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Effect of chromium doping on structural, optical and photocatalytic properties of ZnO nanoparticles

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Pure and chromium doped Zinc Oxide nanocrystals were prepared by simple Co-precipitation method and the prepared nanocrystals were annealed at 450°C for one hour. The effect of dopant concentrations (0.05, 0.075 and 0.1%) on structural, morphological, optical property and photocatalytic activity were analyzed. Optimization of different reaction parameters viz., contact time and pH for better photocatalytic degradation was analyzed using methylene blue as model dye. The results were interpreted in view with the crystallite size and influence of dopant metal. The calculated band gap values are 3.17, 3.4, 3.5 & 3.7 respectively for pure, 0.05, 0.075 and 0.1% Cr doped ZnO nanocrystals. The results revealed that the average crystallite size was 18, 19, 21, and 24 nm, respectively for pure, 0.05, 0.075 and 0.1% Cr doped ZnO nanocrystals. SEM image clearly shows the formation of nanorod like structures. The obtained result shows that 0.05% Cr doped ZnO nanocrystals act as a promising photocatalyst for methylene blue degradation at acidic pH conditions.

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Keywords: Chromium doping, ZnO nanoparticles, Co-precipitation method, Photocatalytic activity

1. Introduction

The textile industry is one of the major consumer of dyes along with different number of chemicals used for dyeing, printing and finishing processes. Organic dyes used in the textile industries is one of the main sources of water pollution due to their non-bio degradability, high toxicity and carcinogenic nature [1]. There are different treatment methods are available and emerged to treat coloured wastewater to meet the environmental demands. Some of them are costly and have various disadvantages [2]. Compared with all other available techniques Advanced Oxidation Process with heterogeneous photo catalyst is an important method, due to complete mineralization [3]. To maintain eco friendly environment there are several photo catalysts were employed [4]. Among them ZnO is important, it is II-VI semiconductor with wide band gap in the ultraviolet (UV) region, i.e., equivalent to or larger than 3.2 eV (k = 387 nm). ZnO shows hexagonal quartzite structure at room temperature. The variety of nanostructures can be synthesized and used to promote the photo-catalytic activity with the illumination of UV radiation. The morphology of nanomaterials are an important key factor that influence their catalytic property. Nanostructures of ZnO are obtained by different methods such as chemical vapor deposition, sol–gel method, sputtering deposition and chemical solution deposition etc. [5-8]. Compared with sol–gel method, other methods shows some limitations during its preparation, for example, controlling the growth of nanostructures is not easy in the microwave and chemical vapor deposition and it may due to the high reaction speed. ZnO nanostructures with novel morphologies are required for variety of applications like in catalysis, cellular imaging, immunoassay, and luminescence tagging, spintronic and drug delivery. Doping of selective elements alter its electronic structure and then influence the structural, optical and catalytic properties. The structural, morphological and optical properties of ZnO nanocrystals are investigated with respect to doping of metals with different concentration [9]. To alter the band gap there are variety of methods are used, among them doping of transition metal ions is important [10, 11]. Based on the theoretical and experimental point of view the transition metal ions doped ZnO nanomaterials is continue to be an important research topic [12]. Among the various dopants, Cr dopant is especially interesting and it has been attracted lots of attention in research [13, 14]. One of the main reasons is that radius of Cr^{3+} is closer to that of Zn^{2+}, which means that Cr^{3+} can easily doped with the ZnO crystal lattice or substitute for the position of Zn^{2+} in ZnO [15]. In particular, unlike many other metals, Cr itself is anti-ferromagnetic and it will not induce an extrinsic ferromagnetism even if Cr clustering occurs. Wu et al prepared Cr-doped ZnO nanowires using solvothermal synthesis for the photocatalytic activity. They reported that the as-synthesized Cr-doped ZnO nanowires were a kind of promising photocatalyst for chemically stable azo dyes under visible light [24].

In this present study the pure and Cr-doped ZnO nanocrystals were synthesized by co-precipitation method and characterized. The photo-catalytic activity of the prepared nanocrystals were analyzed.

2. Experimental procedure

2.1. Synthesis of pure and Cr Doped ZnO nanoparticles

Pure ZnO nanocrystals were prepared using 0.6 M of Zinc sulphate hepta hydrate and sodium hydrogen carbonate solution by co precipitation method. To get homogeneous solution, the solutions were stirred individually using magnetic stirrer. Sodium hydrogen carbonate solution was added drop wise into the Zinc sulphate hepta hydrate solution under magnetic stirring for 30minutes. The precipitate formed was centrifuged, washed and dried. The obtained ZnO nanocrystals was annealed at 450ºC for one hour. To prepare Chromium doped ZnO nanocrystals, 0.05, 0.075 and 0.1% of Chromic Nitrate was added into Zinc sulphate hepta hydrate and sodium hydrogen carbonate solution. The prepared 0.05, 0.075 and 0.1% Cr doped ZnO nanocrystals were centrifuged, washed and dried in a similar way as mentioned above. Finally all the nanocrystals are annealed at 450ºC for one hour.

2.2. Characterization of Cr doped ZnO nanoparticles

The properties of the prepared nanocrystals are analyzed by various characterization techniques. The detailed analysis of structural and morphological analysis of newly synthesized pure and 0.05, 0.075 and 0.1% chromium doped ZnO nanoparticles were done by X-ray diffraction (Rigaku D max-C) with Cu Kα radiation (1.5406 A), scanning electron microscope (SEM with EDXA, Sirion). The optical absorption spectra of ZnO nanoparticles were recorded using a UV-Visible spectrophotometer (JASCO V-570). Photocatalytic activity of the prepared pure and Cr-doped ZnO samples were done using homemade photo reactor and absorbance values were found using UV–Visible spectrophotometer.

3. Results and discussion

XRD pattern of pure and Cr doped ZnO nanoparticles were shown in Fig. 1a & b.

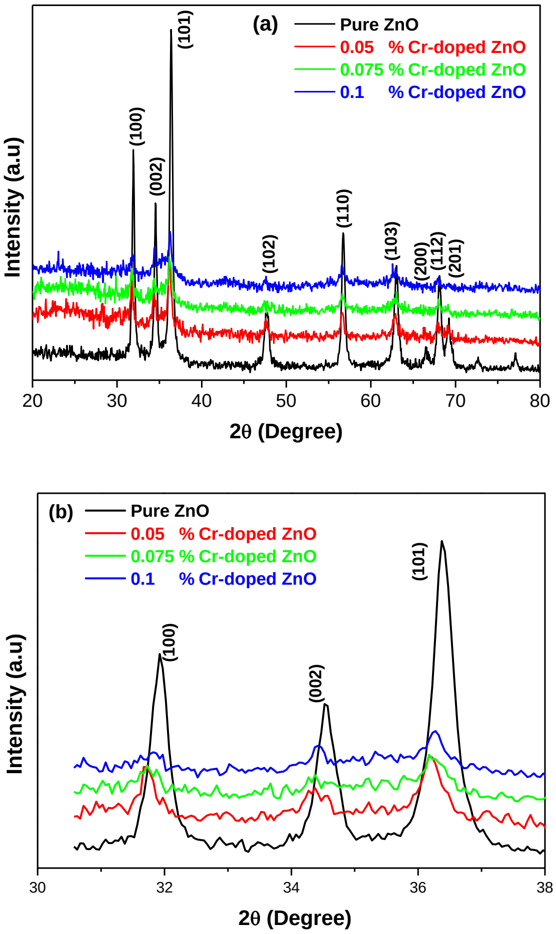

Fig. 1a. XRD patterns of pure and Cr doped ZnO nanoparticles and (b) Shifting of high intense peaks

The image clearly shows that the prepared pure ZnO nanocrystals shows hexagonal wurtzite structure and all the peaks are well matched with standard JCPDS NO: 36-1451 [16]. The Fig. 1b clearly shows the shifting of high intense peaks towards lower angles with increase of Cr content, which prove the doping of Cr on ZnO. Viswanathan et al. [17] reported that this shift in XRD peaks reveals lattice expansion by Cr substitution in ZnO crystal lattice. Also the broadening of XRD peaks exhibit the formation of Cr nanocrystals on ZnO [17]. In addition to ZnO peaks, no other signals appeared in the diffraction patterns, it is due to the low promoter loading (1% w/w). In addition, no variations were observed in the position and shape of the spinel diffraction peaks. The peaks for metallic chromium (FCC) and / or chromium -metal alloys appeared in the XRD patterns and there is no chromium oxide phases (Cr_3O_4) were identified. The average crystallite size were calculated from Scherrer equation [18]. The calculated values are 18, 19, 21, and 24 nm, respectively for pure, 0.05, 0.075 and 0.1% Cr doped ZnO nanocrystals. Most of the theoretical and experimental analysis has demonstrated size-dependent lattice contraction [19]. So, the effect on size would be another possible cause of the lattice contraction due to the surface stress variation. All the XRD diffraction peaks were indexed to hexagonal wurtzite structure. There is no hints of the Cr metal or the Chromium oxides.

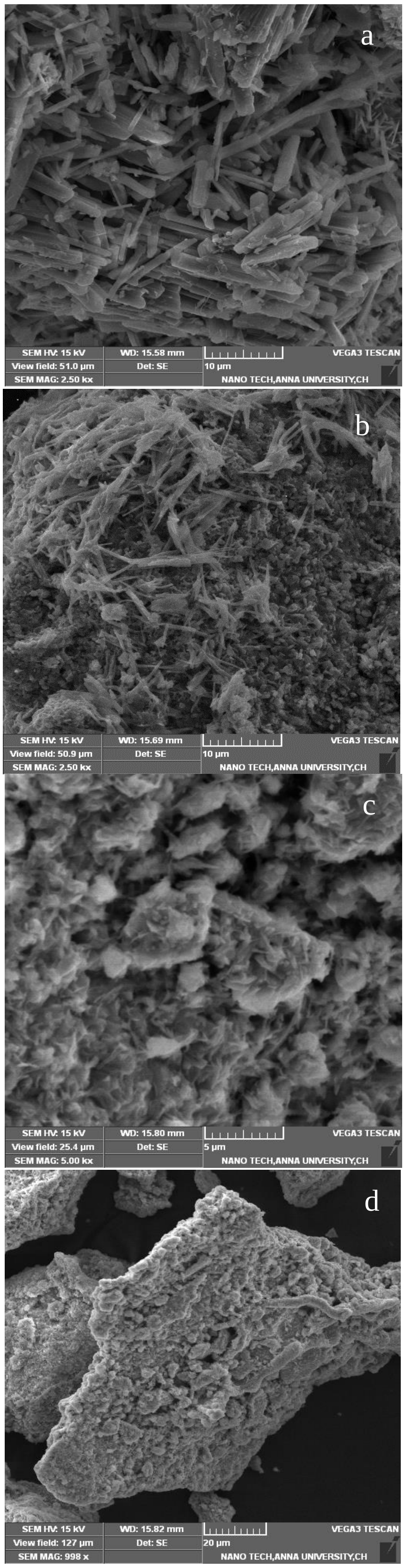

Fig. 2(a,b, c, d). SEM images of pure, 0.05, 0.075, 0.1% Cr doped ZnO nanoparticles

The important reason is that radius parameter of Cr^{3+} is closer to that of Zn^{2+}, which means that Cr^{3+} can easily penetrate into the ZnO crystal lattice or substitute for the position of Zn^{2+} in crystal ZnO. At an outset, this result may originate from the substitution of Cr ions (0.63 Å) at Zn (0.74 Å) sites [15]. The observed values were good agreement with the theoretical values.

Fig. 2 (a-d) shows the surface morphology of pure and Cr doped ZnO nanoparticles. The image clearly shows that the pure ZnO nanoparticles having rod like structure. Whereas the structure of Cr doped ZnO nanocrystals differ from pure ZnO nanocrystals. If the dopant concentration is low the clarity of the Nano rod structure is high order. When compared with pure ZnO, the Cr doped ZnO shows various surface morphology for every doping concentration ratios. The change in surface morphology of Cr doped ZnO nanoparticles due to the addition of dopant on ZnO sites. When the dopant concentration increases the agglomeration of nanoparticles on the surface also takes place due to this the surface morphology also changes.

UV–Visible absorption spectroscopy is an important technique applied to analyse the optical characteristics of Cr doped ZnO nanoparticles. The band gap changes with dopant concentration and the crystal imperfections produced by dopants. The band gap energy also mainly depends on particle size, and oxygen deficiency.

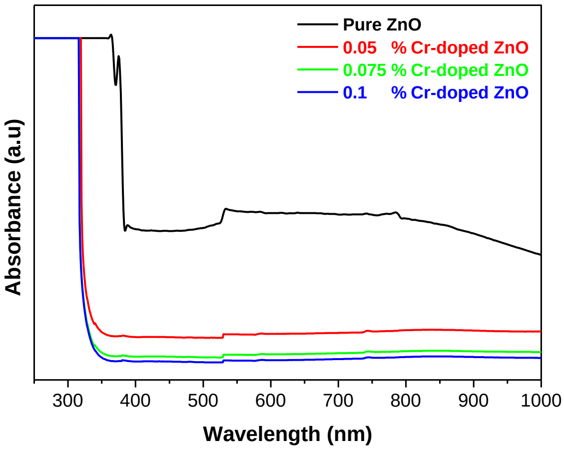

Fig. 3. UV absorption spectra of pure, 0.05, 0.075, 0.1 % Cr doped ZnO nanoparticles

The UV visible absorption spectra of pure and Cr doped ZnO nanoparticles are shown in Figure 3. The strong optical absorbance were identified between 370-388 nm for pure ZnO nanoparticles. But position of the absorption peak was changes with doping concentration, the maximum absorption peak was shifted towards the shorter wavelength (blue shift) for all the concentrations of Cr dopant.

The band gap energy was calculated for all the samples by using Tauc plot [9]. The calculated values are 3.17, 3.4, 3.5 & 3.7 respectively for pure, 0.05, 0.075 and 0.1% Cr doped ZnO nanoparticles. An extrapolation of linear region of a plot was used for the calculation of optical band gap (E_g). The graph clearly shows that the increase of dopant concentration enhances the absorption intensity. This occurs due to the doping of Cr ions on the ZnO lattice by both substitutional and interstitial. The former consists of Cr atoms replacing Zn atoms in ZnO to form chromium oxide, while the latter creates Cr interstitial atoms in the structure. At lower doping concentrations, the doping is usually substitutional doping. For higher doping concentrations, most of the Cr impurities are present as interstitial atoms in the ZnO crystals, which leads to strong absorption.

4. Photo-catalytic activity analysis of Pure and Cr doped ZnO nanoparticles

A specially designed photo-catalytic reactor system was used for photo-catalytic applications. Philips TUV-08 lamp of 15 W with wavelength of 365 nm was kept inside the wooden chamber. The prepared pure and Cr doped ZnO nanocrystals were added in methylene blue (MB) solution, the solution was stirred for 10 min, and then in dark for an hour to achieve adsorption equilibrium. The MB solution was prepared at different pH values such as 2, 4 & 6. The pH of the solution is altered by using 0.1N HCl and 0.1N NaOH solution. The sample was then transferred into photo reactor for UV irradiation. The concentration of MB in the solutions was ascertained by referring to the absorption concentration standard curve which was obtained by measuring the optical absorption of MB at 663 nm using UV–Visible spectrophotometer.

The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak is observed at λ_{max} of 663 (for MB) [16] and it is gradually decreases with increase of irradiation time from 1 hour to 5 hours. The percentage of degradation (% D) was calculated using following equation.

Percentage of degradation (% D) = $(A_o - A_t/A_o)*100$ [19]

Where A_o = absorbance at t = 0 minute
A_t = absorbance at t minute

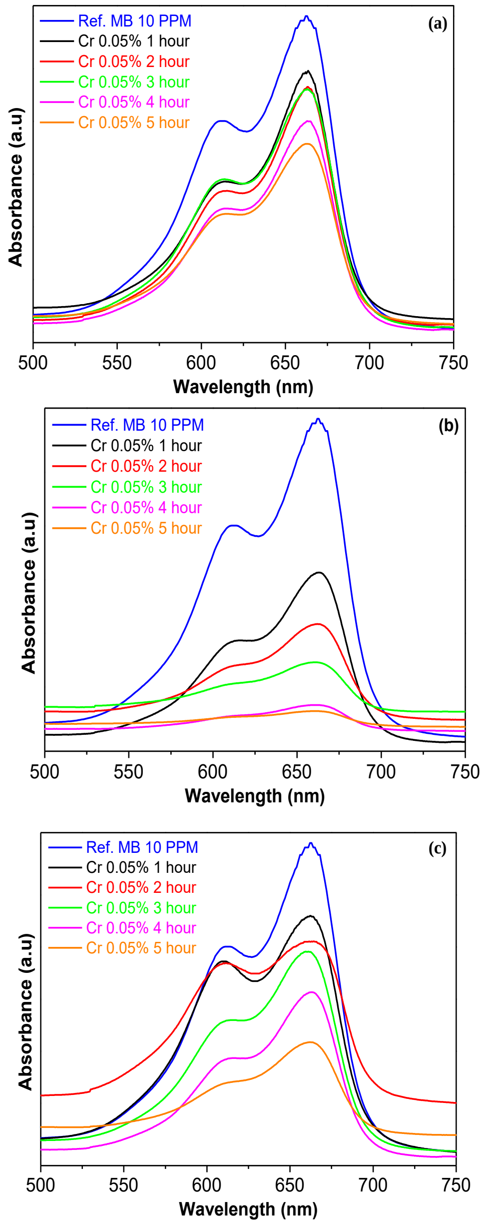

Fig. 4. The time dependent UV-Vis absorption spectra of MB dye degradation of Cr (0.05%) doped ZnO nanoparticles (a) pH = 2, (b) pH=4 & (c) pH=6

For the degradation experiments, fixed amount (0.5 mol/L) of MB dye was taken in a beaker and pure & Cr doped ZnO nanocrystals at various pH (2,4 & 6) were suspended inside the beaker. The beaker was subjected to UV light irradiation kept at a constant distance for fixed interval of time. The graphs were drawn based on the obtained results. The degradation percentage of MB dye increases with increase of time for all the pH conditions. The pH plays an important role in photo-catalytic treatment [20], because Waste water discharged from textile industries into the water sources is of different pH values, so studying the role of pH on decolorization of dye solution is very important. The amphoteric behavior of synthesized ZnO influences the surface charge of the photo catalyst [21]. The pH not only affects the surface properties of ZnO photo catalyst but also influences the degradation of dye molecules by the formation of hydroxyl radicals.

Fig. 4 shows the time dependent UV-Visible absorption spectra of MB dye degradation of Cr (0.05%) doped ZnO nanoparticles for various pH values of MB dye solution. The obtained results clearly shows that at high acidic conditions (pH=2) the degradation increases suddenly with in minimum duration of UV irradiation and then increase gradually with light irradiation time. But for pH=4 the degradation increases gradually with increase of time. It is in contrast with low acidic pH conditions i.e., at pH=6 the degradation percentage is low up to 2 hrs of UV irradiation time.

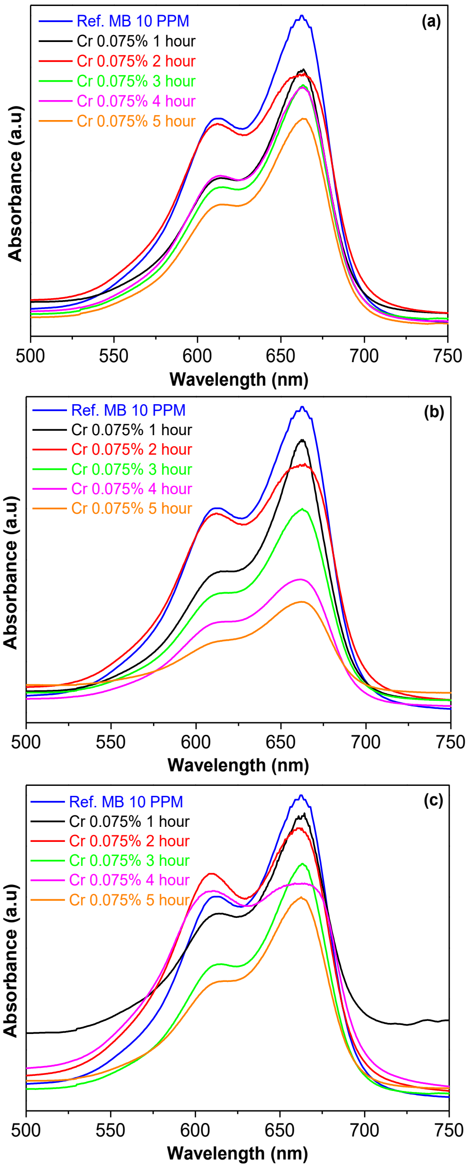

Fig. 5. The time dependent UV-Vis absorption spectra of MB dye degradation of Cr (0.075%) doped ZnO nanoparticles (a) pH = 2, (b) pH=4 & (c) pH=6

The degradation percentage starts to improve for 5 hrs light irradiation. Whereas pH= 2 and 4 exhibit good degradation results than pH=6. The result shows that the decolourisation is high at high acidic medium and gets decreases when the pH of the solution increases. It may due to at acidic pH the hydroxyl radical induces the formation of hydrogen peroxide, which induces the formation of OH radicals and this reaction may initiate the degradation process [22]. The obtained results are similar to the results reported by Ameta et al. [21].

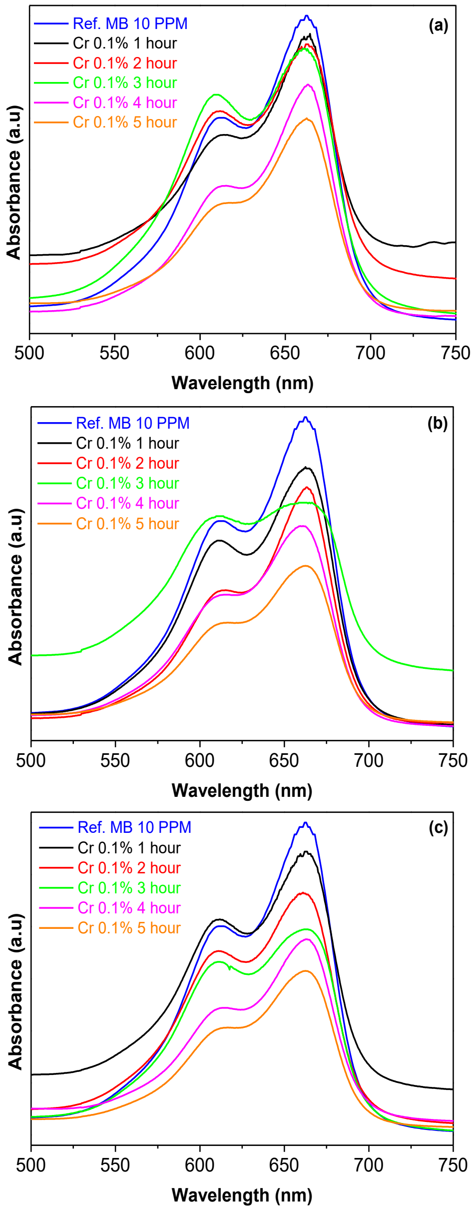

Fig. 6. The time dependent UV-Vis absorption spectra of MB dye degradation of Cr (0.1%) doped ZnO nanoparticles (a) pH = 2, (b) pH=4 & (c) pH=6

The Fig. 6 shows the time dependent UV-Visible absorption spectra of MB dye degradation of Cr (0.1%) doped ZnO nanoparticles for various pH values of MB dye solution. The 0.1% Cr doped ZnO nanoparticles shows same degradation percentage at 5 hours of light irradiation.

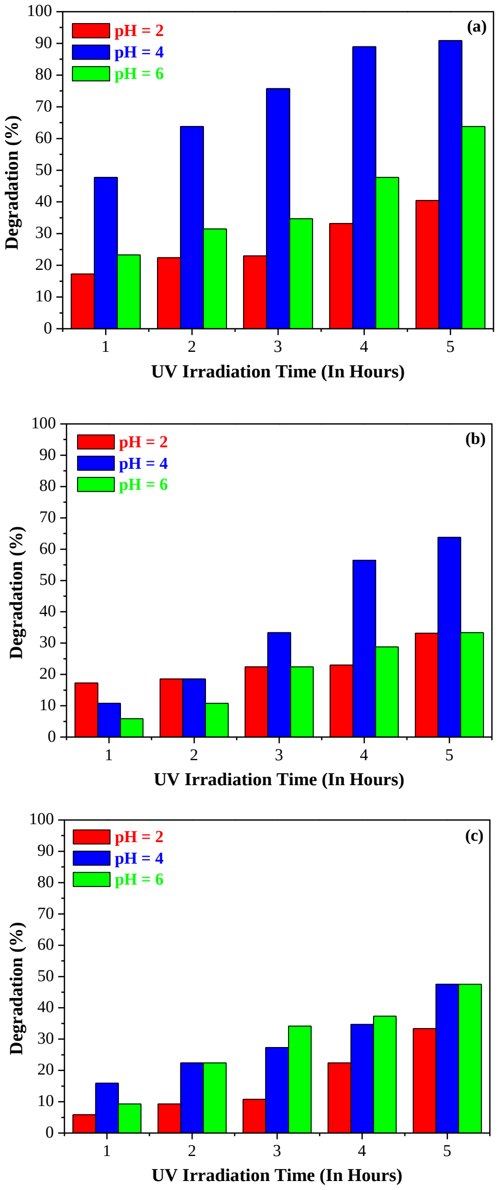

Fig. 7. MB degradation of (a) 0.05%, (b) 0.075% & (c) 0.1% Cr doped ZnO nanoparticles

For 0.05% Cr doped ZnO nanoparticles, the MB dye degradation increases with increase of UV irradiation time. The pH=4 shows better photo-catalytic degradation is than pH=2 & 6. The pH=4 shows maximum MB dye degradation among all other dopant concentrations.

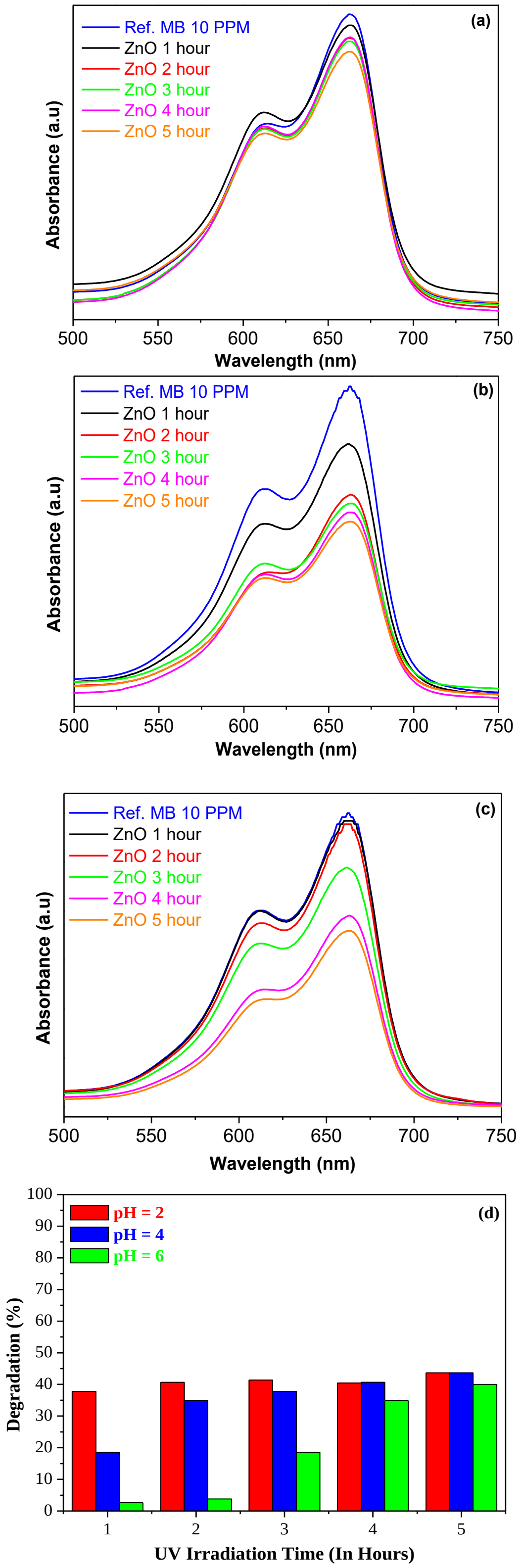

Fig. 8. The time dependent UV-Vis absorption spectra of pure ZnO nanoparticles (a) pH=2, (b) pH=4 & (c) pH=6 and (d) % of Degradation

100mg of 0.05% Cr doped ZnO nanoparticles shows 92.5% dye degradation at 5 hours of UV light irradiation.

The same types of results were obtained for 0.075% Cr doped ZnO nanocrystals.

When the Cr dopant concentration increases from 0.05M to 0.1%, the degradation decreases from 92.5% to 48.5%. Based on the analysis of all the parameters, it was concluded that 0.05% Cr doped ZnO nanocrystals exhibit effective dye degradation for pH=4 MB dye solution. The obtained results are similar to the previous reports reported by Chakrabarti et al (2004) and Elangovan et al. (2016) [16, 23].

5. Conclusion

Pure and 0.05%, 0.075%, 0.1% Chromium doped ZnO nanocrystals were prepared by using Co-precipitation technique. The average crystallite size of the prepared Cr doped ZnO nanocrystals increases with increase of chromium dopant concentrations. The band gap value increases with increase dopant concentrations from 3.17 to 3.7 eV. The photo-catalytic activity of 0.05% Cr doped ZnO nanocrystals shows enhanced photocatalytic degradation of MB dye with 92.5% at 5 hours light irradiation. The obtained result reveals that decolourisation is better at lower pH values.

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