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Preparation, Characterization and Photocatalytic Activity of Ag-Cd-ZnO and Ag-Cu-ZnO Nanostructures

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Abstract

In this study, ZnO nanopowders and ZnO doped with metals (Cu , Ag- doped ZnO) and (Cd, Ag- doped ZnO) were synthesized by the sol-gel method in order to investigation on the co-doping effect on the band gap and photocatalytic activity of ZnO. The synthesized samples are characterized by IR spectroscopy technique. Moreover, the absorption coefficients of the ZnO, Ag-Cd-ZnO and Ag-Cu-ZnO were analyzed by Tauc's approach and the direct band gap is calculated. According to these results, compared with pure ZnO, the band gap of the Ag-Cd-ZnO and Ag-Cu-ZnO decreases and it is dependent on the content of dopands. Furthermore, photocatalytic activity for all samples was investigated under UV irradiation in an aqueous medium. The results have been revealed that Ag-Cd-ZnO and Ag-Cu-ZnO shown more photocatalytic actitivity in comparison with pure ZnO.

Keywords: *Sol-Gel method, Photocatalytic activity, ZnO nanostructure.*

Introduction

In the past decades, the scientific and engineering interest in the application of semiconductor photocatalysis has grown exponentially [1]. ZnO has been widely used as a photocatalyst, owing to its high activity, low cost, and environmentally friendly feature [2].However, due to a wide band gap of 3.37 eV, poor photon absorption of ZnO limits its application in visible light photocatalyst [3]. For the application of photocatalyst, the activity needs to be further improved [4]. The photocatalytic activity of ZnO can be improved by various techniques such as by an increase of surface area, control of the designed shape, incorporating another atom into the lattice and so on. Metal doped ZnO particles have attracted investigations because it is effective

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and practical approach, very easy to apply in many methods for preparing ZnO materials and properties of ZnO nanomaterial highly depend on dopant and nanostructures [5,6].

The doping of metal ions in ZnO nanostructures could enhance the photocatalytic activity of ZnO in some cases. Although the photophysical mechanisms of doped ZnO are not well understood, generally speaking, the formation of shallow charge trapping on the surface of the ZnO nanocrystallites due to the replacementof Zn (II) by metal ions is accepted [1]. Ag is one of the metals that has a beneficial influence on the photocatalytic activity of ZnO particles [6] and Cu is considered as one of the most effective doping elements for improving the activity of photocatalysts[4].

In this study, we have synthesized ZnO nanostructure and ZnO doped with Cu, Ag, and Cd (Cu , Ag- doped ZnO andCd , Ag- doped ZnO), by the sol-gel method with different molar ratioin order to investigation of co-doped effect on band gap and photo-catalytic activity.

Experimental

Materials and Equipment

Zinc acetate ($Zn(CH_3COO)_2$), diethanolamine (DEA), Hydroxyl Propyl Cellulose (HPC), absolute Ethanol, double distilled water, Silver Nitrate ($AgNO_3$), Copper (II) Nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and Cadmium Nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$), acetone (for drying).

All chemicals and reagents were purchased from Merck Chemical Co. and were used without any further purification. IR spectra were recorded with a spectrophotometer Aligenttechnology, carry 600 model. UV-vis spectra were recorded with a spectrometer Perkin Elemer, Lambda 35 model

Sample preparation

All samples were prepared by using the Sol-Gel method with following procedure:

1. Preparation of sample 1: (ZnO)

A: Preparation of solution ***I***

0.2g HPC was dissolved in 30 mL absolute ethanol and was stirred 10 min under hemogenizer, then 0.02 mol $Zn(CH_3COO)_2$ was added solution to and was stirred for 15 min under 60°C.

B: Preparation of solution ***II***

0.8 ml diethanolamine was dissolved in 5 ml absolute ethanol, and then0.2 ml double distilled water was added to solution and was stirred 5 min.

C: Preparation of ZnO:

Solution **II** was added drop wise into solution **I** and was vigorously stirred for 30 min at 60°C. The obtained transparent colloidal suspension was aged 72 h to allow it be formed as a gel. The sample was dried in Oven at 50ºC and ultimately was calcinated at 500ºC for 4 hours.

2. Preparation of sample 1: (Ag,Cd-doped ZnO [dopand]/ZnO=0.02)

*A: Preparation of solution **I***

Solution I was prepared exactly similar to sample 1.

*B: Preparation of solution **II***

$AgNO_3$ and $Cd(NO_3)_2.4H_2O$ was dissolved in 5 ml absolute ethanol with molar ratio [dopand]/ZnO=0.02, then 0.2 ml double distilled water and 0.8 ml diethanolamine was added to solution and was stirred 5 min.

C: Preparation of Ag,Cd-doped ZnO

Solution **II** was added drop wise into solution I and was vigorously stirred for 30 min at 60°C. The obtained transparent colloidal suspension was aged 72 h to allow it be formed as a gel. The sample was dried in Oven at 50ºC and ultimately was calcinated at 500ºC for 4 hours.

3. Preparation of sample 2 (Ag,Cd-doped ZnO [dopand]/ZnO=0.05)

Solution **II** was prepared exactly such as sample 1 but with molar ratio [dopand]/ZnO=0.05 and was added to solution **I**. The other steps are similar to those of the sample 1.

4. Preparation of Sample 3 (Ag,Cd-doped ZnO [dopand]/ZnO=0.1)

Solution **II** was prepared exactly such as sample 1 but with molar ratio [dopand]/ZnO=0.1 and was added to solution **I**. The other steps are similar to those of the sample 1.

5. Preparation of sample 4 (Ag,Cu-doped ZnO[dopand]/ZnO=0.02)

Solution **II** was prepared exactly such as sample 1 but was used $Cu(NO_3)_2.3H_2O$ instead of $Cd(NO_3)_2.4H_2O$ and was added to solution **I**. The other steps are similar to those of the sample 1.

6. Preparation of sample 5 (Ag,Cu-doped ZnO[dopand]/ZnO=0.05)

Solution **II** was prepared exactly such as sample 4 but with molar ratio [dopand]/ZnO=0.05and was added to solution **I**. The other steps are similar to those of the sample 1.

7. Preparation of sample 6 (Ag,Cu-doped ZnO[dopand]/ZnO=0.1)

Solution **II** was prepared exactly such as sample 4 but with molar ratio [dopand]/ZnO=0.1 and was added to solution **I**. The other steps are similar to those of the sample 1. All of steps summarized in below chart (Figure 1).

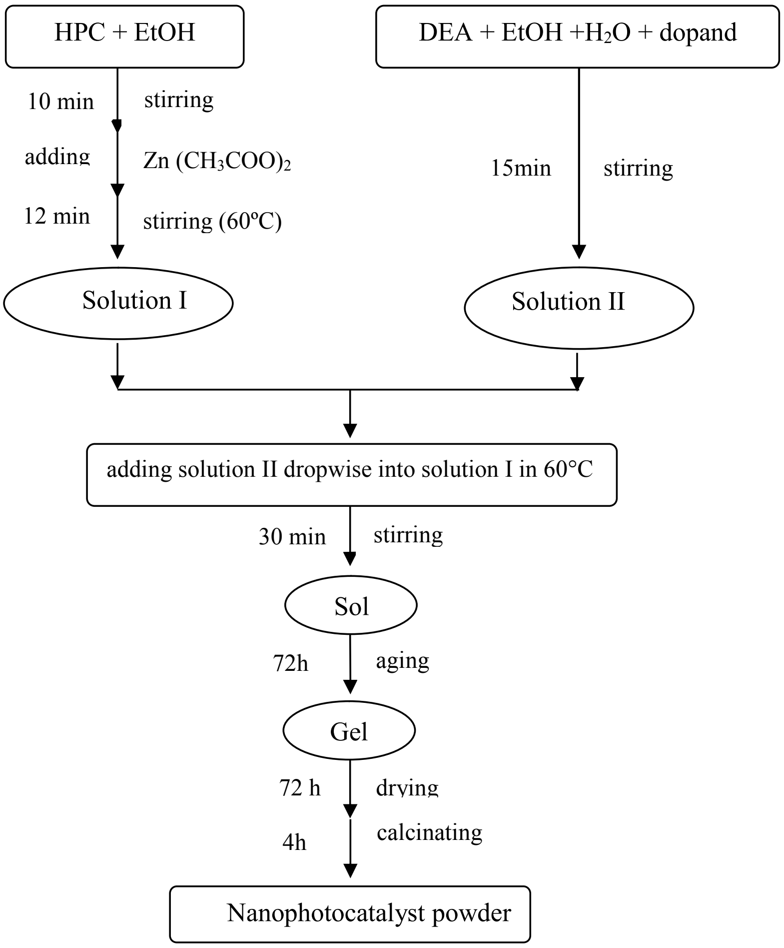

Figure1. sample preparation chart.

Results and Discussion

FT-IR spectroscopy analysis

The characteristic functional groups of the particles were investigated using FTIR spectra and results are shown in Figure 2. According to these results, in all of samples, broad absorption band observedat ~3435 cm^{-1} corresponds to the O–H stretching vibrations of water present in ZnO [7]. The band at~1635 cm^{-1} can be associated with the bending vibrations of H_2Omolecules [8]. It is indicated that there exist large amounts of hydroxyl groups on the surface of ZnO. Compared with the pure ZnO, the intensity of the peaks at 3435and 1635 cm^{-1} is enhanced when the metal-doping content gets to 0.02 mol%. But when the metal-doping content exceeds 0.1 mol%, the intensity of IR peaks at 3435 and 1635 cm^{-1} becomes weaker step by step. It indicates that the concentration of surface hydroxyl groups and active hydrogen-related defects of samples is related to the metal-doping content, which affects the band gap and photocatalytic activity [7].

In addition, a strong absorption band corresponds to the stretching and vibrational modes of metal–oxygen (M–O) appearing between 400 cm^{-1} and 600 cm^{-1} [9]. Moreover, the stretching mode of ZnO nanostructure appears at 546 cm^{-1}.The broad peak observed in the range 460–560 cm^{-1} is the combination of Cu–O and Zn–O vibrations [10-12]. These results show that metal atoms were successfully incorporated into the lattice of ZnO. The absorption bands at 1570 cm^{-1} in samples, is assigned to the residual organic component which might remain adsorbed on the surface of ZnO [11-13].

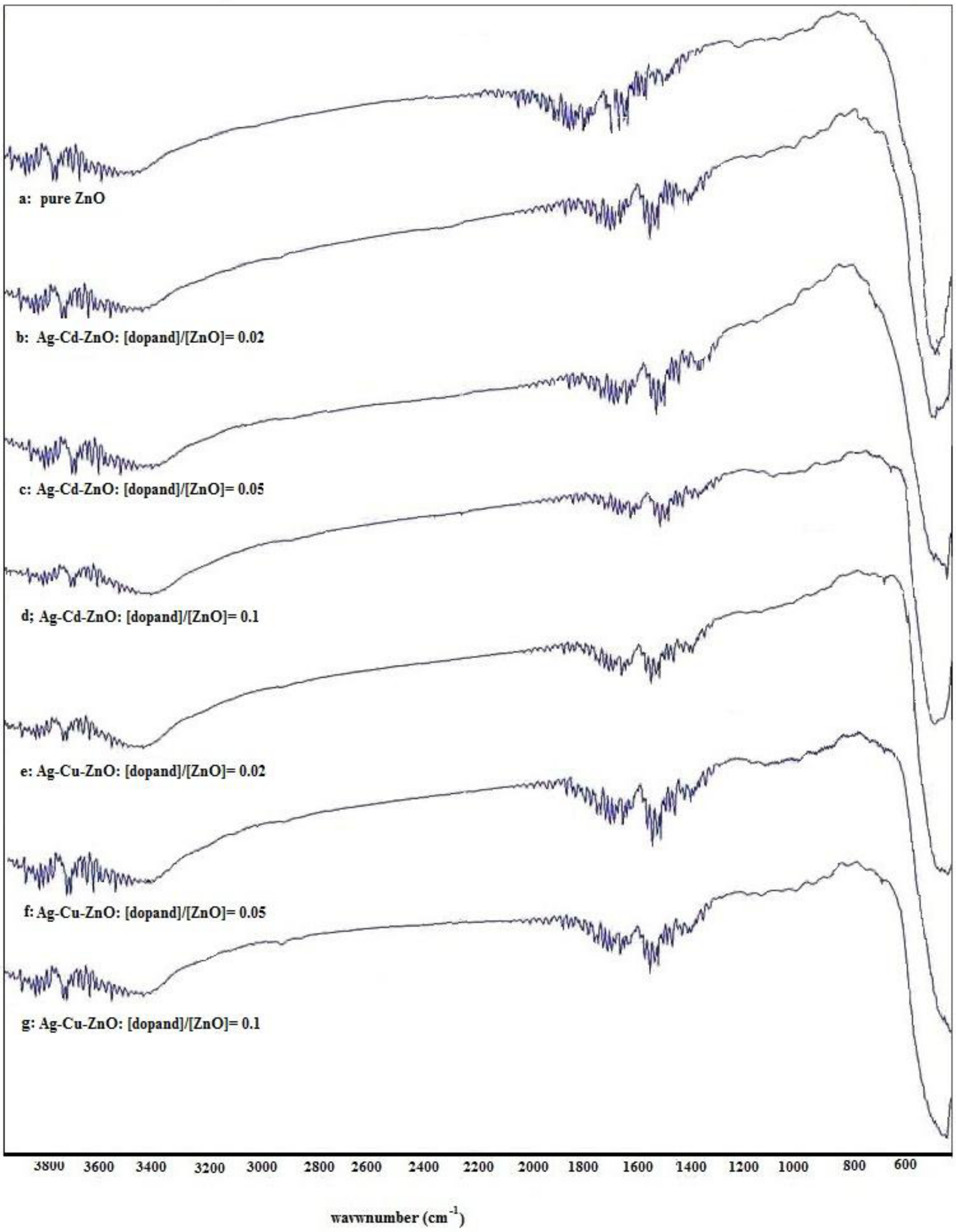

Figure 2. FT-IR spectra of the samples.

UV–visible spectra

UV–vis diffuse reflectance spectroscopy was carried out to investigate the optical properties of the samples. The UV–vis absorption spectra of pure ZnO, and Ag-Cd- ZnO(with different molar ratio between dopand and ZnO) are shown in Figure 3(a). It can be clearly seen that the maximumof the absorbance band shifts slightly toward higher wave length due to Ag-Cd doping. The Ag-Cd- ZnO([dopand]/[Zn]=0.1) shows huge absorption intensity in higher wavelength region. From Figure 3(b), it can be seen that, compared with pure ZnO, the absorption intensity of the Ag-Cu-ZnO increases and a red shift in the absorption with increase in the amount of the content of dopands occur .This could be mainly attributed to the strong interaction between the surface oxides of Zn and dopands [14].

Figure 3(c), shows the Uv–vis spectra of pure ZnO, Ag-Cd-znO and Ag-Cu-ZnO powders for comparing of Cd and Cu effect as dopand. According to results, Cu is more efficiency than Cd and Ag-Cu-ZnO shows more red shift than the adsorption in comparison with Ag-Cd-ZnO sample. These results suggest that, charge transfer transition from the electron donor levels formed by the 3d orbitals of doped Cu^{2+} to the conduction bands of the host materials is easier than charge transfer from the 4d orbitals of doped Cd^{2+}.

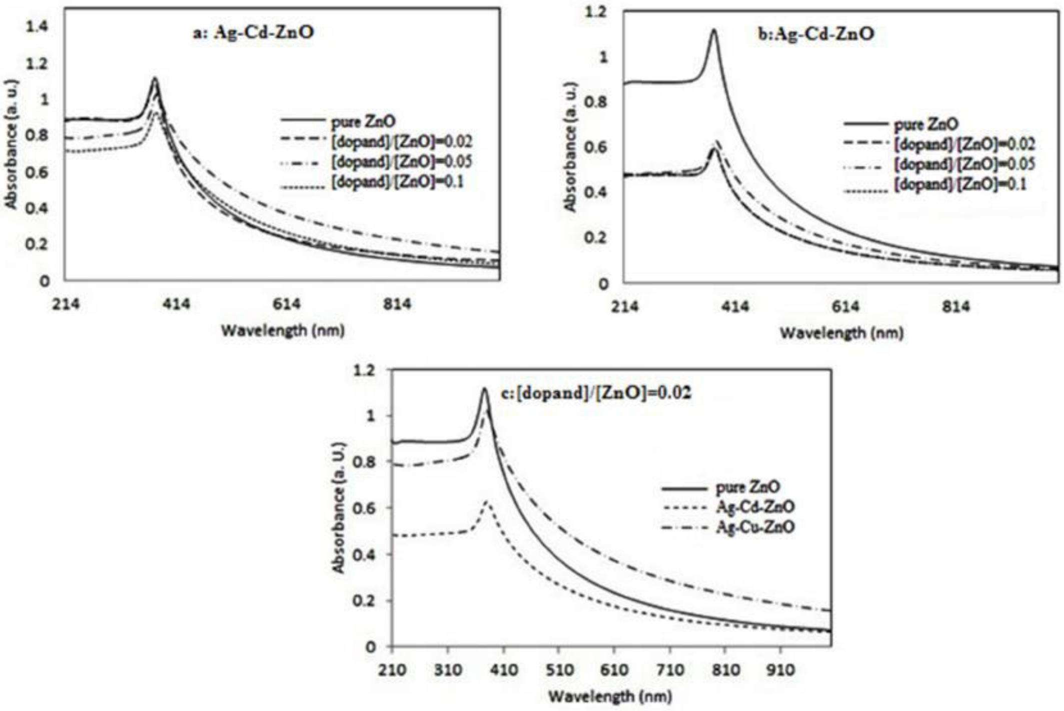

Figure 3. Uv–vis spectra of samples.

Band gap calculation

The absorption coefficients of the ZnO, Ag-Cd-ZnO and Ag-Cu-ZnO are analyzed by Tauc's approach [15], and the direct band gap is calculated using the following equation:

$$\alpha=C\,(h\nu-E_g^{bulk})^2/h\nu$$

Where α is the absorption coefficient, C is a constant, hν is the photon energy and Eg bulk is the band gap.

Table 1 shows that calculated band gap of the samples. According to these results, Ag, Cd and Ag, Cu as well as reduced band gap and it is dependent on the content of dopands. Figure 4, shows the Tauc plots of ZnO, Ag-Cd-ZnO and Ag-Cu-ZnO ([dopand]/[ZnO] molar ratio=0.05). Extrapolation of the linear region of Tauc plot gives a band gap. From Fig. 4, it can be seen that, compared with pure ZnO, the band gap of the Ag-Cd-ZnO and Ag-Cu-ZnOdecreases but Cu is more effective than Cd and these results are consistent with Uv-vis spectra.

Table1. Calculated band gap of samples.

Sample	Mole ratio ([dopand]/[ZnO])	Band gap(eV)
ZnO	--------	3.02
Ag-Cd-ZnO	0.02	2.91
Ag-Cd-ZnO	0.05	2.86
Ag-Cd-ZnO	0.1	2.61
Ag-Cu-ZnO	0.02	2.85
Ag-Cu-ZnO	0.05	2.77
Ag-Cu-ZnO	0.1	2.41

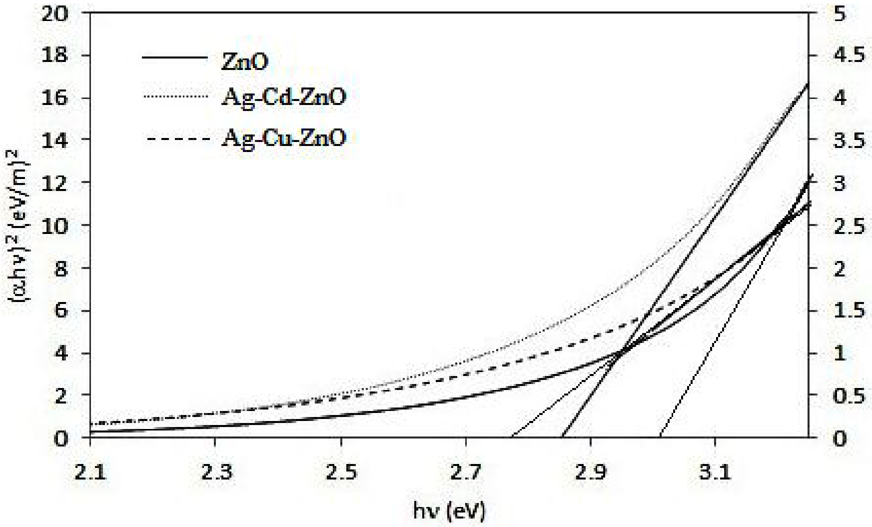

Figure 4. The Tauc plots of ZnO, Ag-Cd-ZnO and Ag-Cu-ZnO ([dopand]/[ZnO] molar ratio=0.05).

Photocatalytic activity

Methylen Blue (MB) dye was used to evaluate the photocatalytic activity of doped and undoped ZnO nanoparticles in response to UV irradiation [18].The solutions of MB (with a concentration of 5ppm) in deionized water were selected as a pollutant solution for photo degradation. These solutions were set in the vicinity of nano photocatalyst powder (0.2g powder in 1L solution) and then were rested for 24 h in the darkness, in order to eliminate the absorptive effect of the solution in the catalyst.

Finally it was placed in the photo-reactor system and Photocatalytic activity was examined under UV irradiation. This photoreactor system consisted of a cubic borosilicate glass reactor vessel with an effective volume of 1000 mL, a cooling water jacket and a 15W UV lamp (Osram)with a quartz cover positioned inside the solution was used as an UV light source. The reaction temperature was kept at 25 ºC using cooling water. MB concentration changing was recorded by an UV spectrometer model Varian.

Results have been shown in Figure 5. According to these results, Compared with the pure ZnO,the Cu-Ag –ZnO and Cd-Ag –ZnO nanostructure obviously displays a higher photocatalytic activity and content of dopands are effective on the activity. It seems that, Cu-Ag –ZnO nanostructure shown the better photocatalytic activity in comparison with Cd-Ag –ZnO nanostructure with the same content of dopands. Similar trend in the band gap studies was observed for photocatalytic activities.

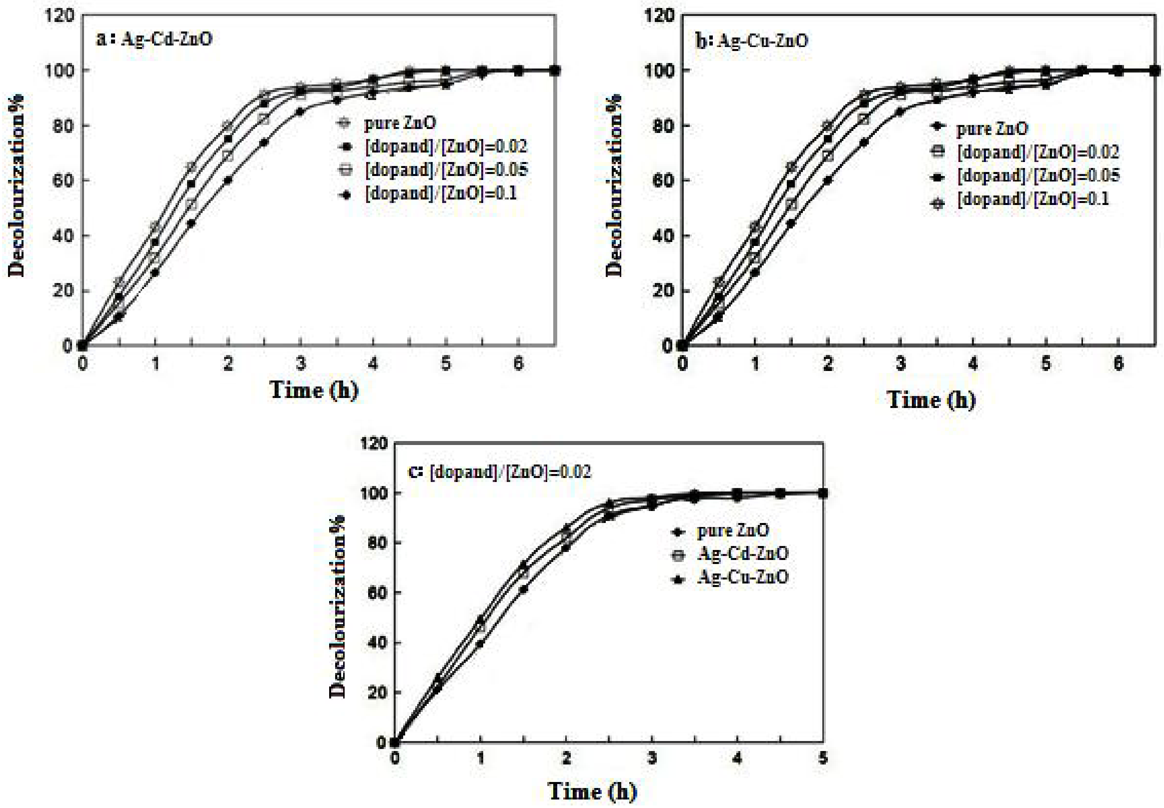

Figure 5. Photodegradation rate of Methylorange solution under UV radiation of samples.

Conclusion

This research has verified that the photocatalytic activity of ZnO nanostructure can be improved using of co-doping. ZnO, Cu-Ag -ZnO and Cd-Ag -ZnO nanostructure samples have been prepared by a sol–gel method. The photocatalytic activity of the samples, were examined for degradation of Methylen Blue in water under UV irradiation in a batch reactor and the photocatalytic activity has been increased with increasing content of dopands.

UV–vis diffuse reflectance spectroscopy showed red shift with co-doping and Cu is more effective than Cd. Moreover, the absorption coefficients of samples were analyzed by Tauc’s approach and calculations confirmed that applications of dopands are very effective on band gaps.

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