absorption for the samples calcined at 700 and 900 °C were 22 and 37 %, respectively. Higher absorption of the sample calcined at 700 °C may be due to higher surface area of this sample. After UV irradiation in the presence of the photocatalyst, the results revealed that the percentage of MO photodegradation using sample calcined at 700 °C is higher than (~95%) of those calcined at 900 °C (~60%). The remarkable photocatalytic performance of the sample calcined at 700 °C may arise from a higher surface area and smaller grain size. Upon irradiation, the electron-hole (e-p) pairs are formed by photoexcitation. These e-p pairs can cause the formation of reactive superoxide radicals. These radical groups may cause the decomposition of organic dyes like MO.

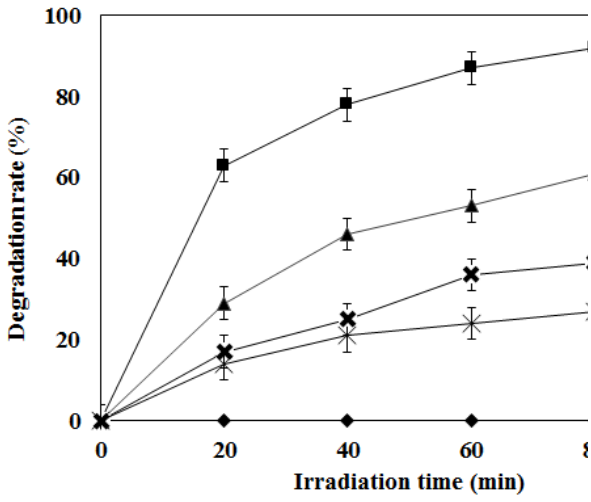

Fig. 6. Photocatalytic activity of the samples calcined at different temperatures

Table 1 compares the photocatalytic efficiency of the $CuAl_2O_4$ synthesized by polyacrylamide gel method with those prepared by other methods. As can be seen, the $CuAl_2O_4$ synthesized by polyacrylamide gel can be considered as a promising photocatalyst for the removal of MO from aqueous solutions. In addition, in the present study, the optimum time for dye degradation was shorter than the others and the amount of photocatalyst was lower in comparison with the $CuAl_2O_4$ prepared by other wet chemical methods which will result in lower operational cost for real-world applications.

Table 1. Compares the photocatalytic efficiency of the $CuAl_2O_4$ synthesized by different methods

Synthesis Method	Calcination Temperature	Particle Size (nm)	Band Gap (ev)	Catalyst Dose (mg)	Solution concentration (mg/l)
Sonochemical	900	18	--	150	10
Sol-Gel	700	10-30	1.77	100	20
Polyacrylamide	700	26	1.79	50	20

4- Conclusion

A nanostructured $CuAl_2O_4$ was prepared via polyacrylamide gel method in order to photodegrade methyl orange dye from aqueous solutions. The characteristics of the composite were studied using XRD, DTA-TG, TEM and UV-Vis spectroscopy. The TEM images demonstrated that the product has a layered structure and each layer is composed of many nanoparticles which are connected to one another. The results showed that the synthesized nanocomposite is a promising photocatalyst for degradation of MO dye. The highest photodegradation (~95%) was achieved for the sample calcined at 700 °C.

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