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Synthesis and Characterization of Metal-Doped (Ni, Co, Ce, Sb) CdS Catalysts and Their Use in Methylene Blue Degradation under Visible Light Irradiation

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Abstract

Metal doped CdS nanoparticles were synthesized by a simple chemical precipitation route with different metals. The obtained nanoparticles were characterized by XRD and UV-vis reflectance spectroscopy. The results indicated that metal-doped CdS catalysts were successfully obtained with cubic structure and 4.0 - 4.5 nm crystallite size. The band gap energies of metal-doped CdS catalysts were estimated using UV-visible reflectance spectra to be about the range of 2.25 - 2.55 eV. Methylene blue was degraded by using metal doped CdS nanoparticles under a 400 W medium-pressure mercury lamp of visible light irradiation (λ > 420 nm). Higher degradation efficiency was achieved by adding metals to the photocatalyst compared with the single CdS catalyst. In this case, the degradation efficiency of Co-CdS catalyst after 4h irradiation time was about 87%.

Keywords

Chalcogenides, Chemical Synthesis, Optical Properties, Photocatalytic Reaction

1. Introduction

Environmental problems associated with organic pollutants provide the impetus for sustained fundamental and applied research in the area of environmental remediation. Semiconductor photocatalysis offers the potential for complete elimination of toxic chemicals through its efficiency and potentially broad ap-

plicability [1]. Dye-related industries such as textile, release various organic pollutants to the atmosphere. If these pollutants are discharged into the environment without any treatment, it will cause extensive toxicity to the various forms of lives. In order to eliminate the potential danger of these organic dyes, many technologies have been developed to treat these pollutants. Photocatalysis is an alternative route for water purification [2]. Photocatalysis is a process by which a semiconductor material absorbs light of energy greater than or equal to its band gap. It causes excitations of valence band electrons in the conduction band. II-VI semiconductors have attracted attention in recent years because of their easy synthesis in the size range and their potential applications in optoelectronic devices, solar cells, photo catalysis, and sensitized solar cells [3].

CdS is an important group of II-VI compound semiconductors with excellent physical properties and wide band gap energy of 2.42 eV. Cadmium sulfide (CdS) has two abilities for photo catalytic reaction: its band gap responses to visible light and its conduction band is more negative than the reduction potential of H^+/H_2 [4]. It is obviously known that CdS has many properties such as crystalline phase, size, morphology, specific surface area which can affect its photo catalytic activity. It has been offered that morphology of photo catalyst could be effective for the constraint of recombination between photo generated electrons and holes and for the separation of H_2 evolution sites from oxidation reaction sites [5]. A favorable shift of the optical response into the visible region occurs subsequently to the doping of transition metal, such as Ni^{2+} and Cu^{2+}. Thus, CdS nanoparticles can also be used as promising catalysts for photocatalytic reactions under visible-light irradiation [6] [7].

Metal doped semiconductors have appealed scientific attention due to their probable applications. Different techniques such as chemical precipitation, hydrothermal method, chemical vapor deposition, spray pyrolysis and other chemical routes have been used to synthesize metal doped CdS. [5] Metal (Ni, Co, Sb, Ce, etc.,) doped CdS has drawn remarkable attention as it presents a great opportunity to combine electrical and optical properties into a single material [5] [8] [9].

Noble metal co-catalysts such as Pt, Pd, and Rh on CdS, can trap light-induced electrons and act as the active sites for H_2 production and degradation of dyes from water. [10] [11]. However, the high cost of noble metals seriously limits their practical application in hydrogen evolution through water splitting, which can well explain why metals are of particular significance as co-catalysts for production of hydrogen and oxygen through water splitting or for degradation of organic pollutants in water and air [12] [13] [14] [15] [16]. With the assistance of cocatalysts, researchers have successfully developed various CdS based photocatalysts possessing visible light catalytic activity, such as NiS/CdS, Ni $(OH)_2$/CdS, and Ni@C/CdS [12] [13] [14] [15] [16]. These modified photocatalysts are valuable, since they can efficiently promote water splitting under visible light irradiation and provide high hydrogen production rates. [17]

A doping effect on metallic chalcogenides is available in the literature [18]

[19] [20], proving that the photoluminescent and electrical features of sulfide nanocrystals. Continuous attempts are being made to synthesize sulfide nanomaterials with controlled sizes, shapes, and phase purity by various chemical routes [21] [22] [23]. Doping cadmium sulfide has attracted considerable attention as it is a convenient way to tailor its physical properties. Recently, spectroscopic studies of transition metal and rare-earth doped nanocrystalline CdS have motivated to develop new and more efficient multicolor phosphor materials [24]. Similarly, the mixed $Cd_{1-x}Zn_xS$ [25], $Cd_{1-x}Mn_xS$, and CdS_xSe_{1-x} nanoparticles system [26] [27] and [28] [29] is studied because of its suitability for optical devices from the near-ultraviolet to the near-infrared [30] and [31]. Investigation of CdS nanostructure has received considerable attention due to its size dependent properties and quantized charging effects on metal nanoparticles and provides the basis for developing new and effective systems. These nanostructures provide innovative strategies for designing next generation energy conversion devices. Incorporate dopants into CdS nanocrystalline have been prepared by various techniques such as, ion exchange reaction, dry process, spray pyrolysis, chemical bath deposition, pulsed laser deposition and sol-gel spin coating method [32] and [33]. In literature, TiO_2-graphene nanocomposite was also used for photocatalytic reactions under visible light and it was showed 93% degradation efficiency with a progress at photocatalytic activity studies [34].

In this study, we investigate optical properties of metal-doped (Ni, Co, Ce, Sb) CdS nanoparticles prepared by chemical co-precipitation method. The prepared samples were characterized using X-ray diffraction and UV/Vis reflectance spectra for studying optical properties. Photocatalytic degradation of methylene blue was performed by using metal doped CdS nanoparticles under a 400 W medium-pressure mercury lamp of visible light irradiation ($\lambda > 420$ nm).

2. Experimental

2.1. Synthesis

In the present study, metal-doped (2% mol) CdS catalysts have been synthesized through chemical precipitation technique. 5 mol aqueous solution of cadmium chloride ($CdCl_2$) (50 ml) and 0.1 mol nickel nitrate (Ni $(NO_3)_2 6H_2O$), cobalt nitrate (Co $(NO_3)_2 6H_2O$), antimony chloride ($SbCl_3$) and cerium chloride ($CeCl_3$) (10 ml) were stirred for 30 min at room temperature, separately. 5 mol aqueous solution of sodium sulfide (Na_2S) (50 ml) was added drop wise to mixed solution and was stirred for 2 h. A yellowish-orange color precipitate was obtained. The nanoparticles were purified by excess distilled water and then the sample was dried at 65˚C for 4 h [35] [36].

2.2. Characterization

The phase as cubic, hexagonal, etc. and the crystallite size of the samples were carried out through X-ray Diffraction Analysis. Structural characterization for the phase identification and crystallite size analysis was carried out by Rigaku Ultima + powder X-ray diffractometer operating at 40 kV and 30 mA with

Cu/Kα (λ = 1.54 Å) radiation. The crystallite size of CdS samples was calculated using Debye-Scherrer equation. UV-V is reflectance and absorbance spectrums were recorded on an Ocean Optics USB-4000 in the range 220 - 1000 nm.

2.3. Photocatalytic Degradation

The photocatalytic reaction was performed in a reactor (250 ml). 50 mg of the catalyst was dispersed in 200 ml of 8 ppm (aqueous) MB dye solution. The reaction mixture was stirred with a magnetic stirrer. It was photo irradiated at room temperature by using a 400-W medium pressure mercury lamp with UV filter (λ > 420 nm). The decomposition of MB dye was measured by UV-V is absorption spectrophotometer at regular intervals of time using (λ_{max} = 665 nm) [37]. The procedure was repeated for all samples.

3. Results and Discussion

3.1. X-Ray Diffraction

X-ray diffraction pattern gives information about crystalline structure and crystallite size. Figure 1 shows the X-ray diffraction pattern of the CdS catalysts with different metals(Ni, Co, Sb, Ce). XRD peaks are found at 2θ values of 26˚, 43˚ and 52˚ approximately, referring to diffraction from (111), (220) and (311) planes, respectively, which has only a single very broad neighbor peak near the (110) line [38]. There were not seen any different peaks corresponding to the metals because of their small quantity (2% mol). Figure 2 shows the XRD pattern of single CdS catalyst. It is clear that, XRD patterns showed for all catalysts

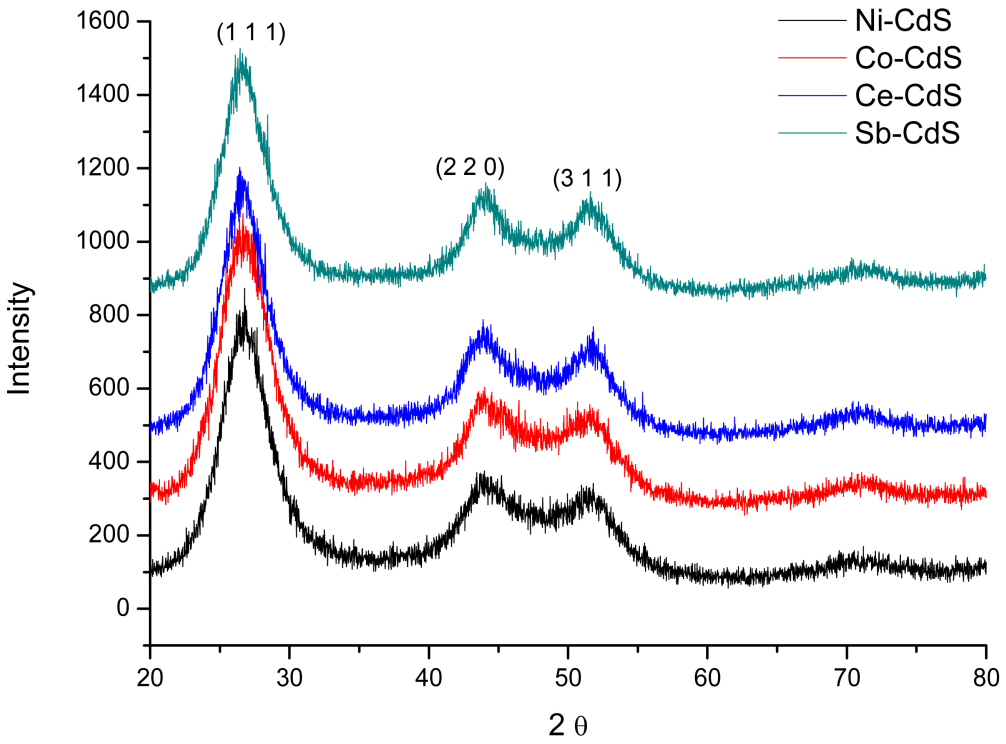

Figure 1. X-ray Diffraction pattern of metal-doped CdS catalysts.

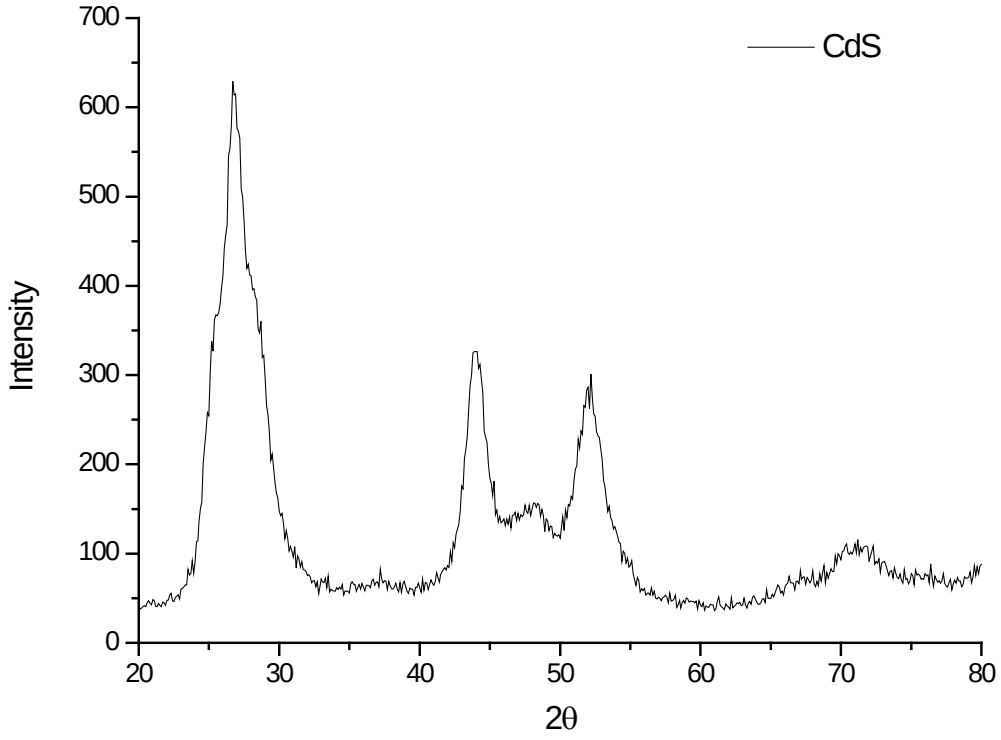

Figure 2. X-ray Diffraction pattern of as-prepared CdS catalyst.

were composed of single cubic phase. **Figure 3** shows standard X-ray Diffraction pattern of cubic CdS (JCPDS-89-0440) and hexagonal CdS (JCPDS-80-0006). The XRD patterns obtained for both single CdS and metal doped CdS corresponded to pure cubic CdS when compared with the standard reference (JCPDS-89-0440). All the peaks in the diffraction pattern is found to be characteristic of CdS, suggesting that incorporation of metals in the sample does not introduce appreciable change in the crystal structure of CdS. But also X-ray diffraction data indicates that the diffraction peak of metal doped CdS plane slightly shifts to larger angle. There is a small shift in broad peaks ofmetal-doped CdS with respect to the pure CdS nanocrystals;this small shift in intensity may be assigned to the presenceof dopant metal in doped nanocrystals. The broadening of diffraction peak provides information about crystallite size. As the width increases, the crystallite size decreases.

The crystallite size was calculated using Debye Scherrer's formula as seen Equation (1) [39]

$$D = \frac{0.9\lambda_{K_{\alpha 1(Cu)}}}{\beta_{2\theta} * \mathrm{Cos}\,\theta_{\max}} \quad (1)$$

where D is the crystallite size, λ is the wavelength of X-rays, β is full-width at half-maxima (FWHM) in radians and θ is the diffraction angle. Corresponding to the maximum intensity peak crystallite sizes were in the range of 4.0 - 4.5 nm as seen in **Table 1**.

Crystallite size of metal doped CdS catalysts were decreased by adding metals as Ni, Co, Sb, and Ce. The diffraction pattern exhibits broad peaks revealing that

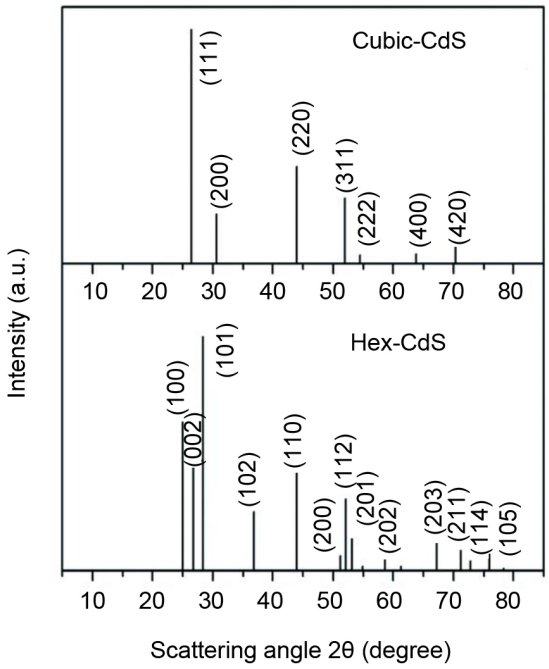

Figure 3. Standard X-ray Diffraction pattern of CdS [40].

Table 1. Crystallite size of metal-doped CdS catalysts from X-ray diffraction analysis.

Catalysts	Crystallite size of metal-doped and single CdS catalysts	
	D (nm)	Phase
Ni-CdS	4.4	Cubic
Co-CdS	4.0	Cubic
Ce-CdS	4.5	Cubic
Sb-CdS	4.5	Cubic
CdS	5.1	Cubic

the prepared particles are of very small crystallite size.

3.2. Diffuse Reflectance

The UV—visible reflectance spectroscopy is an efficient technique to identify the optical properties of CdS particles. **Figure 4** shows the Kubelka Munk function spectrums of the metal doped CdS catalysts. These spectrums exhibit defined reflection edges at 550, 487, 513 and 524 nm, corresponding to band gaps of 2.26, 2.55, 2.42 and 2.37 eV, for metal-doped CdS catalysts, as seen in **Table 2**. For the study of the optical properties of the metal doped CdS nanoparticles, the band gaps were determined, which were calculated by means of the optic reflectance spectrum [39]. Because this is the most accurate way to find the correct band gap value for as-prepared catalysts. Electromagnetic radiation in the range of 440 - 490 nm is known as blue region of the visible light spectrum.

Generally, the wavelength of the maximum exciton reflection decreases when the particle size decreases due to the quantum confinement of the photo-generated electron-hole pairs. But in this study, crystallite sizes were closed to each

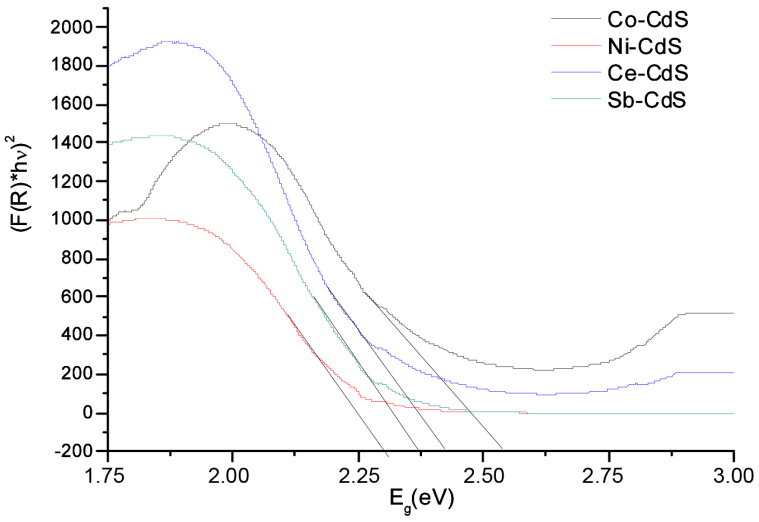

Figure 4. Kubelka-Munk curve of metal-doped CdS catalysts.

Table 2. Band gap values of metal-doped CdS catalysts from UV-vis reflectance spectroscopy.

Catalysts	Band gap values of metal-doped and single CdS catalysts	
	UV-Vis(E_g)-eV	UV-Vis(λ)-nm
Ni-CdS	2.26	550
Co-CdS	2.55	487
Ce-CdS	2.42	513
Sb-CdS	2.37	524
CdS	2.25	552

other as seen in Table 1. So it cannot be said that band gap values were changed because of only the crystallite sizes of the catalysts. It is clearly seen that the band gap of metal doped CdS catalysts were shifted in the blue region [5].

The band gap of CdS is increased by adding metals as seen in Table 2. It means that wavelength which corresponds with band gap is decreased. This decrease is interpreted due to sp-d exchange interaction between the band electrons and the localized d electrons of the metal ions (Co^{2+}, Ni^{2+}, Sb^{3+}, Ce^{3+}) substituting for host ions.

3.3. Photocatalytic Decomposition of Methylene Blue (MB)

Visible light photocatalytic activity of the catalysts was subsequently evaluated by measuring the discoloration of MB in aqueous solution under visible light illumination. The peak maximum for the absorbance spectra of MB at 665 nm decreases gradually with increasing irradiation time [41].

Equation (2) shows % Degradation calculation which is seen below.

$$\%\ \text{Degredation} = \frac{C_{A_0} - C_A}{C_{A_0}} \tag{2}$$

The rate of MB photo degradation in the Co-CdS was higher than that in the

other CdS catalysts; the rate of MB photo degradation in the CdS with metals were also higher than that of the single CdS catalyst as seen in Table 3. In this study, the adsorption time for CdS catalysts keep constant about 30 minutes. The maximum wavelength of MB in the absorption spectra was 665 nm and almost kept the same. After being irradiated for 240 min, the degradation rate of MB with the Co-CdS catalyst was up to 87%. This faster degradation rate of MB with using Co-CdS is referred to the increase in defect sides caused by Co doping, and leading to an enhanced optical absorption in the visible region. Kubelka-Munk curve is also indicated that Co doped CdS slightly placed at the right side of the spectrum, as seen in Figure 4.

Figure 5 shows also the medium pressure mercury (Hg) lamp spectrum with UV filter.

Figure 6 shows the photodegradation of MB in the presence of metal doped CdS catalysts under visible light. The photo catalytic degradation of MB which

Table 3. % Degradation values of metal doped CdS binary catalysts and single CdS catalysts.

Catalysts	% Degradation values of metal-doped and single CdS catalysts
	% Degradation
Ni-CdS	73
Co-CdS	87
Ce-CdS	76
Sb-CdS	70
CdS	68

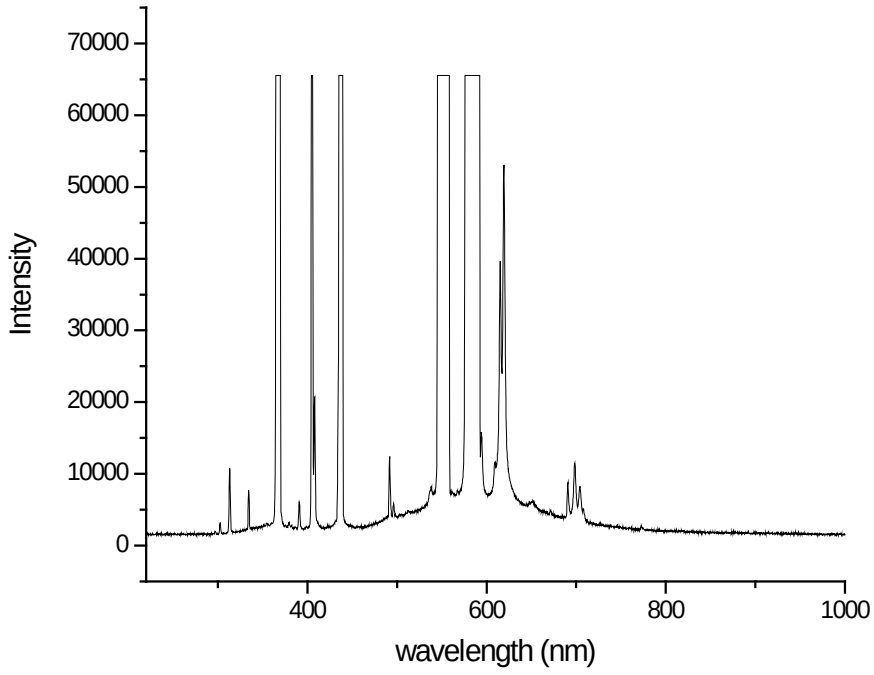

Figure 5. The medium pressure mercury lamp spectrum with UV filter.

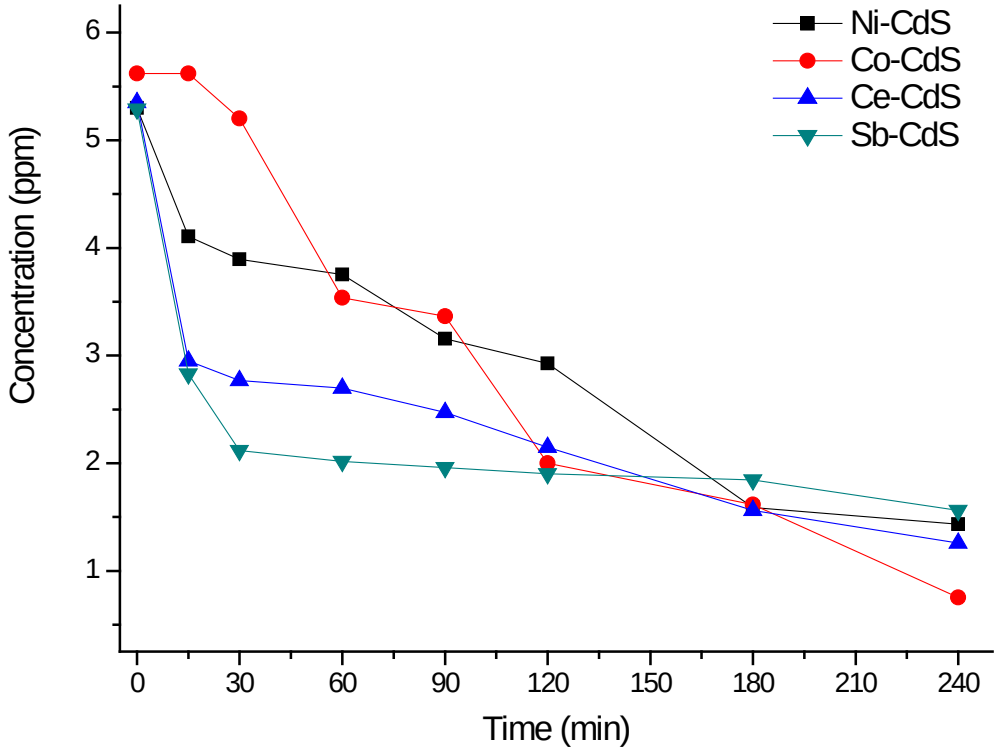

Figure 6. Photodegradation of MB in the presence of metal doped CdS catalysts under visible light.

contains metal doped CdS catalysts under visible light obeys pseudo-first-order kinetics with regard to the concentration of MB, as seen in Equation (3): [40]

$$-\frac{\mathrm{d}C_A}{\mathrm{d}t} = k_{app}C_A \tag{3}$$

The integration of the equation ($C_A = C_{A0}$ at $t = 0$, C_{A0} is the initial concentration in the bulk solution after dark adsorption and t is the reaction time) will prevent with Equation (4):

$$\ln\frac{C_A}{C_{A_0}} = -k_{app}t \tag{4}$$

where C_A and C_{A0} are the reactant concentrations at time $t = t$ and $t = 0$, respectively; k_{app} and t are the apparent reaction rate constant and time, respectively. According to the equation, a plot of ln (C_A/C_{A0}) versus t will yield a slope of k_{app}. Figure 7 shows the the plot of ln (C_A/C_{A0}) versus time for as-prepared catalysts in order to find the k_{app}. The linearity of plot suggests that the photo degradation reaction approximately follows the pseudo-first-order kinetics with a k_{app} of 0.0051 min^{-1}, 0.0086 min^{-1}, 0.0030 min^{-1} and 0.0019 min^{-1} for the degradation under visible light for Ni, Co, Ce and Sb doped CdS catalysts, respectively as seen in Table 4.

It is certain that metal doping on CdS increase the photo catalytic degradation of the MB under visible light. It has been seen that the photo catalytic activity of metal doped CdS is intensely depending on the metal ion type. Doping of Co increases the life time of excited charge carriers, which improves photo catalytic

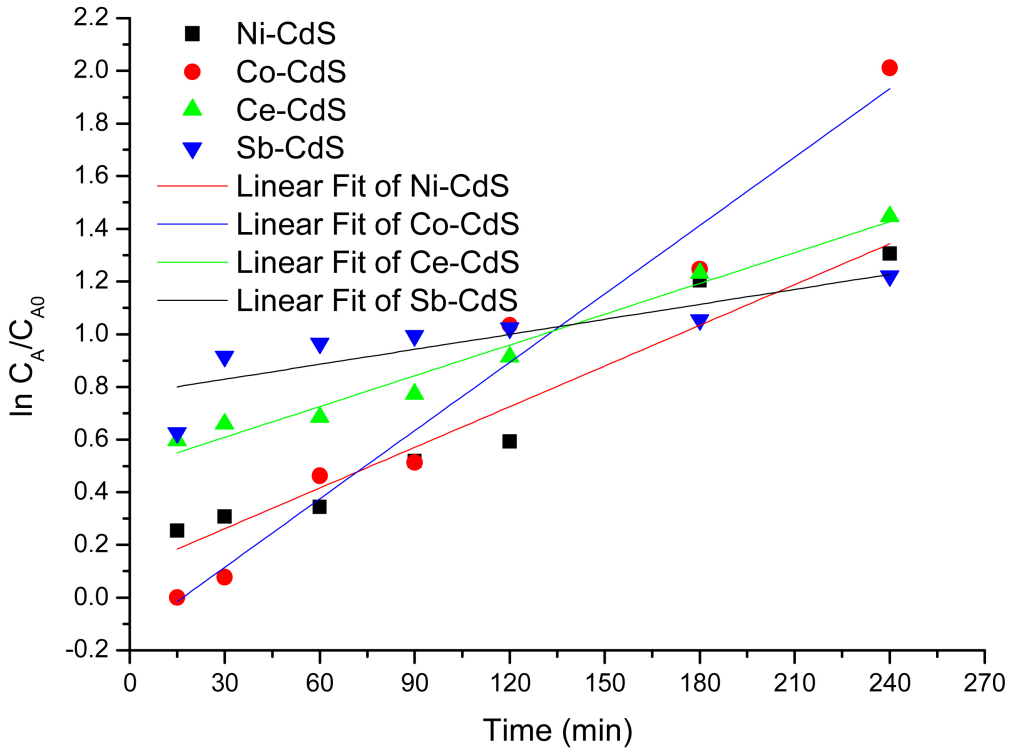

Figure 7. The plot of ln (C_A/C_{A0}) versus time for as-prepared catalysts.

Table 4. Reaction Rate Constants of metal-doped CdS Catalysts.

Catalysts	Reaction Rate Constants of metal-doped CdS Catalysts		
	C_{A0} (ppm)	C_A (ppm)	k*10^{-3} (min^{-1})
Ni-CdS	5.30	1.44	5.1
Co-CdS	5.62	0.75	8.6
Ce-CdS	5.35	1.26	3.0
Sb-CdS	5.30	1.56	1.9

activity. When the doping ion changes, some CdS crystal defects could be caused, and this may act as recombination centers to decrease the photo activity. It is obvious that doping of CdS with metal ions improves photo catalytic activities of CdS, and therefore metal doped CdS is capable of degradation of MB under visible light.

In this study, we assumed that metal ions with CdS generate electron-hole pair at conduction and valence band under visible light. The electrons transfer to the adsorbed MB molecule on the particle surface. The excited electron which comes from the conduction band enters in to the molecular structure of MB and complete degradation of MB. Hole at the valence band generates hydroxyl radical via reaction with water. This obviously indicates that the doped CdS catalysts can be as promising photocatalyst for the environmental detoxification from organic pollutants which can operate under visible light irradiation.

4. Conclusions

This study demonstrated an easy method for preparation of efficient visible light photocatalysts, namely metal doped CdS nanoparticles, by chemical precipitation method. The obtained metal doped CdS nanoparticles exhibit cubic structures with average crystallite sizes in the range of 4.0 - 4.5 nm. Crystallite size of metal doped CdS catalysts was decreased by adding metals as Ni, Co, Sb, Ce.

Optical diffuse reflectance spectra of metal-doped CdS nanoparticles exhibited a blue shift in the visible range compared with bulk CdS. The band gap is increased with adding metals. It means that wavelength which corresponds with band gap is decreased. This decrease is interpreted as mainly due to sp-d exchange interaction between the band electrons and the localized d electrons of the Co^{2+} ions substituting for host ions. The usages of different metals on CdS catalysts are promising work for photocatalytic degradation of methylene blue. Especially, CdS with Co was exhibited larger band gap value than the others and this result was a direct consequence associated with highest % degradation.

Methylene blue was degraded with using CdS and metal doped CdS nanoparticles under visible light irradiation. This study reveals that the photocatalytic activity of the catalysts depends on the metal doping (Ni, Co, Ce, Sb) on CdS. The highest photodegradation efficiency was observed for Co doped CdS with a percentage of 87%.

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