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Facile synthesis of copper doped ZnO nanorods for the efficient photo degradation of methylene blue and methyl orange

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Abstract

In this study, zinc oxide (ZnO) nanorods are doped with copper by low temperature aqueous chemical growth method using different concentrations of copper 5 mg, 10 mg, 15 mg and 20 mg and labeled as sample 1, 2, 3 and 4 respectively. The morphology and phase purity of nanostructures was investigated by scanning electron microscopy, and powder X-ray diffraction techniques. The optical characterization was carried out through UV-Vis spectrophotometer. The band gap of copper doped ZnO has brought reduction at 250-600 nm and it indicates the fewer time for the recombination of electron and hole pairs, thus enhanced photo degradation efficiency is found. ZnO exhibits nanorods like shape even after the doping of copper. The photo degradation efficiency for the two chronic dyes such as methyl orange MO and methylene blue MB was found to be 57.5% and 60% respectively for a time of 180 mins. This study suggests that the copper impurity in ZnO can tailor its photocatalytic activity at considerable rate. The proposed photo

catalysts are promising and can be used for the waste water treatment and other environmental applications.

Keywords: Methylene blue, methyl orange, copper doping, band gap, ZnO nanostructures, photocatalysis

1. Introduction:

Development of any country is depending on the progress made in the industrial products. At the same time, industry produces several pollutants such as effluent, gaseous and solid wastes which bring the severe effect on the life. These pollutants are causing the air pollution and their release into natural water gives water pollution. Among the pollutants, the industrial dyes are creating a significant damage in our environment [1]. Therefore, the degradation of these dyes is a big challenge using a simple strategy and is known as a hot spot for the investigation for improving the quality of environment and ultimately to best of our life [2-4]. The potential and promising strategy is the photo catalysis for the degradation of dyes and it does not produce any secondary pollutants [5]. Also, photo catalysis is economic, nontoxic, consumes less energy, and can be reused [6]. Several, photocatalysts are developed and among them oxide semiconductors are found to be efficient for the photodegradation such as TiO_2 [7, 8] that is intensively used due to its strong absorption in the UV region. However, TiO_2 is associated with certain limitations such as high recombination rate, low quantum yield [9] in water media and wide band gap. The wide bandgap allows TiO_2 to absorb only UV light which is approximately 4% of the white light (Sun light), thus low photo conversion efficiency is so far received in photocatalysis. Because of these reasons both the researchers and industrialists are searching for the alternative potential photocatalysts and in this regard, ZnO has received lot of attention [10] due to its promising properties in the photo catalysis [11,12, 13,14, 15], photo degradation [16], as well as in in other several applications such as gas sensors [17], solar cells [18], transistors [19], light emitting devices [20], and cancer treatment [21]. ZnO has several advantageous features such as inexpensive, earth abundant, can be produced with high yield, environment friendly, chemical and thermally stable [13]. ZnO exhibits better photo catalytic activity than TiO_2 with higher quantum efficiency [22] [23, 24] as it absorbs larger fraction of solar spectrum than TiO_2 . Despite these useful features ZnO also experiences the limitations such as high recombination rate and consequently poor photocatalytic activity is found. The poor efficiency of ZnO is improved through doping that has shown

considerable impact on the optical band of ZnO [25, 26]. Several dopants including Fe, Ag, Ni, Co, Mn and copper are used for ZnO [27-33]. Among them copper shows unique features such as, similar size to that of zinc, improves the separation of charge carriers, possess greater surface area, brings a reduction in the optical band gap and can produces lattice defects in semiconducting photo catalyst [34] and further it facilitates the photo catalytic properties [14], The one dimensional nanostructures such as nanowires/nanorods are the most suitable for the photo catalysis due to their large surface to volume ratio and they play a dynamic role in the photo catalytic activity, thus doping the ZnO by maintaining the morphology is a key challenge with outperform photo conversion efficiency [35].

It has been reported in literature [36-37] that photocatalytic efficiency is dependent upon band gap and increases with decrease in band gap. Abdus Saboor and co-workers [38] succeed in remarkable decrease in band gap by 19.27% with Ag doping and by 18.96% with Nd doped ZnO. A.Modvi and coworkers [39] reduced the band gap of ZnO while inducing copper in combination with transition metals. They achieved band gap reduction by 6.35% with copper doping and upto 11.43% with doping copper in combination with Ag. The effect of copper dopant on the photo catalytic degradation is rarely investigated and further its governing role on the photo degradation efficiency is remained unexplored but this study has shown them systematically.

In this study, we have successfully doped ZnO with copper and maintain the nanorod like morphology. The ZnO nanorods are doped with different copper concentrations such as 5, 10, 15 and 20 mg. The pristine ZnO and copper doped ZnO nanostructures were used to degrade the methylene blue and methyl orange which are known as the most hazardous to the environment. The photo degradation efficiency for both MO and MB are compared, and photocatalytic mechanism has been proposed. We successively reduced the band gap of ZnO from 3.46 (pristine ZnO) to 3.10 eV with increase in copper content up to 20 mg. . It shows a significant effect of copper doping on band gap reduction leading to the increase in photocatalytic efficiency.

2. Materials and Experimental Section

Copper acetate ($\text{Cu}(\text{OAc})_2$), zinc acetate-dihydrate ($\text{ZnC}_4\text{H}_6\text{O}_4$), ammonia solution, and ethanol ($\text{C}_2\text{H}_5\text{OH}$), were of analytical grade and received from Sigma-Aldrich), Karachi Pakistan. The deionized water was used for the preparation of solutions throughout the study.

We used low temperature aqueous method to get ZnO nanorods and their doped samples [40-41]. The zinc acetate dihydrate ($\text{ZnC}_4\text{H}_6\text{O}_4$) and ammonia (NH_3) solutions were mixed in the deionized water and copper acetate ($\text{Cu}(\text{OAc})_2$) was used as dopant source. The dopant concentration was varied such as (5 mg, 10 mg, 15 mg, 20 mg and named as sample 1, 2, 3 and 4 respectively), then subsequently mixed with the precursor solution and uniform mixture was obtained by mechanical stirring for 30 min. The zinc precursor 2.22g of $\text{ZnC}_4\text{H}_6\text{O}_4$ and 5 mL of 25% of ammonia solution was used for the preparation of pristine ZnO and copper doped samples. The growth solution was covered with the aluminum foil and kept in oven at 95 °C for 6 hours. The nanostructured materials were obtained after the growth duration by filtration and dried at room temperature.

The crystalline features of as prepared samples investigated by the powder X-ray diffraction using (Make Panalytical X'Pert Pro $\text{Cu K}\alpha$), and Morphology of as prepared nanostructures was studied using scanning electron microscopy at the accelerating voltage of 3 kV. The photo catalytic and optical band gap studies were carried out by using UV-Vis spectrophotometer.

The photocatalytic study of synthesized pristine and copper doped ZnO nanorods for the degradation of MO and MB was carried out at the different intervals of time and UV light treatment. We have measured the degradation rate of both dyes in aqueous solution using fixed amount of 5 mg photo catalysts. The concentration of MB and MO solution was taken 0.03 mM. The pH for the MB and MO was found 6.79 and 3.65 respectively. The photo catalytic activity was measured at different intervals of time and all other experimental conditions for the samples were same. Typically, in the measurement of photocatalytic activity, we used three 360 nm UV lamps of 10 W each. And fixed amount of photo catalyst and MO/MB were homogenized in 250 mL beaker using ultrasonic bath for 10 mins. Then solution was stirred via magnetic stirring for 30 mins in dark in order to ensure the adsorption-desorption equilibrium state for MO/MB on the surface of photo catalyst. Then UV light was applied to the solutions for different time intervals. During the irradiation of UV light, the suspension was collected and analyzed via UV-visible spectrophotometer (PE Lamda 35) with respect to maximum absorption of MO/MB and to correlate the concentration of the MO/MB in the solution.

The calculation for the degradation efficiency was done via following equation:

$$\text{Degradation efficiency \%} = \frac{C_0 - C_t}{C_0} \times 100$$

Here C_0 is the initial MO/MB concentration (mg/L), C_t shows the MO/MB concentration (mg/L) after at different intervals of irradiation times (t). For confirming the pseudo order kinetics for the MO and MB using UV light as irradiant source and following equation was used

$$\ln C_0/C_t = K_{app} \times t$$

Herein, K_{app} represents apparent rate constant, C_0 represents the initial MO concentration (mg/L) at irradiation time 0 min, and C_t shows the MO/MB concentration for the time t 248 (mg/L). The UV-Visible absorbance spectra were recorded using 5 mg of photo catalyst for the estimation of optical bandgap.

3. Results and Discussionss

The powder XRD was used to investigate the crystallography of as prepared nanostructured ZnO and copper doped ZnO as shown in Figure 1. The ZnO exhibits the wurtzite (hexagonal) phase and with the addition of copper impurity in the precursor of ZnO that did not bring any substantial changes in the intensity of diffraction patterns. The diffraction patterns related to pristine ZnO include 31.737° (010), 34.420° (002), 36.225° (011), 47.515° (012), 56.536° (110), 62.836° (013), 66.304° (020), 67.893° (112), 69.015° (021), and 72.561° (004), 76.891° (022), 81.364° (014), and 89.544° (023) and they are in good agreement with the standard JCPDS card no. 96-900-4182. Besides this, XRD was used record the changes in the crystallinity of copper doped ZnO samples and the patterns are indexed to the crystal planes at slight distortion of angle such as 31.777° , 34.433° , 36.264° , 47.554° , 56.612° , 62.879° , 66.396° , 67.97° , 69.108° , 72.594° , 76.985° , 81.417° and 89.646° seems which indicates that doping has changed the lattice location and which can be assigned to the substitutional doping of copper into ZnO crystal. All the diffraction patterns are in good agreement with the standard JCPDS card no 96-230-0113. The XRD analysis indicates that copper is successfully doped into ZnO and no other impurity such as metallic copper or Cu_2O or CuO was identified.

Figure1: The XRD spectra of undoped ZnO nanorods and copper doped ZnO nanorods with 5, 10, 15 and 20 mg copper dopant concentration

The shape features of as prepared pristine ZnO and copper doped ZnO are investigated by low resolution scanning electron microscopy as depicted in Figure 2. Figure 2a shows the SEM images of 5mg and 10mg copper doped ZnO and Figure 2b for 15mg and 20mg copper doping in ZnO and Figure S1 shows the morphology of pristine ZnO. The length of ZnO nanorods is few microns and diameter is in the range of 200-300 nm. The interesting point in SEM analysis is that before and after the copper doping there is no alternation in the morphology of ZnO and it remains well controlled in length and diameter. The EDS elemental mapping confirmed the uniform distribution of copper into ZnO nanorods and main elements are Cu, Zn and O as shown in Figure S2. The impurity of Cr and Ag is emerged from the substrate.

Figure 2a

Figure 2b

Figure 2: SEM images for ZnO nanorods doped with various concentrations of copper (a) ZnO nanorods doped with 5 mg and 10 mg of copper (b) SEM images of ZnO nanorods doped with 15 mg and 20 mg of copper

The photocatalytic activity of as prepared samples was monitored by the treatment of MB and MO dyes solution with UV light and the relative decrease in the UV-visible light absorption at different intervals of time as shown in Figure 3 for degradation of MO with Copper doping (a-d) and 4 for degradation of MB with copper content (a-d). In each dye solution a fixed amount of photo catalyst was added. The photo degradation efficiency was found increasing with increase in the concentration of copper dopant into the ZnO nanorods.

Figure 3: UV-Vis absorption spectra of various copper doped ZnO nanorods for degradation of MO at different time irradiations of 15, 30, 45, 60, 75, 90 and 105 minutes (e) UV-Visible absorption spectra of pure ZnO at different intervals of time.

Figure 4: Figure 4: UV-Vis absorption spectra of various copper doped ZnO nanorods for degradation of MB at different time irradiations of 20 to 180 minutes at equal intervals of 20 min as compared to (e) pure ZnO for time irradiations of 30 to 360 min at equal intervals of 30 min respectively.

At first photo degradation was performed on pristine ZnO in Methyl Orange (MO) for 360 minutes and it was found that the undoped ZnO progressively degraded up to maximum of 60% efficiency. (Figure 5b)

To investigate the photo catalytic effect of various copper doped ZnO nanostructures in the degradation of MO and it has been shown that copper doping has significantly changed the photo catalytic activity of ZnO when compared to the pristine ZnO as shown in Figure 5 (a). It has been seen that the photo degradation efficiency of ZnO was increased with the addition of increasing amount of copper. The maximum degradation efficiency of (57.5%) was achieved with 10 mg and 15 mg of copper doping into ZnO. Figure 5(c) indicates the pseudo first order reaction and the Figure 5 (d) shows the behavior of various photocatalysts against the time.

Figure 5(e) shows the photocatalytic spectra for the MO at different intervals of time for the pristine ZnO which reveals a long time for the partial degradation of ZnO

It can be clearly observed that doping of copper has considerable time on degradation speed as it took about 360 minutes for undoped ZnO to degrade in MO (Fig: 5b) as compared to copper doped ZnO that took about 105 minutes to degrade enhancing the considerable effect of copper doping.

Figure 5: (a) Photo degradation efficiency of copper doped ZnO nanorods towards MO (b) Photo degradation of pristine ZnO in Methyl Orange (c) Plot of $\ln(Co/Ct)$ versus time for illustrating the kinetics of photo degradation of MO with copper doped ZnO (d) Plot ct/Co versus

time (e) UV-Visible absorption spectra of pure ZnO in the presence of MO at different intervals of time.

Initially pristine ZnO was degraded in Methylene Blue for about 360 minutes. It was found that ZnO degraded progressively up to 46% efficiency as shown in Figure 6b

Further, the dual photocatalytic activity of the prepared copper doped and pristine ZnO samples was investigated for the MB and considerable degradation efficiency was noticed for the copper doped samples as shown in Figure 6. There was a linear relation between the degradation rate with increasing increment of copper dopant into ZnO nanostructures and the degradation efficiency was monitored for the time period of 180 mins. The 20 mg copper doped ZnO nanorods were found to be efficient photocatalyst with a degradation efficiency of (60%) as shown in Figure 6 (a). Figure 6(c) shows the curve fitting which indicates the pseudo second order kinetics, however Figure 6(d) shows the pseudo first order fitting. The obtained value of slopes from the Figure 6(c, d) corresponds to the rate constants. The photo degradation mechanism for the methyl orange and methylene blue based on copper doped ZnO nanorods can be explained on the basis of optical band gap as smaller the band gap few chances for the recombination rate of electron and hole pairs as it gives a short time for the interaction among them. Greater the optical band gap, higher will be time for the interaction of electron and hole pairs that results into the fast charge recombination rate and consequently a poor photo degradation efficiency is found. Figure 6 (e) shows the degradation trend of MB versus degradation time for the pristine ZnO. The pristine ZnO showed the slow kinetics of degradation and a poor degradation activity for the long time around 360 mins. However, the maximum degradation with copper doping was observed in 180 minutes i-e faster than the pristine ZnO. After the comparison of photo degradation efficiency of both dyes, it can be seen that for the copper doped ZnO samples, there is increasing trend of degradation with increasing content of copper; however, for the MO the degradation is limited by 15 mg doped ZnO samples. However, the 20 mg copper doped sample of ZnO has demonstrated slow the degradation rate for MO which can be assigned to greater charge recombination rate of the sample when compared to other copper doped ZnO samples. Based on the degradation efficiency, MO has 57.5 % at time of 105 mins which is smaller than the MB that has 60% degradation efficiency.

Figure 6: (a) photo degradation efficiency of copper doped ZnO nanorods towards MB (b) Photo degradation of pristine ZnO in Methylene blue (c) $\ln C_0/C_t$ versus time (d) Plot of (C/C_0) versus

time (e) UV-Visible absorption spectra of pure ZnO in the presence of MB degradation at different intervals of time.

The UV-visible spectra for the bandgap are shown in Figure 7. It is decreased during the doping of copper into ZnO compared to the pristine ZnO. It is shown that low content of copper has brought reduction in band gap of ± 0.71 at 250-600 nm and overall doped ZnO nanorods exhibit low optical bandgap when compared to the pure ZnO. Also it is worth to mention herein that the reduced band gap has significant effect on photo degradation efficiency.. The measured optical band gap ZnO nanostructures is given in Table 1.

Figure 7: UV-Visible absorption spectra of un doped ZnO nanorods and copper doped ZnO

Table 1: Measured optical bandgap from UV-visible spectra

Name of Samples	Cut of wavelength	Band gap (eV)
Pure ZnO	358.33	3.46
5 mg	380.06	3.26
10 mg	388.02	3.19
15 mg	394.43	3.14
20 mg	400.17	3.10

4. Conclusionss

In summary, ZnO nanorods are successfully doped with different content of copper and were used as efficient photocatalyst for the photo degradation of MO and MB. The XRD study reveals minor crystallographic changes in the ZnO crystal lattice after copper doping and they exhibit the hexagonal phase. Further SEM study confirms no change in the morphology of ZnO with addition of different concentrations of copper. The optical band gap was decreased with increase in the dopant concentration and it prevents the interaction of electron and hole pairs thus charge recombination rate is minimized. Upto 10.4% of decrease in band gap was achieved with copper doping of up to 20mg endorsing the considerable effect of copper doping on optical bandgap. The photo degradation efficiency for the MO was found to be 57.5% and 60% for the MB. The proposed catalysts are promising for the wastewater treatment and other environmental applications.

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Supplementary Data

Facile synthesis of copper doped ZnO nanorods for the efficient photo degradation of methylene blue and methyl orange

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S1: SEM image of pristine ZnO

S2: Elemental mapping and EDS spectra of copper doped ZnO nanorods