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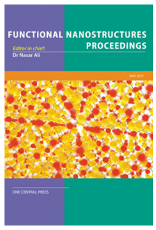

Synthesis and characterization of samarium doped nano ZnO-Ag and its application to photocatalysis

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ABSTRACT

ZnO-Ag photocatalysts were synthesized by simple wet chemical method and samples were calcined at different temperatures. The synthesized nanopowders were characterized by different analytical techniques like XRD, TEM and UV-Vis spectroscopy. The results revealed that the prepared samples were nanometer in size and samarium ions successfully doped into the ZnO lattice. The effect of addition of different concentration of samarium dopant on structural property, optical property, and photocatalytic activity of ZnO-Ag were analyzed. Optical characterizations indicated that the samarium doping can shift the absorption edge of ZnO to the visible range and reduce the band gap. By using methylene blue as a model dye the photocatalytic degradation was studied and the results showed that the samarium doped ZnO-Ag shows higher photocatalytic activity than the pure ZnO.

I. INTRODUCTION

In the recent years, the environmental pollution caused by industries has attracted widespread attention all over the world. These toxic chemicals can have very dangerous effects on biological ecosystems. Many methods have been used to eliminate these pollutions. Among the various treatments, semiconducting photocatalyst using solar energy has been considered as a promising green technique for environmental remediation because it can decompose organic pollutants into CO_2 and H_2O with relatively high efficiency [1]. Among different kind of ceramic semiconductors, ZnO is one of the most promising materials for photodegradation of organic contaminants and it has antibacterial properties. Zinc oxide exhibits energy ban gap about 3.37. This semiconductor is well established and there has been considerable interest in their applications to the area of photocatalysis. Although zinc oxide is a very famous photocatalyst, there are some important chalenges to improve its photocatalytical properties. First, this semiconductor works under ultraviolet light [2]. However, the major part of the solar spectrum includes of visible light. Second, rapid recombination of electron and hole pairs in zinc oxide can reduce the effective degradation of pollutants [3]. Many researches have been done in the world to tackle these problems. Three important strategies can be applied to improve the photocatalytic efficiency of ZnO. First one is the coupling of two semiconductors. Second one is to add metal ion dopants as modifiers into the matrix of zinc oxide. The third one is adding conducting metals like Ag or Au into zinc oxide. These three methods not only inhibit e-h recombination but also increase the onset wavelength response range into visible region [3-5]. In the present research we want to use two of these strategies simultaneously to improve the photocatalytic efficiency of zinc oxide. Therefore, the aim of this study is to synthesis samarium doped nano ZnO-Ag via sol-gel method. Optical properties and photocatalytic activity of synthesized samples were studied.

II. EXPERIMENTAL PROCEDURE

Zinc acetate, silver nitrate and samarium nitrate as metal precursors were purchased from Merck, Germany. Deionized distilled water was used throughout experiments. First, zinc acetate, samarium nitrate and silver nitrate were dissolved in distilled water. Then, aqueous ammonia was added drop-wise to reach a pH of 7 and the stirring was continued for 60 min. A gel was formed and it was allowed to age overnight. It was dried at

100 ˚C for 12 h and calcined at 500 ˚C for 2 h in a tube furnace. Photocatalysis experiments were done with 250W UV lamp as the source of irradiation above the samples. Photocatalytic properties of samples were studied by UV/Vis Spectrophotometer (OPTIZEN 322OUV) with methylene blue (MB) dye as the water pollutant model. At all photocatalytic experiments, 0.01 g of prepared samples after calcination was added into 10 ml aqueous solution of MB (10 ppm). X-ray diffraction analysis was carried out to study structure of samples using a Philips TW3710 X 'Pert diffractometer with CuKα radiation. The morphology and particle size of the samples were observed using transmission electron microscope (TEM, Philips-Model:MC30). UV–vis spectroscopy was used to investigate optical properties of the samples on a Shimadzu spectrophotometer (model UV-1601 PC).

III. RESULTS AND DISCUSSION

XRD patterns of pure ZnO, ZnO-Ag, and Sm-doped ZnO-Ag calcined at 500 ˚C are shown in Fig. 1 (a). The peaks related to the ZnO hexagonal wurtzite phase (JCPDS Card no. 89-1397) can be seen in all samples. In addition in the ZnO-Ag, and Sm-doped ZnO-Ag samples there is a secondary phase, which can be indexed to the structure of metallic silver (JCPDS Card no. 87-0720). No other phases like Ag_2O were detected, showing the high purity of the nanoparticles obtained. The presence of Ag_2O, in ZnO-Ag sample calcined at 500 ˚C, is unlikely. It was reported that Ag_2O decomposes to Ag at the calcination temperatures higher than 400 ˚C [6]. By adding samarium to the samples there are no new phases in the patterns and just the intensity of peaks decreases. It shows adding samarium reduces the crystallinity of the ZnO and Ag phases.

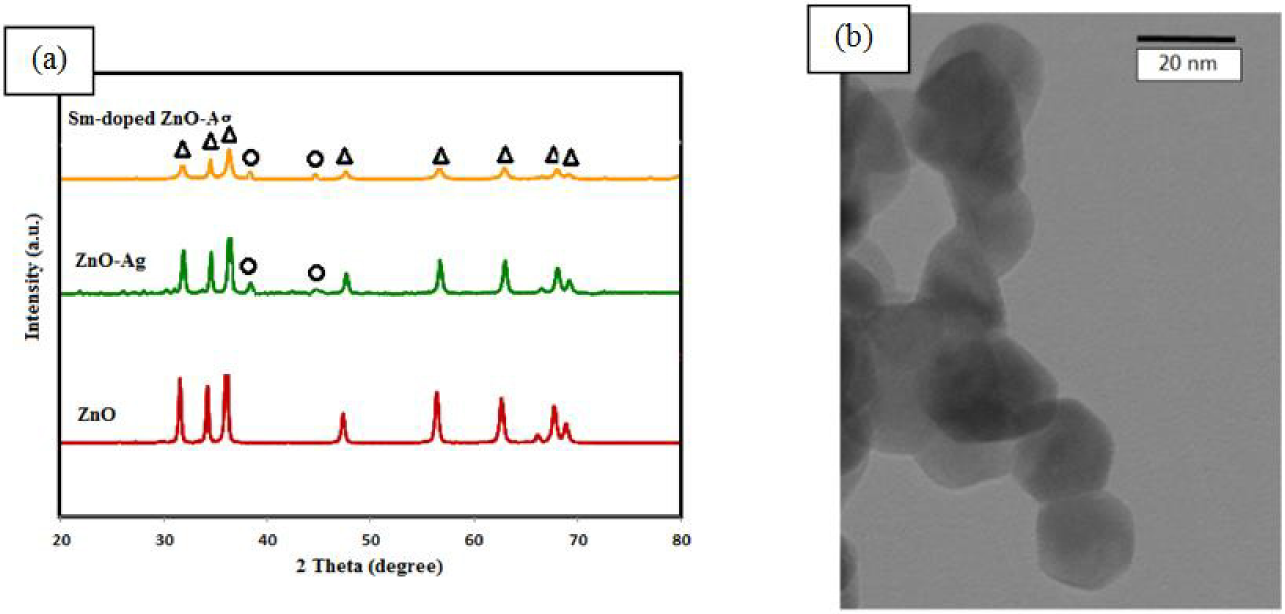

Figure 1 (a) XRD patterns of pure ZnO, ZnO-Ag, and Sm-doped ZnO-Ag calcined at 500 ˚C and (b) TEM image of Sm-doped ZnO-Ag calcined at 500 ˚C.

Fig. 1 (b) displays the TEM of Sm-doped ZnO-Ag sample. The TEM image reveals that the powders consist of the aggregated particles with irregular or hexagonal morphology. The average diameter of agglomerates is about 20 nm.

UV-Vis spectrophotometer is used to investigate the optical properties of pure ZnO and ZnO-Ag, and Sm-doped ZnO-Ag powders. The band gap of powders has been calculated using Tauc's formula which represents the relationship between absorption coefficient (α) and photon energy (hυ). The optical band gap energy values (E_g) were calculated by an extrapolation of the linear part of $(\alpha h\upsilon)^2$ versus hυ plot as shown in Fig. 2 (a). It is observed that the band gap value of Sm-doped ZnO-Ag (3.21eV) is less than that of ZnO-Ag (3.26) and pure zinc oxide (3.28eV). The optical absorption of a semiconductor has an important effect on its photocatalytic activity. The reduction in E_g with adding dopant may result in an increase in the formation rate of e-h pairs and better absorption of solar energy on the photocatalyst surface.

The effect of vanadium concentration on the phocatalytic activity of ZnO was shown in Fig. 2 (b). As can be seen the Sm doped ZnO-Ag sample show better photodegradation efficiency than the ZnO-Ag and pure ZnO. The improved photocatalytic activity of the Sm doped ZnO-Ag compared to other samples indicates the reduced recombination rate and better e-h separation in this sample. In addition, the reduction in the band gap energy of vanadium-doped samples (Fig. 2 (a)) in comparison with other sample may be another reason for higher photocatalytic performance.

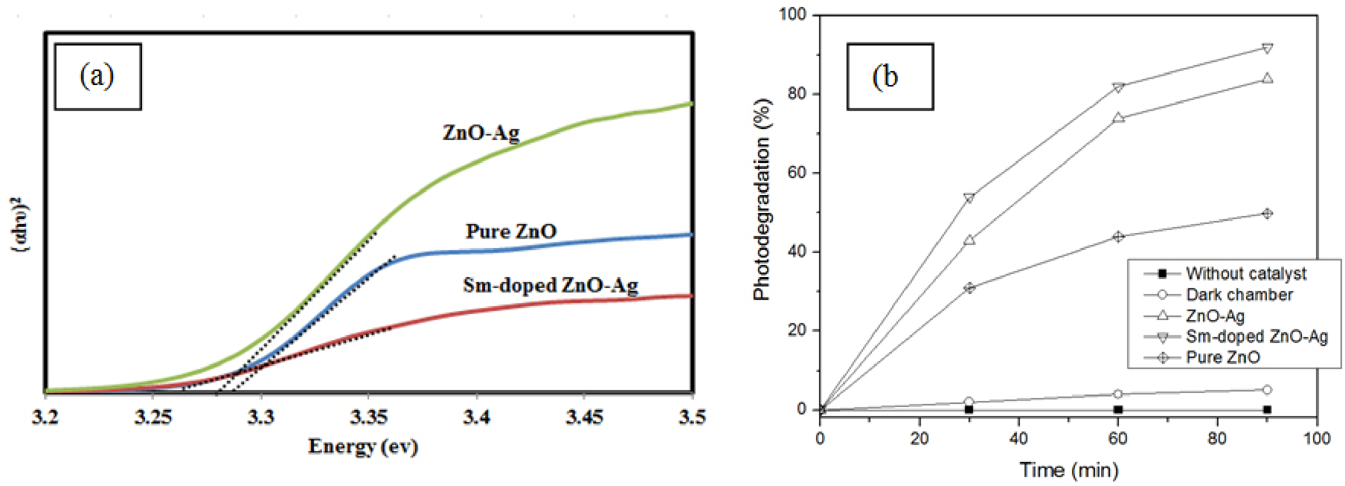

Figure 2 (a) The plots of $(\alpha h\nu)^2$ versus photon energy (hν) and (b) photodegradation efficiency of pure ZnO, ZnO-Ag, and Sm-doped ZnO-Ag calcined at 500 ˚C.

It was suggested that photo excited electrons transferred from Ag to ZnO due to surface plasmon resonance that could reduce the recombination of electron–hole pairs and increase lifetime of the electron–holes pairs, improving the degradation efficiency [7]. In addition, by adding samarium defects are formed in the ZnO lattice to trap the e or h, therefore, recombination is inhibited and subsequent photolytic reactions can occur with higher efficiency [4,8,9].

IV. CONCLUSION

In the present study, Sm doped ZnO-Ag was successfully obtained by a sol-gel method. The crystal structure, morphology and band gap of the samples were characterized by XRD, TEM, and UV–vis spectroscopy. TEM results showed that nanoparticles are composed of the aggregated particles with irregular or hexagonal morphology. Band gap energy of zinc oxide reduced from 3.28 eV to 3.21 eV with adding Ag and samarium. Photocatalyst results showed that Sm doped ZnO-Ag sample exhibit better photodegradation efficiency than the ZnO-Ag and pure ZnO samples.

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