



Synthesis of NiWO₄ nanostructure and NiWO₄/CdO nanocomposites as an effective photocatalyst for enhanced degradation and removal of organic contaminant

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Abstract

NiWO₄ nanostructure and NiWO₄/CdO nanocomposites have been prepared through a new rapid co precipitation in presence of tween 80 as capping agent at 500 for 30 min. This study aimed to investigate the effects metal to capping agent ratios on the morphology and particle size of final products. Furthermore, due to occurrence of red shift in nonanocomposite, during the coupling of CdO into NiWO₄, photocatalytic properties of final products were improved which lead to improve photo-destruction efficiency for rhodamine B from 78 to 90%. The as-obtained NiWO₄/CdO nanocomposites was analyzed by ultraviolet–visible spectroscopy, transmission electron microscopy, field emission scanning electron microscopy, vibrating sample magnetometer, and X-ray diffraction.

1 Introduction

Due to industrial wastewater usually contains toxic organic compounds that can be harmful to human health, natural environment, and wildlife many wastewater processes' studies were extensively carried out in the past few decades. Photocatalysis is a promising method to deal with such wastewater [1–5]. Light assisted-photocatalyst materials (photocatalyst materials in assistance with light) break down the organic pollutants to innocuous the substances such as water, carbon dioxide, or other species in wastewater. The primary advantage of photocatalysis is that it never requires secondary disposal methods. Other treatment techniques such as adsorption by activated carbon and air stripping merely accumulate pollutants by carrying them over to the adsorbent or air. As a result, these pollutants will never be converted to non-toxic chemicals [6–11].

NiWO₄ have attracted much attention due to their interesting size and shape dependant optical, magnetic and electronic properties [12–15]. Transition metal tungstates have many applications, such as in gas sensors, optical fibres, humidity sensors, pigments, catalytic and biological activity

[16–23]. NiWO₄ is well known as a suitable medium in photocatalytic system. There is no report to prepare NiWO₄/CdO nanocomposites and evaluate their photocatalytic behavior.

This paper takes a new rapid co-precipitation synthesis of neat NiWO₄ nanostructure and NiWO₄/CdO nanocomposites composites by focusing on the impact of various factors and preparation condition such as with the molar ratio of polymer to metal on morphology, and size of as made samples. Effect of coupling CdO with NiWO₄ to reduce band gap and improve photocatalytic activity of catalyst on degradation of different organic dyes under visible light were performed.

2 Experimental

2.1 Materials and characterization

The chemicals [i.e. Ni(NO₃)₂·6H₂O, Na₂WO₄·2H₂O and Cd(NO₃)₂·6H₂O] were obtained from Merck Co. and were used as received. The magnetic properties, at room temperature, were evaluated with an alternating gradient force magnetometer (AGFM) instrument (Meghnatis Daghigh Kavir Co., Kashan Kavir, Iran) by scanning the magnetic field between ± 10,000 Oe. The X-ray diffraction (XRD) patterns were acquired using a Philips, XRD instrument with an Ni-filtered CuKα radiation. The field emission scanning electron microscopy (FESEM) images

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were recorded using a LEO 1455VP instrument after coating a very thin layer of Pt (using a BAL-TEC SCD 005 sputter coater) on the samples, to induce conduction to the sample surface, prevent charge accumulation, and help obtain improved contrast. DRS spectrum of the as-produced NiWO₄/CdO nanocomposites has been detected with the aid of ultraviolet–visible spectroscopy (UV–Vis) spectrophotometer (Shimadzu, UV-2550, Japan).

2.2 Synthesis of NiWO₄ nanoparticles

Here in NiWO₄ nanostructure were prepared by co-precipitation method. We followed a step-by-step procedure to make NiWO₄. Firstly, we dissolved 1 mmol of Na₂WO₄·2H₂O in hot water (typically 70 °C). Secondly, it was added drop-by-drop to a 20 ml hot solution (50 °C) containing 1 mmol of Ni(NO₃)₂·6H₂O and 3 mmol tween 80 with magnetic stirring. We regulated the pH of gained solution in 5–6. Afterwards, under constant magnetic stirring, the resultant solution was heated at 90 °C for 15 min, and then we permitted the system to cool to normal temperature. Subsequently, we collected the obtained precipitation by filtration, and washed several times with absolute ethanol and distilled water. Finally, the obtained precipitation was washed three times with distilled water, dried, and calcined at temperature 500 °C for 60 min.

2.3 Synthesis of NiWO₄/CdO nanoparticles

The as-prepared NiWO₄ nanoparticles from last past step were dispersed in a mixture of 50 ml of water. The dispersion was gently stirred for 10 min to become homogenous. A mixture of Cd and tween were inserted into the solution for 15 min at 70 °C. Then, solution of NiWO₄, Cd²⁺ and capping agents was mixed with 50 ml solution of NaOH with a concentration of 2.5 mol/l and was mixed with above mentioned solution under magnetic stirring for 10 min at constant temperature 25 °C. Finally, the obtained precipitation was washed three times with distilled water, dried, and calcined at temperature 500 °C for 60 min. Reaction conditions are listed in Table 1.

Table 1 The preparation conditions of the NiWO₄/CdO nanocomposites

	Capping agents	Molar ratio (M:capping agents)	Molar ratio (Ni ²⁺ :Cd ²⁺)	Temperature (°C)	Product
1	PEG	0.5:1	1:0	500	NiWO ₄
2	PEG	1:1	1:0	500	NiWO ₄
3	PEG	1:1	1:1	500	NiWO ₄ /CdO
4	PEG	1:1	1:2	500	NiWO ₄ /CdO

2.4 Photocatalytic evaluations

The degradation of rhodamine B (Rh B) were investigated to access the photoactivity of NiWO₄/CdO nanocomposites. In order to achieve this aim, photocatalytic degradation was accomplished in a 100 ml beaker including 50 ml of 2 × 10⁻⁵ M Rh B and 0.03 g of the catalyst at room temperature. The suspensions were aerated to achieve balance between the organic molecules and the catalyst surface for 30 min. Then, the mixture was inserted inside the photo-reactor which the vessel was 20 cm away from the visible source of 400 W Osram lamp. The light source and quartz container were placed inside a black box to barricade UV leakage. Aliquots of the mixture were taken at definite interval of times during the irradiation and after centrifugation the samples were pursued by a UV–Vis spectrometer. The photocatalytic degradation percent was calculated via the following equation (Eq. 1):

$$\text{Degradation rate (\%)} = 100(C_0 - C_t)/C_0 \quad (1)$$

In which C₀ and C_t are the absorbance value of solution at 0 and t min, respectively.

3 Results and discussion

Nowadays, extensive research has been conducted to obtain optimal sample through change of capping agent and concentration [1, 24–34]. Nanoparticles were prepared with molar ratio of metal to PEG (0.5:1) and (1:1). As a result, with increase in ratio of capping agents, the size of nanoparticles reduced, as shown in Figs. 1 and 2. Consequently, nanoparticles in sample two was chosen for synthesis of nanocomposites. In Fig. 3 the nanocomposites with the molar ratio of PEG to metal (1:1) have been shown. Therefore, particles with proper size distribution was produced.

To elucidate the more details of shape and grain size of the NiWO₄/CdO nanocomposites prepared (sample no. 3), transmission electron microscopy (TEM) analysis was performed. The TEM images (Fig. 4) indicate that quasi-spherical NiWO₄/CdO nanocomposites with diameter in range of 32–57 nm are sintered together.

Production of nanostructures (Fig. 5) have been shown in XRD pattern of NiWO₄ nanoparticles gained with the molar

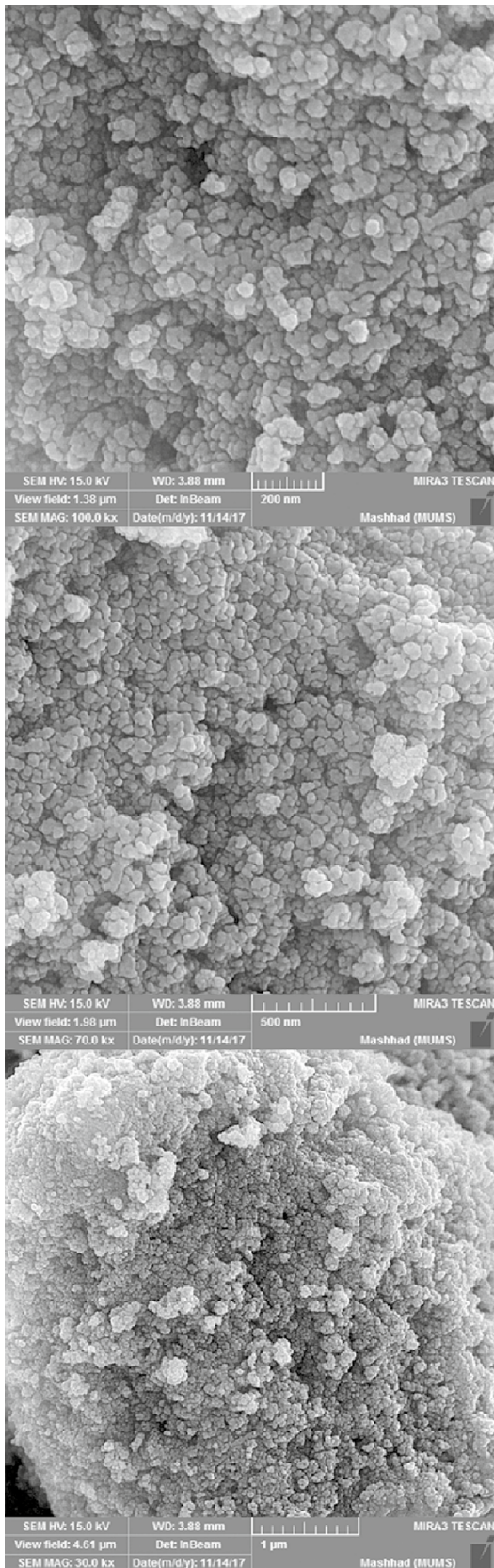


Fig. 1 SEM images of NiWO_4 nanoparticles obtained with the molar ratio of PEG to metal (0.5:1) (sample no. 1)

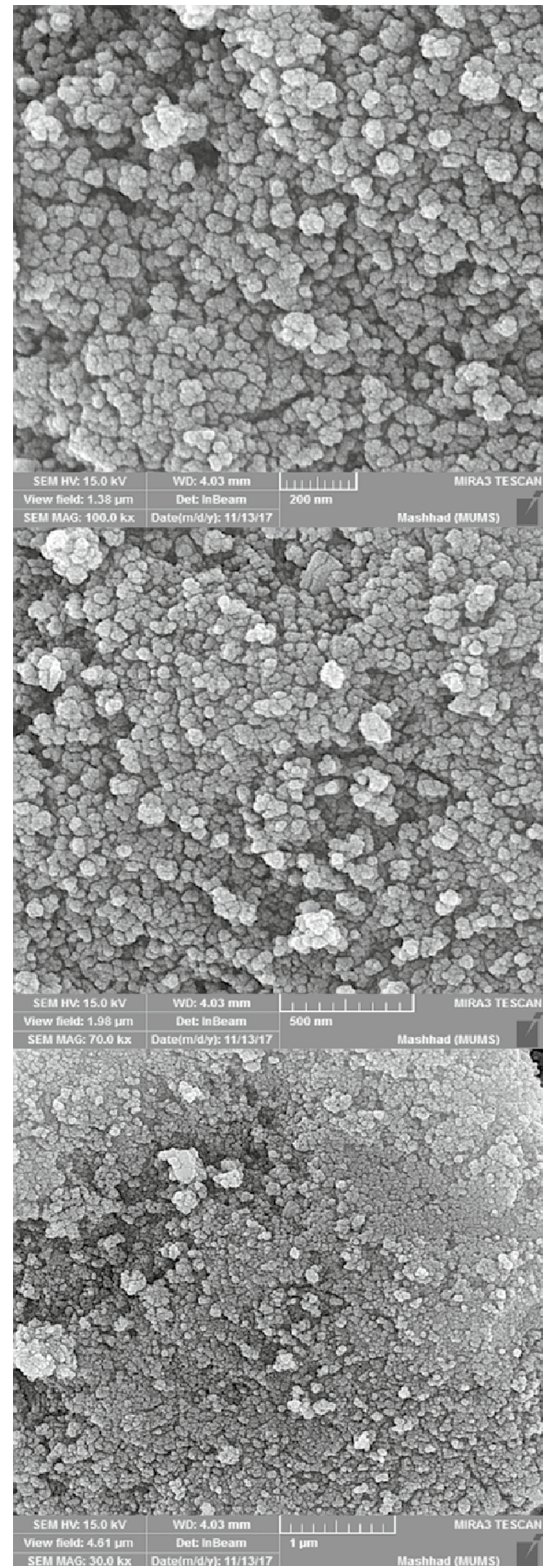


Fig. 2 SEM images of NiWO_4 nanoparticles obtained with the molar ratio of PEG to metal (1:1) (sample no. 2)

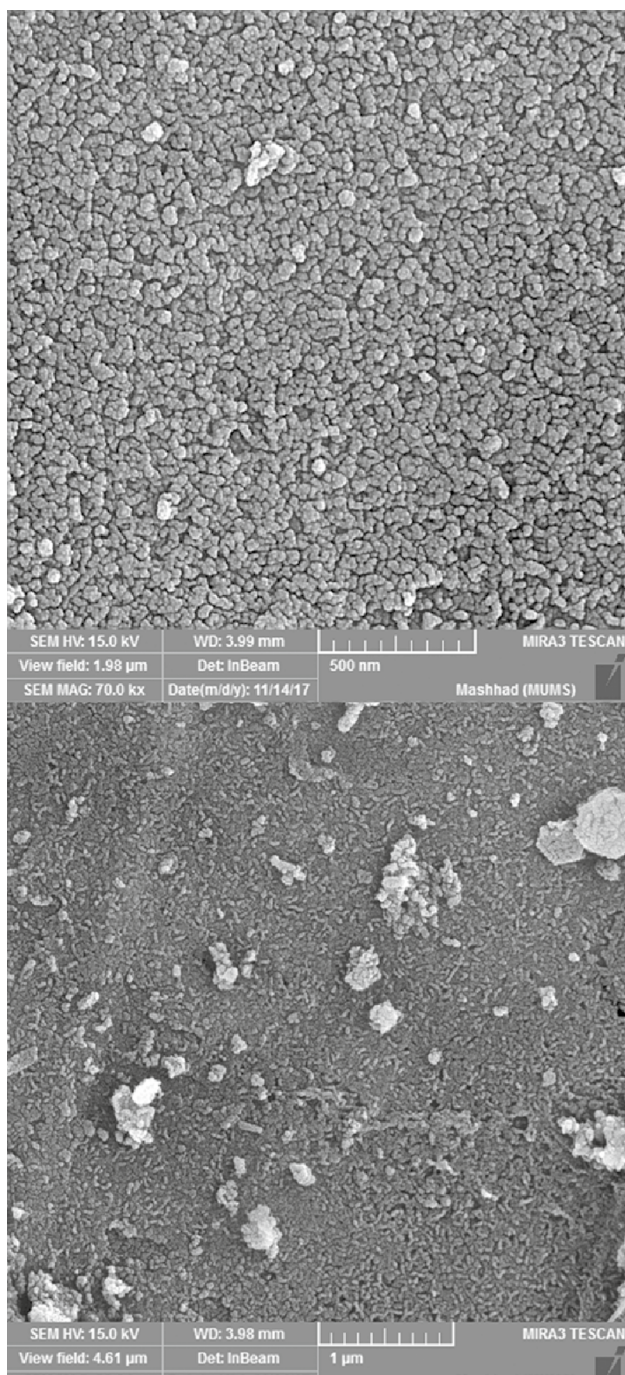


Fig. 3 SEM images of NiWO₄/CdO nanocomposites obtained with the molar ratio of Ni²⁺ to Cd²⁺ (1:1) in the presence of capping agent PEG (sample no. 3)

ratio of PEG to metal (1:1) (sample no. 2). Then, The XRD pattern of NiWO₄/CdO nanocomposites with the ratio of Ni²⁺ to Cd²⁺ (1:1) and with the molar ratio of PEG to metal (1:1) have been displayed in Fig. 6 (sample no. 3).

As our findings show, all prepared nanocomposites are pure and have two phases including, the phase of NiWO₄

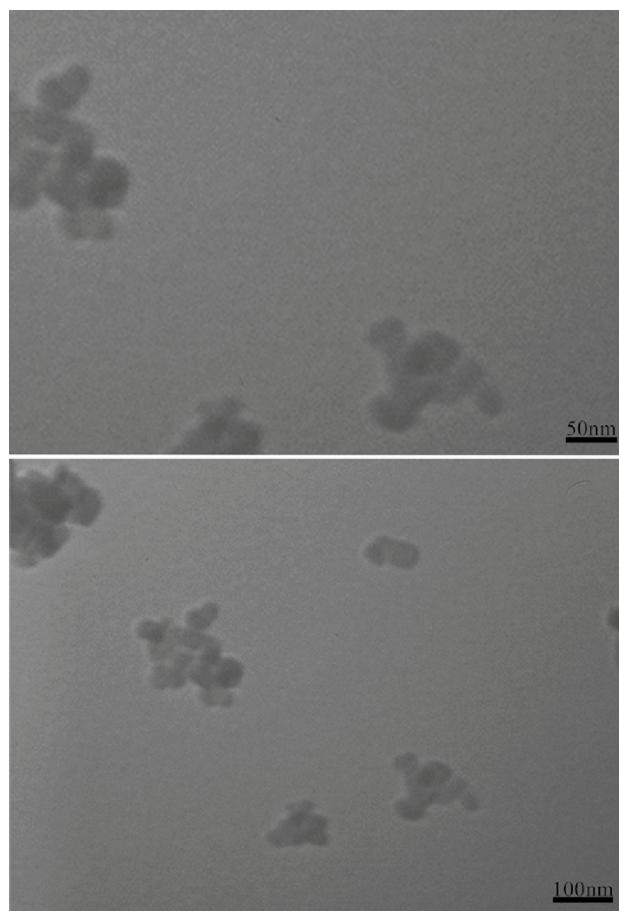


Fig. 4 TEM image of NiWO₄/CdO nanocomposites obtained with the molar ratio Ni²⁺ to Cd²⁺ (1:1) in the presence of capping agent PEG (sample no. 3)

and CdO with crystal structure of monoclinic (JCPDS 15-0755) with space group *P2/c* and cubic (JCPDS 75-0592) with space group *Fm-3m* respectively. Considering Figs. 5 and 6 and Scherrer equation, the crystallite diameter (D_c) of products can be obtained as following:

$$D_c = K\lambda/\beta \cos \theta; \quad (2)$$

In which K is the so-called shape factor, which commonly takes a value of approximately 0.9, β is the breadth of the noticed diffraction line at its half intensity maximum, and λ is the wavelength of X-ray source applied in XRD. The domain sizes of evaluated crystalline have been found out to be 22.6, and 25.4 nm, respectively.

The magnetic properties of NiWO₄/CdO nanocomposites that calcined at 500 °C have been studied by vibrating sample magnetometer (VSM) method (Fig. 7, sample no. 3). The VSM data demonstrated that the NiWO₄/CdO nanocomposites have paramagnetic properties and the magnetization of products is about 0.12 emu/g at room temperature.

Fig. 5 XRD pattern of NiWO₄ nanoparticles obtained with the molar ratio of PEG to metal (1:1) (sample no. 2)

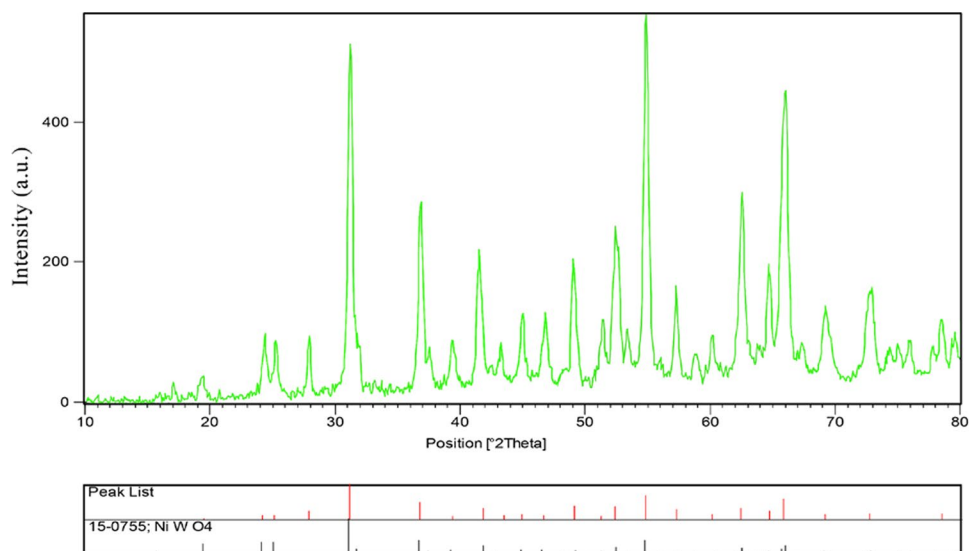
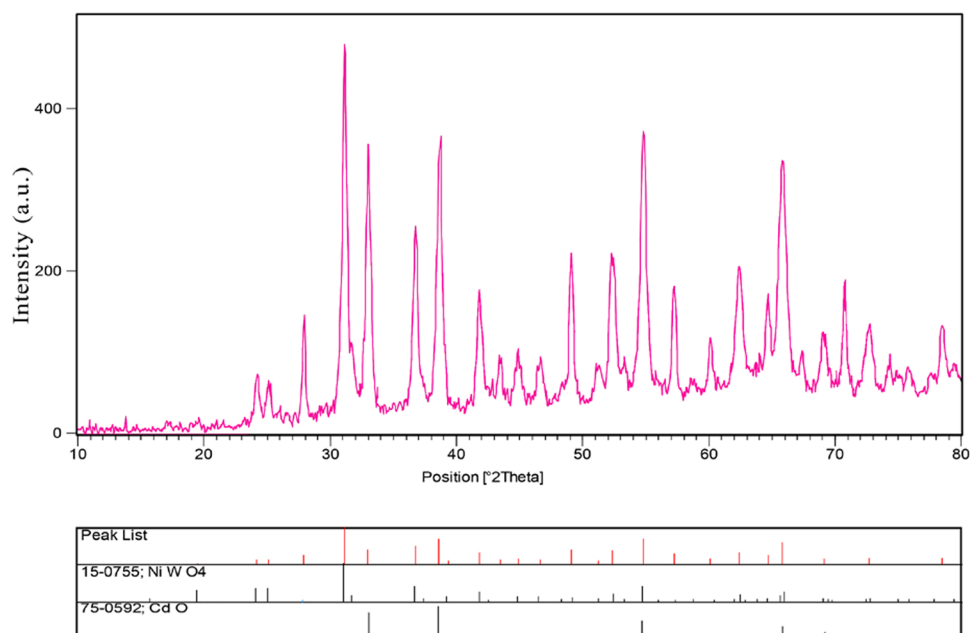


Fig. 6 XRD pattern of NiWO₄/CdO nanocomposites obtained with the molar ratio of Ni²⁺ to Cd²⁺ (1:1) in the presence of capping agent PEG (sample no. 3)



The NiWO₄/CdO nanocomposites are well known that the band-gap of the nanostructures materials plays a key role in utilizing photocatalytic applications. Given that the band-gap of the materials has a critical role in there photocatalytic applications, the diffuse reflectance spectroscopy (DRS) of NiWO₄/CdO nanocomposites (Fig. 8) was obtained and used for determining the band-gap value (E_g) based on the equation below:

$$(Ah\nu)^n = (h\nu - E_g) \quad (3)$$

In which $h\nu$ represents the photon energy, B is a constant value, A is the absorbance, and n is a constant which depends on the nature of the electronic transition. Using

extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ curve in return $h\nu$ to the energy axis, the energy gap of the samples (E_g) was found. The value of band-gap (E_g) for NiWO₄/CdO nanocomposites was 2.66 eV.

A photocatalytic test as blank has been illustrated in Fig. 9. To verify the stability of Rh B under ultraviolet light, the blank test was carried out without catalyst powder. The efficiency of the blank test is 4% resulting in a relatively good stability. We have displayed the impact of molar ratios of PEG to metal of (0.5:1) and (1:1) on photocatalytic behavior of the NiWO₄ nanoparticles at the temperature 500 °C (sample nos. 1 and 2). In the presence of optimum reaction conditions, molar ratios of PEG to metal of (1:1), destruction percentage was 78% at 200 min. The effect of the molar ratio

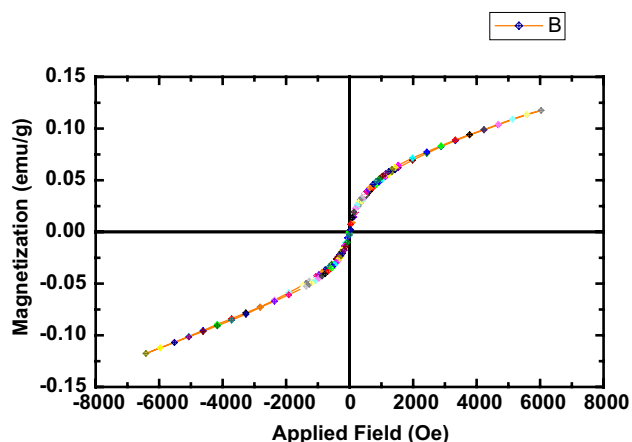


Fig. 7 VSM curve of of NiWO₄/CdO nanocomposites obtained with the molar ratio of Ni²⁺ to Cd²⁺ (1:1) in the presence of capping agent PEG (sample no. 3)

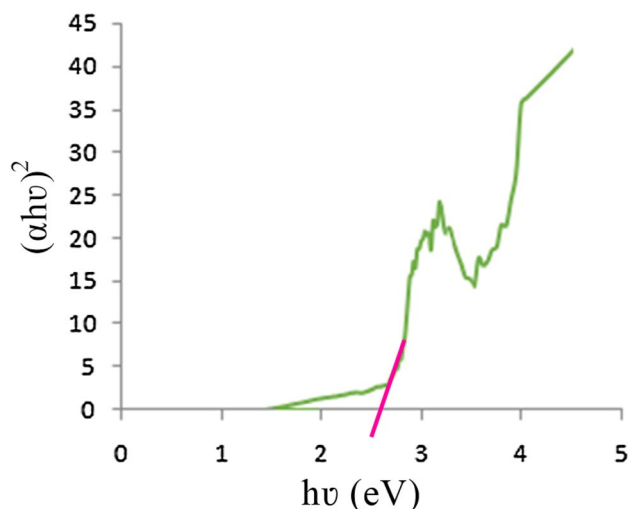


Fig. 8 Tauc plot pattern of NiWO₄/CdO nanocomposites obtained with the molar ratio of Ni²⁺ to Cd²⁺ (1:1) in the presence of capping agent PEG (sample no. 3)

of Ni²⁺ to Cd²⁺ of (1:1) and (1:2) on the Rh B destruction, has been presented in Fig. 9 (sample nos. 3 and 4). As it demonstrates, the quantities of samples are positively correlated with the percentage of destruction. The destruction rate for (1:1) and (1:2) mg of picked samples were 90, and 92% respectively. Due to an inconsiderable difference between photocatalytic activity of (1:1) and (1:2) of samples, only 2%, and tangible dissimilarity of the second samples for this behavior, the optimum and appropriate value for NiWO₄/CdO nanocomposites were chosen to be molar ratio of Ni²⁺ to Cd²⁺ of (1:1).

The probable mechanism of the photocatalytic degradation of Rh B can be summarized as follows:

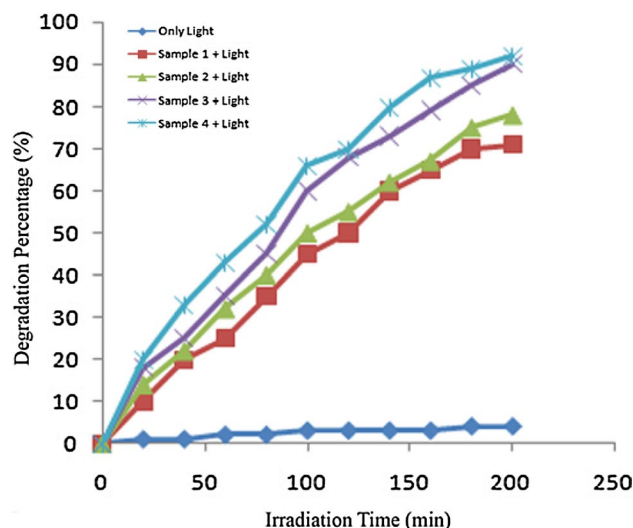
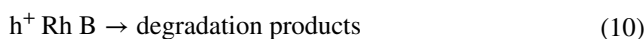
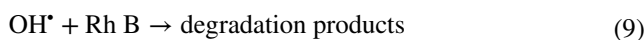
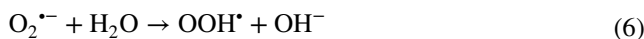
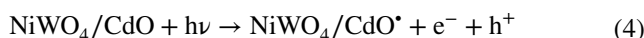


Fig. 9 The photocatalytic behavior of NiWO₄ nanostructures (sample nos. 1 and 2) and NiWO₄/CdO nanocomposites (sample nos. 3 and 4) under visible light

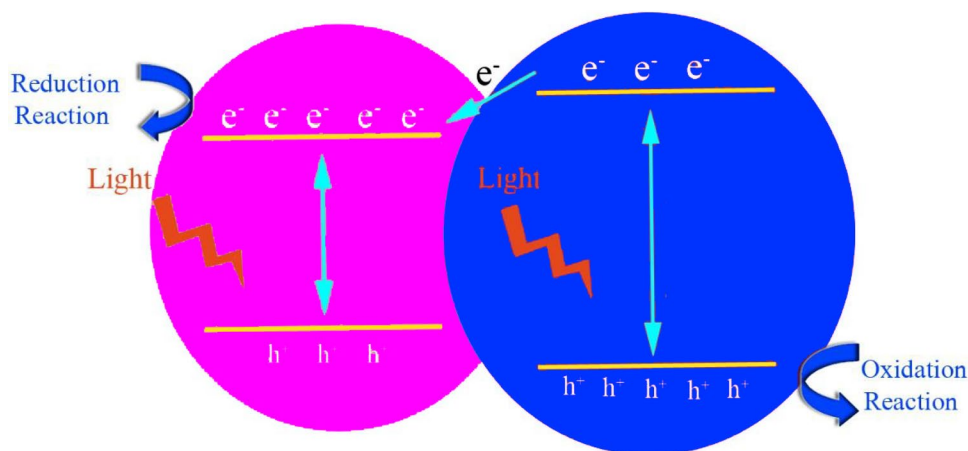


The composition procedure of contaminant for the NiWO₄/CdO nanocomposites has been shown in Scheme 1.

4 Conclusions

In summary, a new co-precipitation process has been carried out for the preparation of the NiWO₄ nanostructure and NiWO₄/CdO nanocomposites, for the first time. The synthesis of NiWO₄ nanostructure and NiWO₄/CdO nanocomposites were appraised through different parameters such as molar ratio of PEG to metal and Ni²⁺ to Cd²⁺ and reach conditions of optimum shape and size. It was found that optimum shape and size can be obtained with the usage of PEG, as a capping agent, and the molar ratio metal to PEG (1:1) and Ni²⁺ to Cd²⁺ (1:1). 90% degradation of Rh B demonstrates that as obtained NiWO₄/CdO nanocomposites is a suitable candidate in waste water purification under visible light.

Scheme 1 Schematic illustration of charge transfer in a coupled semiconductor system (NiWO₄/CdO nanocomposites)



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