Synthesis and Characterization of Cr-N-P-TRI Doped ZnO Nanoparticles for Photocatalytic Degradation of Malachite Green Under Visible Radiation.

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ABSTRACT

Zinc oxide (ZnO) nanoparticles were synthesized by direct precipitation method via the hydrolysis and oxidizing process. $ZnCl_2$ was dissolved in distilled water with continuous stirring. Modified photo catalysts (chromium-doped ZnO and nitrogen phosphorus co-doped ZnO) were synthesized by the incipient wetness impregnation method and by mixing as-synthesized ZnO, and each chickpea and rice respectively whereas chromium-nitrogen phosphorus tri-doped ZnO (CrNPZ) nanomaterials were prepared from the already prepared ZnO and BNP co-doped ZnO nanomaterials, respectively. The as-synthesized photo catalysts were investigated by X-ray diffraction (XRD), Fourier Transform Infrared spectrometer (FTIR), and UV–Vis spectrophotometers to study crystalline phase, molecular interaction and functional group, and band gap determination, respectively. Photocatalytic degradation of malachite green using as-synthesized photo catalysts was studied under visible as well as without irradiations. Highest photocatalytic degradation efficiency of chromium-nitrogen phosphorus tri-doped zinc oxide (CrNPZ) is attributed to the lower rate of recombination of the photo-generated electrons and holes as well as to its lower band gap energy.
Keywords: Nanoparticles; X-ray diffraction; FT-IR; malachite green dye; Chromium-Nitrogen Phosphorus tri-doped ZnO (CrNPZ)

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INTRODUCTION

Nanoparticles, smaller than several tens of nanometer in primary particle diameter, frequently show behavior which is intermediate between that of a macroscopic solid and that of an atomic or molecular system. The dimensions of these particles make them ideal candidates for the nanoengineering of surfaces and the fabrication of functional nanostructures that are useful in optoelectronics, chemical and biosensors, drug delivery, catalysis, etc. Nanoparticles of semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron oxide (F_2O_3) and cadnium sulfide (CdS) have attracted extensive attention as a photocatalyst for the degradation of organic pollutants in water and air[1].

Recently, nitrogen-doped ZnO sample has been synthesized by grinding the ZnO and urea mixture and the subsequent calcinations at 400°C [2]. The synthesized sample has exhibited photoabsorption in the region of visible light wavelength. In addition, the sample has shown excellent photocatalytic ability. Li and Haneda [3] synthesized colored N-containing ZnO powder with high surface area. Ultraviolet–visible spectra indicated that the photocatalyst powder could absorb not only ultraviolet light like pure ZnO powder, but also part of the visible-light. The photocatalytic performance of N-containing ZnO powder was superior to feature was also observed on N-doped ZnO thin films [4] . These results indicated that the doped nitrogen atoms in a ZnO crystal lattice could significantly improve the optical absorption properties of ZnO.

In recent years, there has been great interest in biomorphic mineralization a technique that employ nature living things as template for mineralization to produce biotemplate materials with morphologies and structures resembling those of the templates[5]. Besides, nature living things can also act as bio-precursors for mineralization, for them possess many desirable elements that can be potentially be employed as chemical components of the materials to be produced. For example, some plants accumulate metal elements such as Ni, Co, Cd and Au are most biomass contains abundant nonmetallic elements such as C, H,O,N and P[6]. Crop seeds, containing abundant N and P elements, can be employed as non-metallic precursors for mineralization to synthesize N-P co-doped metal oxide. Crop seeds are composed of various chemical compositions, mainly starches, proteins and fats, among which starches and proteins are hydrophilic colloids, favorable for the infiltration of metal-ion solution. Moreover, crop seeds contain abundant N and P elements in different forms, e.g. as storage proteins, enzymes, phyticacids, phospholipids, phosphoprotein and so forth. These N and P elements are expected to be retained and self-doped in to mental oxide. These characteristics make crop seeds appropriate biogenic nonmetallic precursors for producing doped metal oxide. Metal oxide photocatalyst have become a focus of attention due to their possible application to degradation of environmental organic pollutants and the conversion of solar-energy [7]. As a suitable alternative photocatalys to TiO_2, ZnO has a similar band gap energy (3.2 eV) to TiO_2, larger quantum efficiency and higher photocatalytic efficiencies than TiO_2 [8]. It has also suggested that ZnO costs lower than TiO_2 for decolorization of organics in aqueous solutions [9]. However, the photocatalytic decolorization can only proceeds under UV irradiation because it has wide band gap and absorb UV light with ≤ 387nm [10] . Unfortunately solar spectrum consists only 5–7% of UV light, the other 46% and 47% of the spectrum are visible light and infrared radiation, respectively. This minimal extent of UV light in the solar spectrum has particularly ruled out the use of natural source of light for photocatalytic decomposition of inorganic contaminants and bacteria disinfection from water and air on large scale[11]. To sensitize ZnO to visible light and enhance its photocatalytic activity, many effort have been made, such as noble metal deposition [12], composite semiconductor[13] metal doping [14],rare earth doping [15], nonmetal doping [16] and so forth. Among these, nonmetal doping has been reported to be an effective way by many researches [17,18].Nonmetal doping could form a localized state slightly above the valence band in the band gap, causing bad narrowing and it could also reduce the formation energy of oxygen vacancies, which are energetically favorable for the enhancement of light absorption and photocatalytic activity [19,20].

To the best of the researchers' knowledge, no work is reported on the effect of ZnO nanoparticles modified with Cr-N-P tri doping for degradation of malachite green. Therefore, the impetus behind this study is to study the effect of Cr –N-P tri doping in ZnO nanoparticles on the photocatalytic degradation of malachite green.

MATERIALS AND METHODS

Synthesis of photocatalyst

Preparation of Zinc oxide nanoparticles

ZnCl$_2$ (0.5mol) was dissolved in 100 mL of distilled water with continuous stirring. NaOH solution was added into the beaker drop by drop until the pH of the solution became 12. During the addition of NaOH solution, white particles were started to precipitate and finally the sedimentation process was finished at pH 12. White particles were washed three times with distilled water and dried for 24 h at 80°C. At this point, the white product did not show high crystalline since it consists of ZnO and Zn(OH)$_2$. Annealing at 600°C for 3h was necessary to obtain high crystalline ZnO.

Preparation of BNP-ZnO nanoparticles

Two kinds of crop seeds were employed as bio-precursors to synthesis biogenic N-P co-doped ZnO nanoparticle namely; Chickpea (Cicer arietinum) and Glutinous rice (O.sativa L.).Seeds of rice mainly contain starches. Starches in this seeds are mixture of amylose and amylopectin while seeds of chickpea mainly contain proteins and fats, respectively.

15 gm of each crop seeds were taken and cleaned with pure water three times to remove the tastae (coat).The coatless crop seeds were treated with 100 ml of 5%HCl solution for 12 h to get rid of K, Ca and S ions. The solutions were rinsed with pure water. Then 10 gm of ZnO was taken and mixed with each of crop seeds. The reaction is assumed to have been under gone grinding together by using mortar and pestle. Then the samples were dried in an oven at 80°C for 24 h.At this point we do not get the pure BNP-ZnO because starches and proteins were hydrophilic colloids, containing many functional groups such as hydroxyls and carbonyls, Zn ions were easily introduced in to seeds. So, calcining at500^{o}cfor 2 h, with a ramping rate of 1^o_C / min.

Preparation of Cr-doped ZnO nanoparticles

The doping concentrations, 10% (mol), of Cr–ZnO were prepared by the incipient wetness impregnation method. 2.214 g of chromium nitrate nonahydrate [Cr (NO$_3$)$_3$·9H$_2$O] was dissolved in 100 ml of deionized water and then was added to 10 g of undoped ZnO and the mixture was stirred continuously for 1 h. The product was allowed to settle down for 24 h, filtered with membrane filter and washed three times each with DI water and ethanol. The filtered/washed precipitate was dried at 105^{0}C for 12 h, after drying was calcined at 550^{0}C for 2 h in programmable furnace [21].The product obtained was labeled as chromium-doped Zinc oxide (CrZ).

Preparation of Cr-N-P-tri doped ZnO nanoparticles

5 g of each crop seeds were transferred to a ceramic crucible and 0.153 g synthesized Cr-doped ZnO nanoparticles were added into nanoparticles. After agitating with glass rod then, was calcinated at 600°C, cool to room temperature and labeled as Cr-N-P tri-doped ZnO (CrNPZ).

Characterization

X-ray diffraction (XRD) study

X-ray diffraction patterns of as synthesized photocatalysts were obtained using a BRUKER D8 (West Germany) X-ray diffraction (XRD) equipped with a Cu target for generating a Cu Kα radiation wavelength (λ = 1.5406 A°) at GSE. The measurements were made at room temperature accelerating voltage and the applied current is 40 kV, 100 mA respectively. The instrument was operated under steps can type with step time and degree (2θ) of 1s and 0.020°, respectively for the range of 4° to 64°. The average crystallite size of the as-synthesized photocatalysts can be calculated using the Debye-Scherrer formula, as used by[22].

$$D = \frac{K\lambda}{FWHM \cos\theta}$$

where D is the average crystallite size, λ is the wavelength of the X-ray = 0.15406 nm for Cu target Kα radiation, FWHM is the full width at half – maximum of an XRD peak and θ is the Bragg's angle.

Absorption edge determination

The light harvesting capacities and absorption edge of as-synthesize nanoparticles were determined by using UV-VIS absorption spectra, record on SANYO UV-Vis spectrophotometer model (SP65) in the spectral range of 200-800 nm. The same quality for all the CrBNP-ZnO and undoped ZnO samples were taken during the measurement. Band gap energy of the as-synthesize photocatalysts were obtained using the relation[23].

$$E_g = \frac{1240}{\lambda}$$

Where, E_g-is band gap energy and λ- is maximum wavelength (nm) corresponding to absorption edge of nanoparticles.

Fourier transforms infrared (FT-IR) study

Surface structure of all samples was characterized by a shimadzu 8400S (German) Fourier transform infrared (FT-IR) spectroscope. Measurements were performed with pressed pellets make using paraffin as diluents. The FT-IR spectrum was collected between the wave numbers of 400 and 4000 cm^{-1}.

Photocatalytic degradation studies

Catalytic activities of the as-synthesized photocatalysts were studied for degradation of malachite green (MG). The experiments were carried out under dark and visible light (619 nm) using as-synthesized photocatalysts. First 0.0102 g of MG was dissolved in 500 ml of deionized water and MG solution was prepared. 0.1 g of ZnO sample was disperse in 100ml of MG solution in reactor tube. ZnO aqueous suspension was stirrered in dark for 1 hr and purge for 20 min to reach its adsorption equilibrium. Degradation was monitored by taking sample solution at 0, 12, 24, 36, 48, 60, 72, 84, 96, 108 and 120 min respectively during the irradiation time. These sample solutions were centrifuge with 3000 rpm for 3 min. Then, the supernatants were tested by using UV-Vis spectrophotometer to get absorption spectra. Percentage degradation efficiency (% DE) of the sample was calculate by:

$$\% \, DE = \frac{Ao - A}{Ao} X \, 100$$

Where A_0 is absorbance of dye at initial stage, A_t is absorbance of dye at time "t".

RESULTS AND DISCUSSION

XRD analysis

The XRD patterns of calcined ZnO (Zc), Cr-doped ZnO (CrZ), N-P co-deped ZnO (Chickpea),N-P co-doped ZnO (Rice) and Cr-N-P tri-doped ZnO (CrNPZ) are shown in Figure 1. The diffraction peaks at scattering angles (2θ): 31.77, 34.42, 36.34, 47.54, 56.60, and 62.86 corresponds to the reflection from (100), (002), (101), (102), (110), and (103) crystal planes for all as-synthesized powders suggesting pure hexagonal wurtzite structure of ZnO[24].

In the XRD spectra of modified ZnO, there is a replication of all peaks which appeared in the ZnO spectra. The peaks appeared in NPZ and CrZare broader than those for pure ZnO. There are additional, extra peaks appeared in the XRD spectra of CrZ, which may be due to the presence of small amount of $Cr(NO_3)_3$

impurity in Zc[25].It is noted that all the catalysts are in the form of nanoparticulates with average crystallite sizes ranging from 41.6 to 48.1 nm. Compared to calcined ZnO, the average crystallite size for the CrZ sample decreased, implying that doping Cr within ZnO restrains the increase of grain size [26].The average crystallite size of the as-synthesized photocatalysts can be calculated using the Debye-Scherrer formula, as used by [22].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the average crystallite size, λ is the wavelength of the X-ray = 0.15406 nm for Cu target Kα radiation, β is the full width at half – maximum of an XRD peak and θ is the Bragg's angle. The most intense peak (101) in the XRD patterns was used to calculate the average crystalline size. The calculated average crystallite size (D) of the photocatalysts is given in Table 1.

Table 1: Average crystallite size (D) of as-synthesized photocatalysts

Sample	2θ (Degree)	β (Radian)	D (nm)
Zc	36.357	0.00358	48.1
CrZ	36.34	0.00368	46.7
CZ	36.378	0.00373	46.2
RZ	36.373	0.00377	45.7
CrNPZ	36.372	0.00413	41.6

Orders of average crystallite size (D) of as-synthesized photocatalysts are: CrNPZ< RZ < CZ <CrZ< ZC.

Figure 1: XRD spectra
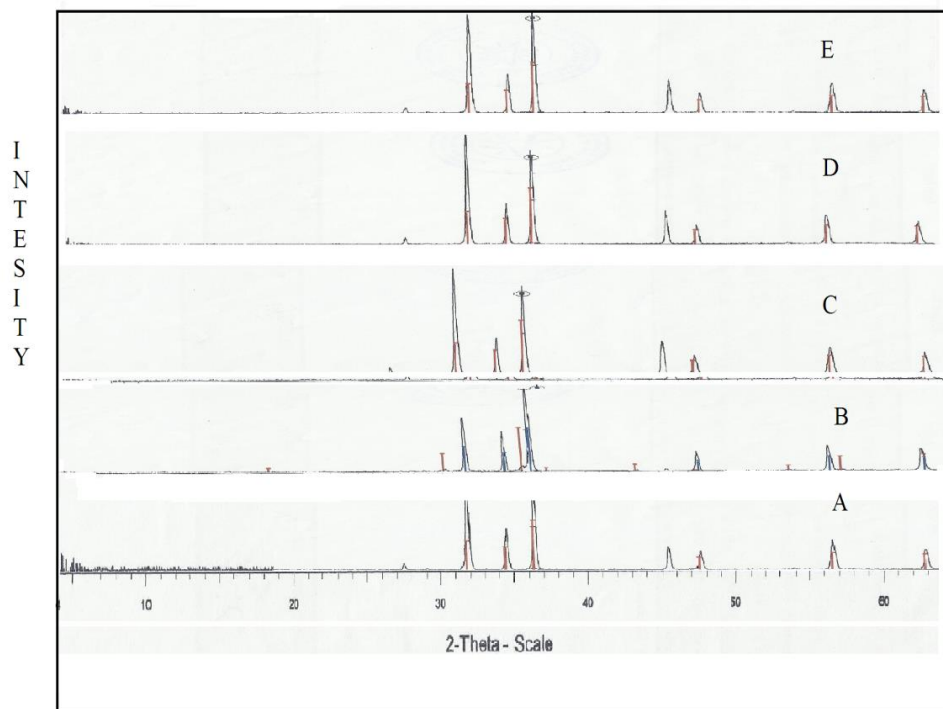
A) CalcinedZnO B) Cr-dopedZnO C) Chickpea-doped ZnO
D) Rice-doped ZnO E) Cr-N-P tri-dopedZnO

Figure 2: UV-Visible absorption spectra of undoped zinc oxide (absorption edge 386 nm).
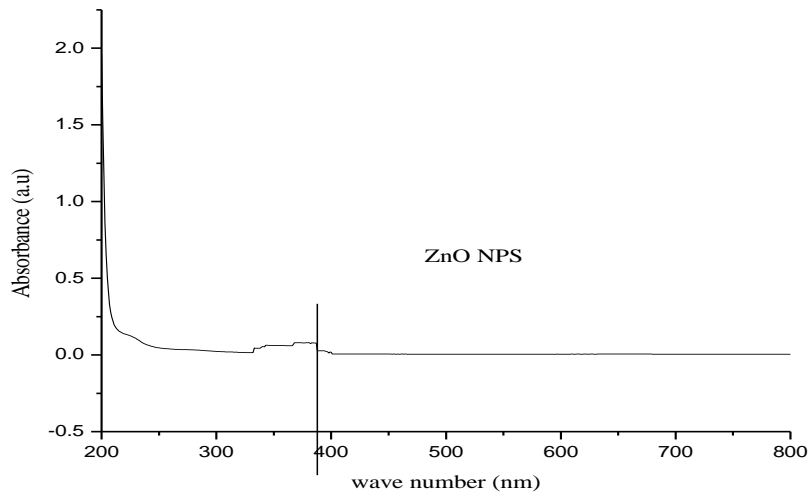

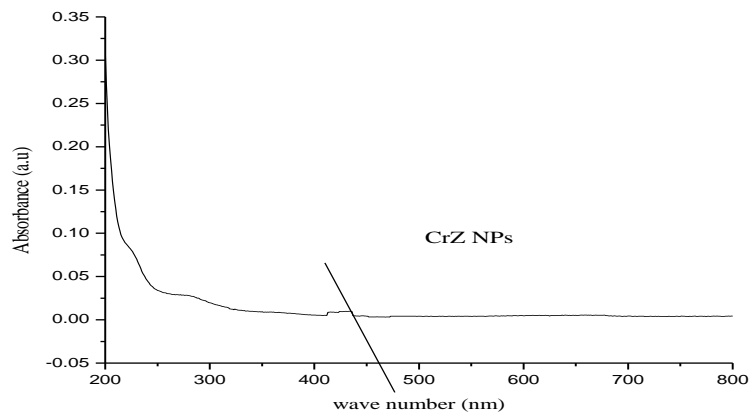**Figure 3: UV-Visible absorption spectra of Cr-doped zinc oxide (absorption edge 464 nm).**

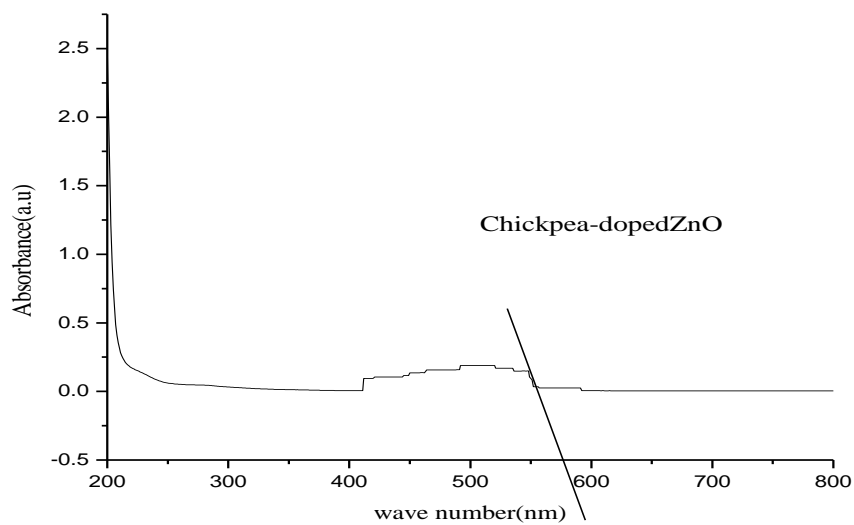**Figure 4: UV-Visible absorption spectra of chick-doped zinc oxide (absorption edge 577 nm).**

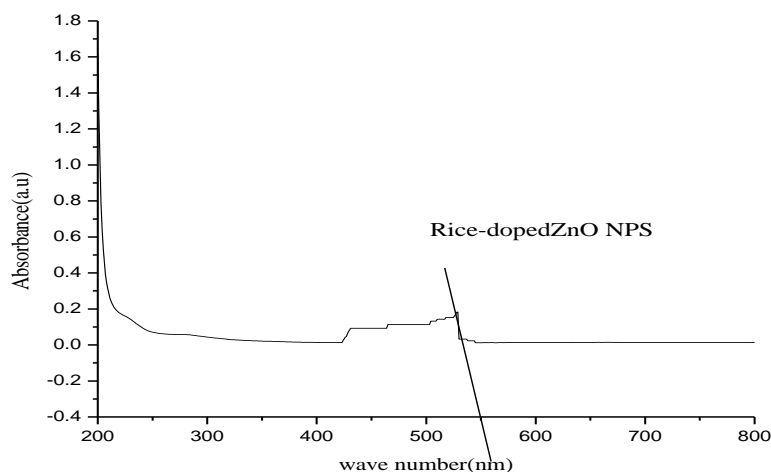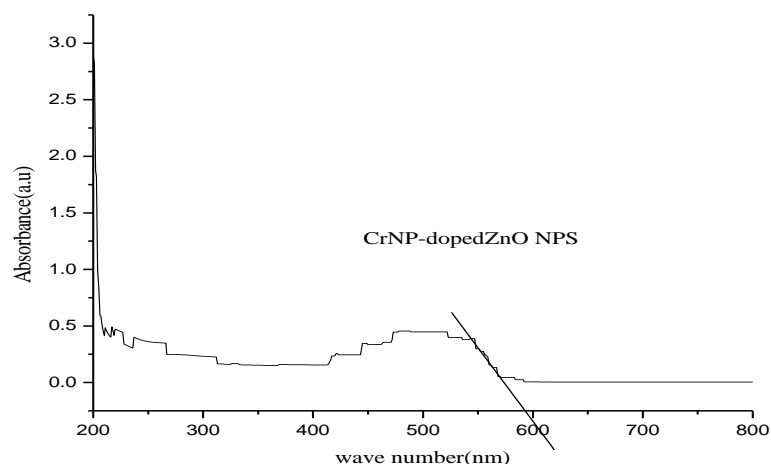**Figure 5: UV-Visible absorption spectra of rice-doped zinc oxide (absorption edge 551 nm).**

Figure 6: UV-Visible absorption spectra of CrNP-doped zinc oxide (absorption edge 588 nm).

UV-Vis absorption spectra analysis

The optical absorption spectra were determined using UV/Vis spectroscopy. UV/Vis absorption spectra of the as-synthesized photocatalysts: Zc, CrZ, CZ, RZ and CrNPZ are shown in Figures 2-6. Absorption edge for Zc, CrZ, CZ, RZ and CrNPZ are: 386, 464, 577, 551 and 588 nm, respectively. The sample Zc shows the band gap absorption at 386 nm, corresponding to an intrinsic absorption of ZnO. This absorption peak is red shifted as compared to the bulk exciton, which is due to the size effect of the nanostructures. It is clear that the absorption wavelength range of chickpea and rice - ZnO powders are shifted to longer wavelength as compared with pure ZnO powder, and its absorption intensity is also increased.

The narrowing of band gap due to N and P doping may be due to the delocalized N and P 2p states, thus greatly contributing to the formation of VB with the O 2p and metal 3d states. Consequently, the mixing of the N and P 2p states with VB increases the width of the VB itself, thus narrowing down band gap. Undoped ZnO shows steep edge which is a typical characteristic of direct allowed transition between valence and conduction band corresponding to the transition between p state of oxygen and s state of zinc (figure 4). On the other hand, Cr-doped ZnO shows shifting absorption edge to visible light region. The band gap is therefore found to decrease. Thus, the reduction in the band gap can be attributed to the transitions between the valance and conduction bands and also due to the exchange interaction between the d electrons of Cr^{3+} ions. For Cr doped ZnO nanoparticles d-orbital of chromium mixed with the zinc orbital may act as a valence band.

On the other hand conduction band may be consisting of mixture of Cr orbital and oxygen orbital. The optical absorption edges of the catalyst CrNPZ obviously shifted further to the visible region compared with the CrZ , CZ and RZ a significant enhancement of the visible-light absorption is obvious, due to may be synergetic effect.

Band gap energy (Eg) of the as-synthesized photocatalysts was calculated using the equation depicted below [23].

$$Eg = \frac{1240}{\lambda} \, eV$$

Where, E_g is band gap energy in electron volts and λ is wavelength (nm) corresponding to absorption edge.

The E_g of photocatalysts Zc, CrZ, CZ, RZ and CrNPZ were found as 3.21, 2.67, 2.15, 2.5 and 2.11 eV, respectively

FT-IR analysis of photocatalysts

Figure 7-11 shows the FTIR spectra of calcined ZnO (Zc), Cr-doped ZnO (CrZ), N-P co-doped ZnO (NPZ) (chick pea-ZnO), N-P co-doped ZnO(Rice-ZnO) and Cr-N-P tri-doped ZnO (CrNPZ) photocatalysts, respectively. The broad band 3512- 3450 cm^{-1} was observed in all samples which may be due to the vibration mode of OH group of water adsorbed molecule (Ahmed, *et al.*, 2011) indicating the existence of small amount of water absorbed by the photocatalysts. Absorption bands at 494 cm^{-1}, 454 cm^{-1}, 774cm^{-1}, 481 cm^{-1}and 467cm^{-1} is observed in the spectra of Zc, CrZ, chickpea-doped ZnO, rice-doped ZnO and CrNPZ photocatalysts, respectively which is assigned to the stretching vibrations of Zn−O (υZn−O). In addition, the peaks at 2859 cm^{-1}, 2912 cm^{-1}, 2925 cm^{-1},2925 cm^{-1}, 2939 cm^{-1}was observed which is due to symmetric C-H stretching and the peak between 1210-1140 cm^{-1} was observed due to symmetric P=O stretching mode frequencies in Figures 9-13, due to may be effect of diluents (paraffin)and the other peaks that appear at 1462 and 1377 cm^{-1} in all photocatalysts may be due to O-C-O stretching vibrations CO$_2$originated from atmospher and also for absorbance spectra showing in the range 1400 - 2200 cm^{-1} region, N-doped ZnO has very strong absorption peaks [27].
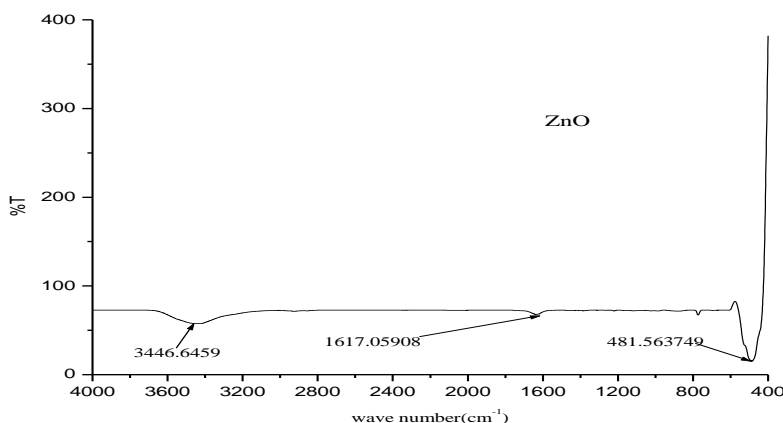
Figure 7: FTIR spectra of ZnO

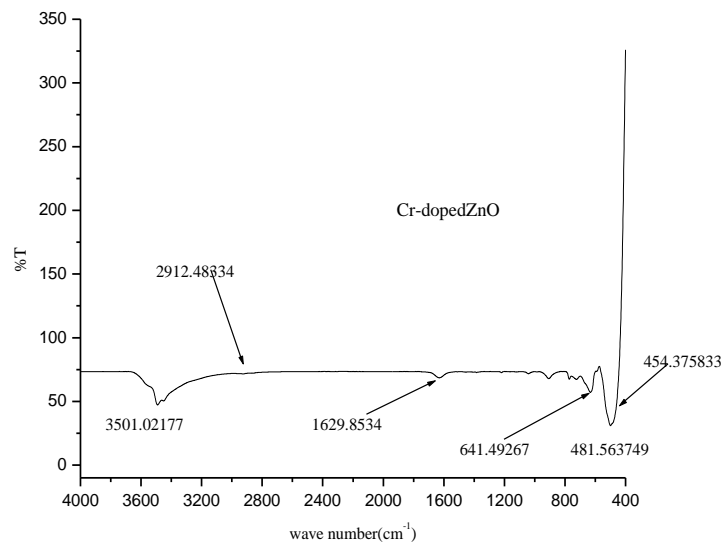**Figure 8: FTIR spectra of Cr- doped ZnO**

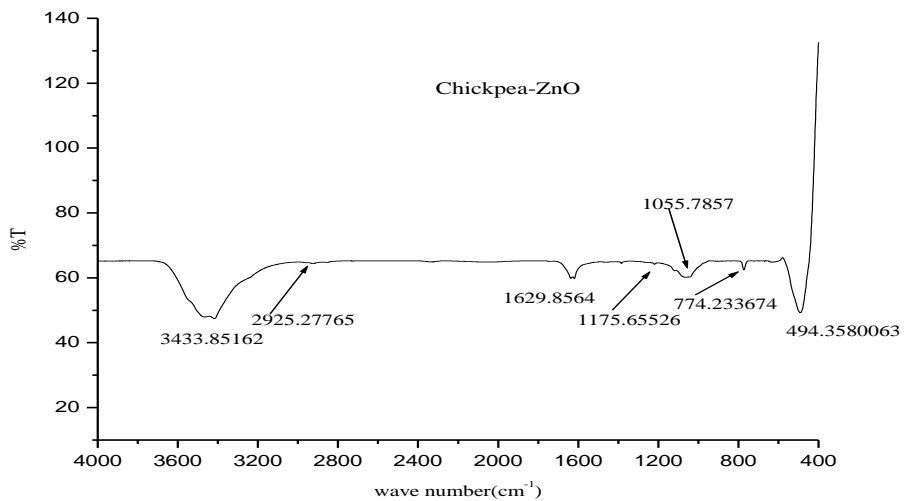**Figure 9: FTIR spectra of chickpea-doped ZnO**

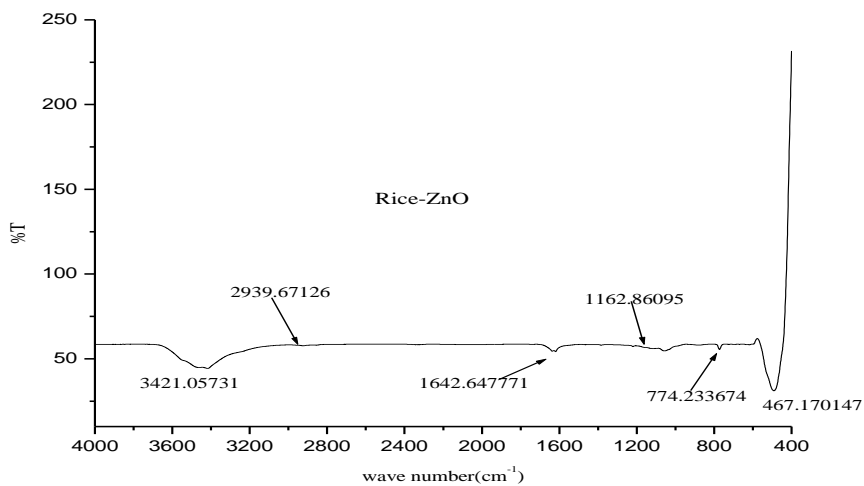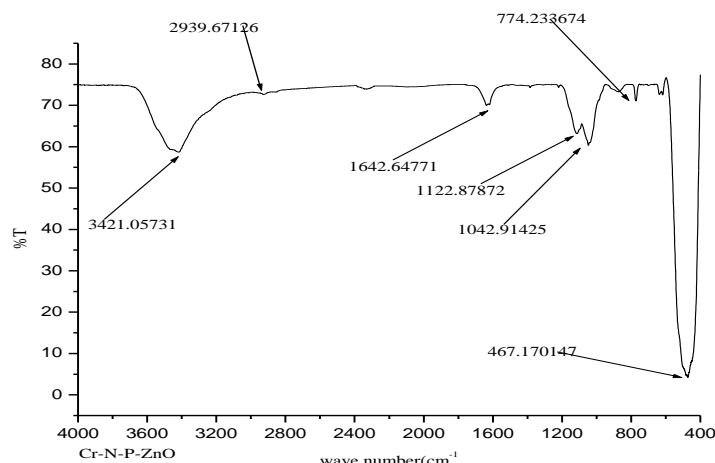**Figure 10: FTIR spectra of Rice-doped ZnO**

Figure 11: FTIR spectra of CrNPZ

Photocatalytic Degradation Study

The photocatalytic activities of as-synthesized nanomaterials were investigated for the degradation of malachite green (MG) dye solution under dark and visible light in 619nm. Percent adsorption values of MG as a function of time under no-irradiation are given in Table 2. The photocatalytic degradation values as a function of time under visible irradiation was presented in Tables 3. Plots of percent adsorption as a function of time under no-irradiation is given in Figure 10 and plots of percent degradation as a function of time under visible irradiations is given in Figure 11. The percentage adsorption of MG in dark (without irradiation) using the photocatalysts ZC, CrZ, NPZ(chickpea-doped ZnO),NPZ(rice-doped ZnO) and CrNPZ at 120 minutes were 7.4%, 4.0%, 3.5%, 3.0%, and 8.6%, respectively. The percent adsorptions of MG in dark are used as reference as zero minute irradiations [25].

Table 2: Percentage degradation of malachite green dye under dark (without irradiation) as a function of time using different as-synthesized photocatalysts

| Time	ZcCrZ	CZ	RZ	Cr	NPZ	ZC	CrZ	ChickpeaZ	RiceZ
0	0	0	0	0	0	0	0	0	0
12	0.257	0.152	0.174	0.325	0.257	0.051	0.152	0.068	0.235
24	0.456	0.232	0.204	0.650	0.772	0.355	0.232	0.204	0.650
36	1.070	0.533	0.476	0.975	1.158	0.560	0.533	0.476	0.975
48	1.570	0.761	0.7473	1.300	2.188	1.070	0.761	0.747	1.300
60	2.080	0.914	0.951	1.626	3.475	2.080	0.914	0.951	1.626
72	3.399	1.752	1.359	1.952	4.118	4.008	0.990	1.359	1.952
84	4.008	2.513	1.834	2.276	5.405	5.631	1.752	1.834	2.276
96	5.631	3.275	2.310	2.602	6.692	6.850	3.275	2.310	2.602
108	6.850	3.656	2.989	2.764	7.593	7.360	3.656	2.989	2.764
120	7.366	4.037	3.465	3.008	8.623	8.270	4.037	3.465	3.008

Photodegradation under visible radiations are found to be 57.6%,68.0%, 74.0%, 70.0%, 86.7%, for Zc, CrZ, CZ, RZ and CrNPZ respectively. The photocatalytic degradation of malachite green was found to be of first order. In case of CrZ under visible light irradiations, Cr can entrap the photo-generated electrons there by reducing probability of electron hole recombination, and hence increase photocatalytic activity. In case of NPZ e^{-1} - h^+ recombination might have been delayed by the addition band introduced. The red shift observed by the biodopants on ZnO electronic structure supports the incorporation of additional bands. The order of photocatalytic efficiency of as-synthesized nanomaterials under visible radiation was: CrNPZ> CZ>RZ >CrZ>ZC whereas under dark it was: CrNPZ> ZC >CrZ>CZ >RZ.

Table 3: Percentage degradation of malachite green dye under visible irradiation as a function of time using different as-synthesized photocatalysts

| Time (min)	ZC	CrZ	ChickpeaZ	RiceZ	CrNPZ
0	0	0	0	0	0
12	6.55	8.45	20.45	13.33	12.34
24	14.05	17.29	34.98	21.83	26.12
36	23.012	26.88	45.65	33.34	36.68
48	31.21	32.22	53.32	41.12	49.65
60	37.02	37.54	62.54	49.23	57.34
72	40.78	43.64	66.54	54.12	68.73
84	45.54	48.21	68.20	58.69	75.57
96	49.43	53.54	69.40	62.43	79.45
108	53.74	60.39	72.21	66.73	83.54
120	57.64	68.01	74.05	70.01	86.65

Adsorption of dye molecules on the photocatalyst (ZnO) is a prerequisite for photo degradation; a corollary is that the photoinduced reaction occurs on the catalyst surface rather than in solution bulk. The photocatalytic degradiation efficiency of NPZ (chickpea doped ZnO) and NPZ(rice doped ZnO) shows higher photocatalytic activity than Zc under visible light irradiations. This may be due to narrowing of band gap energy on co-doping of nitrogen and phosphorus to zinc oxide (Chen *et al.*, 2009). CrZ shows higher photocatalytic activity than Zc under visible light irradiations. This may be explained by ability of Cr to trap electrons from CB. This process reduces the e^- and h^+ recombination at ZnO surface. Therefore, a more effective electron and hole transfer occurs to the electron acceptors and electron donors, respectively adsorbed on the surface of the particle than in the case of Zc. The photocatalytic activity of CrNPZ is large compared to other as-synthesized photocatalysts under study in Visible light irradiations. This is due to synergetic effect of electron trapping by Cr-doping and band gap narrowing by N-P co-doping ZnO nanoparticles.

Figure12: Plot of percentage degradation of malachite green dye under without irradiation as a function of time using different as-synthesized photocatalysts
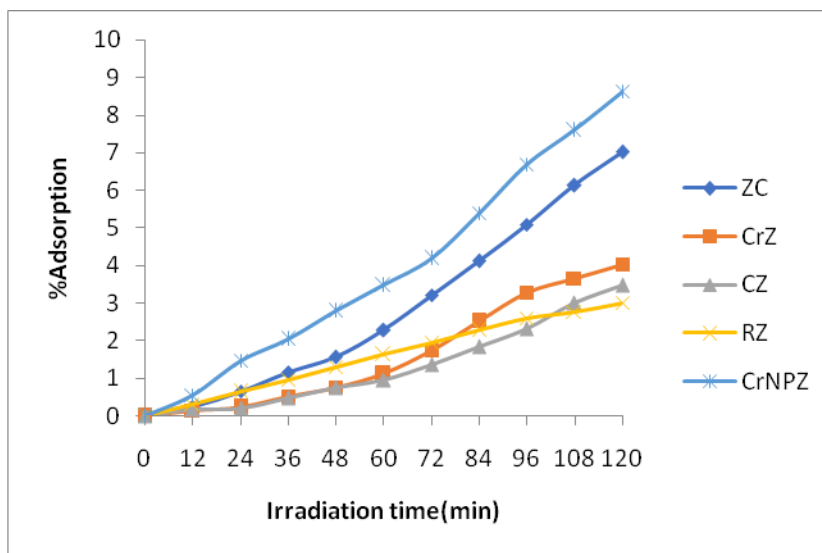
[Zc = calicinate zinc oxide,Crz = chromiumzinc oxide, CZ = chickpea zinc oxide,RZ = rice zinc oxide and CrNPZ =chromium-nitogen-phosphoruse zinc oxide]

Figure 13: Plot of percentage degradation of malachite green dye under visible irradiation as a function of time using different as-synthesized photocatalysts.
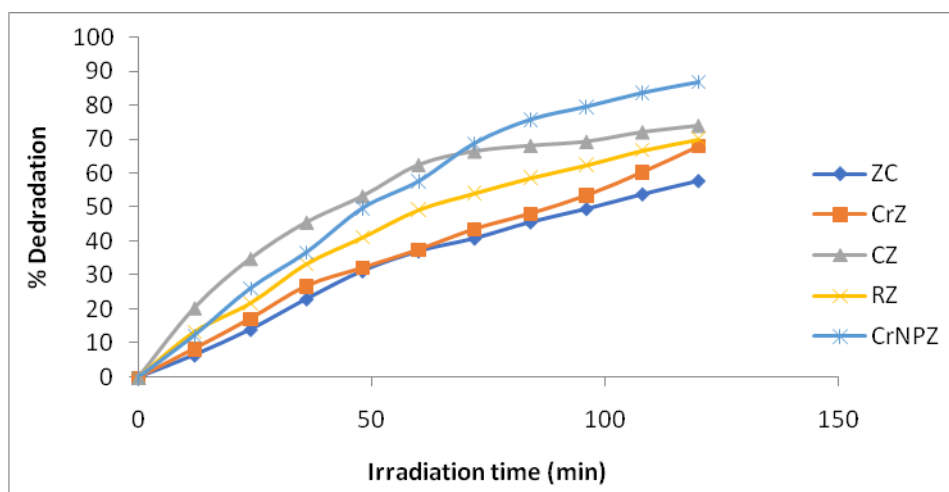
Photocatalytic efficiency is a function of oxygen vacancies and defects in ZnO. These vacancies and defects inhibit the e^- - h^+ recombination process by capturing photoinduced electrons and holes and hence improve photoactivity. Moreover, oxygen vacancies also promote the adsorption of O_2 which is converted into superoxide radicals ($^{\bullet}O_2^-$) by interacting with photo-induced electron. These $^{\bullet}O_2$ radicals are active to promote the oxidation of organic substances by forming other radicals such as $^{\bullet}OH$, $HO_2^{\bullet}$ (Patilet al., 2010).

CONCLUSION

Nano-sized photocatalysts: ZnO, Cr-doped ZnO, NP doped ZnO(chickpea) and NP doped ZnO (rice) and Cr-N-P tri doped ZnO were synthesized. XRD spectra for these photocatalysts showed that these doped ZnO have wurtzite crystalline structure. UV-Vis absorption spectra suggest that there is band gap narrowing of ZnO on doping Cr^{+3}, chickpea as well as rice.

N and P doping into zinc oxide modifies its electronic properties leading to the optical absorption of zinc oxide well extended to the visible light region. Whereas doping Cr in ZnO reduces e^- - h^+ recombination. Hence, doping Cr^{+3} has synergetic effect for photocatalytic degradation of malachite green.

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