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The effect of size of the CuO Nano leaves on the sunlight driven Photocatalytic properties

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Abstract - *Copper oxide nano leaves were synthesized using surfactant assistant wet chemical method. Using various concentration of Polyvinyl pyrrolidone (PVP) as surfactant, four copper oxide nano materials were synthesized. Crystalline nature, crystallite size of CuO materials were studied using X-ray Diffraction pattern. Nano leaves morphology of the materials was confirmed by scanning electron microscope. Sunlight driven photo catalytic properties of the materials have been studied using Congo red as a model contaminant.*

Key words: **Copper oxide, PVP, Photocatalytic, Congo red, sunlight**

1. INTRODUCTION:

Our water resources contaminated by the waste water released by many industries like textile industry, leather industry, hair-colouring industry, food industry, paper industry etc. More than 10000 different commercial dyes and pigments exist and 700000 tons are produced per year worldwide [1]. During the process in the industries, the excess dyes are made to lost in water resources and pollute the water. The harmfulness of the dyes creates the necessity to do the removal process. On the basis of SciFinder data source Malka etal [2] told in his review paper, 50% to 70% of the dye production in global is azo dyes but the manuscripts on the removal of azo dyes in the presence of visible light are low. Most of the semiconductor oxides studied for their catalytic properties but colored semiconducting oxides have capability to expand the wavelength absorption in visible region [3]. CuO is favorable cause its ease of preparation, non-toxic and stability. Considering all these factors, in the present work CuO nano leaves were synthesized and utilized as a nano catalyst for the removal of azo dye (Congo red) in the presence of sunlight. The CuO has been published as a good photo catalyst in many reports, [4-9] but photo catalytic properties for the degradation of organic dyes directly related to synthesis technique, particle shape and size. In the present case Copper oxide nano leaves were synthesized by simple wet chemical method using PVP K_{30} as surfactant

2. MATERIALS AND METHODS

Cupric nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$] (Himedia 99.5% purity), PVP K_{30} (M.W= 40,000) (Himedia)and sodium hydroxide pellets [NaOH] (Nice chemicals) are the chemicals used in this experiment. They were analytical reagent grade and used without further purification. Copper oxide was prepared by surfactant assistant wet chemical method. 0.1M of cupric nitrate solution and 0.2 M of NaOH solutions were made separately using deionized water. With the blue colored cupric nitrate solution, PVP was added and allowed to stir with warm heat until it dissolved. Freshly prepared sodium hydroxide solution was added drop by drop with continuous stirring until the solution pH reached to 11. Meanwhile, the continuous addition of NaOH solution changed the blue color solution to greenish blue precipitation and then it turned into black. The precipitation was then washed several times by distilled water and ethanol using suction funnel. Washed samples were dried at room temperature for 24 hrs. Then it was kept in oven at 120° C for 10 hrs. Following the above procedure using different concentration of PVP such that 0.005M, 0.01 M, 0.05M and 0.1 M was added and four samples were synthesized and named as PVP (0.005), PVP (0.01), PVP (0.05), and PVP (0.1) respectively.

2.1 characterizations

The XRD pattern was recorded by XPERT-PRO diffractometer using Cu-Kα radiation (λ=1.54 Å) in order to confirm the crystalline nature and to determine the phase present in the prepared materials. FTIR spectrum was recorded by KBr pellet technique from 400cm^{-1} to 4000 cm^{-1} using spectrum RXI Perkin Elmer spectrometer SEM analysis was carried out using scanning electron microscope Carl Zeiss EVO 18 at 25KX magnification. UV-visible absorbtion spectrum was recorded using. Lamda 35 Perkin Elmer spectrophotometer.

2.2 Photo catalytic experiment

Photo catalytic properties synthesized CuO nanomaterials were studied using the degradation of Congo red dye under the sunlight. The experiment was carried out from 10.30 am

to 2.30 pm in order to get relatively uniform intense light energy. The luminosity of sun light at time of experiment was measured using a sun meter and it is found to be as 950 to 1100 watts/ m^2. 10 mg of synthesized nano CuO powder was dispersed in 100 ml of an aqueous solution of Congo red solution with initial concentration of 10 ppm was taken in four glass beakers and they kept under sunlight. After every hour 2ml solution from each beaker was collected separately and absorption was read out using a UV visible spectrometer Lamda 35 Perkin Elmer spectrophotometer from the wavelength of 200 to 1200 nm.

3. RESULTS AND DISCUSSIONS

3.1XRD analysis

Fig - 1 shows the XRD pattern of the CuO sample with different concentrate of PVP. Relatively broadening in the peaks revealed the formation of nano crystalline CuO. XRD Patterns for all the samples is in a uniform manner (ie) the peak positions present in same direction. This shows that change in concentration of PVP does not affect the crystal growth direction. All the peaks indexed to monoclinic crystal system which is good agreement with JCPDS No. 80-1916. Crystallite size was calculated for high intense peak using Scherer's formula [10]

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

Where D is the crystallite size, λ is the wavelength used in the experiment; β is the full width at half maximum and θ is the diffraction angle. The calculated crystallite sizes are 35.7, 32.0, 28.1, and 22.2 nm for PVP (0.005), PVP (0.01), PVP (0.05) and PVP (0.1) respectively. This result confirmed that increment of surfactant decreases the particle size.

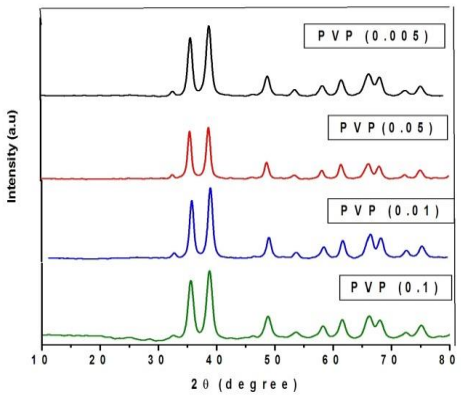

Fig - 1: XRD patterns of the CuO nanoleaves.

3.2 FTIR Analysis

Fig 2 shows the FTIR spectra of CuO nano materials prepared with different concentration of PVP. Well defined absorption bands were observed at 427, 511 and 605 cm^{-1} which is assigned to the metal – oxygen bonds confirms the Cu-O stretching bond present in the synthesized materials. According to standard spectrum of CuO peak should be at the frequency range 725 cm^{-1}. In the present case peaks are blue shifted due to nano size of synthesized particles. Small and wide band at 3699 cm^{-1} assigned to the vibrational modes of O-H bond. It may be of H_2O molecules physic-absorbed on the surface of CuO. The absence of well-defined peak at 1045 and 650 cm^{-1} confirms the absence of other phases Cu (OH) and Cu_2O respectively. Thus the FTIR confirms the functional groups and also the phase purity of the synthesized materials.

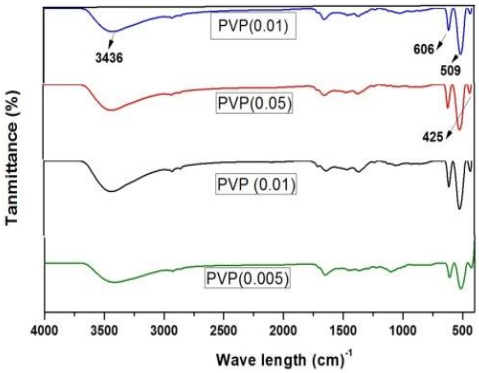

Fig -2: FTIR spectrum of synthesized copper oxide nano leaves

3.3. SEM Analysis

Morphology of the synthesized nano materials examined by the SEM was shown in Fig-3. SEM reveals nano leaves morphology for all the synthesized materials for PVP (0.005) and PVP (0.01) leaves are narrow and lengthy leaves were obtained. But in the case of PVP (0.05) and PVP (0.1) leaves are shortened and broadened. This difference in morphology shows that change of concentration of PVP altered the shape and size of nano leaves.

3.4 Photo catalytic analysis

The copper oxide dispersed in Congo red solution absorb the sunlight photons and produces the electron hole pairs. The electrons and holes reacted with O_2 and H_2O respectively and produce OH radicals. These OH radicals are highly reactive and it can cause the rupture of the cyclic structure of Congo red molecule and degraded to CO_2 and H_2O [11]. Congo red has a strongest absorbance in 495 nm. Photocatalytic activities of copper oxide nano leaves are evaluated by monitoring the decomposition of Congo red by decrement of the peak with time. Fig- 4 shows the UV absorption spectra of Congo red with copper oxide materials with different concentration of PVP. Fig 5 shows that PVP

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(0.005), PVP(0.01), PVP(0.05), PVP(0.1) degraded the Congo red in to 55.5%, 64.5%, 84.2%, 100% after 4 hours illumination of sunlight. PVP (0.1) is exhibiting excellent photo catalytic activity than other samples.

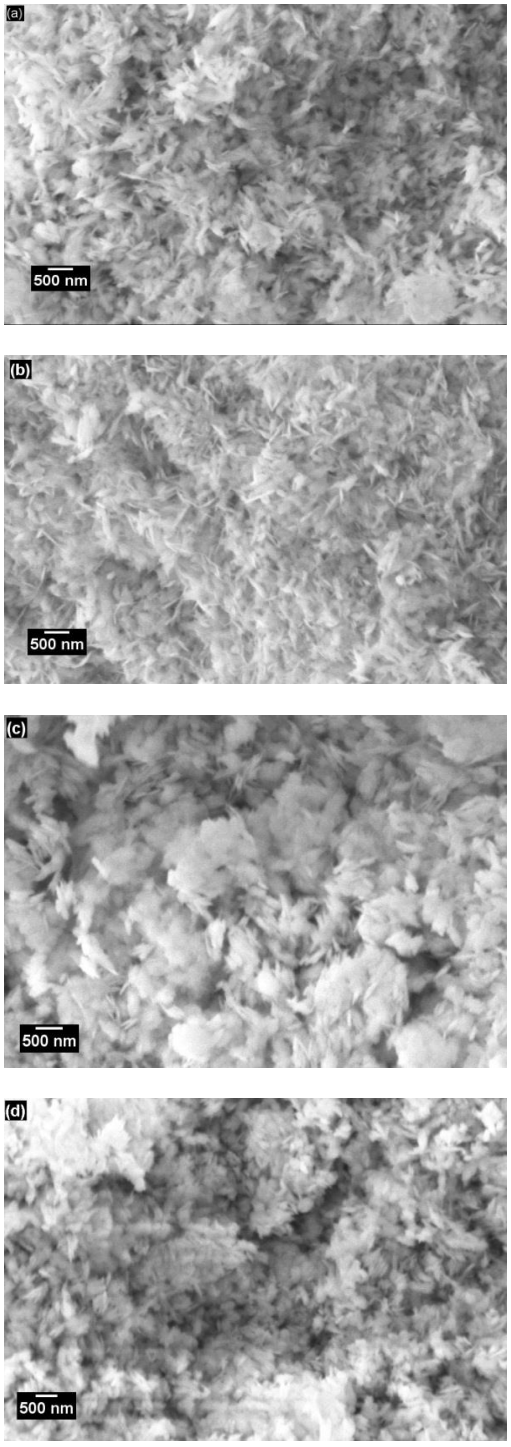

Fig- 3: SEM images of CuO nano leave (a) PVP(0.005) (b) PVP(0.01) (c) PVP (0.05) (d) PVP (0.1)

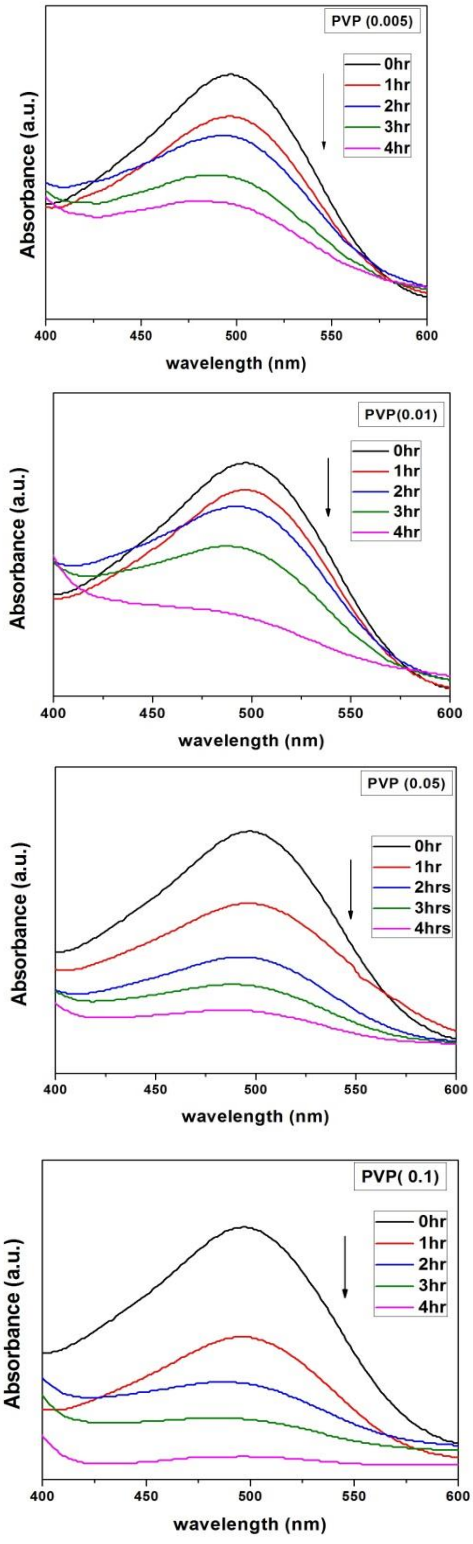

Fig-4: Degradation of Congo red in the presence of synthesized CuO nano leaves.

XRD and SEM confirm that PVP (0.1) has small particle size. Small particle and the high surface to volume

ratio is the reason for this high activity. The high concentration of PVP creates more surface defects by reducing the particle size and may reduce the bulk defects by increasing the regularity of the grains. Bulk defects acts as center for recombination of electron hole pair. Increasing of bulk defects increase the recombination possibility and lowers photocatalytic activity. In the case of surface defects, they increase the charge separation and improve the photo catalytic activity [12].

4. Conclusions

Copper oxide nano leaves were synthesized by simple wet chemical method using PVP as surfactant. Crystallite size calculated from XRD confirmed that increment in concentration of PVP reduces the particle size. SEM Photographs elucidated the nanoleaves morphology. Photo catalytic experiment results that PVP (0.1) exhibited higher photocatalytic activity than other samples. 100% degradation of congo red solution is obtained by PVP (0.1) Copper oxide nano leaves.

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