Fabrication, structural and optical properties of Ni and Cr doped ZnO nanocomposites for photocatalyst under UV light

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Abstract: *This report deals on the construction of undoped and Ni, Cr co-doped ZnO (NCZ) nanocomposites (NCs) which were prepared by facile precipitation method. Also, the investigations of their structural, optical, luminescence and photocatalytic performance were performed via XRD, SEM, UV-Vis DR Spectroscopy, PL Spectroscopy and photocatalytic activity respectively. Undoped and 5 M% of Ni and Cr co-doped ZnO NCs show the medium structural effect and they have uniformly distribution in their morphology. Optical bandgap has a blue shift from 3.19 eV to 2.99 eV, which is a desirable property for electronics and photocatalytic properties. A broad photoluminescence peak appears in NCZ around 515nm which corresponds to blue-green emission range, hence it is useful for optoelectronics devices specifically blue LEDs. Enhanced photocatalytic activity is seen in the NCZ nanocomposites and it takes 240 mins to degrade the 82% of MB dye. This photocatalytic activity of NCZ NCs is higher than undoped and doped nanomaterials.*

Keywords**: **ZnO Nanocomposites, Ni, Cr co-doped, Blue emission, Photocatalyst

1. Introduction

Semiconductor photocatalysis and electronics has attracted wide research interest because, it has emerged as one of the most promising elucidations for functionalities of desirable electronics, environmental problems related to organic pollutants as well as toxic contaminants in water and air. Among the metal oxides, TiO_2 has been studied widely owing to its superior photocatalytic properties [1], whereas other metal oxides have received less attention. Zinc oxide (ZnO) has a significant wide and direct bandgap semiconductor ((~3.3eV) binding energy 60 meV)) compared to TiO_2 and has been used as an environmental photocatalyst under UV light irradiation. Also its high catalytic efficiency, low cost, and environmental sustainability, high stability, make it suitable for applications in water and air purification, optoelectronics and so forth [1-2]. In this work, Ni and Cr doped ZnO NCs were prepared through precipitation method which is a simple, low temperature and eco-friendly synthesis way. The photodegradation of methylene blue (MB) was used to evaluate the photocatalytic performance of the materials. This surface modification induces an increase of the absorption properties of UV light. And a possible mechanism of photocatalysis under UV and visible light was also discussed.

2. Synthesis

Zinc nitrate (0.1M), nickel nitrate (0.005M) and chromium nitrate (0.005M) were dissolved in 50 ml of ethanol and 50ml of deionized water mixture through continuous stirring for 8 hours at 50°C. Simultaneously, 0.1g of PVP and 0.1g of citric acid were added in the solution as a stabilizer, and reaction catalyst also. Moreover 0.3M of NaOH is added to the particular solution for which the pH value was conserved at 10, with resulting in a blue dark precipitate and it has aged through overnight [2]. This solution was heated by microwave oven at 600W for 10mins with ultrasonication for in 30 mins to get dispersed nano materials. The obtained product was placed in a hot air oven at 150°C for 10 hours, finally, it is moved to anneal in the furnace at 550°C for 3hr to stabilize the nanomaterials. A similar procedure was followed to synthesis undoped ZnO, Ni doped ZnO and Cr doped ZnO nanomaterials. Prepared samples are labelled as follows; (Ni:Cr-0M: ZnO (PZ), Ni-0.005M: ZnO (NZ), Cr-0.005M: ZnO (CZ) and Ni-0.005M: Cr-0.005M: ZnO (NCZ)).

3. Results and Discussion

3.1 Structural analysis

Fig. 1 shows the XRD pattern recorded using powder X-ray diffractometer (Rigaku miniflex II) of all samples. XRD spectra show broad peaks at the positions of (100) and (101) which are in good agreement with the standard ZnO (JCPDS Card file 36-1451, a = b = 3.249 Å, c = 5.206 Å) and indexed to the hexagonal wurtzite structure [3]. Furthermore, it can be seen in doping materials (NZ, CZ and NCZ) there is no change in the ZnO peaks with the existence of Ni and Cr peak, which indicates Ni and Cr ions are present with the Zn oxides lattices (JCPDS card file (NiO-71-1179) and (CrO-89-3079)). XRD pattern show good crystallinity, and there is no other impurity peaks are observed, hence the synthesized NPs have single-phase sample formation.

Table.1 Structural parameters of undoped and Ni, Cr doped ZnO nanocomposites

S. No	Samples	Crystalline size (nm)	Lattice Parameters	
			a=b (nm)	c (nm)
1.	PZ	44.5	3.2710	5.2075
2.	NZ	33.5	3.2626	5.2204
3.	CZ	33.6	3.2641	5.2338
4.	NCZ	25.6	3.2508	5.2331

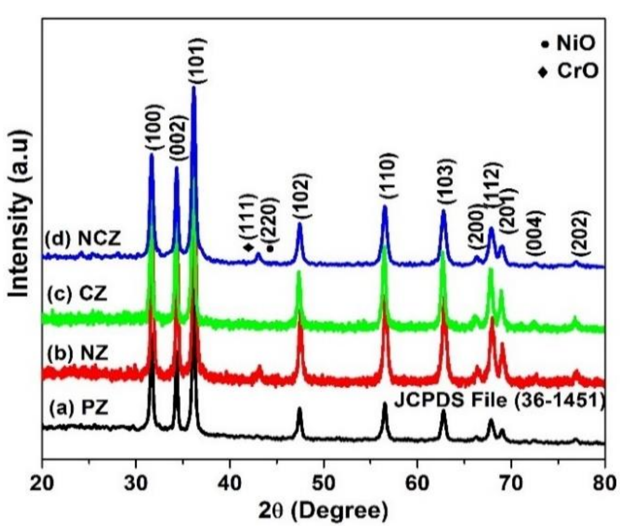

Fig. 1 XRD pattern of prepared samples

Furthermore, it can be seen in doping materials (NZ, CZ and NCZ) there is no change in the ZnO peaks with the existence of Ni and Cr peak, which indicates Ni and Cr ions in the Zn oxides lattices and it will be confirmed to JCPDS card file (NiO-71-1179) and (CrO-89-3079) also. XRD pattern show good crystallinity [3], and there is no other impurity peaks are observed, hence the synthesized NPs have single-phase sample formation. The crystallite size was estimated using Scherrer's formula ($D = \frac{k\,\lambda}{\beta \cos\theta}$), Where, β = full width half maximum (FWHM), K = grain shape dependent constant (0.9), λ = wavelength of incident beam (1.5406 Å), θ = Bragg Reflection angle in degree. The deduced crystallite sizes are ranging from 44-25nm for different NPs (Table 1).

3.2 Morphology and analysis

Scanning Electron Microscopy (SEM) is one of the capable techniques for the surface analysis of the samples and to investigate the size also. Using SEM - JEOL Model JSM 6390LV, the surface morphology of the NCZ nanocomposites were recorded and shown in Fig 2. The entire SEM images obviously show the average sizes of the nanoparticles are in nanometer scale. It is observed that the synthesized nanoparticles are uniformly distributed throughout the surface. These images revealed that grown nanoparticles were almost in spherical shape.

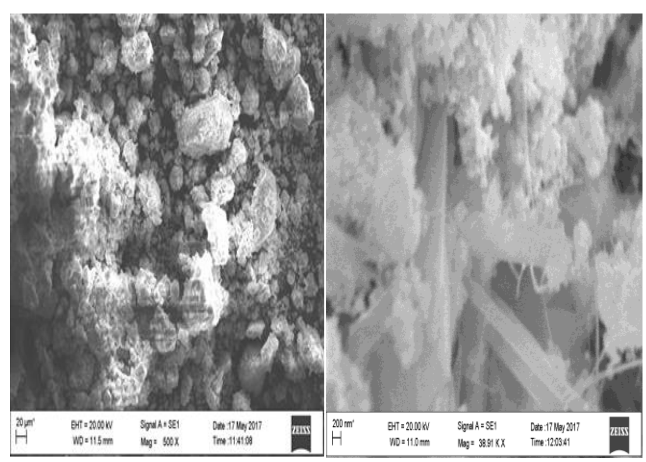

Fig.2.SEM images of NCZ samples

3.3 UV- Vis DR Spectroscopy

The absorption spectra (Fig.3) of all prepared samples are analyzed using UV- Vis Spectroscopy (Ocean Optics USB4000 Spectrophotometer). The cut-off wavelength for PZ is 243 nm, whereas all other doping nanoparticles have much more defect of red shift upto 250, 252 and 261nm also. The doping metal ions with their electron density in ZnO leads to change in the conduction band level of the nanoparticles and give modification to the particular bandgap.

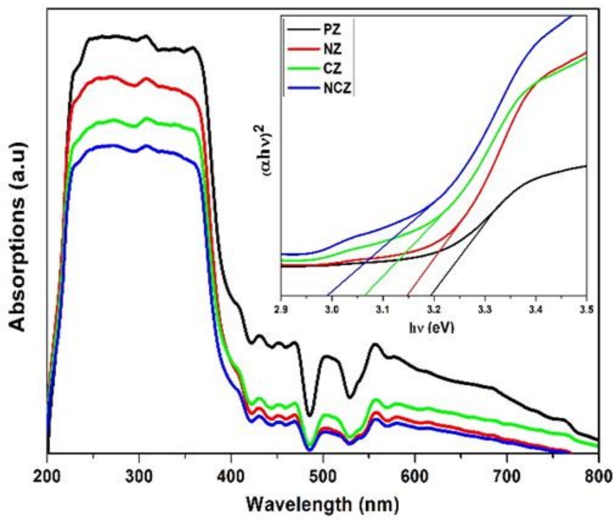

Fig.3 Optical absorption spectra and bandgap evaluation (insert)

These shifts towards the higher energy wavelength of UV- light suggesting the bandgap narrowing in the doped compounds which is confirmed via tauc plot analysis of spectroscopic data (Fig 4). The tauc plots are drawn using Tauc equation $(\alpha h\nu)^2 = A\ (h\nu - Eg)$, where, ν is the frequency of light, A is a constant, h is the planck's constant, and Eg is energy bandgap of the material. The bandgap calculated for the PZ, NZ, CZ and NCZ nanocomposites were 3.19, 3.15, 3.06 and 2.99eV respectively. It is observed that the bandgap decreases with adding the dopant ions. The percentage of dopant material is playing a vital role in the determination of the bandgap, and this tuning at bandgap can be applied to design colour LEDs in the field of photo electronics and photocatalyst.

3.4 Photoluminescence Spectroscopy

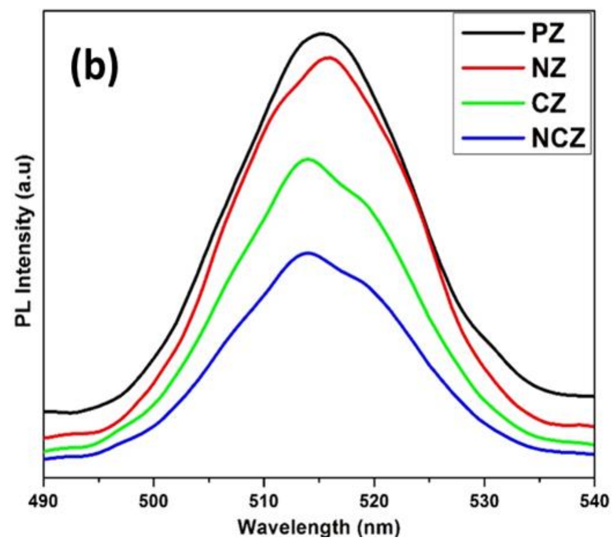

Fig. 4 PL spectra of prepared samples

PL Spectroscopy is an effective technique to study the electronic band structure and charge carrier trapping which is carried out by Perkin Elmer LS45 spectrometer. All the samples have sharp emission (Fig.4) band around 515nm in the blue-green region due to the emission from band to band transition (Excitation wavelength λ = 360nm). And they are related to non-stoichiometric intrinsic defects and the same may be caused by the occurrence of oxygen vacancy can occurred [6]. Likewise, Ni and Cr co-doped ZnO material is exhibiting the low intensities, which means good probability of electron-hole recombination, which allows it for numerous applications like sensing, LEDs and photocatalyst.

3.5 Photocatalytic activity

To investigate the photocatalytic activity of the as-prepared PZ, NZ, CZ and NCZ nanomaterials 0.1g of catalyst was added into a 100-mL of millipore water with 20ppm of MB solution and kept ready for the degradation process. A high-pressure halogen lamp with the biggest emission wave of 365 nm was used as the UV light source.

3.5.1 The degradation process of MB

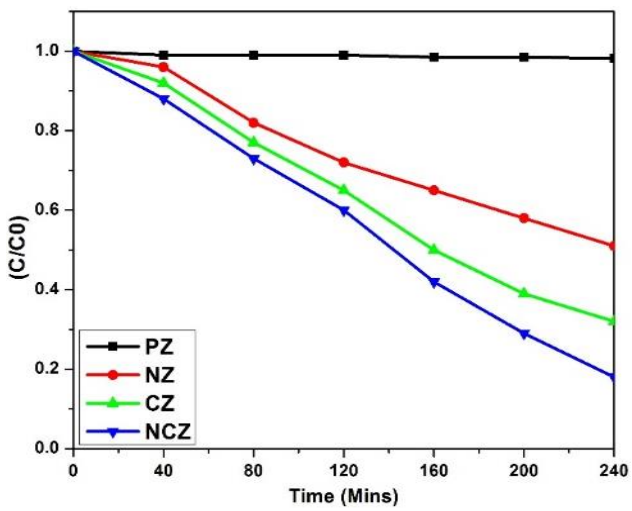

Fig.5 Photocatalytic degradation efficiency of MB dye under UV light in 240 Mins

$$(D\%) = \frac{C_0 - Ct}{C_0} * 100 \quad \text{----- (1)}$$

To realize and elucidate the changes occurred in molecular structure of MB in the presence of nanocomposites under UV light irradiation, UV–Vis spectra changes were recorded in the dye solution over various time intervals. The main absorption peak of MB molecule locating at 664 nm in the presence of valuable NCZ nanocomposites decreases rapidly with extension of the exposure time. The undoped, NZ and CZ nanocomposites have degraded 61 % of MB in 240 mins, and the NCZ NCs has the degradation of 82% at the same time. Decomposition efficiency (Fig. 5) is calculated using the formula (eqn.1).

The decomposition efficiency of NCZ nanocomposites was comparatively higher than the others. Reaction kinetics of NCZ nanocomposites being higher than undoped ZnO nanocomposites. Reaction mechanism as follows (eqn 2-5) [5-7]

$ZnO + h\nu \longrightarrow ZnO + (e^- + h^+)$ --------- (2)
$e^- + O_2 \longrightarrow O^-_2$ --------- (3)
$h^+ + OH \longrightarrow OH^\cdot$ --------- (4)
$OH^\cdot/O^-_2 + dyes \longrightarrow CO_2 + H_2O$ --------- (5)

4. Conclusion

The Ni, Cr and co-doped ZnO NCs were synthesized by precipitation method and their structural, optical, and photocatalytic performances were investigated. The XRD pattern reveal the formation of prepared samples are hexagonal wurtzite structure with average crystalline size of ~45nm. SEM images reveal the NCZ NCs which are in spherical shape with the particles are uniformly dispersed. The UV-DRS spectra reveal that significant decreases in optical bandgap of the single doping and co-doping in Ni and Cr ions (3.19eV to 2.99eV). Interestingly, all the samples have good luminescence property with the strong blue emission at 515nm and hence they are very useful in the fabrication of LED devices and the finest electron-hole recombination are valid. Enhanced the photocatalytic activity is observed in NCZ nanocomposites which takes 240 mins to degrade the 82% of MB, under UV light.

References

[1] B. Subash, B. Krishnakumar, M. Swaminathan, and M. Shanthi Langmuir 2013, 29, 939–949

[2] Ranjani Viswanatha, Sameer Sapra, Subhra Sen Gupta, B. Satpati, B. N. Dev, and D. D. Sarma, J. Phys. Chem. B 2004, 108, 6303-6310

[3] Xianming Hou, Lixia Wang, Gu Hea Jingcheng Hao, CrystEngComm, 2012, 14, 5158–5162

[4] Xiao Liu, Baosheng Du, Ye Sun, Miao Yu, Yongqi Yin, Wei Tang, Chong Chen, Lei Sun, Bin Yang, Wenwu Cao, and Michael N. R. Ashfold ACS Appl. Mater. Interfaces 2016, 8, 16379−16385

[5] Suresh Kumar, Virender Singh Amit Tanwar, J Mater Sci: Mater Electron, 2016 27, 2166–2173

[6] V. Pandiyarasan S. Suhasini J. Archana M. Navaneethan M. Abhijit Y. Hayakawa H. Ikeda et al, Applied Surface Science, 2016, 12, 202

[7] Bappaditya Pala, D. Sarkara, P.K. Girib, Applied Surface Science 2015, 356, 804–811

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