PREPARATION AND VISIBLE-LIGHT PHOTOCATALYTIC PROPERTIES OF $BiFeO_3$ BY CO-PRECIPITATION METHOD

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SUMMARY

In this study, nano $BiFeO_3$ powders were successfully synthesized by co-precipitation method which dissolved PVA in water with Bi/Fe/PVA = 1/1/3 molar ratio, at pH = 12. Research results showed that $BiFeO_3$ nano powders have been formed at a temperature of 110ºC after 4 hours of drying. When materials were calcined at higher temperatures, from 250ºC to 550ºC for 2 hours, $BiFeO_3$ appears more frequently, with a particle size of about 100nm. However, the material system had not achieved pure monophasic state, still had some other phases like Bi_2O_3, $Bi_{25}FeO_{40}$ and substrate. Differential thermal analysis method (TG/DTA), X-ray diffraction method (XRD), scanning electron microscopy method (SEM) were used to study the structural characteristics of materials. The study determined the effect of calcination temperature (250, 350, 450, 550ºC), pH values (1, 3, 6, 9, 12), presence of H_2O_2 on photocatalytic ability of the material formed in the treatment of RY160 in the visible light region. The dye concentration was determined by the method of Ultraviolet – visible spectroscopy (UV-Vis) at 425 nm. Experimental results showed that, the RY160 degradation efficiency of BFO materials varied significantly when changing the pH and H_2O_2 was attended. The calcined materials were presented with high performance. Specifically, at pH = 3, added 1mL H_2O_2, the RY160 decomposing efficiency of BFO450 up to 100% after 90 minutes of lighting.

Keyword: Bismuth ferrite ($BiFeO_3$), co-precipitation method, effect of pH, nano powders, photocatalytic degradation, Reactive Yellow 160.

1. INTRODUCTION

The use of photocatalyst materials to convert sunlight energy into chemical energy in the treatment of environmental pollutants is one of the research directions that many scientists are interested in as it is environment-friendly, less energy consuming and has good results in prospect. Most studies on photocatalytic materials decompose toxic organic compounds under ultraviolet radiation, typically TiO_2 (Thammasak Rojviroon, 2012). However, ultraviolet energy only accounts for about 8% of the total solar radiation energy. A large part of the unused solar energy is the energy of the radiation in the visible light region. Therefore, it is necessary to research and develop materials with photocatalytic activity in the visible light region to turn solar energy into advantage.

Bismuth ferrite, $BiFeO_3$ (BFO), is one of the main multiferroic perovskite oxides, ABO_3 form brings about high efficiency in the treatment of organic compounds in water due to its high catalytic activity, low band gap energy is about 2.2 eV (Y.Hu. et al., 2011; F.Gao. et al., 2007), thus being able to catalyze in visible light. On the other hand, $BiFeO_3$ nano powders has chemical stability, showing ferromagnetism at room temperature, so it can be reused (C. Hengky, 2010; G.L.Yuan, 2006). Therefore, recent research on $BiFeO_3$ for photocatalytic orientation in general and for other applications in particular focus on finding the manufacturing process for pure single-phase products of $BiFeO_3$ at low temperature and pressure, simple reaction conditions. So far, there has been many methods used to synthesize BFO, such as solid state method (Nguyen Van Dang, 2007), sol-gel process (J.Wei, et al, 2012), gel burning, hydrothermal methods (Bing Liu, et al., 2011; Dao Ngoc Nhiem, 2015), microwave synthesis (U.A.Joshi, et al., 2008), thin film method (K. Saito, et al, 2006)... but obtaining pure $BiFeO_3$ with a simple, cheap process from easy-to-find precursors is still a challenge for scientists. In this article, BFO was prepared by co-precipitation from two solutions containing Fe^{3+} and Bi^{3+} in which dissolved PVA water is used as a solvent. Furthermore, the pH values of the solutions were altered by sodium hydroxide used as a precipitating agent. The brown red precipitate is dried and calcined to facilitate the formation of the $BiFeO_3$ crystalline phase, removing the volatile inorganic component and burning PVA.

2. RESEARCH METHODOLOGY

2.1. Chemicals, equipment

Chemicals: $Bi(NO_3)_3$ 0.1M; $Fe(NO_3)_3$ 0.1M; NaOH 5M; PVA; H_2O_2 30% and distilled water with analytical cleanliness; Yellow active 160 solutions (RY160) are prepared from standard solutions of concentration of 1000 mg/l.

Equipment: IKA C-MAG HS4 magnetic stirrer (Malaysia), Memmert heating and drying ovens (Germany), Pioneer Ohaus analytical balance (USA) with accuracy of 0.0001g, kiln (China), Yellow 15 watt Led bulb with wavelength range of 570 - 590 nm.

2.2. Materials synthesis

Pour PVA into the water and stirred for about 30 min at 80°C to form a clear solution, then slowly add the $Bi(NO_3)_3$ and $Fe(NO_3)_3$ solutions with molar ratio of metal/PVA being 1/1/3, adding NaOH to the reaction solution to maintain pH = 12 to get the reaction product. These precipitates were washed several times with distilled water to remove unreactant products and then filtered. The brown red precipitate were dried for 4 hours at 120°C and calcined at temperatures of 250ºC, 350°C, 450°C and 550°C for 2 hours. The phase identification of the sample was examined on X–ray diffractometer and differential thermal analysis. The morphology of the prepared particles was observed using scanning electron microscope.

2.3. Material properties testing methods

The properties of BFO materials are identified by the following methods:

Differential thermal analysis method (TG/DTA) was performed on TG - DTA/DSC Setaram at the VNU University of Sciences with a heating speed of 10ºC/min from room temperature to 900ºC in the air. The information obtained from the thermal diagram showed the process of allotrope transformation and the decomposition process, allowing the calculation of thermodynamic values that occurred when raising heat.

X-ray diffraction method (XRD) conducted on D8 Advancer - Bruker machine, radiation CuKα with wavelength λ = 1,5406 Å at the VNU University of Sciences. XRD is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition and physical properties of materials.

Scanning electron microscopy (SEM) was used to determine the shape and structure of surface materials with magnification that can be changed from 10 to 10,000 times with clear images, two-dimensional display. SEM results of the study were obtained from Nova Nano SEM 450 machine at the VNU University of Sciences.

2.4. Methods of investigating photocatalytic ability of materials

BFO nanopowders were tested for the removal of Reactive Yellow 160 (RY160) from aqueous solutions via batch experiments. Prepare 500ml of RY160, concentration of 10 mg/L were prepared by standard solution and pH was adjusted by solution of H_2SO_4 1M and NaOH 1M; Then, added with H_2O_2 and materials. The reaction solution was stirred on a magnetic stirrer at a speed of 120 rpm and was irradiated under visible-light irradiation with wavelength range of 570 – 590 nm. After the treatment time: 15, 30, 60, 90 minutes, the concentration of RY160 is determined by the UV-Vis method with a maximum absorption wavelength of 425nm on HARCH DR3900 meter, at the Chemical Lab, Vietnam National University of Forestry.

The RY160 degradation percentages is determined by the formula:

$$H(\%) = \frac{C_0 - C_t}{C_0} x100$$

In which: C_0, C_t is concentration of RY160 in the pre-treated sample (0 minutes) and t minutes after processing.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Bismuth ferrite

3.1.1. Differential thermal analysis result

The dry precipitated sample was investigated by thermal analysis, the results were shown in figure 1.

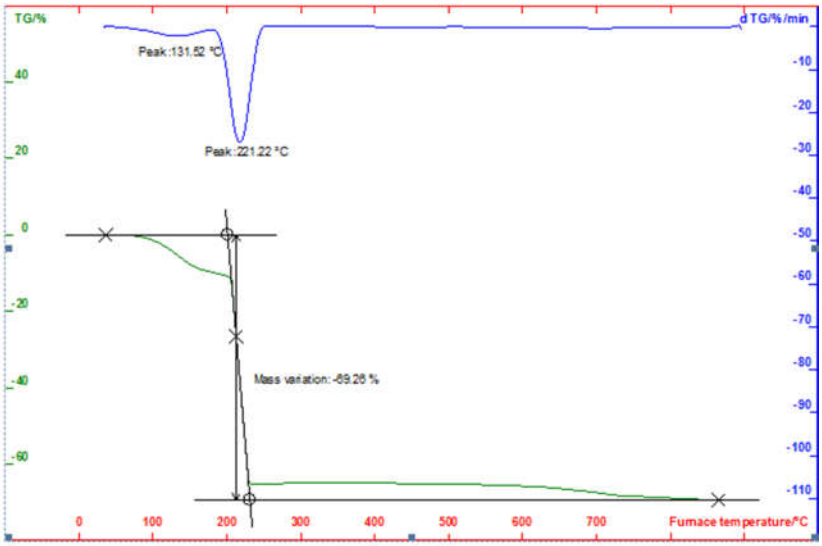

Figure 1. TG – DTA diagram of precipitation sample

The data shows an endothermic peak with a maximum at T_{max} = 221ºC resulting in a mass loss up to nearly 70% of the total weight in the temperature range from 90ºC to 230ºC corresponds to the process of evaporation, decomposing organic compounds and forming $BiFeO_3$ crystals. When the temperature is above 700ºC, the material loses a small amount of mass, maybe from this temperature range the material starts to become pyrolysis, the perovskite structure is broken.

3.1.2. Chemical composition of materials

Figure 2 shows the X-ray diffraction pattern of BFO powders calcined at different temperatures. The products after synthesis process is BFO, BFO250, BFO350, BFO450, and BFO550 respectively, were analyzed by XRD method to determine the phase composition of the material.

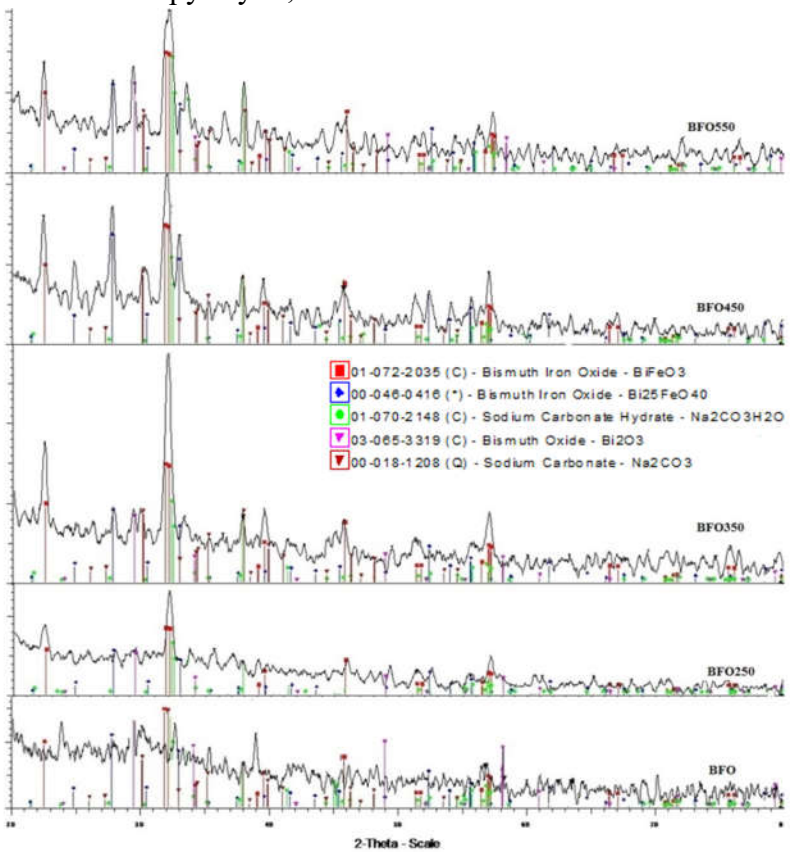

Figure 2. XRD diagram of the BFO material system is calcined at different temperatures

For the powders synthesized at 120ºC (BFO), there are secondary phases Bi_2O_3 and $Bi_{25}FeO_{40}$ and the beginning of the $BiFeO_3$ phase formation. Diffraction peaks of $BiFeO_3$ is not high, in the system of materials existed Bi_2O_3 phase with great intensity and substrate. At 250ºC, the $BiFeO_3$ peak increases slightly, the presence of unexpected phases is Bi_2O_3 and $Bi_{25}FeO_{40}$ decreased. As the temperature continued to rise to 350ºC, the signal of the $BiFeO_3$ phase increased sharply, at this temperature the formation of the $BiFeO_3$ crystal phase was stable, clearly. With increasing the calcination temperature, $BiFeO_3$ keeps constant with enhanced peak intensity and peak quantity, which is consistent with the thermal analysis results. Thus, compared with the method of synthesizing $BiFeO_3$ materials by solid state method (Nguyen Van Dang, 2007), the crystal phase temperature has been reduced from 830ºC to 350ºC. This phase formation temperature is equivalent to the result of synthesizing materials according to sol - gel method (Nguyen Thi Ha Chi, 2015). However, by the co-precipitation method, the material system has not achieved pure monophasic state but still has some other phases like Bi_2O_3, $Bi_{25}FeO_{40}$.

3.1.3. SEM Image

Surface morphological characteristics of BFO materials before and after calcination were shown on SEM images in figures 3 and 4.

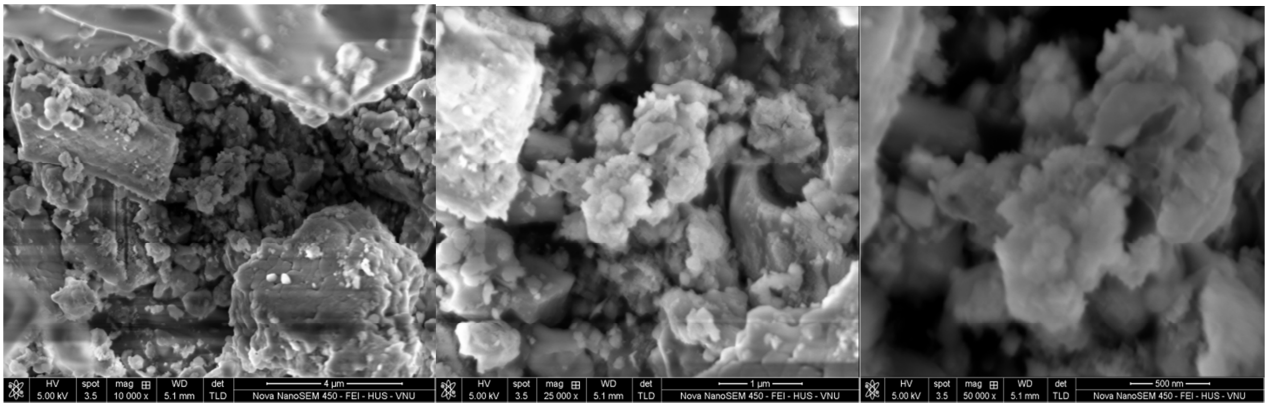

Figure 3. SEM image of BFO at magnification size of 10000, 25000 and 50000 times

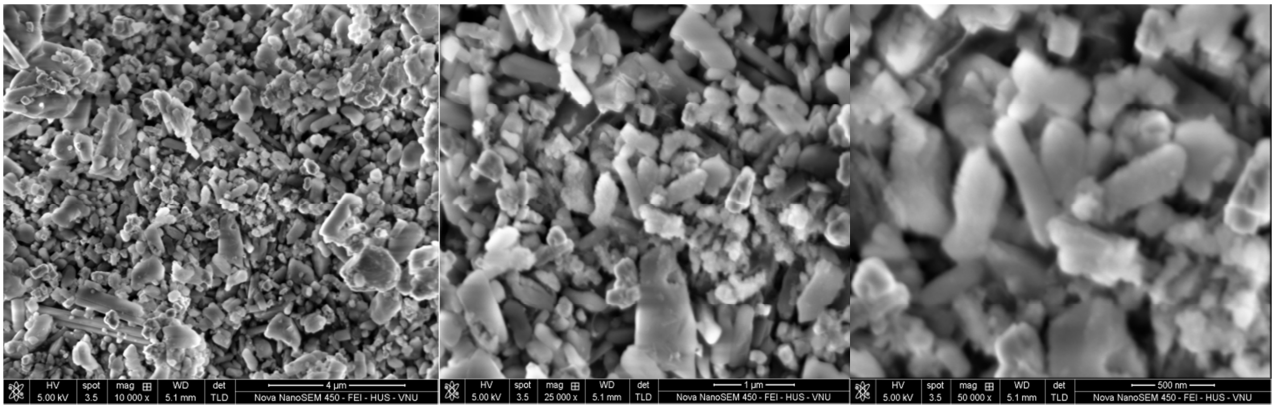

Figure 4. SEM image of the BFO450 at the room size of 10000, 25000 and 50000 times

SEM images show morphology of the material system changed before and after calcination. With unburnt BFO material, the surface structure is not clear, cohesive, large size about 500 nm and uneven. After heating, BFO450 is cylindrical, the particles are uniform in size and small - about 100 nm.

3.2. Photocatalytic ability of materials

3.2.1. Effect of calcination temperature on dye decomposing efficiency

Experiments to investigate RY160 photodegradation ability of the materials are

carried out in light boxes with a dye solution concentration of 10 mg/L, ratio BFO mass: dye solution volume is 1g/L, photodegradation time of 90 minutes, supplemented with 1mL H_2O_2, pH = 3. After testing, the RY160 solution was analyzed for the concentration and processing efficiency of baked materials at varied temperatures. The results were shown in figure 5.

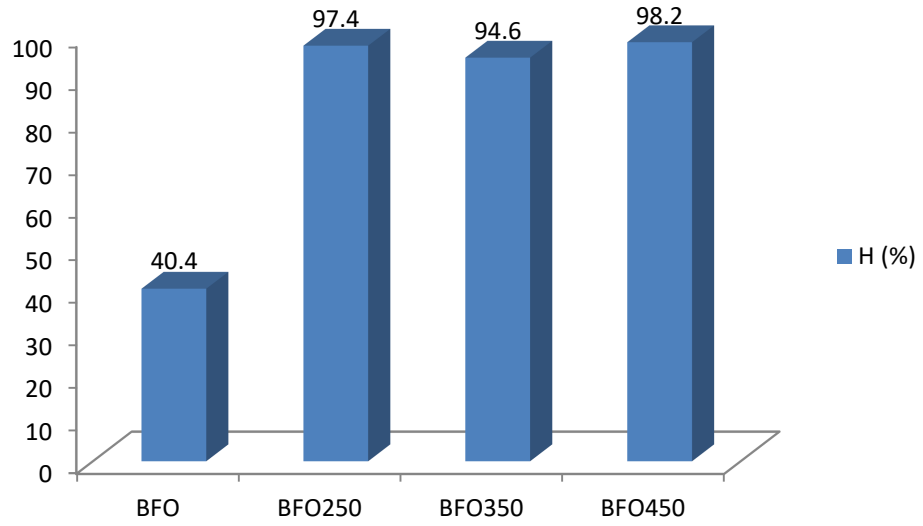

Figure 5. The effect of calcination temperature on RY160 decomposing efficiency

The results showed that $BiFeO_3$ materials are capable of fairly good RY160 treatment and all 3 phases of materials have the ability to photocatalytic decomposition of Reactive Yellow 160. The calcined materials are presented with higher performance than ones. This can be clearly seen when comparing the treatment performance of unburnt BFO material with the occurrence rate of less $BiFeO_3$ phase, more Bi_2O_3 and $Bi_{25}FeO_{40}$ phases, the degradation percentages is only 40.4%. After heating at 250ºC, 350ºC, 450ºC, the intensity of occurrence of the $BiFeO_3$ crystal phase increased sharply, the efficiency also increased to 95 - 98%. The photocatalytic capacity of 3 types of calcined materials at different temperatures is not much different. This is consistent with the results of thermal analysis and XRD analysis when the heating temperature is increased, the material system is relatively stable, the signal of BFO phases is similar, so the treatment abilities of these materials not much different.

3.2.2. Effect of pH

The pH of dye solutions were adjusted to 1, 3, 6, 9 and 12 pH values. 0.5 gram of photocatalyst was mixed with 500 mL of RY160 solutions at concentration 10 mg/L, lighting for 90 minutes, with additional 1ml of H_2O_2. After testing, the RY160 solution was analyzed for concentration and calculated the dye removal percentage of the object at different pH conditions. The results were shown in figure 6.

The results indicate that, when changing pH the ability to decompose the color of the material varies greatly. In an acidic environment, the photocatalytic ability of the material is best. RY160 decomposition efficiency up to 99 - 100% after 90 minutes of reaction. When changing the pH to the neutral environment, the processing ability of the material is poor, the efficiency is only 6 - 7%. When pH increases gradually to alkaline environment, the percentages of removal dye increases slightly but the efficiency is low, only 18%. Thus, the optimal condition for photocatalytic reaction to treat RY160 of BFO material system is acidic, at pH = 3.

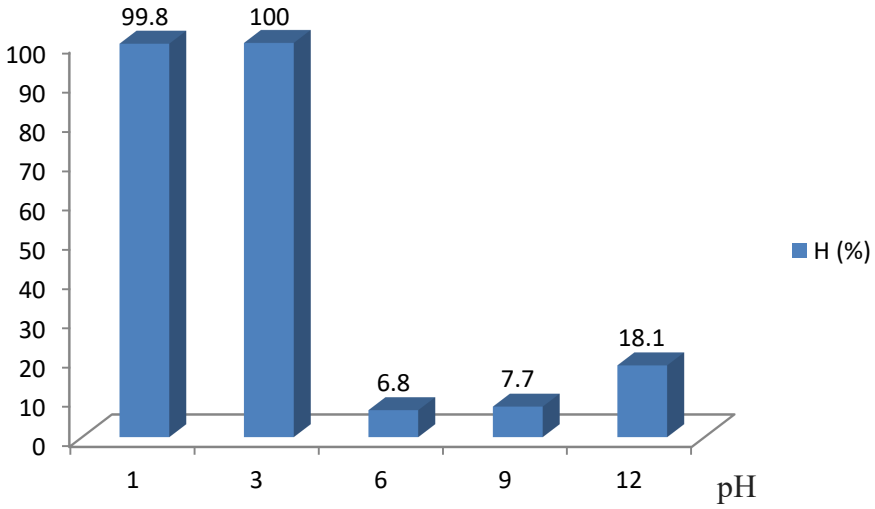

Figure 6. RY160 decomposition ability of BFO450 materials at different pH levels

3.2.3. Effect of H_2O_2

Photodegradation test was performed to assess the role of H_2O_2 on the catalytic ability of materials in light boxes with an initial concentration of RY160 of 10 mg/L, with 0.5g of material in 500 mL of solution. The amount of H_2O_2 is changed from 0, 0.5, 1 mL, pH = 3. After the intervals of 15, 30, 60, 90 minutes, the RY160 concentration was determined as above.

The effect of H_2O_2 on photodegradation process illustrated in figure 7 that, the RY160 degradation efficiency of BFO materials increased significantly when H_2O_2 was present. When H_2O_2 is absent, the dye decomposition time is long, the efficiency is low, after 90 minutes, it only reaches 75.8%. When H_2O_2 is present, the decomposition rate of RY160 increases sharply. Specifically, when adding 0.5 ml H_2O_2, after 60 minutes the performance reached 86.4% and increased to 94.4% after 90 minutes. When increasing the amount of H_2O_2 to 1ml, after 15, 60 minutes of irradiation, the percentage reached 75.1% and 100% respectively. It can be affirmed that H_2O_2 plays an important role in RY160 treatment performance and shortens the reaction time of BFO due to H_2O_2 itself being a strong oxidizing agent, which can create free radicals when received energy from light radiation. It is these free radicals that increase the number of free radicals in the color solution that leads to an increase in the degradation efficiency of RY160.

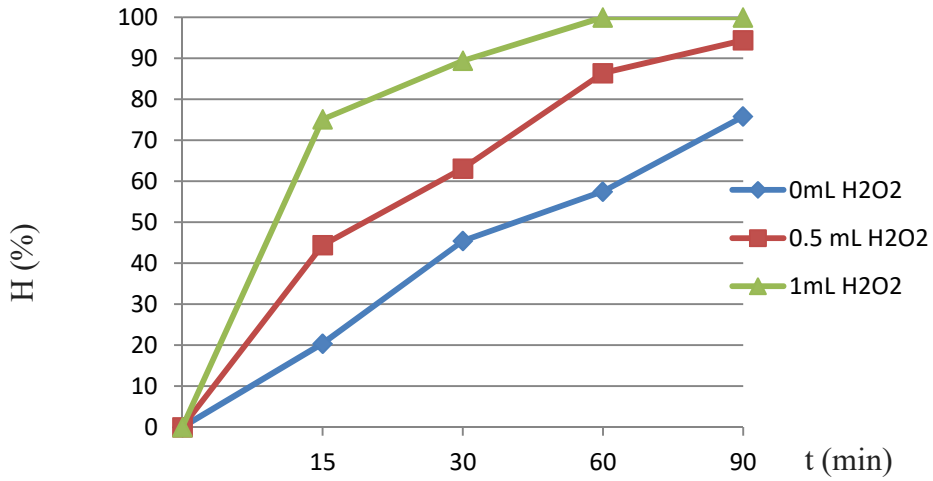

Figure 7. The effect of additive H_2O_2 on photodegradation efficiency

4. CONCLUSIONS

By co-precipitation method combined with PVA dispersant, $BiFeO_3$ powders have been synthesized under low temperature conditions, short synthesis time, and nanometer crystal size with perovskite $BiFeO_3$ crystal structure. The temperature affected the crystal structure of the material, when the temperature increases

above 250°C, the rate of $BiFeO_3$ phase appears more with a cylindrical crystal structure, uniform size ≤ 100 nm.

The effect of temperature on the phase formation, morphological structure and the pH of dye solution, H_2O_2 were found as the more effective factors affecting the photodegradation process. The results showed that when the material was calcined at 450ºC; pH of the dye solution in a strong acidic environment, about pH 1 - 3, the RY160 photocatalytic ability of the BFO system has the highest efficiency, about 99.8 - 100% in 90 minutes of lighting with the presence of 1ml H_2O_2 with 1 g of $BiFeO_3$ material in 1 liter of solution.

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NGHIÊN CỨU TỔNG HỢP VÀ KHẢ NĂNG QUANG XÚC TÁC CỦA VẬT LIỆU $BiFeO_3$

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TÓM TẮT

Trong nghiên cứu này, vật liệu nano $BiFeO_3$ đã được tổng hợp thành công bằng phương pháp đồng kết tủa trong nước có hòa tan PVA với tỉ lệ Bi/Fe/PVA = 1/1/3, tại pH = 12. Kết quả nghiên cứu cho thấy, vật liệu nano $BiFeO_3$ đã được tạo thành ở nhiệt độ 110ºC sau khi sấy 4h. Khi tiến hành nung vật liệu ở nhiệt độ cao hơn từ 250ºC đến 550ºC trong 2h, cường độ xuất hiện của $BiFeO_3$ lớn hơn, có kích thước hạt nhỏ hơn 100 nm. Phương pháp phân tích nhiệt vi sai (TG/DTA), phương pháp nhiễu xạ tia X (XRD), phương pháp kính hiển vi điện tử quét (SEM) đã được sử dụng để nghiên cứu đặc trưng cấu trúc của vật liệu. Nghiên cứu đã xác định được ảnh hưởng của nhiệt độ nung, pH, H_2O_2 đến khả năng quang xúc tác của vật liệu tạo thành trong việc xử lý phẩm vàng RY160 ở vùng ánh sáng khả kiến. Nồng độ chất màu được xác định bằng phương pháp quang phổ hấp thụ phân từ (UV-Vis) tại bước sóng 425 nm. Kết quả thực nghiệm cho thấy, tại pH = 3, có mặt 1ml H_2O_2, vật liệu BFO450 cho hiệu suất xử lý RY160 đạt cao nhất 100% sau 90 phút chiếu sáng.

Từ khóa: Ảnh hưởng của pH, Bitmut ferit ($BiFeO_3$), phản ứng quang xúc tác, phẩm vàng RY160, phương pháp đồng kết tủa, vật liệu nano.

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