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APPLICATION OF EUROPIUM-DOPED ZNO NANOWIRES AS A PHOTOCATALYST

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ABSTRACT

Eu doped ZnO Nanowires (ZnO:Eu NWs) were grown on glass substrate by simple and cost effective chemical bath deposition (CBD) method. The structural properties of ZnO: Eu NWs were investigated by X-ray diffraction (XRD) , for different concentration of Eu in ZnO:Eu NWs. Maximum shifting of 2θ is observed for 3% Eu doping . Nanowire structure is observed in SEM of the undoped and Eu doped NWs samples. The photocatalytic activities of the as-synthesized sample were evaluated by the degradation of methyl orange in aqueous solution under ultraviolet (UV) light for different time interval of absorption. The photo catalytic results indicate that the as prepared ZnO:Eu NWs of maximum doping shows better photocatalytic activity than undoped ZnO NWs.

Keywords: ZnO nanowires; Eu doping**;** Photocatalyst.

1. Introduction:

ZnO is a semiconductor material with a direct wide band gap 3.37 eV and a large exciton binding energy 60meV at room temperature [1]. One-dimensional (1D) nanostructure, zinc oxide (ZnO) nanowire is one of the most important materials for nanotechnology in modern research. 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 present in 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 interact with water(H_2O) or hydroxyl ion($OH^{-)}$ 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 photocatalyst. The RE ions of lanthanide series such as Sm3+, Nd3+,La3+, Dy3+, and Ce3+ are promising material in photocatalytic activities than pure ZnO [8-10]. 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. 0.35% Eu doped NWs thin film among the different %Eu in 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(MO) photodegradation were investigated and discussed. Doping of Eu delay the recombination rate of the electron-hole pairs which is very important to eliminate the organic dye pollutants in waste water [12].

2. 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 0.375M 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 is used as 99%:1%,98%:2% and 97%:3% were mixed in DI water and seeded substrate immersed in the prepared aqueous solution for 5h at temperature 95

^{0}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:

$$PDE(\%) = (A_0\text{-}A)/ A_0 \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where, A_0 and A are the UV–Vis absorption of MO solution and MO solutions in suspension after time t.

3. Result and discussion:

X-ray diffraction (XRD) is used to investigate the phase structure and lattice parameters of the undoped and ZnO: Eu NWs of zinc nitrate: europium oxide in 99%:1%,98%:2% and 97%:3%. XRD pattern for different concentration of 1%Eu, 2%Eu and 3% Eu is recorded in the 10°–70° range. The diffraction peaks of undoped ZnO sample appeared at 2θ = 31.82∘, 34.48∘, 36.30∘, 47.58∘, 56.62∘, 62.88∘,66.40∘, 68.00∘, and 69.12∘ which were, respectively, identified to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) diffraction planes of wurtzite hexagonal ZnO structure in accordance with the database of the JCPDS number 36–1451 [8]. The XRD pattern matches the lattice spacing of crystalline ZnO in the wurtzite structure having space group:P63mc. The high intensity of the ZnO peaks clearly indicates good crystallinity of the undoped ZnO NWs and different %Eu doped ZnO NWs samples. The possible substitution of Zn ions with Eu ions in all ZnO: Eu NWs, the angle shift of 2ɵ as a function of doping was observed. This peak shifting may be attributed to the lattice mismatching of the crystal.

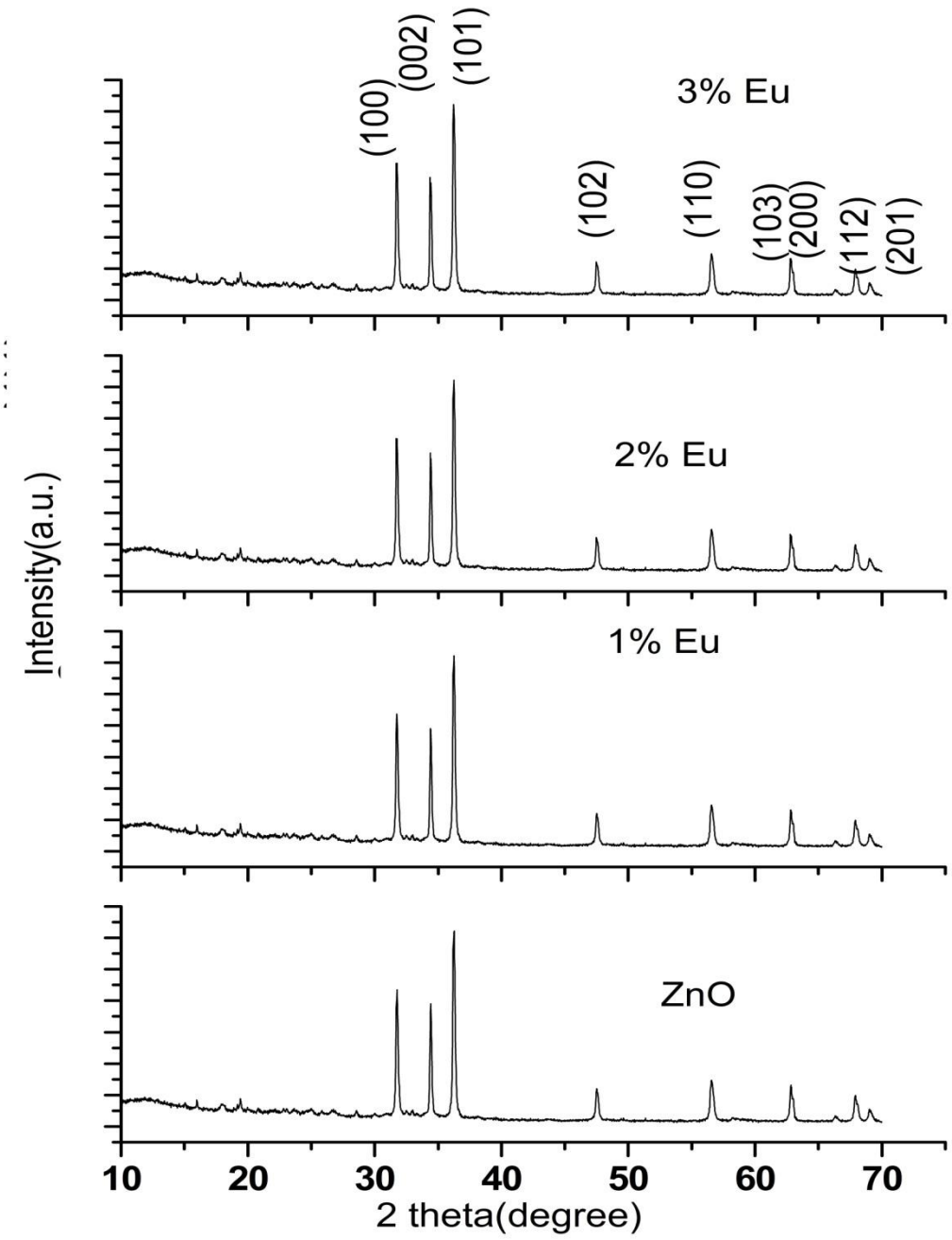

Fig.1 XRD patterns of the as-synthesized undoped ZnO NWs and Eu-doped ZnO NWs of zinc nitrate: europium oxide in 99%:1%,98%:2% and 97%:3%. at 2θ of 10∘–70∘ synthesized by CBD for 5 h

The broadening of the diffraction peaks is an indication that the synthesized materials are in nanometer regime.

Morphologies of the pure and ZnO:Eu NWs of 3% Eu doping samples were characterized by the SEM are shown in Fig:2.

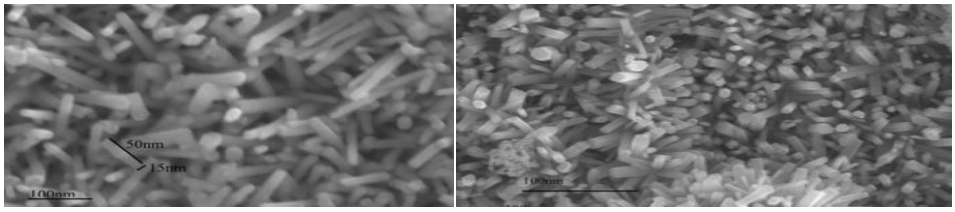

Fig:2: (A) SEM of Undoped ZnO NWs (B) SEM of (97%:3%) of ZnO:Eu NWs sample

Doping of Eu in Zno NWs prepared by CBD method is confirmed by the given EDS spectra of (97%:3%) ZnO:Eu NWs sample in Fig.3.Eds spectra shows that maximum 0.35atomic% of Eu is doped via CBD method at 95^0C of bath temperature.

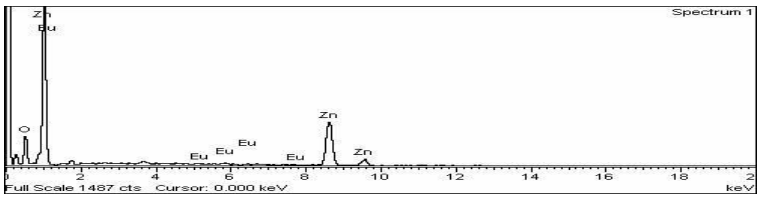

Fig.3: EDS of ZnO:Eu NWs thin film

Photo catalysis utilizes semiconductor photocatalysts as ZnO and (97%:3%) 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].

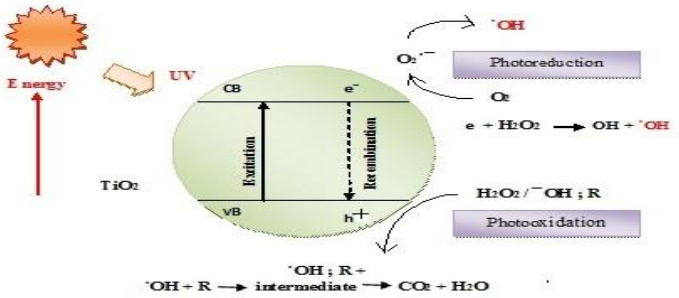

Fig.4: Mechanism of photocatalysis activity [15]

To evaluate photocatalytic activity of undoped and (97%:3%) 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 (97%:3%) 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.

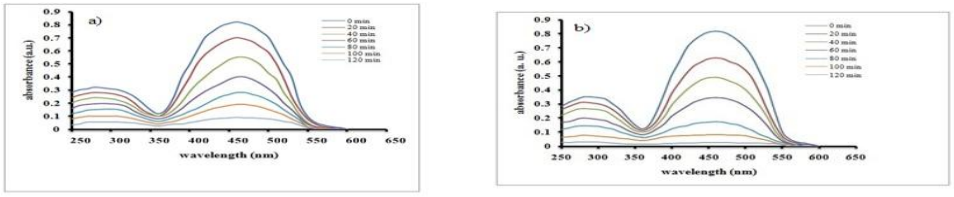

Fig. 5: UV-vis spectra in various times for degradation of MO with (a) Undoped ZnO NWs thin film and (b) ZnO:Eu NWs thin film.

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 120min, higher than that of the undoped ZnO NWs

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