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VIETNAM ACADEMY OF SCIENCE AND TECHNOLOGY

THE 11th INTERNATIONAL WORKSHOP ON ADVANCED MATERIALS SCIENCE AND NANOTECHNOLOGY

PROCEEDINGS

PUBLISHING HOUSE FOR SCIENCE AND TECHNOLOGY

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MEE-P05

Synthesis, characterisation, photocatalytic and antibacterial activities of Ag-doped ZnO nanoparticles

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Abstract. Synthesis, characterization, photocatalytic, and antibacterial properties of Ag-doped ZnO nanoparticles were presented in this work. The nanoparticles were synthesized by the combustion method using polyvinyl alcohol (PVA) as an agent. The structure of nanoparticles were characterized using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD revealed a single-phase hexagonal structure in all samples, except for the 5% Ag-doped ZnO. TEM indicated that most particles had a spherical shape, with grain sizes ranging from 10 to 30 nm in diameter. Scanning electron microscopy (SEM) showed the porous surface of the sample. Both the shape and grain size of the nanoparticles were influenced by the Ag ratio and annealing temperatures. Rhodamine B was used as a representative dye pollutant to assess photocatalytic activity. The results demonstrated that Ag-doped ZnO nanoparticles exhibited superior photocatalytic properties compared to pure ZnO nanoparticles, with the 3% Ag-ZnO sample showing the best photocatalytic and antibacterial activity.

Keywords: Ag-doped ZnO; nanoparticles, photocatalytic properties, antibacterial, PVA; combustion method.

1. Introduction

Metal oxide nanomaterials play a crucial role in many areas of chemistry, physics and materials science. They belong to a family of nanomaterials that have been manufactured on a large scale for both industrial and household applications, and they hold promise for future applications [1].

Among metal oxides, zinc oxide has a wide range of applications in different areas because of its unique photocatalytic, electrical, electronic, optical, dermatological, and antibacterial properties [2].

The photocatalytic degradation of organic pollutants in water and air, using semiconductors such as TiO_2, ZnO, and some other oxides has been the focus of research recently due to their prospects in the environmental detoxification [3].

The quantum efficiency of ZnO is also significantly larger than that of TiO_2 and sometimes it has revealed better activity than TiO_2. Besides, ZnO is available at a low cost and it absorbs over larger fraction of the solar spectrum than TiO_2, it is considered to be a more suitable material for the photocatalytic degradation of organic pollutants [4]. Morever, it is a bactericide and is effective in inhibiting inhibit bacteria [5].

Transition metal such as Ag doped nanostructure is an effective method to enhance photocatalytic and antibacterial activity of ZnO, which can further improve by the changes in doping concentrations of doped materials [6].

Many methods have been described in the papers for the synthesis of ZnO nanomaterials such as hydrothermal methods [7], sol–gel method [8], chemical vapor deposition [9], laser synthesis [10], magnetically assisted synthesis [11],...

In the recent years, combustion synthesis (CS) has become an effective, low-cost method for the production of various industrially useful materials. Today CS has become a very popular approach for the preparation of nanomaterials. The extensive research carried out in the last five years emphasized the CS capabilities for materials improvement, energy saving, and environmental protection [12, 13].

In this paper, we present the results of a study on synthesis, characterization, photocatalytic activity and bactericidal properties of Ag-doped ZnO nanoparticles, which were synthesized by combustion method using a polyvinyl alcohol (PVA) agent.

2. Experimental

The metal nitrate solutions in the predetermined molar ratio Zn^{2+}:Ag^{+} were mixed with a precalculated amount of PVA. The obtained solution was magnetically stirred at 80^0C. As water evaporated, the solution turned into a very viscous gel. After drying, the gel was further heated to form a crystal phase.

The thermal analysis was performed on TGA/DTA Analyzer DTG 60H (Shimadzu, Japan) in the air with the heating rate of 100C/min.

The structure and grain size, morphology of of nanoparticles were characterized on an X-ray diffractometer (XRD) Bragg-Brentano with Cu-K$_\alpha$ in the range 2θ = 20 – 80° with a step size = 0.02 a transmission electron microscope (TEM) (JEM-1010, JEOL, Japan) operated at 60 kV.

The photocatalytic performances of the Ag-doped zinc oxide particles were evaluated by cleaning rhodamin B (RDM B) in water under UV irradiation. In a typical process, 0.1g of the catalysts was added into 50 mL RDM B solution with a concentration of 10 mg/L.

The antibacterial property of Ag-doped ZnO samples was tested bioactive with Escherichia coli ATCC (American Type Culture Collection) 25922 strain. The antibacterial activity of the synthesized ZnO nanoparticles was evaluated using bacterium as per the colony count method.

3. Results and discussion

3.1. Pyrolysis of gel

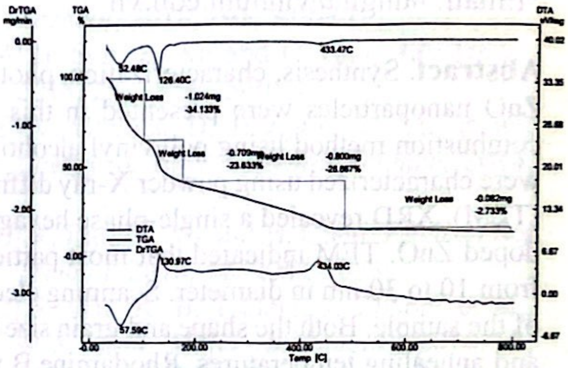

Figure 1. TGA-DTA curves of gel.

The pyrolysis of the gel-precursor was monitored by thermal analyses in Fig. 1. According to the TGA curve, the weight decrease terminated around 500°C. Before 100^0C, the weight loss of about 34.1% was associated with to the vaporization of physically absorbed water on gel. In the range of temperature 100-200°C, the first exothermic peak at about 131°C with a weight loss of 23.6% could be due to incomplete decomposition of PVA. Corresponding to a wide temperature region from 200 - 500^0C, the weight loss (accompanying exotherms in the DTA thermogram) showed the fire of PVA being left in the gel with nitrates acted as an oxidizer. During the combustion, large amounts of gases such as H_2O, CO, CO_2 and NO are liberated [14]. At a temperature higher than 500^0C, the final weight loss corresponded to the formation of crystal phase.

3.2. Synthesis of Ag-doped ZnO nanomaterials

To find the heating temperature for the formation of Ag doped ZnO phase, 3%Ag doped ZnO was chosen to be synthesized under conditions: pH=3, PVA/metal mole ratio of 2:1, gel formation temperature 80°C, and various heating temperatures (300, 400, 500, 600 and 800°C).

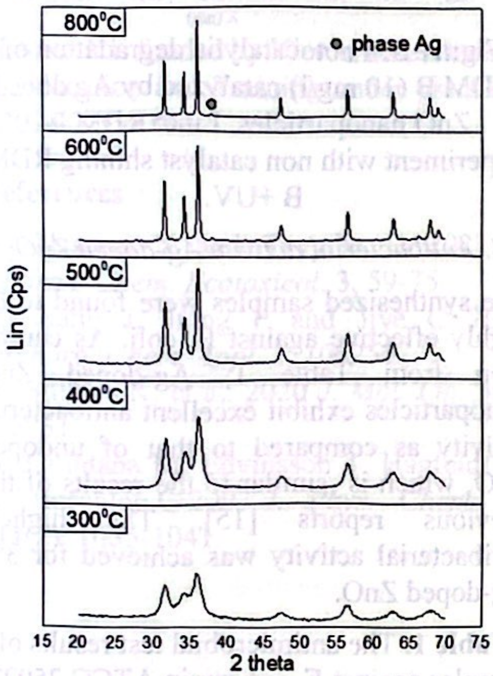

Figure 2. XRD patterns of the 3%Ag doped ZnO powder samples prepared by heating the precursor at designated temperature for 1 h.

Figure 2 presents XRD patterns of the obtained powders. All the diffraction peaks can be indexed to be in agreement with the ICDD Reference Pattern: zinc oxide, PDF2 card: 01-070-8072, which corresponds to hexagonal wurtzite structure. No peaks of impurity are observed except for the sample heated at 800°C. These results confirmed the formation of single phase hexagonal ZnO. The most prominent peaks observed in the patterns corresponded to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 0 3), (1 1 2), (1 0 4) planes. From the results above, x% Ag-ZnO with x = 0; 1; 3; 5 were synthesised under the same conditions.

The XRD patterns of x%Ag-doped ZnO were shown in Fig. 3. The samples with doping concentrations lower than 5% show a pure ZnO phase (PDF2 card: 01-070-8072). This result indicated that Ag ions are incorporated into ZnO at either the interstitial or the substitute sites. Samples with higher Ag concentrations show impurity peak (phase Ag), suggesting that the solubility of Ag in ZnO is lower than 5%. Due to the low Ag solubility in ZnO, we focus on the 0- 3% doped samples. These samples had the hexagonal system structure of ZnO from PDF card 01-070-8072.

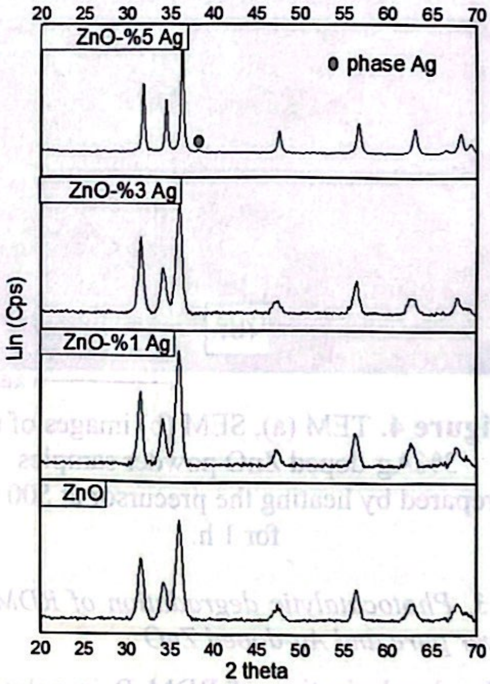

Figure 3. XRD patterns of x%Ag-ZnO with different Ag contents: x = 0, 1, 3, 5.

TEM and SEM images of 3%Ag-doped ZnO were shown in Fig. 4 . The TEM micrograph clearly showed nanostructure homogeneities with the sample's spherical morphologies. The TEM observation also showed the nanospheres with an average diameter of 15 -20 nm. The crystallite size was calculated from XRD data using the Scherrer formula. It is found to be 14.1 nm in agreement with the particle size obtained from TEM.

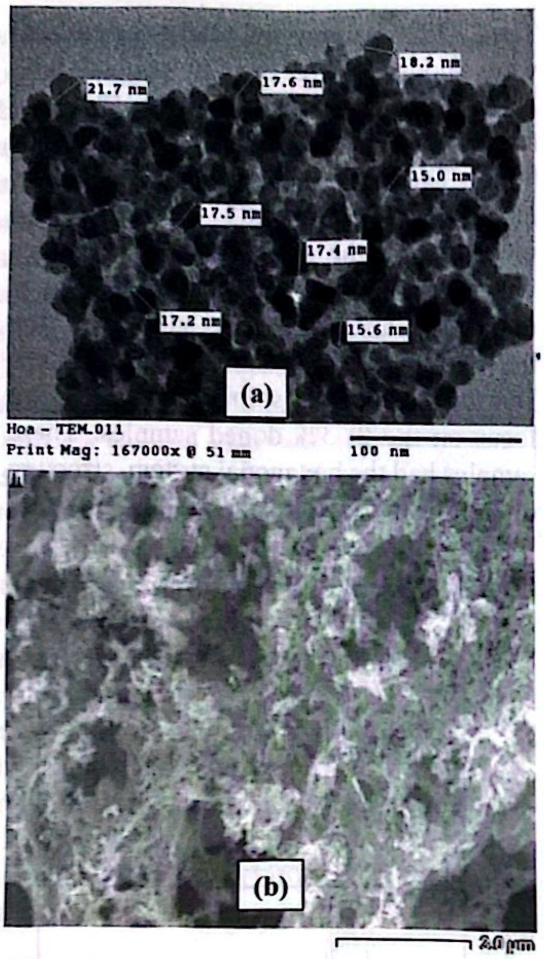

Figure 4. TEM (a), SEM (b) images of the 3%Ag-doped ZnO powder samples prepared by heating the precursor at 500 °C for 1 h.

3.3. Photocatalytic degradation of RDM B over pure and Ag-doped ZnO

The decolorization of RDM B in solution was observed in terms of change in intensity at λ_{max} of the dye. In photocatalytic degradation experiments, prior to irradiation, the aqueous solution was stirred continuously in the dark for 60 min to ensure adsorption/desorption equilibrium. Rate of decolorization was observed in terms of change in intensity at λ_{max} of the dye (Figure 5). The order of photocatalytic activity of Ag-doped ZnO was as follows: 3 >1 > 0 mol %, which suggested that the Ag^+ doping enhanced the photocatalytic activity. The 3%Ag-ZnO photocatalyst exhibited the highest photocatalytic decolorization efficiency.

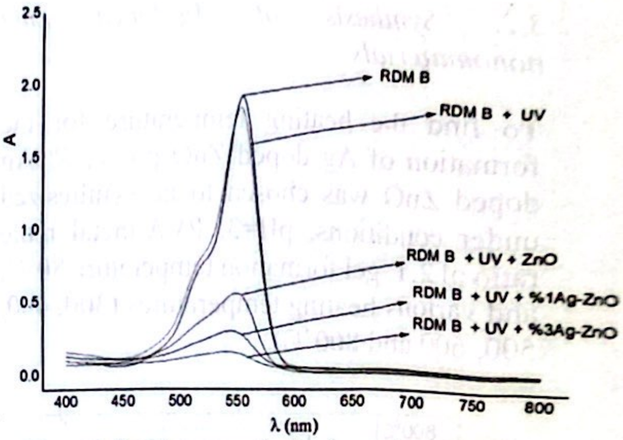

Figure 5: Photocatalytic degradation of RDM B (10 mg/l) catalyzed by Ag doped ZnO nanoparticles. Line: RDM B- experiment with non catalyst shining RDM B +UV.

3.4. Antibacterial activity Ag-doped ZnO

The synthesized samples were found to be highly effective against E. coli. As can be seen from Table 1, Ag-doped ZnO nanoparticles exhibit excellent antibacterial activity as compared to that of undoped ZnO, which is similar to the results of the previous reports [15]. The highest antibacterial activity was achieved for 3% Ag-doped ZnO.

Table 1. The antimicrobial test results of samples against *E. coli* strain ATCC 25922.

Samples	Results					
	10^{-3}		10^{-5}		10^{-7}	
	$\overline{D}$	S	$\overline{D}$	S	$\overline{D}$	S
Ref. sample	283.67	21.73	170.33	3.58	155.33	8.33
ZnO	9.00	7.94	3.33	3.51	1.67	1.53
1%Ag-ZnO	3.67	3.51	1.67	0.58	0	-
3%Ag-ZnO	0.67	0.58	0.33	0.58	0	-

D: average number of viable cells.

4. Conclusions

Pure ZnO and x% Ag-doped ZnO nanoparticles (0 % ≤ x ≤ 5 %) were synthesized by combustion method using polyvinyl alcohol (PVA) agent. XRD analyses showed the single phase of hexagonal structure (PDF2 card: 01-070-8072) in all the samples (exception sample with dopping Ag content 5%). TEM images indicated that the particles were spherical in shape with grain size of nanoparticles ranging from 10 to 30nm. The study found that Ag-doped ZnO nanoparticles exhibited better photocatalytic and antibacterial activity than the pure ZnO. The 3% Ag-doped ZnO showed the highest antibacterial and photocatalytic activity.

Acknowledgments

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