Full length article

Synthesis, characterization and optical properties of sulfur and fluorine doped ZnO nanostructures for visible light utilized catalysis


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Zinc oxide and sulfur/fluorine doped ZnO with nanosphere structure are synthesized by facile low cost solid state route. The synthesized material was characterized using XRD (X-ray diffraction), FE-SEM (Field emission scanning electron microscopy), photoluminescence spectroscopy and electrical conductive gas sensor measurements. FE-SEM images are showing spherical aggregated particle morphology, in the case of Fluorine doped ZnO showing flaky pastry shapes and sulphur doped ZnO shows particle with aggregated morphology. DRS and absorbance spectra is utilized to calculate the band gap values of the respective sample. The as prepared materials shows efficient activity towards methylene blue dye degradation and in future it could be utilized in improved photo catalytic and dye sensitized solar cell applications.

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1. Introduction

Different kind of semiconductor metal oxide with nanostructures morphology such as TiO₂, ZnO, Fe₂O₃, ZrO₂, Nb₂O₅, Al₂O₃, and CeO₂, have been successfully reported as promising photo electrodes in the field of catalysis, solar cell and sensor applications [1–5]. Among the above-mentioned metal oxide nanostructures, the usage of TiO₂ and ZnO is of very much interesting due to potential candidates as photo electrode used in solar cell and photo catalytic applications [6–10]. However, the advantage obtained by improved surface area of the nanoparticle film is exposed by the effectiveness of charge collection by the synthetically modified electrode [11].

Compared with titania, ZnO is a wide band gap semiconducting materials. Also, it can be used as a catalyst for photocatalytic degradation of various organic dyes as well as textile dying wastewater to remove organic pollutants under UV–vis light irradiation. In order to improve the activities of the catalyst various non-metal dopants were doped with ZnO. Here, we have doped two non metals such as Sulfur and Fluorine. Sulfur doped zinc oxide shows faster and higher electron mobility with similar band gap and conduction band energies. Also, it gives better optical and electrical and photocatalytic activities
due to their higher electro negativity and difference in size of S and O. The direct wide bandgap of ZnO semiconductor is (\(E_g = 3.4\) eV) altered by incorporation of hetero atom like sulphur and fluorine by various route [12].

Recently, Jothi Ramalingam et al., reported various synthetic methodology development for gallium doped ZnO with different nanostructure morphology such as nanodisk and nanoflowers thinfilms are successfully used as gas sensor applications. Gallium doping into ZnO matrix is further improve the conductivity of the ZnO by three times higher compared to pristine ZnO. Ga-doped ZnO was reported by our group in the past with nanodisk and nanoflower morphology for possible UV-light, gas sensor and bio-compatible, bio-imaging cell labeling techniques [13,14]. Doping of heteroatom in ZnO matrix result in alter the bang gap values to enhance the faster electron recombination process upon irradiation of light.

Various methods have been adopted for the synthesis of ZnO such as chemical vapor deposition, pulsed laser deposition etc. But these methods require sophisticated instruments and severe working condition such as higher temperature higher pressure and long time. Since the ball milling process is simple and environmentally friendly method, we have used to synthesize ZnO as well as S and F doped ZnO in this study. In the present study hetero atom such as sulfur and fluorine are incorporated in ZnO with wurtzite structure. The crystalline phase, surface and visible light harvesting capacity of prepared ZnO composite materials are further characterized by XRD, SEM and DRS techniques.

2. Experimental

2.1. Synthesis of fluorine and sulphur doped ZnO

The bulk ZnO is used to prepare the fluorine and sulphur doped ZnO composites. The appropriate amount of (0.25 g and 0.5 g of sodium fluoride mixed with 1 g of ZnO separately) and mixed to decrease the particle size of the as prepared mixture by ball milling process. Thiourea is used as sulphur source to prepare the sulphur doped ZnO samples. The same procedure is adopted to prepare the Sulfur doped ZnO composites. The XRD pattern of the powder sample is recorded using Miniflex 600. The band gap values are calculated using kubelka munk equation by diffuse reflectance spectroscope (JASCO UV–vis spectrophotometer V550 ISV469), FE-SEM images are recorded using JSM-T 220A, JEOL to study the respective morphology characterizations.

The solar harvesting ability of the prepared Sulfur and fluorine doped ZnO based materials were analysed by photosensitive degradation/decolouration studies of Methylene blue (MB) under sunlight. MB is an industrially important organic dye and is used widely in many fields like textiles. It is widely used in chemical and biological fields. The dyes like methylene blue from the industries, causes pollution and many of these are toxic, having highly intense colour, carcinogenic, mutagenic and teratogenic for living organisms. Molecular formula of MB is \(C_{16}H_{18}N_3SCl\) and molecular weight is 319.85 g/mol.

Requisite amount of the material was added into MB solution (1 M) and kept under sunlight for irradiation. Small aliquots were withdrawn at particular intervals and absorbance was recorded using UV–vis spectroscope (Perkin Elmer-USA model Lambda 35). Experiments in dark also were conducted.

3. Results and discussion

3.1. XRD analysis

X-ray diffraction analysis was used to identify the crystalline behaviour of the ZnO as well as sulphur and fluorine doped ZnO. The XRD (X-ray diffraction) pattern of undoped ZnO, sulphur, fluorine doped ZnO are shown in Fig. 1. The results clearly indicates that, ZnO exist in wurtzite structure with highly crystalline in nature. The hkl values such as (002), (101), (103), (200), (201) and (202) noticed at 2-theta values of 32.5°, 34.47°, 36.1°, 62.4°, 67.0°, 68.8° obtained in ZnO are very much similar to the JCPDS file card 22-1087.

The XRD patterns is used to calculate the average crystallite size and is evaluated by using Debye–Scherer’s equation

\[D = 0.98\lambda/\beta \cos \theta\]

Where, \(D\) is average crystallite size, \(\beta\) is full width half maxima (FWHM), \(\theta\) is Bragg’s angle and \(\lambda\) is the wavelength of CuK\(\alpha\) radiations.

After doping of Fluorine and sulphur into ZnO matrix is not alter the crystalline phase of the original ZnO. It can be observed that there is a shift in the XRD pattern of sulphur and fluorine doped ZnO. Comparing with undoped ZnO, the diffraction angle of the S-doped and F-doped peaks shifted towards higher diffraction angle, with F and S doped Zinc oxide. Since, the S atom higher than that of O atom, also, the ionic radius of S atom is larger than that of O atom, it can be easily occupies the O atom which is resulted in increase the lattice constant. In the same manner F is higher than that of O, it is also easily occupied in the lattice. Also, the FWHM of the S doped ZnO is higher than that of ZnO which result in increase in the defects. There is a slight variation observed in decrease in intensity of the respective plane values of doped ZnO.
3.2. DRS studies

Diffuse reflectance studies are important to calculate the bandgap values of the as-prepared samples. Tauc relation is involved in the estimation of the optical band gap. Fig. 2 shows the DRS studies of ZnO, S, F doped ZnO. Diffused reflectance is converted into an absorption coefficient by the Kubelka–Munk function as given below

$$\alpha = F(R) = \frac{(1-R)^2}{2R}$$

where, \(F(R)\) is Kubelka–Munk function, \(\alpha\), the absorption coefficient, \(R\), the reflectance. Then the Tauc relation becomes,

$$F(R) = A(h\nu - E_g)^n$$

where \(n=2\) and \(1/2\) for direct and indirect transition, respectively, from which direct and indirect band gaps could be calculated. The plots of \((F(R)h\nu)^2\) versus \(h\nu\) for all samples are shown in Fig. 2(a–d).

Here we have observed that, the undoped ZnO has the bandgap value of 3.37 eV. Fig. 2(a and b) shows the sulfur incorporated ZnO prepared by ball milling process and it shows higher impact in alteration of band gap values for ZnO. Initially 0.25 g of thiourea is incorporated into 1 g of ZnO. Here, we have observed that there is decrease in the band gap value compared to undoped ZnO. Also, further we increase the amount of thiourea into 0.50 g, the band gap value increased compared to the addition of 0.25 g of thiourea into 1 g of ZnO. Hence, \(S(1)\) ZnO shows more reduced band gap value compared to \(S(2)\) ZnO and undoped ZnO. From the results, we can conclude that, less amount of sulfur incorporation in ZnO causes effective alteration in band gap values compared to higher amount of sulfur source addition. These results reverse in the case of fluorine addition in ZnO.

Fig. 2(c and d) shows the fluorine incorporated ZnO prepared by ball milling process. Here, when we added 0.25 g of sodium fluoride into 1 g of ZnO, the band gap value decreases to 3.2 eV which is less than that of undoped ZnO. But, further increases in the doping 0.50 g of sodium fluoride into 1 g of ZnO, there is a slight variation and the band gap value reduced into 3.16 eV which is less than that of \(S(1)\) and undoped ZnO. Indirectly it reflects the effect of fluorine addition impact the alteration in band gap structure and reduces the gap of energy levels internally. From these results, one can clearly understand the alteration occurred in band gap structure of ZnO and reduced band gap values changes the rate of electron
mobility in band gap structure upon visible light driven catalysis process. Fig. 2e shows the overall DRS spectra of as prepared S, F doped ZnO samples. There is clear shifting in the peaks are observed in the spectra.

3.3. SEM analysis

Scanning electron microscopy used to identify the surface morphology of the prepared ZnO as well as S and F doped ZnO. Fig. 3(a–c) shows the SEM images of the F doped ZnO. SEM images indicate that the flaky pastry shapes were obtained with slight aggregation in the particle morphology. But the particles are not even in shape and size. Compared to lower magnified images (1 μm), higher magnified SEM images (100 nm) showed the plate like morphology formation.

Fig. 4(a–c) shows SEM images of the S doped ZnO. Here the samples have uniform spherical shape morphology formation for Sulfur doped ZnO. There is no platy or flaky type morphology observed like fluorine doped ZnO. But, the particles in the lower magnified images (1 μm) all the particles are almost even in size and shape of the morphology. But, when we compare with higher magnified SEM images (100 nm), there is no formation of spherical shape morphology. Instead of that, there is a formation of very small rectangle and square type morphology of sulfur doped ZnO formed. Therefore, sulfur doping is more effective in reducing the bandgap value of ZnO and it will enhances the electron mobility and feasible the recombination rate [15]. MB is a potential cationic dye with two intense absorption bands at 290 and 661 nm ranges. The absorption at 661 nm belongs to the orange region and that is why the compound is blue colored. The visible range has two peaks around at 610 and 660 nm due to the formation MB dimers and monomer respectively. Generally, UV–vis spectrum shows only absorption corresponding to MB monomer at 660 nm. The photosensitive action of sulfur and fluorine doped ZnO can cause degradation/decolouration in the presence of solar light. The degradation leads to the formation of harmless inorganic anions such as nitrate, chloride, sulphate etc. The reaction taking place during the degradation of MB can be represented as below;

\[
\text{C}_{16}\text{H}_{18}\text{N}_{3}\text{SCl} + 2\text{CO}_{2} \rightarrow 16\text{CO}_{2} + 6\text{H}_{2}\text{O} + 3\text{NH}_{4} + \text{SO}_{4}^{2-} + \text{Cl}^{-}
\]

The observed reduction in MB concentration (Fig. 5a and b) under sunlight in presence of prepared materials confirms the photosensitive activity of the S, F doped ZnO based materials. At 4 h, the degradation rate of MB solution is more for the F-ZnO materials than S-ZnO i.e., the characteristic absorption bands of MB solution at the ~610 nm were significantly
Fig. 3. SEM images of S doped ZnO.

Fig. 4. SEM images of F doped ZnO.
decreased in intensity for the F doped materials. It suggests that the nitrogen doping level has an obvious influence on the photocatalytic activity of F-ZnO. The absorbance spectrum of a blank MB solution without any photosensitive material kept in the dark shows no degradation at all. Another MB solution kept in the light without any photosensitive materials shows very little reduction in intensity in 4 h. It is observed that the degradation is more for the material with higher concentration of nitrogen. The degradation increases as the F:Zn ratio increases. This is due to the fact that the photosensitive action of the materials under solar light increases when the nitrogen get doped into the materials since it can shift the absorption edge of the materials to the visible region than undoped ZnO.

Fig. 5b shows the degradation of MB solution in presence of S-ZnO as a function of time. As the time increases the degradation also increases and at 6 h, MB is completely degraded as indicated by the very less intense absorption pattern in the visible region. The degradation of MB occurs by the reaction of electrons and holes generated by the photosensitive materials with MB. The fast degradation of MB solution occurs on F-ZnO materials is due to the effective absorption of solar energy by the NT materials and thus reduce the electron-hole recombination. This will enhance the photosensitive activity of the prepared materials.

3.3.1. Conclusion
Flourine and sulfur doped ZnO is synthesized by simple and facile one step method. The as prepared materials shows reduced band gap values for hetero atom doped ZnO and hence it will enhance the electron capture upon irradiation of visible light absorption, which is clearly confirmed by DRS analysis. Lower amount sulfur addition causes reduce the band gap value of ZnO compared to fluorine addition. The present study concludes sulfur doping is more effective in reducing the bandgap value of ZnO and it will enhances the electron mobility and feasible the recombination rate upon photo light irradiation and solar cell applications.

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References


