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Electrochemical Synthesis of ZnO:CuO Nanocomposites for Photodegradation Studies of Cibacran Brilliant Yellow Dye and Textile Dyeing Industry Effluent

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Abstract

Zno:Cuo nanoparticles are synthesised by electrochemical method and were characterised by UV-visible spectroscopy, infrared- spectroscopy, scanning electron microscopy, X-ray diffraction, positron annihilation lifetime spectroscopy and density measurements. The band gap energy of ZnO:CuO nanocomposite was 3.05 eV. The size was found to be 9.9nm by XRD studies. The nanocomposites consist of more defects and vacancies than ZnO. The photocatalytic efficiency of the sample was investigated systematically on Cibacran brilliant yellow 3G-P dye and a textile dyeing industrial effluent.

Keywords: *Cibacran Brilliant Yellow 3G-P Dye, Electrochemical Synthesis, Positron annihilation lifetime spectroscopy, ZnO:CuO nanocomposites.*

1.0 Introduction

Mixed metal oxide nanoparticles are a very important class of materials which find their applications in optoelectronics, data and energy storage, solar cells, catalysis etc. Dyes may be natural, synthetic and xenobiotic compounds that transform the surrounding world to look more beautiful through colours. However, the release of coloured industrial effluents represents a serious environmental threat and raises a public health concern. Colour removal or degradation of dyes from textile industrial effluents, has become a great challenge these days, and to date, environmental scientists are still working on the most effective, economical and environmentally friendly procedures for the treatment of colour or dyes present in the industrial effluent samples. They are working towards an effective method for the decolorisation or degradation of dyes[1]. The excess or unused dyes or colours present in industrial effluents pose a serious threat to the environment as they are the source of unpleasant scenes of water bodies, they are also harming the biota of the waterbodies, they are posing to block the solar radiations reaching the water bodies. Many researchers are working towards the decolorisation demineralisation or degradation of dyes so that it can stop the harm caused. The most trustworthy and notable technique for the removal of dyes or colours from effluents is learned as Advanced Oxidation Processes (AOPs), and this reaction is catalysed by metal oxide semiconductors in the presence of solar radiations[2]. So this technique is termed as heterogeneous photocatalysis. Studies show that the decolorization of dyes is more effective when the heterogeneous photocatalysts size is in the nano range, because of their better reactivity, and high surface area for reaction to happen. This has created lots of interest in present-day researchers to synthesise nanoparticles

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of trivial ZnO and TiO_2 photocatalysts. The ZnO and TiO_2 photocatalysts have been advantageous because of their high chemical stability, non-toxic, and is of less expensive. The only disadvantage that they are facing is the narrow absorption of solar radiation. This gap in the trivial photocatalysts has motivated to preparation of mixed metal oxide nanoparticle photocatalysts through electrochemical methods for the dye degradation studies of industrial effluents. An attempt to increase the visible range of solar spectrum for photocatalytic reaction to happen[3] based on these considerations and to broaden the range of visible light photo-response and to improve the separation of photo-generated electron-hole pairs simultaneously, herein we synthesise copper oxide coupled ZnO nanocomposites as photocatalysts for the degradation of Cibacran Brilliant Yellow dye and textile dyeing industry effluent.

2.0 Experimental

2.1 Materials and Methods

All chemicals used were purchased from Alfa Aesar and were of analytical grade purity. The metal wires (Zinc and copper) and Cibacran Brilliant Yellow 3G-P dye were purchased from Sigma-Aldrich. The textile dyeing industrial effluent was collected from the dyeing industry located in Ranganathpura industrial estate, Bangalore, India. The solutions were prepared using distilled water. Absorption spectra, FTIR spectra, crystallographic interpretations and morphological features of the semiconductors were studied on UV-visible spectrophotometer, Systronics 117, FT/IR-4100 type A spectrometer, X-ray diffractometer (Rigaku, Mini Flex II desktop XRD) and scanning electron microscopy (SEM model LEO 440) respectively.

2.2 Electrochemical Synthesis of ZnO:CuO Nanocomposites

Zinc and Copper wires were taken and fixed was made anodic, the counter electrode was platinum and the dissolution of Zn and Cu gives Zn(II) and Cu(II) ions which are electrochemically reacted with aqueous $NaHCO_3$ (0.5%) (electrolyte) to form Zn(II) and or Cu(II) oxide/hydroxide. The experiment was carried out for 3 hrs on a magnetic stirrer at room temperature (10mA, 6V); the solid or precipitate obtained was ZnO:CuO nanoparticles which were subjected to wash with distilled for removal of excess $NaHCO_3$. The ZnO:CuO nanoparticles were dried at a high temperature of 250°C - 400°C to ensure the removal of water content and to convert all metal hydroxides to metal oxides. The synthesis of mixed metal oxides was found to take place at the interface or close to the electrode within the electrical double layer[4]. The proposed electrochemical reaction is as follows:

$$Zn \rightleftharpoons Zn^{2+} + 2e^-$$

$$2NaHCO_3 + 2e^- \rightleftharpoons 2CO_2 + 2Na + 2OH^-$$

$$Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2$$

$$Zn(OH)_2 \rightleftharpoons ZnO + H_2O$$

$$Zn + 2NaHCO_3 \rightleftharpoons ZnO + 2CO_2 + 2Na + H_2O$$

The overall reaction is

In general,

$$M + NaHCO_3 \rightleftharpoons MO + CO_2 + Na + H_2O$$

$$Zn \xrightarrow[NaHCO_3]{Cu} ZnO{:}CuO$$

2.3 Determination of Photocatalytic Activities

Cibacron Brilliant Yellow 3G-P (CBY) solution was prepared by dissolving 0.872mg/l in distilled water. This solution was further used in investigating the photocatalytic activities of the commercial ZnO and ZnO:CuO nanoparticles in comparison. Further the photocatalytic activity of commercially available ZnO and the prepared ZnO:CuO nanoparticles were carried out in sunlight at every 30 min time interval, 2ml of colloidal solution was drawn followed by centrifugation at 800 rpm to remove the dispersed catalysts if any and the absorption studies were carried on. The Chemical Oxygen Demand (COD) was found by the dichromate oxidation method[5].

3.0 Results and Discussion

3.1 UV-Visible Absorption Studies

UV–visible absorption studies of ZnO:CuO nanoparticles

over the range 200-800 nm showed a maximum at 510nm, which says that the ZnO:CuO nanoparticles are active under visible light. Through extensive literature studies the energy of the band gap could also be estimated as 3.05 eV for ZnO:CuO nanoparticles. This is also supported by the noticeable colour of the photocatalyst which was observed to be pale blue. This may be due to the presence of CuO in addition to ZnO and there is a chance of redshift[7]. Also by literature, it can be said that favourable doping of Cu^{2+} in the lattice of Zn as the ionic radius of Cu^{2+} (0.72 Å) is very close to that of Zn^{2+} (0.60 Å). Therefore, we can say that the band gap can be narrowed by the donor levels of Cu 3d orbitals[8].

3.2 Infrared Spectral Studies

The IR spectrum of the ZnO:CuO nanoparticles is shown in Figure 1. For metal oxides, absorption peaks are noticed generally below 1000 cm^{-1}. A peak at 613 cm^{-1} corresponds to Zn-O bonds. A peak at 614 cm^{-1} and 675 cm^{-1} corresponds to Cu-O bending. The peak at 1367 cm^{-1} and 1739 cm^{-1} indicates the formation of ZnO and CuO respectively. The M-O frequencies observed for nanoparticles of ZnO:CuO is evidenced by literature[9].

3.3 Scanning Electron Microscopy

Through SEM studies, the morphology of the samples was detected. The SEM micrograph (Figure 2) of the ZnO:CuO solids shows that it consists of semi semi-crystalline nature of nanoparticles.

3.4 X-Ray Diffraction

XRD pattern of ZnO:CuO is shown in Figure 3, dominant peaks are observed. The size of the ZnO:CuO

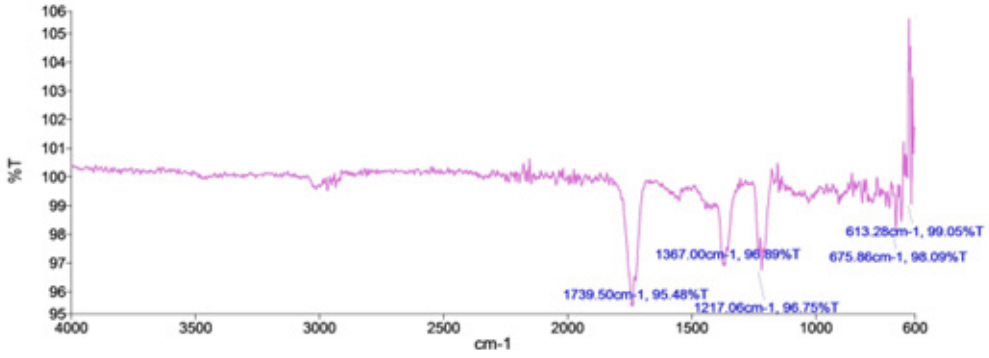


Figure 1. IR spectrum of ZnO:CuO nanoparticles.

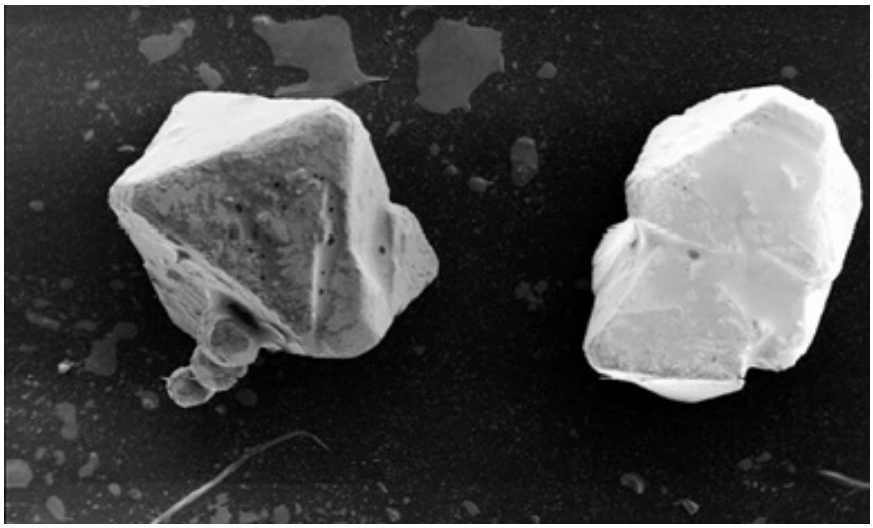


Figure 2. SEM Image of ZnO:CuO nanoparticles.

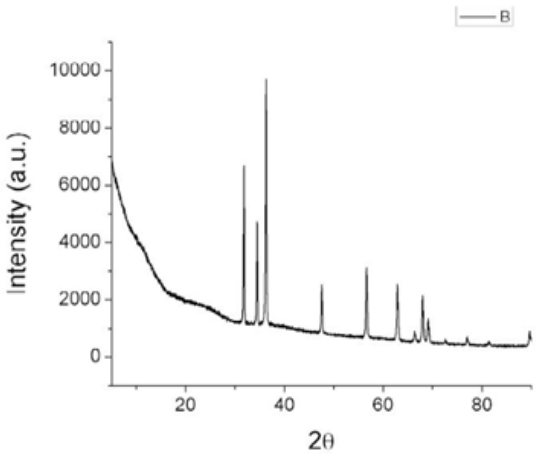


Figure 3. XRD plot of ZnO:CuO nanoparticles.

nanoparticles was noted as 9.9 nm, the crystal system is orthorhombic with unit cell volume 1028.55 Å^3, the (hkl) values according IUCR and α = β = γ = 90°, a ≠ b ≠ c, (a = 17.28 Å, b = 8.10 Å, c = 7.34 Å) (JCPDS 09-0492). The diffraction peaks at 35.760° and 37.040°, corresponding to (1 3 1) and (1 0 3) respectively of the CuO phase are also observed which also confirms the inclusion of Cu in the ZnO matrix[9].

3.5 Positron Annihilation Lifetime Spectroscopy

A two-state trapping model is followed. The parameters obtained in the PALS study are tabulated in Table 1.

3.6 Photocatalysis and COD Measurements

The decolorisation of dye solution was happening at a much higher rate in the presence of ZnO:CuO nanoparticles at varying time intervals in comparison to commercially available ZnO. Thus, it can be said that the photocatalytic decomposition of dye is more in the presence of ZnO:CuO nanoparticles. According to first-order reaction kinetics, the rate of photocatalysis for ZnO:CuO nanoparticles was observed to be 4.183 x 10^{-3} min^{-1} which is notably higher than the obtained for ZnO 2.350 x 10^{-3} min^{-1}.

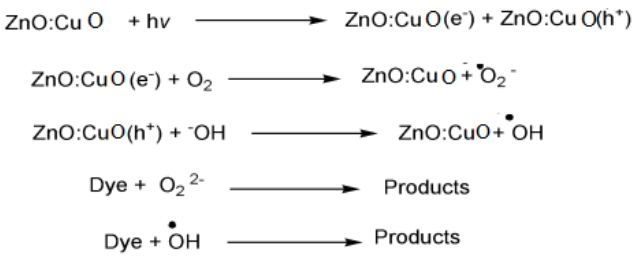
The decolourisation of dye solution and Chemical Oxygen Demand (COD) was measured at regular time intervals. The working concentration of dye solution was kept in the range of 1x10^{-6}M to 12x10^{-6}M with ZnO:CuO nanoparticles and then was exposed to sunlight, at every 30 min of time interval 2ml of the dye solution was drawn and absorption at the transmission of light was measured and every of 2 hrs time interval COD was measured using the titrimetric method. The photocatalytic efficiency for ZnO:CuO nanoparticles and ZnO were found to be 94.13% and 57.46% respectively.

The following reaction mechanism was proposed for dye degradation[10]:

$$\text{Photodegradation efficiency} = \frac{\text{Initial COD - Final COD}}{\text{Initial COD}} \text{ X 100}$$

Table 1. PALS results of ZnO and ZnO:CuO nanoparticles

Parameters	ZnO	ZnO:CuO
τ_1(ps)	171	260
I_1 (%)	-	91.52
τ_2 (ps)	230	562
I_2 (%)	-	8.48
τ_{mean} Lifetime (ps)	-	285
τ_{Bulk} Lifetime (ps)	181	272
λ_B Annihilation (ns)$^{-1}$	-	3.671
K Trapping Rate (10^9)s^{-1}	-	0.175
τ_2/τ_B	1.27	2.06
Defect Concentration C=Ad (K/μ) (10^{15}) cm		4.847



3.7 Effect of pH

The pH of the solution plays an important role in the photocatalysis reactions. The pH was made acidic or basic by adding 0.001M HNO_3 or 0.001M NaOH solution respectively. The optimum pH was found to be 6.6 at near neutral pH.

3.8 Effect of Initial Cibacron Brilliant Yellow 3G-P Concentration

The maximum concentration of Cibacron Brilliant Yellow 3G-P dye that the ZnO:CuO nanoparticles could decolourise was found to be 2.0×10^{-6} M. A little increase in concentration was blocking the catalytic activity of nanoparticles and the rate of degradation was affected.

3.9 Effect of Catalyst Loading

To find out the optimum catalyst loading on the photodegradation rate of Cibacron Brilliant Yellow 3G-P, the amount of ZnO:CuO nanoparticles varying from 500 to 2000 mg/L was considered for study. The optimum catalyst loading was nearly 800ppm.

3.10 Reuse of the Photocatalyst

For the cost-effectiveness of the photocatalysis of Cibacron Brilliant Yellow 3G-P dye the re usage of the photocatalyst was examined. After the first attempt at dye degradation, the photocatalyst was separated by centrifugation and was washed thoroughly with distilled water till the pH of the solution became neutral, then subjected to dry in a hot air oven. The so-obtained reused ZnO:CuO nanoparticles were then again used for dye degradation at optimum conditions. The efficiency was lesser compared to a fresh photocatalyst[11].

3.11 Textile Effluent Treatment Using ZnO:CuO Nanoparticles

Textile effluent was collected from a dyeing industry located in Ranganathpura Industrial area, Bangalore, India. The effluent collected contained some solid particles and was intensely coloured. The effluent was filtered and then diluted with distilled water (1:1 V/V) for further studies as stated above with optimum conditions, the photocatalysis was carried out.

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