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SYNTHESIS AND CHARACTERIZATION OF EUROPIUM-DOPED ZINC OXIDE NANOWIRES AS A PHOTOCATALYST

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Undoped and Eu doped ZnO Nanowires (ZnO : Eu NWs) were grown by simple and cost effective chemical bath deposition (CBD) method. The structural and morphological properties of ZnO : Eu NWs were investigated by X-ray diffraction (XRD) , SEM and EDS. EDS results show 0.35 atomic % Eu is doped by using this method. The particle size, dislocation density and strain are calculated from XRD.The photocatalytic activities of the as-synthesized sample were evaluated by the degradation of methyl orange in aqueous solution under ultraviolet (UV) light. The photo catalytic results indicate that the prepared ZnO : Eu NWs shows better photocatalytic activity than undoped ZnO NWs and it could be considered as a promising photocatalyst for dye waste water treatment.

KEYWORDS: ZnO nanowires; Eu doping**;** CBD method, Photocatalyst.

INTRODUCTION

One-dimensional (1D) nanostructures, zinc oxide (ZnO) nanowire is one of the most important materials for nanotechnology in today's research. ZnO is a semiconductor material with a direct wide band gap 3.37 eV and a large exciton binding energy 60 meV at room temperature [1]. ZnO is also biodegradable, biosafe and biocompatible, for medical and environmental applications [2]. It crystallizes in two main forms such as hexagonal wurtzite and cubic zinc blende. In recent years organic dyes in waste water have become one of the main pollutants in our daily lives. Semiconducting photocatalyst are the promising material to degrade the organic pollutants in waste water because they proved to be the highly efficient catalysts for environmental remediation and energy conversion purposes [3, 4]. In photo catalytic process, valence band holes generated by photons from light source such as UV and visible light interact with H_2O or OH^- adsorbed on the catalytic surfaces to generate hydroxyl radical (OH), and electrons in the conduction band interact with adsorbed O_2 to yield O_2^- radical**.** ZnO is a low cost, environmental friendly semiconductor material, which shows high thermal and optical stability. ZnO shows better performance in degradation of several organic contaminants in both acidic and basic media, which has stimulated many research groups to further explore the properties of ZnO in many photocatalytic reactions [5-7]. Due to its wide band gap at RT it is suitable as a host matrix for optically active impurities like rare-earth

ions. RE doped semiconductors have been studied for their potential use in integrated optoelectronic devices and photocatelyst [8-9]. In these materials, the excitation of the RE cations occur by the recombination of photo generated carriers of the ZnO and energy transfer from the semiconductor to the RE ions [10]. Eu doped ZnO (ZnO : Eu) NWs synthesized by chemical bath deposition (CBD) shows better photocatalytic activity than undoped NWs [11]. The photocatalytic activities of the as-synthesized undoped and Eu doped samples for the methly orange photodegradation were investigated and discussed.

Experimental details

All the reagents involved in the experiments were of analytical (AR) grade and were utilized without further purification. ZnO : Eu NWs were grown on glass slides via a two-step chemical process. In the first step, a thin seed layer of ZnO nanoparticles was prepared on glass substrate by sol-gel method by ethanolic solutions of 0.375 M zinc acetate dehydrate and monoethanolamine (MEA). For undoped ZnO NWs 25 mM zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) in molar ratio 1 : 1 is dissolved in deionized water (DI). For Eu doping zinc nitrate: europium oxide (97% : 3%) were mixed in DI water and seeded substrate immersed in the prepared aqueous solution for 5h at temperature 95°C in CBD. The crystal structure of ZnO : Eu NWs was characterized by XRD, Bruker/Lynx Eye 1D-PSD and SEM images were taken on a JEOL JSM-5600.

Photo-catalytic experiments were carried out using a home-made photo-reactor and a 340 W mercury lamp for UV radiation. In a typical experiment, 100 mL of aqueous Methyl Orange(MO) with an initial concentration of 10 mgL^{-1} (pH 7.0, maintained by added NaOH or HCl) were placed in a beaker, the photo catalyst (10mg L^{-1}) added and the suspension stirred for 30 min in the dark, at room temperature, to ensure the establishment of the adsorption/desorption equilibrium. The UV lamp was turned on while the suspension was magnetically stirred. At fixed intervals of time, 3 mL of sample were withdrawn, centrifuged, and the transferred into a spectrophotometer cell for measurement of the absorbance of MO. Absorbance measurements were also recorded in the range of 250-650nm, using a UV-Vis spectrophotometer.

Finally, photocatalytic degradation efficiency (PDE) of MO solutions was calculated with the following formula:

$$\mathrm{PDE}(\%) = \frac{A_0 - A}{A_0} \times 100 \quad \ldots (1)$$

where, A_0 and A are the UV–Vis absorption of MO solution at time t = 0 and after time t respectively.

Result and discussion

X-ray diffraction (XRD) is used to investigate the phase structure and lattice parameters of the undoped and ZnO : Eu NWs. XRD pattern recorded in the 10°–70° range. The pattern matches the lattice spacing of crystalline ZnO in the wurtzite structure having space group : $P6_3mc$. The high intensity of the ZnO peaks relative to the background clearly indicates good crystallinity of the undoped and doped samples. To confirms the possible substitution of Zn ions with Eu ions in ZnO : Eu NWs, the angle shift of 2 theta for the ZnO (101) peak as a function of doping was observed. This peak shifting may be attributed to the lattice mismatching, lattice distortion, strain of the crystal. Particle size, strain, dislocation density

and some other physical quantities are calculated by XRD for undoped and ZnO : Eu NWs are given in Table 1.

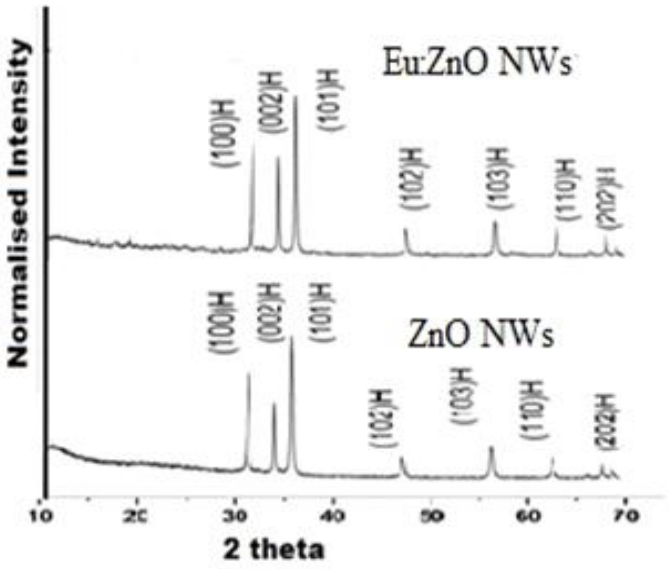

Fig. 1. XRD of undoped and Eu doped ZnO NWs

Both the samples showed a single-phase nature with a hexagonal wurtzite structure. The average grain size (D) of the sample is calculated with the help of Scherrer formula using the diffraction intensity of (101) peak .

$$D = k\lambda/(\beta \cos\theta) \quad \ldots (2)$$

where λ is the X-ray wavelength, β the full width at half maximum (FWHM) of the ZnO (101) line and θ is the diffraction angle. The broadening of the diffraction peaks is an indication that the synthesized materials are in nanometer regime. Strain and dislocation density values compiled in Table 1 were calculated by the following formula:

$$\text{strain} \quad \varepsilon = \beta . \text{Cot} \square / 4 \ (\text{lin}^{-2}\, m^{-4}) \quad \ldots (3)$$

$$\text{dislocation density } \delta = 1/D^2 \ (\text{lin}\ m^{-2}) \quad \ldots (4)$$

Table 1. Value of particle size, strain, dislocation density calculated from XRD

Sample	2(theta)	hkl	d(A^0)	A(A^0)	FWHM (Degree)	Crystalline size D (nm)	Strain	Dislocation density
Eu: ZnO NWs	36.355	(101)H	2.47E-6	3.5E-6	0.305	25.8	0.0047	4.3E+12
Undoped ZnO NWs	36.399	(101)H	2.47	3.49	0.5	16.3	0.0066	3.57E+15

Morphologies of the pure and ZnO : Eu NWs samples were characterized by the SEM are shown in Fig. 2.

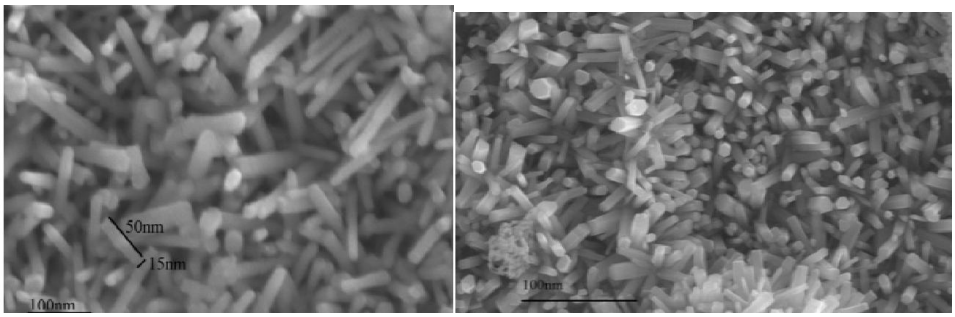

Fig. 2. (A) SEM of Undoped ZnO NWs (B) SEM of Eu : ZnO NWs

Doping of Eu in Zno NWs prepared by CBD method is confirmed by the given EDS spectra in Fig. 3.

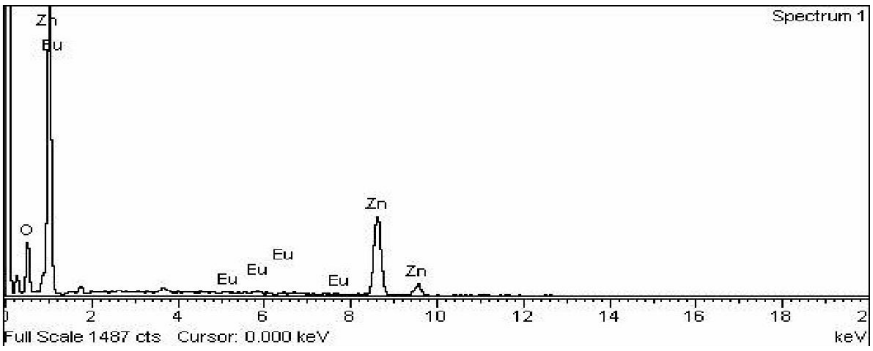

Fig. 3. EDS of ZnO : Eu NWs thin film

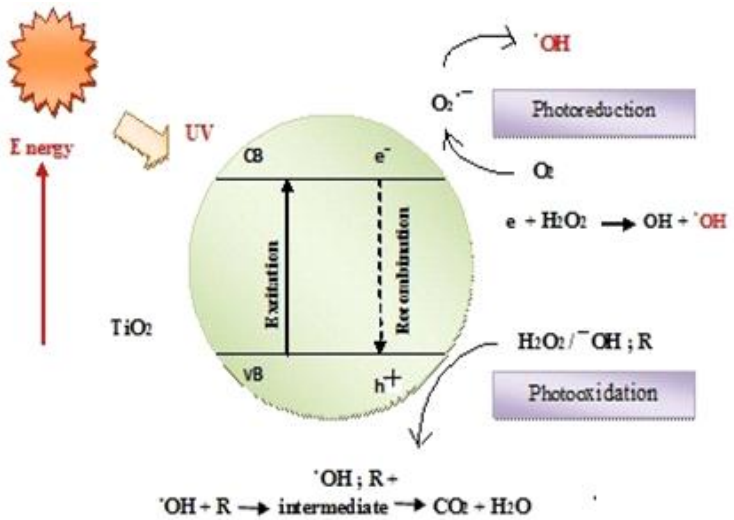

Fig. 4. Mechanism of photocatalysis activity [15]

Photocatalysis utilizes semiconductor photocatalysts as ZnO and ZnO : Eu NWs to carry out a photo-induced oxidation process to break down organic contaminants , pollutants and inactivate bacteria and viruses [12-14]. Fig. 4 illustrates the process of photocatalysis [15]. When photons with energies greater than the band gap energy of the photocatalyst are

absorbed, the valence band (VB) electrons are excited to the conduction band to facilitate a number of possible photoreactions. The photocatalytic surface with sufficient photo energy leads to the formation of a positive hole (h+) in the valence band and an electron (e−) in the conduction band (CB). The positive hole could either oxidize organic contaminants directly or produce very reactive hydroxyl radicals (OH•). The hydroxyl radicals (OH•) act as the primary oxidants in the photocatalytic system [16], which oxidize the organics. The electron in the conduction band reduces the oxygen that is adsorbed on the photocatalyst. Heterogeneous photocatalysis using semi-conductors is an effective method to destroy a wide range of organic pollutants at ambient temperatures and pressures [17, 18].

To evaluate photocatalytic activity of undoped and ZnO : EuNWs samples, degradation of MO under UV light irradiation was considered. Fig.5 shows the variation of absorbance versus wavelength for the degradation reaction on undoped and ZnO : Eu NWs. It is evident that MO has some small absorption peaks in visible range and a large absorption peak in the UV range. Under the light irradiation, intensity of the absorption peaks gradually decreases without any changes in position of the peaks.

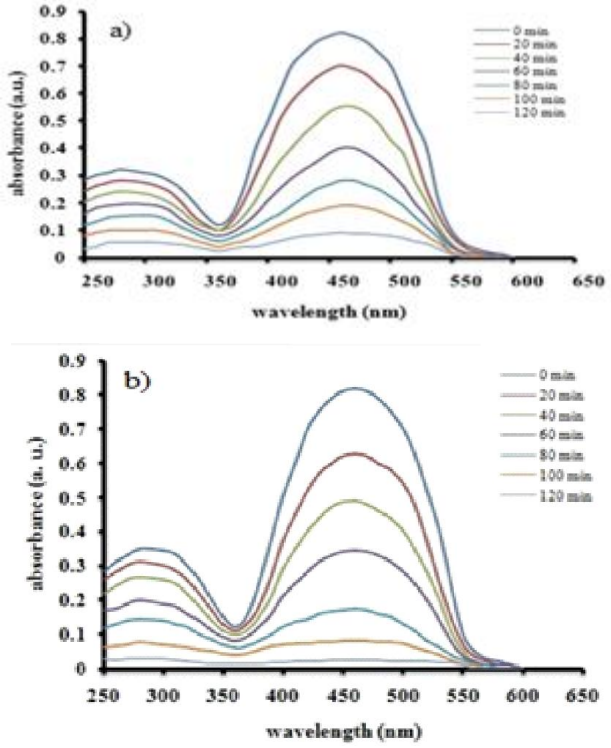

Fig. 5. UV-vis spectra in various times for degradation of MO with (a) Undoped ZnO NWs thin film and (b) ZnO : Eu NWs thin film.

Figure 5(a) shows that the photo catalytic activity of undoped sample shows the degradation of MO is 14% after 20 min irradiation and after 120 min the PDE (%) is 87%. ZnO : Eu NWs sample shows the highest photocatalytic activity, and more than 97% of MO molecule was decomposed in 120 min. Fig. 5 (b) shows MO degradation by the ZnO : Eu NWs catalysts synthesized by 23% after 20 min . However, after the irradiation for 120 min, the peaks nearly disappeared; achieving 97% degradation in this case.

Conclusions

The characterization result show that the as-synthesized undoped and ZnO : Eu NWs as a photo catalyst belong to the hexagonal wurtzite structure. The photocatalytic activities of the as-synthesized nanostructure have been evaluated by the degradation of MO in aqueous solutions under UV-light irradiation. The MO decolorization efficiency of ZnO : Eu synthesized by CBD method is achieved at 97% within 120 min, higher than that of the undoped ZnO NWs.

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