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Effect of Gadolinium on the properties and photo-catalytic applications of ZnO nanocrystals

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ABSTRACT

Various weight % of Gadolinium doped ZnO nanocrystals were prepared by using simple co-precipitation method. All the prepared Gd doped ZnO nanocrystals are annealed at 450°C. The synthesized nanocrystals are characterized by using various techniques like X-ray diffraction, scanning electron microscope and UV-Vis spectroscopy. The influence of various weight % of Gadolinium doping on structural, optical and photo-catalytic performance of the ZnO nanocrystals has been investigated. Photo-catalytic decolourization was analysed for Gadolinium doped ZnO nanocrystals by using Methylene blue as model dye. It has been found that 0.075% Gd doped ZnO nanocrystals shows enhanced catalytic performance.

Keywords

Gadolinium-zincoxide, co-precipitation, photo-catalytic, Methylene blue, Electron microscoppy

Academic Discipline and Sub-Disciplines

Applied Physics, Advanced in Nano science and Technology

SUBJECT CLASSIFICATION

Advanced in Nano science and Technology, Nano technology

TYPE (METHOD/APPROACH)

Precipitation – co-method

1. INTRODUCTION

In recent years extensive research is being carried out on Zinc Oxide, because ZnO, a versatile II-VI multifunctional semiconductor with esthetic morphologies, has attracted a great deal of attention in the material research field due to direct wide band gap (3.37eV) and large excitation binding energy (60 meV) For ZnO nanostructures, the doping of selective elements is an effective technique to modify its electronic structure and then affect the electrical, optical, and magnetic properties, which are crucial for their practical application. ZnO has many advantages such as less expensive, non-toxic, and can be synthesized easily.Compared with all other industries textile industry alone produces major wastewater with huge chemicals and dyes. To remove these colours so many conventional and non-conventional treatments are employed and emerging day by day. Most of them are costly and having so many disadvantages.

In recent years broad investigation is focused on zinc oxide based photo-catalysts, the main reason is its broad range of properties [1]. Compared with all other wide band gap semiconductors ZnO alone shows many advantages like non-toxic, inexpensive and easy synthesize. In addition to these properties, ZnO is a promising material for purification techniques because of its better performance in the degradation of organic dyes in both acidic and basic media [2-3].

However, there are some limitations for using ZnO nanoparticles in photo-catalytic and other optics related applications, since it shows short diffusion length of photo-generated electron–hole pair and poor utilization of solar energy [4-5]. In ZnO nanostructures the doping of lanthanide metal ions is an important technique to alter its electronic structure and then it influences the structural, optical and photo-catalytic properties [6-8]. To the best of our knowledge there is no work on Gd doped ZnO nanocrystals for photo-catalytic applications

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2. EXPERIMENTAL

To prepare pure and Gd doped ZnO nanocrystals AR grade of Zinc Acetate, sodium hydroxide, Gadolinium Nitrate and Methylene blue were purchased from Merck specialities private Limited, Mumbai and used without further purification. All the solutions were prepared using double distilled water. For photocatalytic degradation, methylene blue dye (M = 319.85 g/mol, $C_{16}H_{18}N_3SCl$) was used.

Pure and Gd doped ZnO nanocrystals were prepared by simple precipitation method using zinc acetate and sodium hydroxide as precursors. To prepare pure ZnO nanocrystals, 1M aqueous solution of zinc acetate Zn $(CH_3COO)_2.2H_2O$ was kept under constant stirring and 1 Molar aqueous solution of sodium hydroxide (NaOH) was added drop by drop. Now it makes the formation of white precipitate. The precipitate was washed several times using de-ionized water and ethanol to

remove the byproducts which were bound with the nanoparticles and then dried in air atmosphere at about 80°C. Finally the prepared nanoparticles were annealed at 450°C for 1 hour.

Similarly, to prepare gadolinium doped ZnO nanocrystals high purity gadolinium nitrate was used for chemical reaction. The required amount of gadolinium nitrate (0.05 0.075 and 0.1 %) was added into the aqueous solution of zinc acetate. Then aqueous soluton of sodium hydroxide was added drop wise to the above mentioned solutions, the obtained precipitate was centrifuged and annealed in a similar way as mentioned above.

The crystal structure was identified by using X-ray diffraction studies and it was recorded using PANalytical X-ray diffractometer with nickel-filtered CuKα radiation (30kV, 30mA) of wavelength 1.5406 Å. The surface morphology of the samples was determined by using scanning electron microscope (JEOL JS-6390) equipped with an energy dispersive spectrometer (EDS: Oxford Instruments). The optical properties were studied using absorbance spectra recorded on a UV – VIS double beam spectrometer (SYSTRONICS: AU-2707) in the range of 190–900 nm.

Photo-catalytic reactor system was designed by using wooden chamber and 15 W, UV lamp with wavelength of 365 nm was kept inside the wooden chamber. For photo-degradation measurement, the prepared nanocrystals such as pure, 0.05, 0.075 and 0.1 % Gd doped ZnO nanoparticles (1 g/l) was added in 50 ml aqueous solution of methylene blue (MB; 20 mg/l at natural pH = 6.5).

The mixture solution was stirred for 10 min to disperse the catalyst in MB solution, and the solution was kept in dark for an hour to achieve adsorption equilibrium. The sample was transferred into the photocatalytic reactor for UV exposure and the lamp was turned ON. The UV irradiation was performed for different light irradiation time such as 1 hr, 2 hr, 3 hr, 4 hr and 5 hr at room temperature. The concentration of MB in the solution was ascertained by referring to an absorption concentration standard curve that was established by measuring the optical absorption of methylene blue at 665 nm by UV–Vis spectrometer.

3. RESULTS AND DISCUSSION

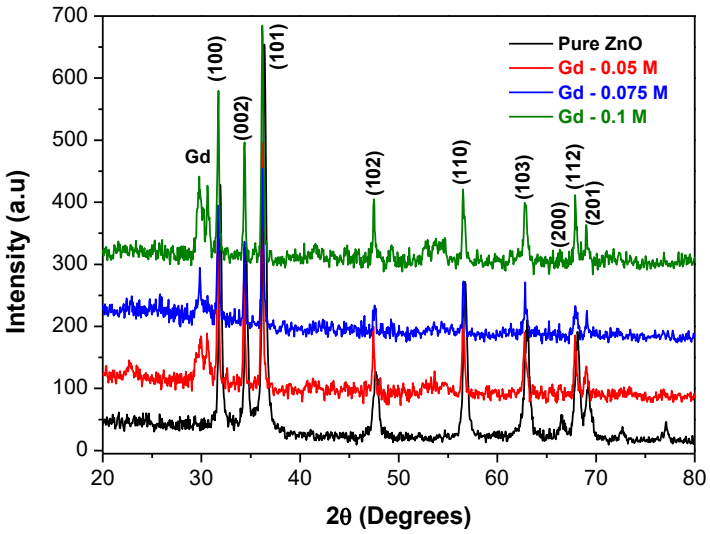

Figure 1. X-ray diffraction patterns of pure and Gd doped ZnO nanocrystals

Figure 1 shows the X-ray diffraction pattern of pure and Gd doped ZnO nanocrystals. The polycrystalline wurtzite structure of ZnO is confirmed from the strong and sharp peaks of X-ray diffraction pattern (Ref. Code: 00-005-0664). The intense peaks located at 31.7°, 34.4° and 36.4° are corresponds to (100), (002) and (101) planes of ZnO. Similarly other peaks found at 47.5°, 56.6°, 62.8°, 66.4°, 68.2°, and 69.2° are corresponds to (102), (110), (103), (200), (112), and (201) planes of the wurtzite structure. In addition to this X-ray diffraction pattern of Gd doped ZnO samples show a small peak at 2θ=29.9° and which is due to the doping of Gd. The intensity of this peak increases with increase of Gd percentage from 0.05% to 0.1%. This pattern also clearly shows that the peak positions of ZnO are not much changed due to the doping of Gd, which confirms that there is no additional phase formation [4].

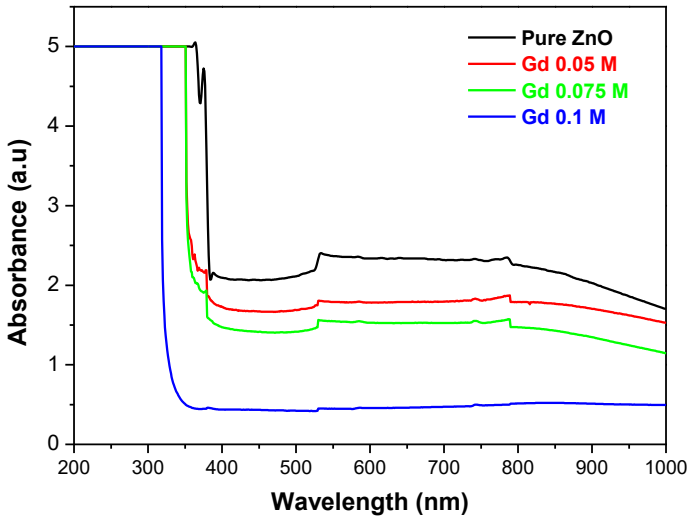

Figure 2. UV–vis absorption spectra of pure and Gd doped ZnO nanocrystals

The UV–vis absorbance spectra of the Gd doped ZnO nanoparticles are shown in Figure. 2. The spectrum clearly shows the decrease in the absorbance at 350 to 400 nm and it can be assigned to the intrinsic bandgap absorbance of ZnO due to the electron transitions from the valence band to the conduction band. And also there is a blue shift of the absorbance edge for the nanocrystals prepared with different percentage of Gd ions. It is due to the variation of particle size, changes in the surface microstructures and morphology. The band gap of the prepared pure and Gd doped samples have been calculated by the extrapolation of the absorption edge onto the x-axis and the calculated values are 3.27, 3.38, 3.45 and 3.84 eV for pure, 0.05, 0.075, and 0.1 % Gd doped ZnO nanocrystals respectively. It clearly shows that the band gap increases with increase of Gd content. It may due to the formation of new defects and also Gd atoms substitute for Zn atoms due to the electro negativity and ionic radius difference [1, 14]. ZnO is an n-type semiconductor and its Fermi level is present inside the conduction band. The doping of Gd ions contributes more electrons, and this may be due to lower electron affinity of GdO when compared to ZnO. Thus the radiative recombination of these excitons may lead to a blue shift.

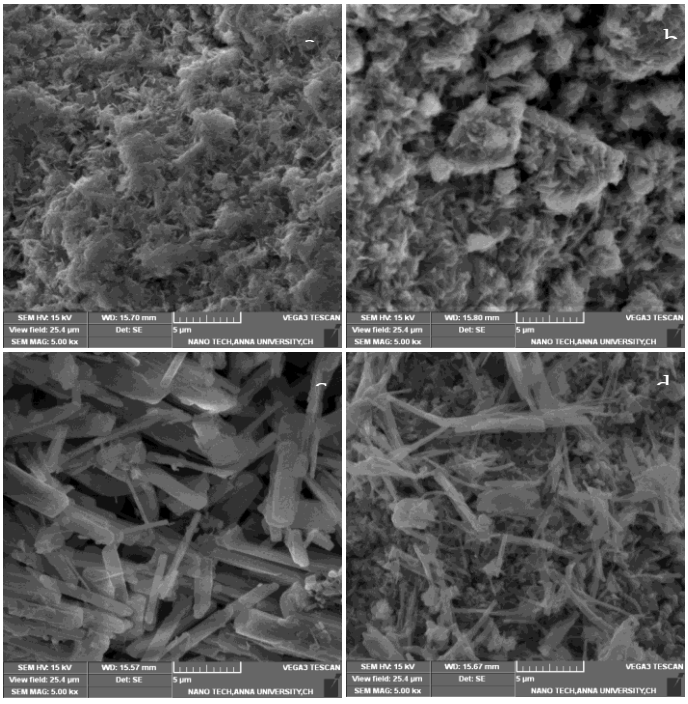

Figure 3. SEM images of (a) pure and (b-d) 0.05, 0.075 and 0.1% Gd doped ZnO nanocrystals

Figure 3(a-d) shows the surface morphology of the pure and Gd doped ZnO nanocrystals. Figure 3(a) clearly shows that pure ZnO nanocrystals exhibit particle like structure. When Gd is doped with ZnO it promotes the formation of rod like structure. When the concentration of Gd is increased it promotes the size of the nanorod and it is shown in Figure 3(c). The reason for the increase of particle size at higher concentration is the increased alkalinity and it favors for grain growth. Due to this particle size increases with increase of Gd concentration.

Time dependent UV-vis spectra of Methylene blue dye degradation using Gd doped ZnO nanocrystals are shown in Figure 4(a-c). The rate of decolourization was recorded with respect to the change in the intensity of absorption peak in the visible region. The prominent peak is observed at ~655 nm which decreases gradually with the increase of irradiation time from 1 h to 5 h. For the degradation experiments, methylene blue dye was prepared at three different pH values

(pH=2,4 and 6) and it is taken in three different beakers and the 0.05, 0.075 and 0.1% Gd doped ZnO nanocrystals were added. The beakers were subjected to UV irradiation light (8 W Philips bulb TUV-08) kept at a distance of 15 cm for fixed interval of time. The graph clearly shows that 0.1% Gd doped ZnO nanocrystals shows enhanced catalytic activity than the other crystals irrespective of irradiation time.

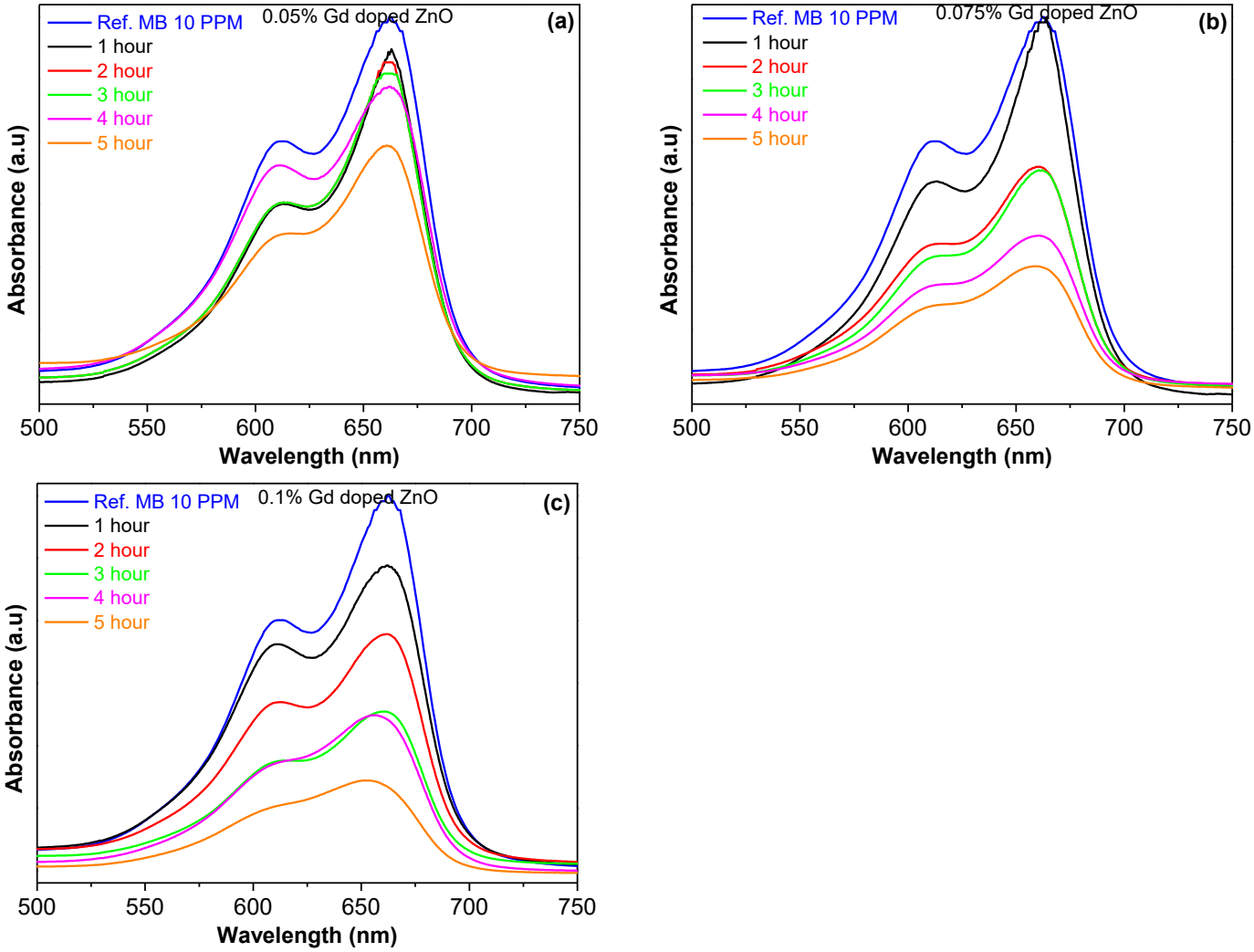

Figure 4. Time dependent UV-vis spectra of Methylene blue subjected to Gd doped ZnO nanocrystals

Figure. 5 (a–c) shows the effect of irradiation time of Gd doped ZnO nanocrystals on the methylene blue decolourization. It can be observed that for pH values and lower irradiation time the decolourization is very less (<10%) whereas at higher pH values the rate of decolourization is ~20 to 40% even at lower light irradiation time. The doping concentration also changes the rate of decolouriztation it may due to the total active surface area present on the catalyst. It is clearly evident from the SEM images of the prepared samples. Compared with all other SEM images 0.075% Gd doped ZnO shows more rod like structures. Hence availability of more active sites on the catalyst and it will enhance the decolourization [15]. And also the presence of more negative surface charge on the catalyst surface will readily attract the methylene blue molecule and degrade it.

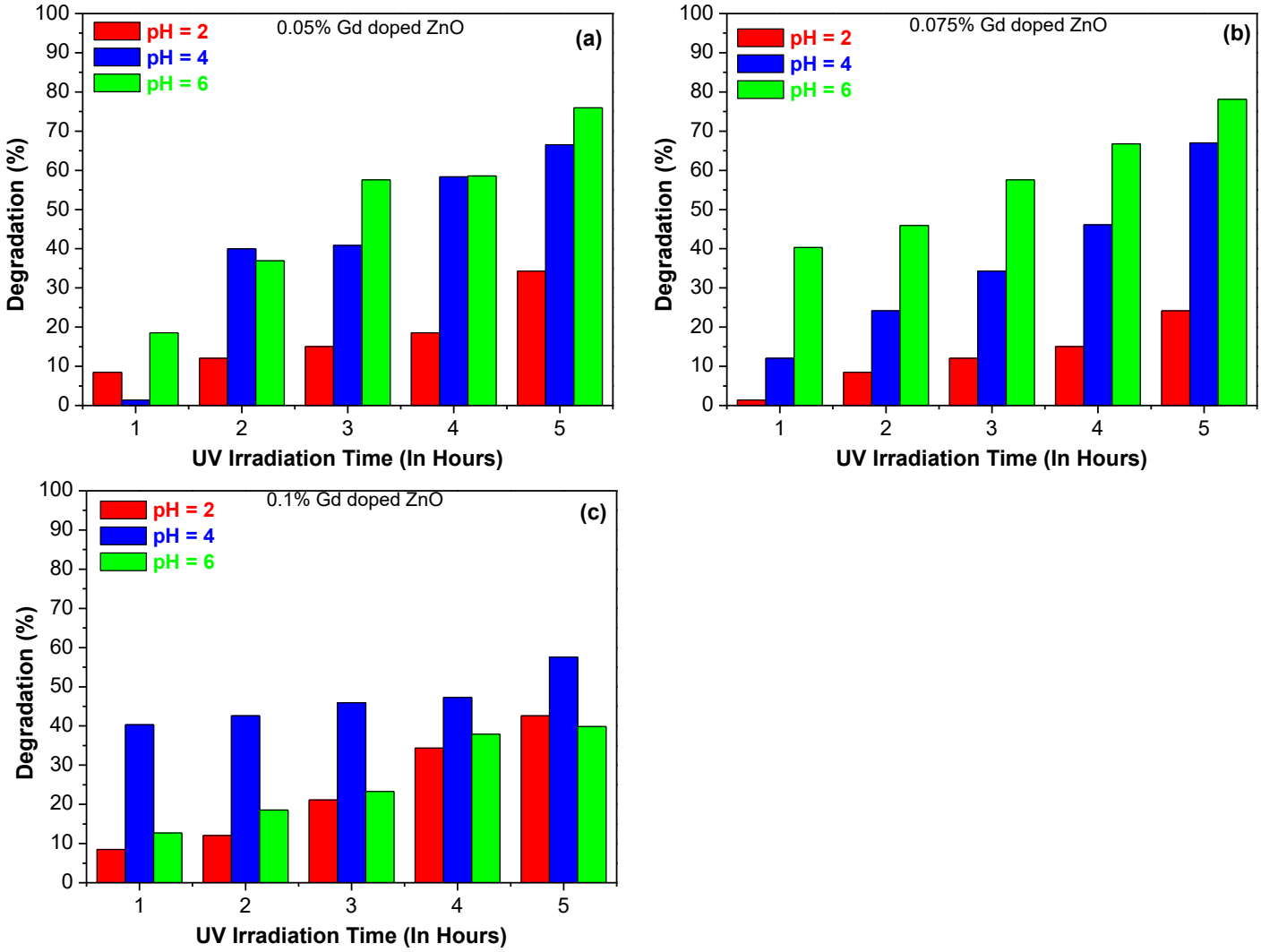

Figure 5. Effect of irradiation time of UV on Methylene blue for different pH values

4. CONCLUSION

Various weight % of Gadolinium doped ZnO nanocrystals were prepared by using simple precipitation method and all the prepared samples are annealed at 450°C. All the prepared samples are characterized by using various techniques like X-ray diffraction, scanning electron microscope and UV-Vis spectroscopy. The effect of Gadolinium doping on structural, optical and photo-catalytic performance of the ZnO nanocrystals has been investigated. Photo-catalytic decolourization was analysed for Gadolinium doped ZnO nanocrystals by using Methylene blue as model dye. It has been found that Gd doping enhances the photo-catalytic performance at higher pH values of Methylene blue.

5. REFERENCES

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