

RESEARCH PAPER

Hydrothermal Synthesis of Photo-catalyst and Photo-luminescence Polymer-CdS Flexible Nanocomposites

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ARTICLE INFO

Article History:

Received 05 October 2018

Accepted 10 December 2018

Published 01 January 2019

Keywords:

Cadmium sulphide

Nanocomposite

Nanostructures

Photo-catalyst

Photo-luminescence

ABSTRACT

CdS nanoparticles are II-VI group semiconductors in nature with suitable band gap for photoluminescence and photo-catalyst applications. CdS nanostructures were synthesized via a facile precipitation method in the presence of green capping agents such as starch, glucose, gelatin, salicylic acid in the green solvent of water. The influence of concentration, surfactant, precipitating agent on the particle size and shape of the products were examined. Then for preparation of polymer based nanocomposites, cadmium sulphide nanoparticles were added to poly styrene, poly vinyl alcohol, cellulose acetate and acrylonitrile-butadiene-styrene polymers. The prepared samples were characterized by X-ray diffraction pattern (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared (FT-IR) spectroscopy. The photocatalytic behaviour of cadmium sulfide was evaluated using the degradation of three azo dyes (methyl orange, acid violet 49 and acid black 1) under ultraviolet and visible light irradiation. Our results confirm preparation of pure semiconductor nanoparticles and polymer-based thin film nanocomposite with both appropriate photo-luminescence and photocatalytic performance simultaneously. Interestingly outcomes show photocatalysts can photo-degrade toxic dyes in less than 15 min.

How to cite this article

Mirsharifi S, Pakpour F, Ghanbari D. Hydrothermal Synthesis of Photo-catalyst and Photo-luminescence Polymer-CdS Flexible Nanocomposites. *J Nanostruct*, 2018; 8(3): 112-123. DOI: 10.22052/JNS.2019.01.012

INTRODUCTION

Semiconductor nanoparticles nowadays found considerable applications in different area of science and technology such as biology [1], bio-labelling [2, 3], molecular biotechnology [4, 5, 6], construction of lasers [7], nano-electronic devices [8], and many others. It is well-known that the optical properties of these materials strongly depends on the size of the particles [9-14], so they are extensively studied for applications in optoelectronics and photonics such as solar cells, photodiodes, LEDs [15], nonlinear optics and heterogeneous photo-catalysis [16].

CdS belongs to group II-VI semiconductors which attracted a huge interest because of its exceptional size dependence physical and chemical properties. It was shown that the band gap of nanosized CdS particles could be reached to a value of 2.42 eV as the size of the particles reduced to a few nm [17]. With decreasing the particle size the onset of absorption shifted to higher energies resulted to size quantization effects [18].

In recent years CdS nanoparticles were synthesized and characterized via different chemical, physical and biological [19-22] methods.

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In this research we aim to synthesize CdS nanostructures via a facile and low cost method in the presence of green capping agents such as starch, glucose, gelatine, salicylic acid in the green solvent of water.

MATERIALS AND METHODS

Cd(NO₃)₂ · 4H₂O, NaOH, polyvinyl alcohol (PVA), polystyrene (PS), acrylonitrile butadiene styrene (ABS), cellulose acetate (CA), ethyl cellulose (EC), acetone, dichloromethane, starch, glucose, gelatin, salicylic acid and poly vinyl alcohol were purchase from Merck company. In this study we used a simple co-precipitation and hydrothermal method for producing nanostructures. Water and ethanol was used as solvent; sugar and natural materials as surfactants. We did not use harmful chemical solvents. XRD analysis was done to determine the structural characterization of synthesized nanoparticles. It was done with CuKα radiation (λ = 1.5418 Å) in 2θ = 10-80 degrees. The morphology and particles size were estimated using scanning electron microscopy (SEM). A

KYKY-EM3200 instrument was used to get SEM images. To prevent charge accumulation, prior to taking images, the samples were coated by a very thin layer of Au (using a BAL-TEC SCD 005 sputter coater) to make the sample surface conductor and obtaining a better contrast. In UL-94 a bar shape specimen of plastic 130 × 13 × 1.6 mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each).

Synthesis of CdS nanoparticles

0.1 g of Cd(NO₃)₂ · 4H₂O and 0.024 g of thiourea were separately dissolved in 100 ml of distilled water and mixed. NaOH solution (1 molar) gradually was added to this solution until a pH of 10 is reached. The solution was stirred for 30 minutes and allowed formed sediment to deposit. Deposited sediment was washed with distilled water and then the precipitate was calcined at a temperature of 75 °C. The resulting product is cadmium sulfid nanoparticles. Fig.1 shows the schematic diagram for experimental setup for preparation of CdS nanoparticles and

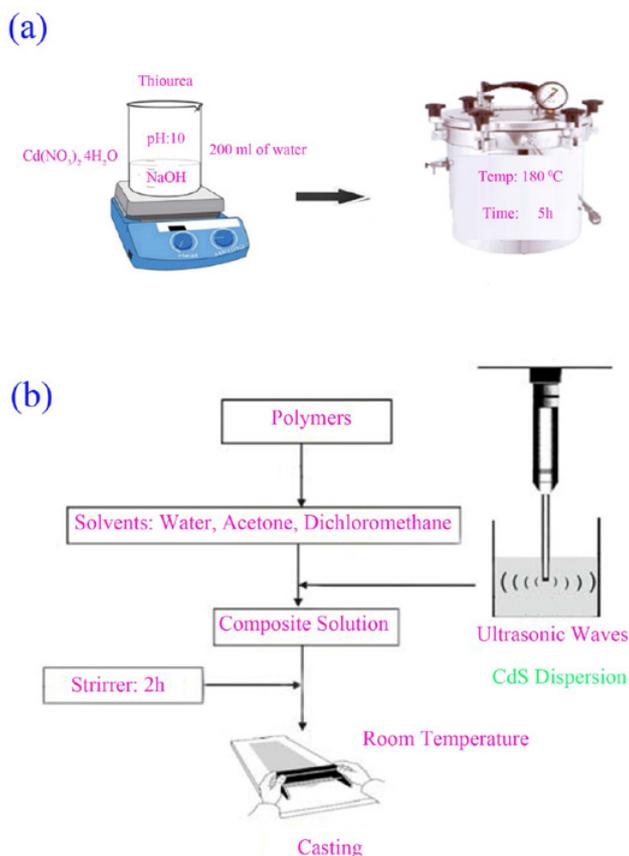


Fig. 1. Preparation of CdS nanoparticles and polymeric nanocomposites

nanocomposites used in this method. Fig. 2 shows the proposed energy diagram of CdS based for photo-degradation application.

Synthesis of PVA-CdS nanocomposite

0.1 g of CdS separately dispersed in 100 ml of appropriate solvent, and then 1g of polymer was dissolved in solvent (water for PVA, acetone for cellulose acetate and dichloromethane for PS and ABS). The solution was stirred for 60 minutes and then casted on the glass surface and remained for 24 hours at room temperature.

Photo-catalytic degradation process

0.1 g of catalyst was applied for degradation of 10 ml solution. To obtain a better availability of the surface, the solution was mixed by a magnet stirrer

for 60 minutes in darkness and then the adsorption of the dye by catalyst was studied. Three 8 W UV lamp which was located in a quartz pipe in the middle of the reactor was used to irradiate the solution. The concentration of the sample was determined by UV-Visible spectrometry after it was filtered and centrifuged.

RESULTS AND DISCUSSION

The structure and crystallinity of the synthesised CdS nanoparticles was demonstrated by XRD pattern in Fig. 3. The XRD pattern shows the typical diffraction pattern of pure hexagonal phase (JCPDS No.: 01-0780) with P63mc space group which is consistent with pure cadmium sulfide.

The composition of the PVA-CdS nanocomposite was also studied. As the figure depicts poly vinyl

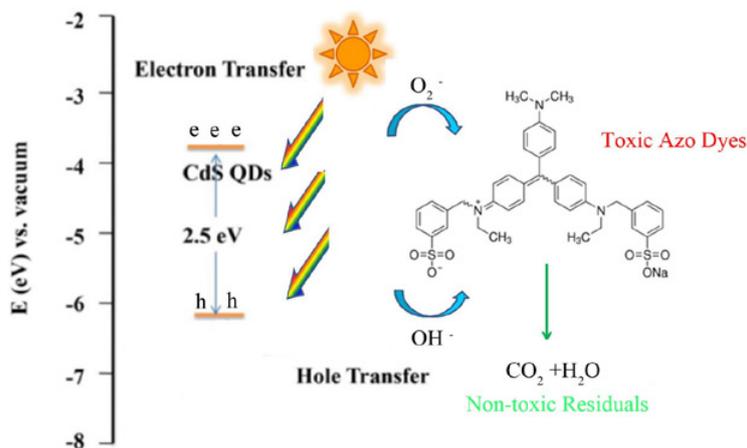


Fig. 2. Proposed energy diagram of CdS applied for photo-degradation

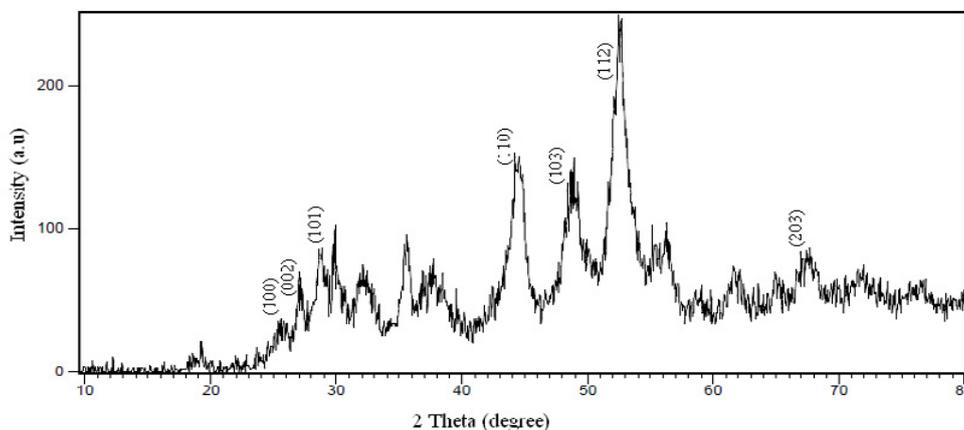


Fig. 3. XRD pattern of CdS nanoparticles

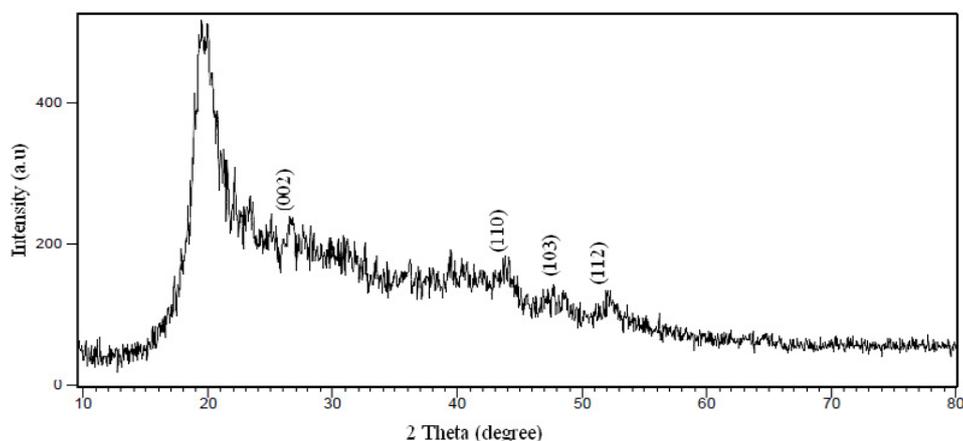


Fig. 4. XRD pattern of PVA-CdS nanocomposite

alcohol has broad peak around 2θ :18-21° which is the characteristic peaks of the PVA. Presence of pure hexagonal phase (JCPDS No.: 01-0780) in the semi-crystalline polymer matrix was confirmed and is illustrated in Fig. 4.

The crystalline diameter, $D_c = 0.9\lambda/\beta\cos\theta$, was measured using Scherrer equation, β is width of the diffraction peak at half maximum intensity, λ is the X-ray wavelength (K_α of Cu= 1.54 Å). The average crystalline diameter for CdS and PVA-CdS nanocomposite are about 11 and 10 nm respectively. It proposes that nanoparticles have good dispersion in the matrix and the crystals were covered by polymeric matrix and as a result lower crystallite size was achieved for polymer based nanocomposite.

The morphology, shape and diameter of the spherical was estimated by scanning electron microscopy (SEM). Figs. 5 exhibits CdS nanoparticles obtained by precipitation in 100 ml of solvent with starch as a green, biocompatible and cost-effective capping agent. According to SEM images the average particle size is found to be around 49 nm. As another green capping agents and surfactant various sugars were applied. In this work non-toxic surface active agents were applied that they should be able to dissolve in water rapidly, cover the ions and nucleolus appropriately and be removed by a simple washing and separation and don't remained on the final products. Figs. 6 show SEM images of CdS nanoparticles synthesized in the presence of glucose surfactant. The average particle size is calculated to be around 44 nm.

The effect of a green macro molecule on the size of the particles was also investigated; SEM

image of CdS nanoparticles prepared by gelatin coating is shown in Fig. 7. The average particle size is calculated to be around 43 nm.

The influence of the lipophilic mono hydroxyl

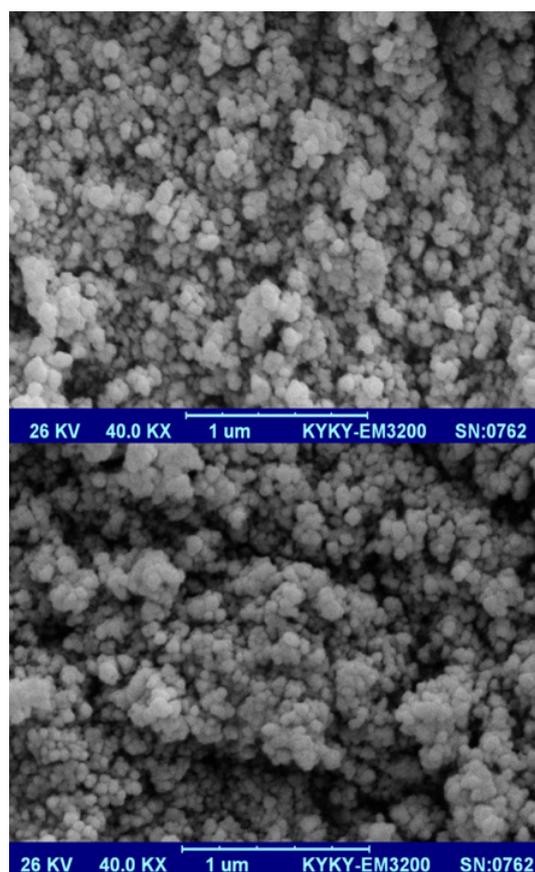


Fig. 5. SEM images of cadmium sulfide nanoparticles prepared in the presence of starch.

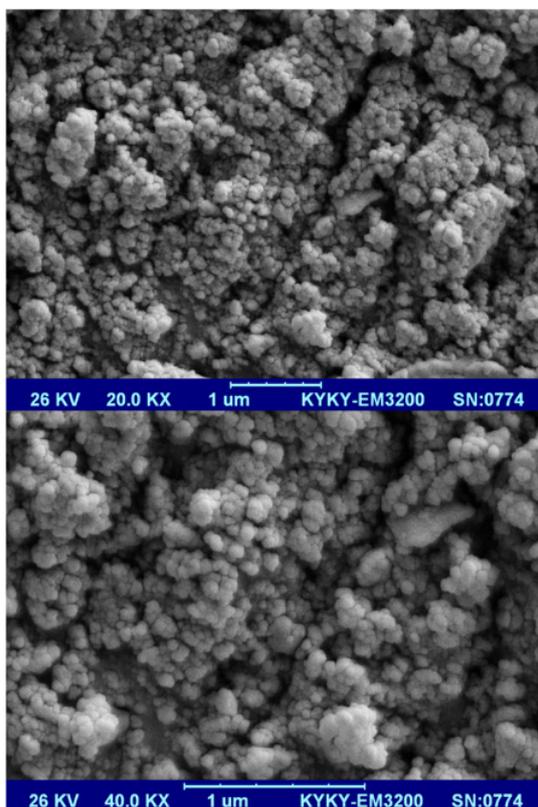


Fig. 6. SEM images of CdS nanoparticles with glucose

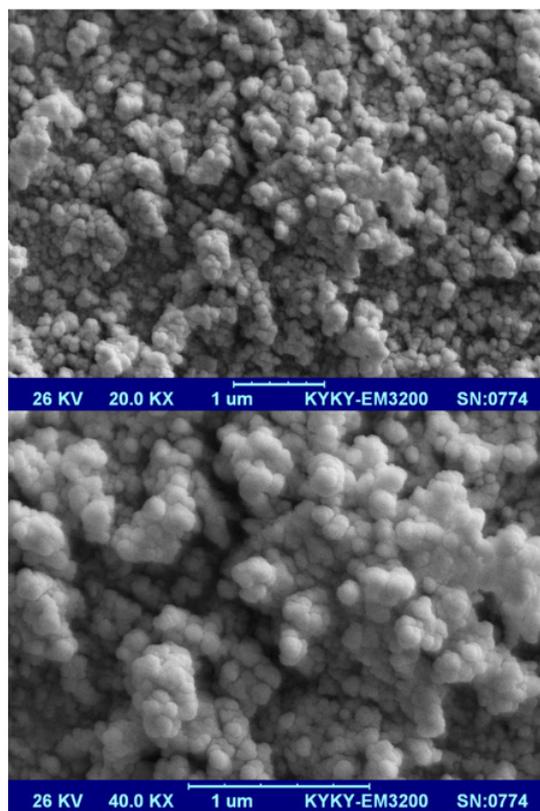


Fig. 7. SEM images of CdS nanoparticles with gelatin

benzoic acid on the shape and dimension of the chalcogenide was also examined; SEM images of cadmium sulfide prepared with salicylic acid coating are shown in Figs. 8. The average particle size is calculated to be around 42 nm.

Transmission electron microscopy image of the cadmium sulphide in the Fig. 9 confirms preparation of mono-disperse semiconductor with average diameter less than 80 nm.

Fig. 10 illustrates SEM images of the poly styrene-CdS nanocomposite. The images approve the presence of nanoparticles in the polymer matrix. Polymer chains cover nanoparticles, however because of suitable dispersion, only some of the nanoparticles are presented in the polymer matrix. The average size was estimated to be around 43 nm. The results confirmed that all synthesized nanostructures were formed from nanoparticles with average diameter size less than 70 nm.

FT-IR spectrum of the as synthesized CdS nanoparticles by salicylic acid sample is shown in Fig. 11., The spectrum shows prominent bands near 3424 cm^{-1} , which are attributed to the

stretching modes and O-H vibrations of the free or adsorbed water. Peaks at 620 , 653 and 720 cm^{-1} are related to Cd-S bonds. The weak band near 1016 cm^{-1} is assigned to C-O bending vibration and the adsorptions of 1384 cm^{-1} are related to salicylic acid.

Fig. 12 shows the FT-IR spectrum of the polystyrene-CdS nanocomposite. The band at 1452 , 1492 and 1601 cm^{-1} are related to aromatic C=C stretching vibration mode from styrene block. The band at 2924 and 2850 cm^{-1} were assigned to aliphatic C-H bonds stretching vibration mode. Absorptions at 3081 , 3059 and 3025 cm^{-1} are corresponding to aromatic C-H bonds. The peaks at 540 and 699 cm^{-1} confirm presence of Cd-S bonds in the poly styrene matrix.

FT-IR spectrum of the synthesized cellulose acetate-CdS nanocomposite is shown in Fig. 13, The spectrum show bands near 3488 cm^{-1} , which are attributed to the stretching modes of O-H vibrations of the free or absorbed water, also the band at 1751 cm^{-1} was assigned to C=O stretching vibration. And peaks at 903 , 1052 , 1253 cm^{-1} was assigned to C-O stretching vibration mode. A

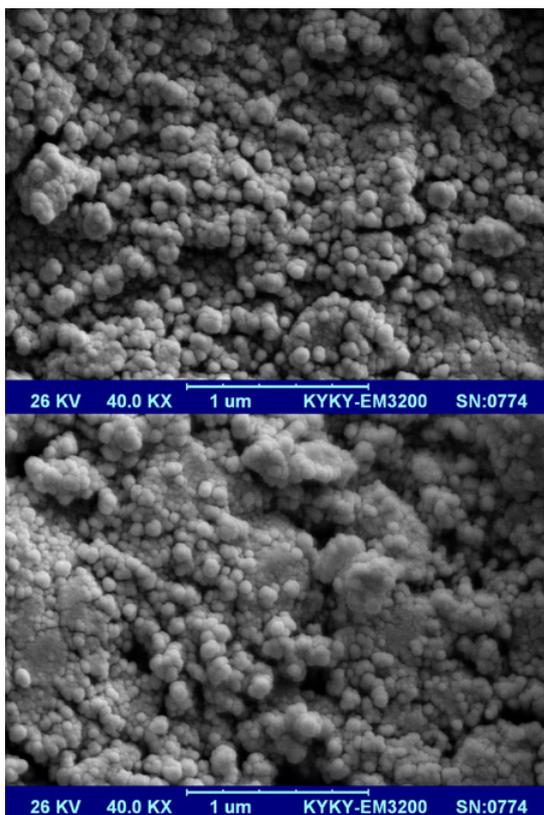


Fig. 8. SEM images of CdS nanoparticles with salicylic acid

peak at 1370 cm^{-1} is related to bending mode of O-H bonds. The absorption at 558 cm^{-1} approves existence of cadmium sulphide in the cellulose

acetate.

FT-IR spectrum of the synthesized ABS-CdS nanocomposite is depicted in Fig. 14, the spectrum show bands near 2237 cm^{-1} was stretching to $\text{C}\equiv\text{N}$ bending vibrations mode. The band at 2923 cm^{-1} was assigned to aliphatic C-H bonds stretching vibration mode. Absorptions at 3082 and 3061 cm^{-1} are corresponding to aromatic C-H bonds. The peak at 548 cm^{-1} confirms presence of Cd-S bonds in the acrylonitrile-butadiene-styrene matrix.

Photo-luminescence of pure CdS in water under UV irradiation and in the presence of starch, salicylic acid and solvent of ethanol are shown in Figure 15a-d respectively. As outcomes approve all semiconductor samples illustrate excellent luminescence radiation under UV excitation. Results also show the products have photo-luminescence under visible solar excitation.

Acid black 1, methyl orange and acid violet 49 as typical organic pollutants were employed as targets because of the relative stability of their molecular structure. The result of the test showed that the prepared nanoparticles could be used to improve environmental problems associated with organic and toxic water pollutants.

Maximum absorption peaks (λ_{max}) of organic dyes that were used for degradation under UV light are obtained from UV-vis absorption spectra and were confirmed by scientific literature. The photo-catalytic activity of the nanoparticles was examined by observing the degradation of organic

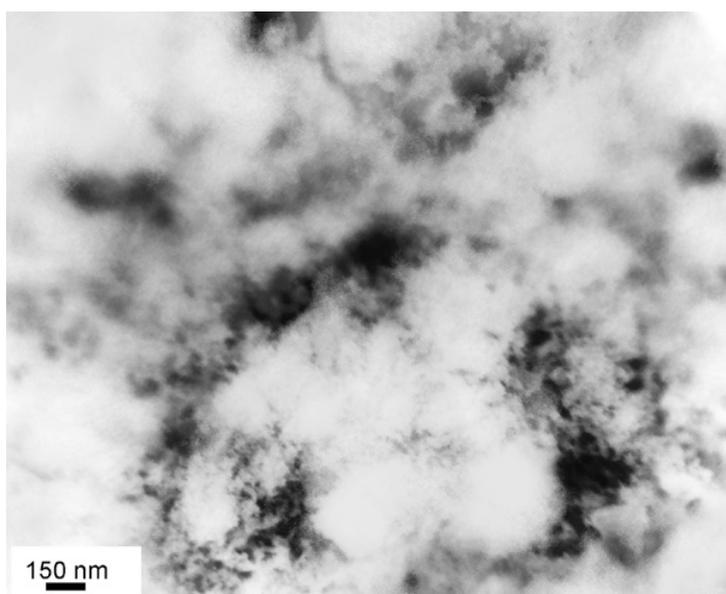


Fig. 9. TEM image of CdS nanoparticles

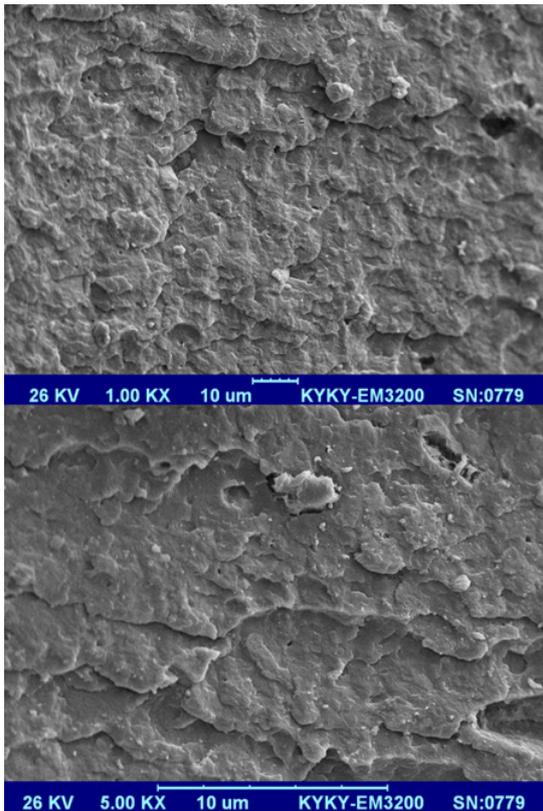


Fig.10. SEM images of the polystyrene-CdS nanocomposite

dyes in an aqueous solution, under UV irradiation. As time increases, organic dyes are adsorbed on the surface of the nanoparticles catalyst, until the absorption peaks (λ_{max}) of acid black 1, methyl orange and acid violet 49 decrease and vanish around 25 min, 10 min and 45 min respectively. UV-vis absorption spectra of blank acid violet 49 and in the presence of CdS photo-catalyst are shown in Fig 16a and 16b respectively. UV-vis absorption spectra of blank acid black 1 and in the presence of CdS photo-catalyst are shown in Fig 17a and 17b respectively [23].

The dyes concentration decreased rapidly with increasing UV-irradiation time. Organic dyes decompose to carbon dioxide, water and other less toxic or nontoxic residuals. The changes in the concentration of dye are illustrated in Fig. 18.

Thermal gravimetric analysis of poly vinyl alcohol-CdS nanocomposite is shown in Fig. 19. Initial temperature of thermal decomposition (Tonset) of the nanocomposite is increased and degradation of nanocomposite shifts towards higher temperature in the presence of CdS nanostructures.

Cadmium sulfide has barrier effect to decrease the product volatilization and heat transport in decomposition of the polymer. So residual amount

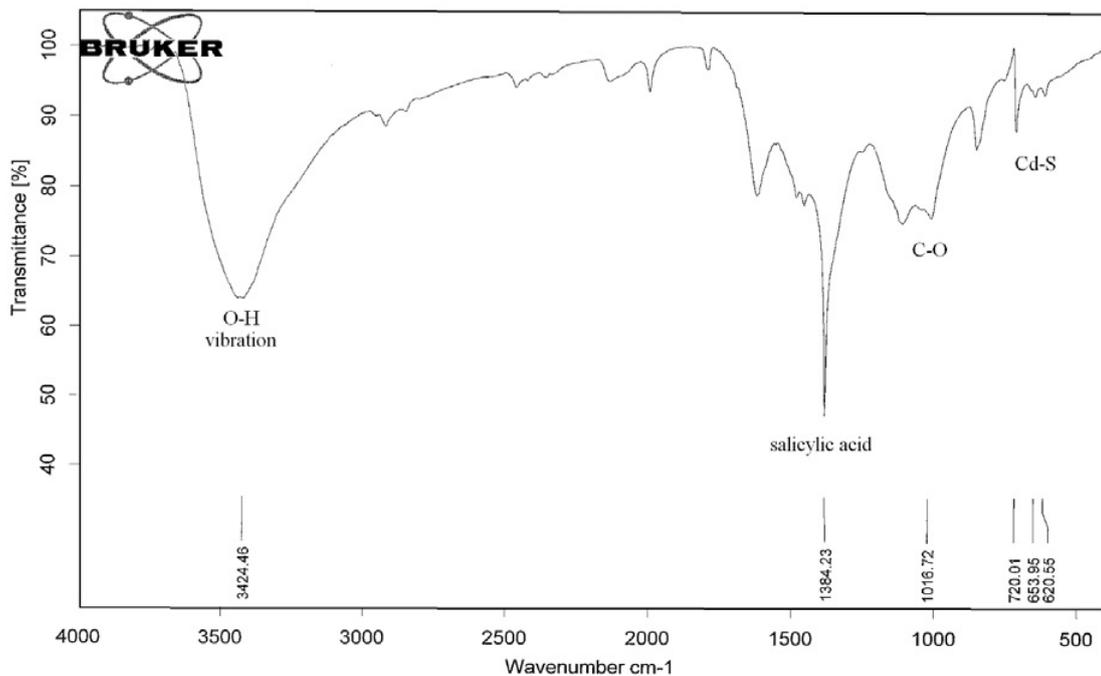


Fig. 11. FT-IR spectrum of CdS nanoparticles

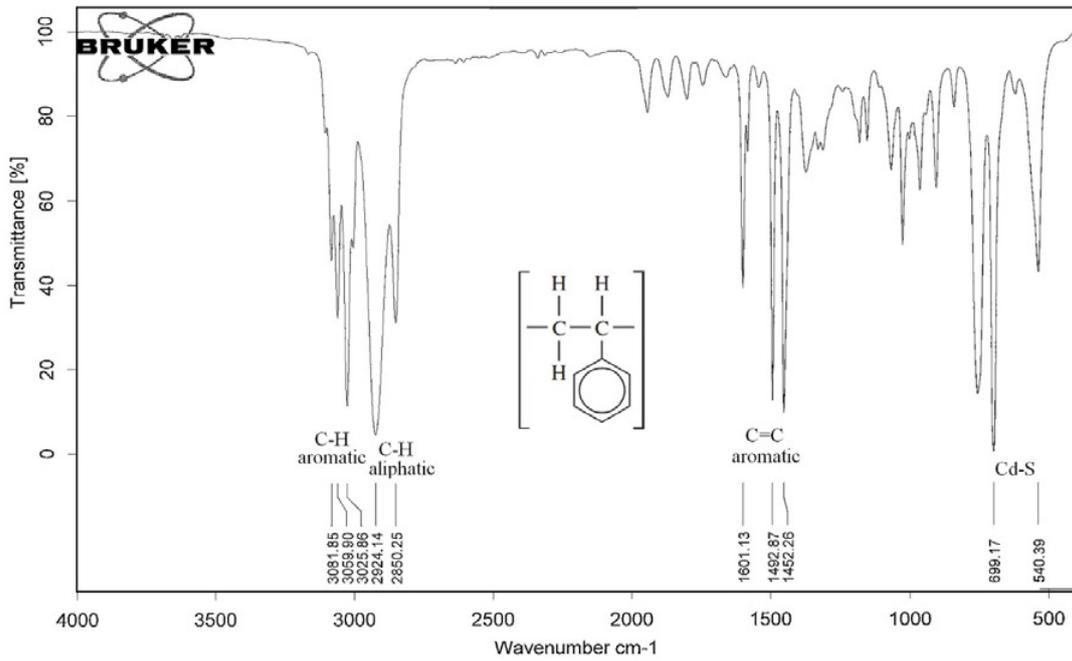


Fig. 12. FT-IR of polystyrene-CdS nanocomposite

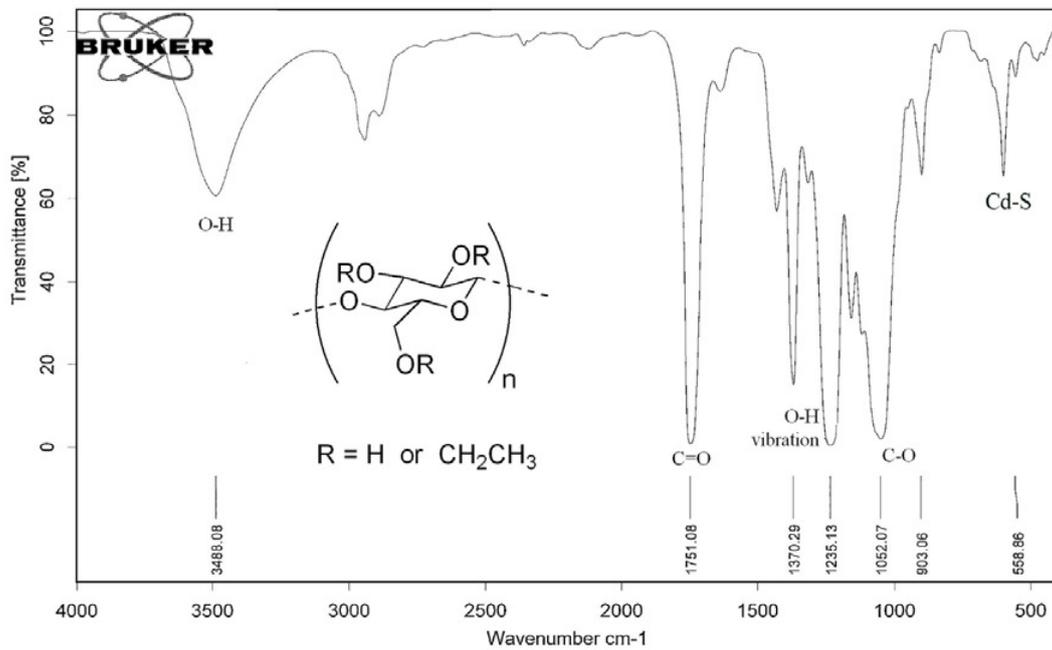


Fig. 13. FT-IR of cellulose acetate-CdS nanocomposite

of organic-inorganic nanocomposite is higher than pure PVA. It can be used as an inorganic char that prevent propagation of fire and heating.

The effect of CdS nanostructure on the flame

retardant properties has been considered using UL-94 test. The results of UL-94 test for PVA-CdS nanocomposites is V-1. A V-1 classification is received by a sample with maximum combustion

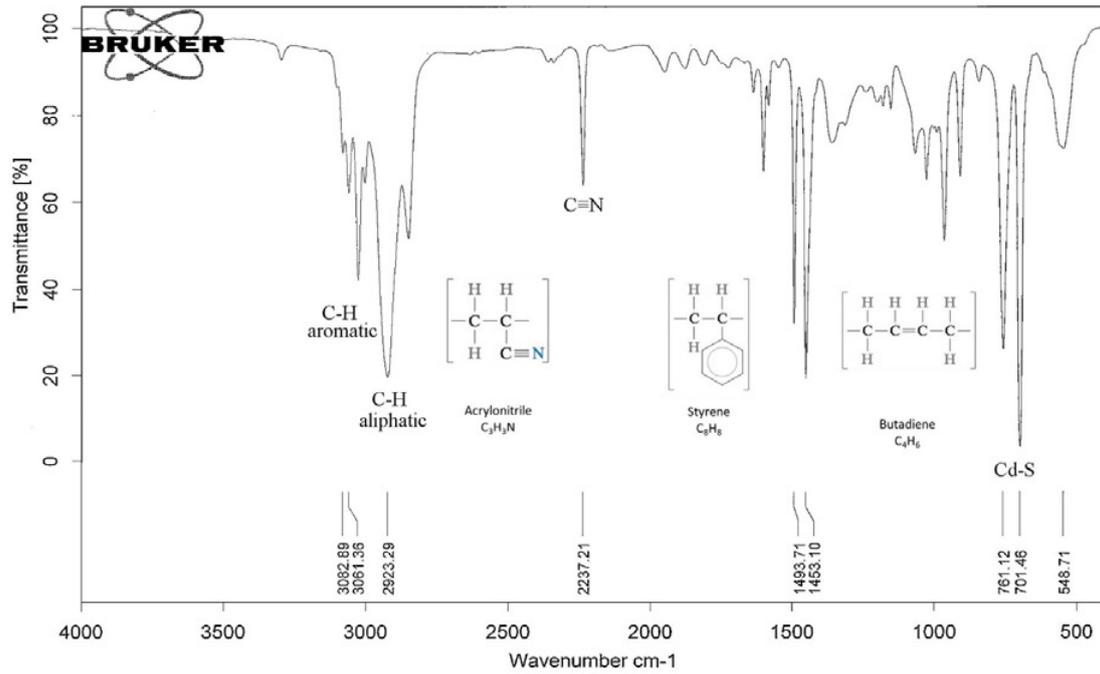


Fig. 14. FT-IR of ABS-CdS nanocomposite

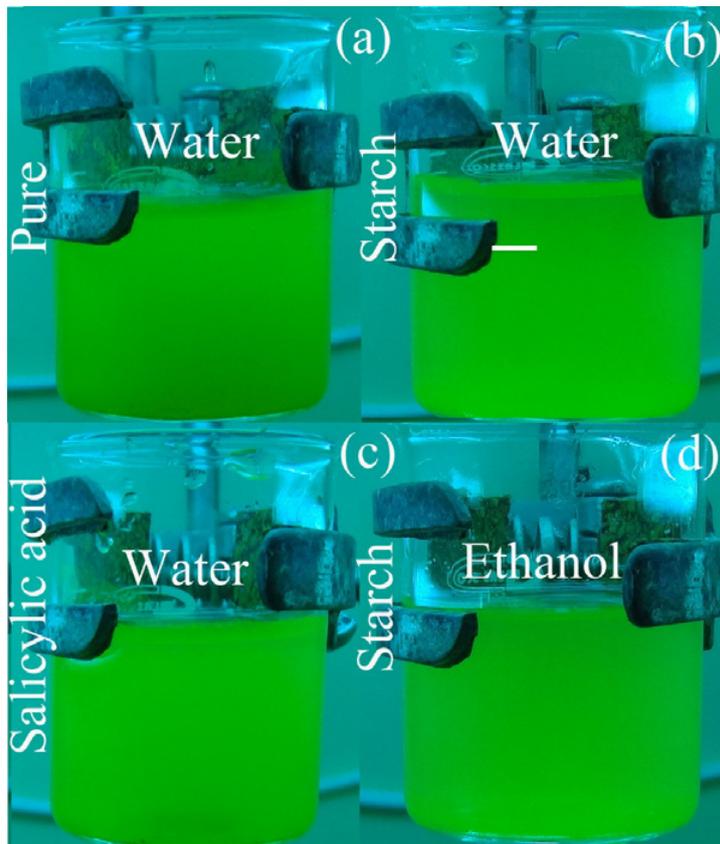


Fig. 15. Photo-luminescence of CdS in water under UV irradiation (a) pure (b) in the presence of starch (c) salicylic acid, and (d) ethanol

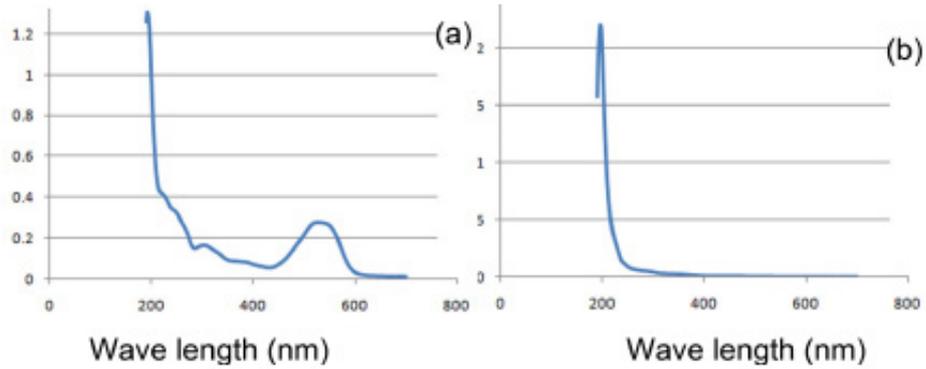


Fig. 16. UV-Vis absorption spectra of (a) blank acid violet 49 (b) in the presence of CdS photocatalyst

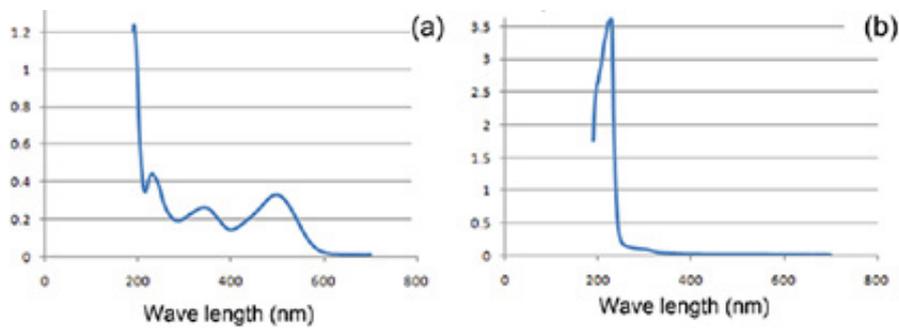


Fig. 17. UV-Vis absorption spectra (a) blank acid black 1 (b) in the presence of CdS photocatalysts

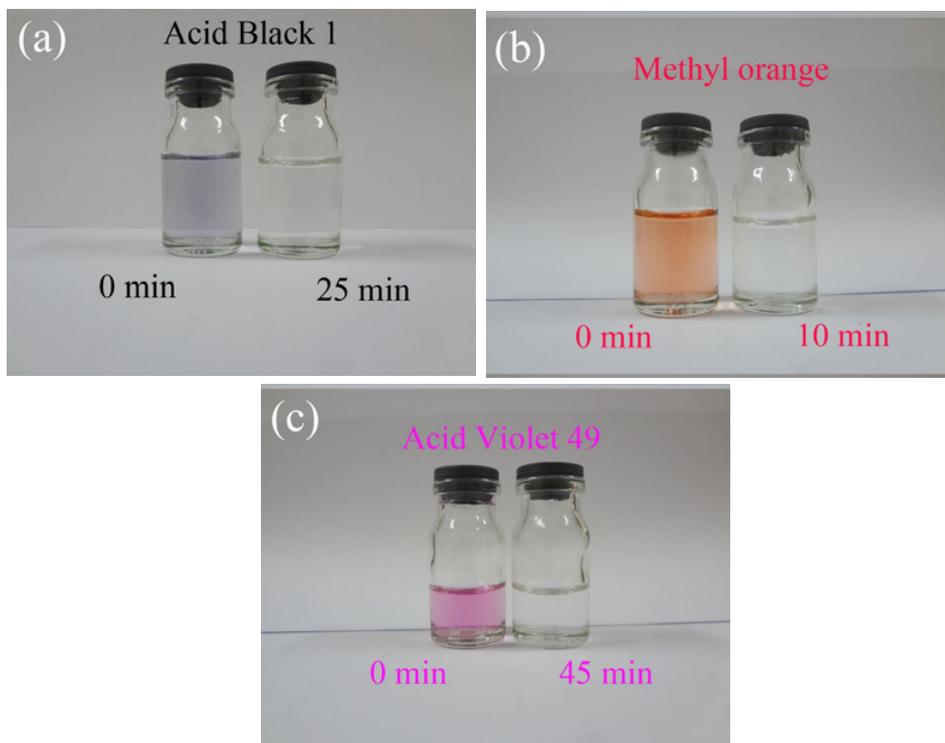


Fig. 18. Photo-degradation of (a) acid black 1 (b) methyl orange (c) acid violet 49

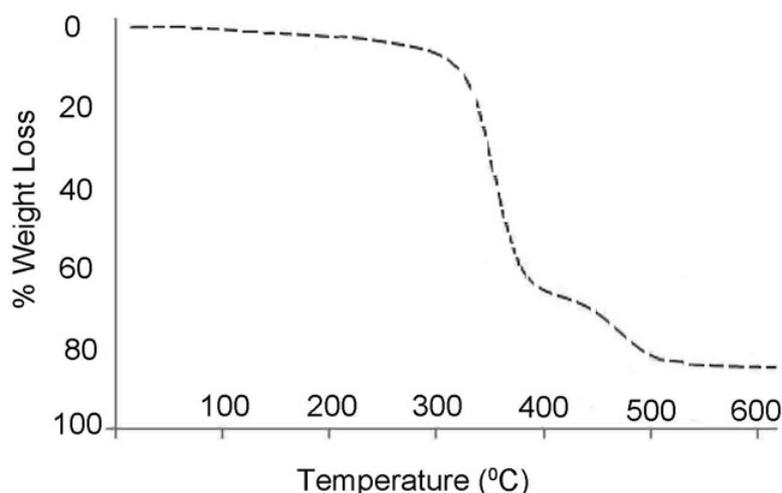


Fig. 19. Thermal gravimetric analysis of PVA-CdS nanocomposite

time lower than 30 s, drips of particles are allowed as long as they are not inflamed. The results show that the CdS nanostructures enhance the flame retardant property of the PVA matrix.

CONCLUSIONS

In conclusion, mono-disperse of the CdS nanoparticles were synthesized by a facile hydrothermal reaction. Then CdS were added to the four various polymers matrixes for preparation of polymer based nanocomposites. Nano-Characterization about size, purity and morphology of the cadmium sulphide, PVA-CdS, PS-CdS, ABS-CdS, Cellulose acetate-CdS and Ethyl cellulose-CdS nanocomposite were reported. The photocatalytic activity of CdS with three azo dye acid black 1, methyl orange and acid violet 49 were examined under ultraviolet light. Results also show suitable photo luminescence of the cadmium sulphide under visible and ultraviolet irradiation.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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