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Enhanced Photo catalytic properties of CuO nano sponge using Igepal CA 210 as surfactant

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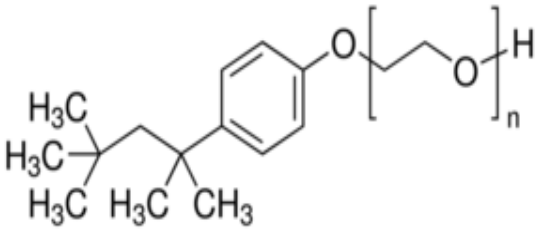
ABSTRACT

The copper oxide nano sponge like material was synthesized by simple solid state reaction method at low temperature using Igepal CA 210 as a surfactant. Three samples were synthesized by changing the concentration of the surfactant such that 0M, 0.05M, and 0.1M. Influence of Igepal on the structural, morphological and optical properties of CuO nanomaterial were analysed and reported. Sunlight driven photo catalytic properties of synthesized materials were analysed using Congo red as model dye. Degradation ability of the CuO nano materials synthesized with different ratio of surfactant was compared and discussed.

Keywords: Copper oxide, Nanoparticles, Structural, Igepal, Photo catalysis, Kubelka-munk

I. INTRODUCTION

The matter at Nano scales can perform better functions compare with the bulk materials. As the size and morphology of the materials changes, resulting properties of the materials changes noticeably. To synthesize better performance materials, many synthesis techniques have been used. In which, the parameters precursor materials, reducing agents, annealing temperature, and using surfactant are changed. Surfactant is a surface active agent which lowers the surface tension and so reduces the particle size and limits agglomeration. It also acts as a template for nano-particle formation during synthesis and produces the materials with different morphology. Number of surfactants has been used to synthesize copper oxide materials which is an important industrial material that can be used in many applications. Some of surfactants used to synthesize copper oxide nano materials are PEG (Poly Ethylene glycol) [1], PVA(polyvinyl alcohol) [2], Chitosan [3], SDS (sodium Dodecylsulfate), Triton X-100 [4], CTAB (Cetyl trimethyl-ammonium Bromide) [5], Amino acids [6], starch [7], glycerol [8] and so on. In this current study Igepal CA 210 (Octyl phenol ethoxylate) which has the following structure was used as a surfactant to synthesize copper oxide nano material and the photocatalytic properties were analyzed under the sunlight. Vo Thanh Son et al reported the synthesis of Fe_3O_4 nano particles using the Igepal Co 520 surfactant [9]. Synthesis of copper oxide using Igepal as surfactant is not reported earlier, to the best of our knowledge.



II. METHODS AND MATERIAL

A. Synthesis of catalyst

Cupric nitrate trihydrate [Cu $(NO_3)_2 \cdot 3H_2O$] (Himedia 99.5% purity), sodium hydroxide pellets [NaOH] (Nice chemicals), Igepal CA 210 $(C_2H_4\ O)_n.C_{14}H_{22}O$ (Sigma Aldrich) are the analytical grade chemicals used in this experiment without any further purification.

4.83g (0.1M) of cupric nitrate and 1.6 g (0.2) sodium hydroxide pellets were grounded using the agate and mortar for 30 minutes. The resulted blue colour pasty copper hydroxide was washed well with de-ionized water and ethanol several times. Then the material was kept in a furnace at 300° C for 5 hrs. This yields the black colour CuO material. To synthesize CuO with surfactant, cupric nitrate was grounded well with Igepal

for 20 minutes and then the same procedure was followed. Here copper hydroxide was first washed well with ethanol in order to remove Igepal since it is immiscible with water. Then it was washed using de-ionized water. Three samples were synthesized such that IG (0) without Igepal, IG (0.05) (2.5 ml (0.05M) of Igepal) and IG (0.1) (5ml (0.1M) of Igepal)

B. Characterizations

The XRD pattern was recorded by XPERT-PRO diffractometer using Cu-Kα radiation (λ=1.54 Å). FTIR spectrum was recorded by KBr pellet technique from 400cm^{-1} to 4000 cm^{-1} using spectrum RXI Perkin Elmur spectrometer. UV visible diffusion reflection spectrum was recorded using Lamda 35 Perkin Elmer spectrophotometer from the wavelength of 200 to 1200 mm. SEM images were taken using Carl Zeiss EVO 18 electron microscope at 25 KX magnification. The BET surface area was calculated by nitrogen adsorption technique at liquid nitrogen temperature, using Micromeritics ASAP 2020 porosimeter.

C. Photocatalytic experiment

Photocatalytic properties of synthesized CuO nano materials 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 was found to be in the range of 950 to 1100 watts/ m^2. 100 ml of Congo red solution (10 ppm) was taken in three glass beakers. 10 mg of catalysis were mixed with each beaker and kept under sunlight. After every hour 2ml solution from each beaker was collected separately and absorption was read out using a UV visible spectrometer.

III. RESULTS AND DISCUSSION

A. Characterization of Photocalyst

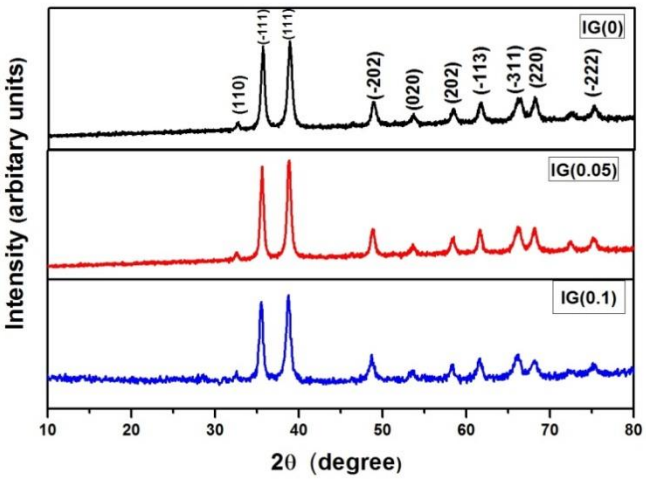


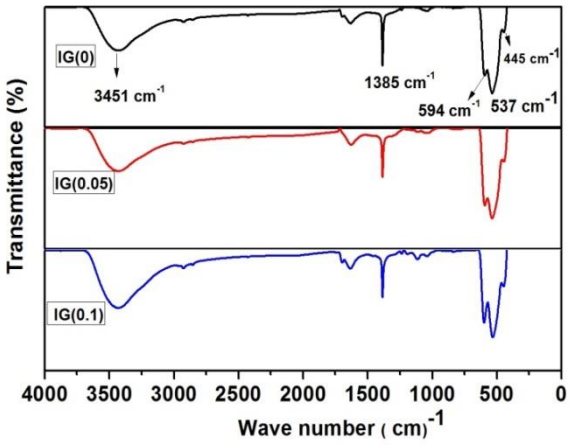
Figure 1: XRD Pattern of IG(0), IG(0.05), IG(0.1)

Fig. 1 shows the XRD pattern of the synthesized materials which reveals the relatively broad peaks and it confirms the nano crystalline nature of the materials. The pattern does not contain any impurity peaks which confirm the purity of the materials and phase. All the diffraction peaks are indexed to monoclinic system which is well matched with JCPDS card no. 80-1916.The crystallite size calculated using Debye – Scherrer's were 44, 37 and 25 nm for the materials IG(0), IG(0.05) and IG(0.1) respectively. The small crystallite size of IG (0.1) than IG (0) confirms that the surfactant igepal reduces the crystallite size. The cell parameters calculated using UNIT CELL software and theoretical values from the JCPDS data have been tabulated in table 1. Table I depicts that all the synthesized materials are in the same monoclinic structure. β value of unit cells and cell volume of IG (0.05) and IG(0.1) are almost same, but less than the value of IG(0). These results confirm that surfactant affect the unit cell parameters and shape. BET surface area of IG(0) and IG(0.1) was also given in table I. BET surface area values show that the surface area is higher for material with smaller particle size.

FTIR spectrum of synthesized nano CuO materials is shown in Fig. 2. The peaks at 445, 537 and 594 cm^{-1} represent the metal - oxygen stretching vibration which confirms the formation of copper oxide. Bending vibration of OH ions which indicates the presence of the physically adsorbed water on the surface of the material observed at 1628 cm^{-1}. No peaks in the region 600 to 650, confirms the absence of another phase Cu_2O and so the phase purity of the materials [10].

TABLE 1. Crystallographic Data of Cuo Nanomaterials Calculated Using The Unit Cell Software

Samples a b c β cell volume BET surface area	
Theoretical values	4.692 3.428 5.137 99.546 81.50
IG(0)	4.689 3.420 5.119 99.49581 80.99 32.94 m^2/g
IG(0.05)	4.811 3.197 4.429 92.79353 68.24
IG(0.1)	4.796 3.210 4.429 92.66817 68.13 37.46 m^2/g



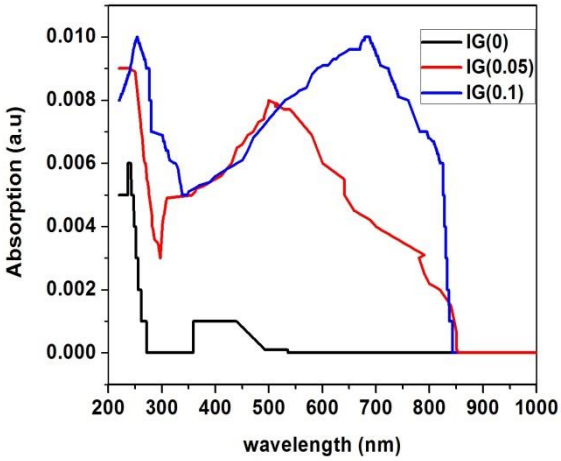


Figure 2: FTIR spectrum of IG(0), IG(0.05), IG(0.1) copper oxide nano structures

UV diffusion reflection spectrum and Tauc's plot of IG(0), IG(0.05), IG(0.1) was given in Fig. 3(a) and 3(b) respectively. Fig 3(a) clearly shows that sample IG(0) have a small absorbance peak in the region of wavelength from 358 – 492 nm whereas IG(0.05) and IG(0.1) samples shows a broad absorption band from 300 – 850 nm with the peak value 507 and 340 – 840 nm with the peak value 680 respectively. Since the absorption occurs at visible region, synthesized CuO materials can be used as sunlight photocatalysts.

The band gap of the materials calculated using Kubelka-munk equation

$$\alpha h\upsilon = K(h\upsilon - E_g)^2 \text{ --------- (1)}$$

where $\alpha = (1 - R)^2 / 2R$, $R = 10^{-A}$. A is an optical absorption, h is Planck constant, υ is photon frequency, K is constant [11]. The band gap of the synthesized materials IG(0), IG(0.05), IG(0.1) calculated using

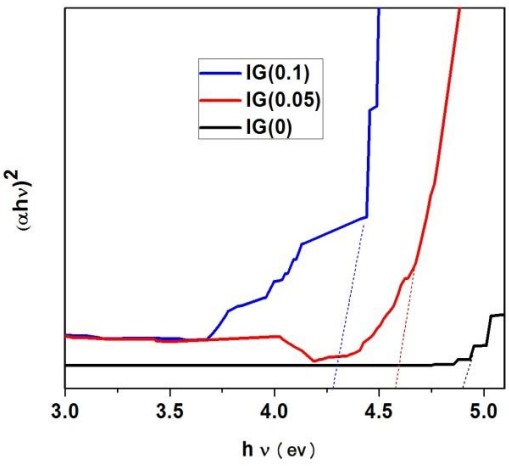


Figure 3 : (a) UV- Visible DRS absorption spectrum (b) Tauc's Plot of of IG(0), IG(0.05), IG(0.1) CuO nano materials

equation 1 is 4.91, 4.59, 4.27. Band gap decreases with the increment of of Igepal the surfactant even though the particle size decreases. This may be due to changes in electronic structure of the materials with the change of morphology which is caused by increment of surfactant. Band gap of the synthesized materials is higher than the

band gap of the bulk CuO (1.8 eV). This blue shifted is due to the quantum confinement effect [12].

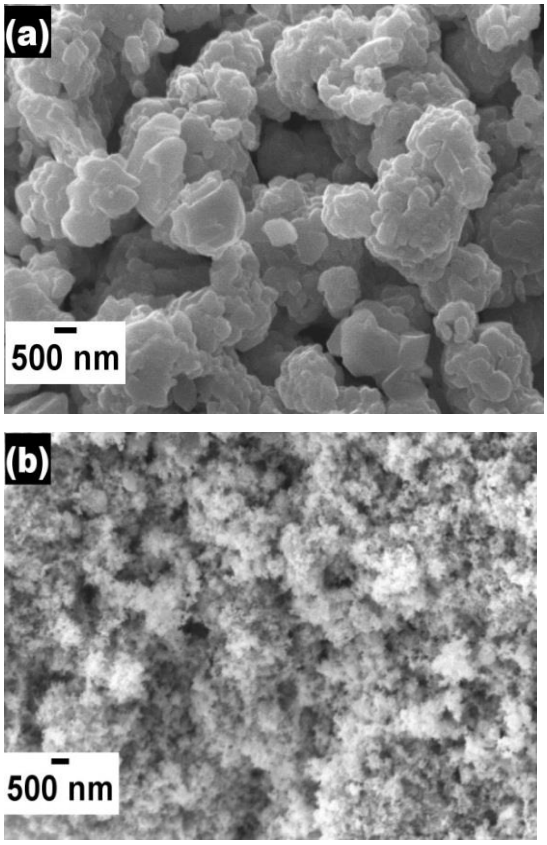
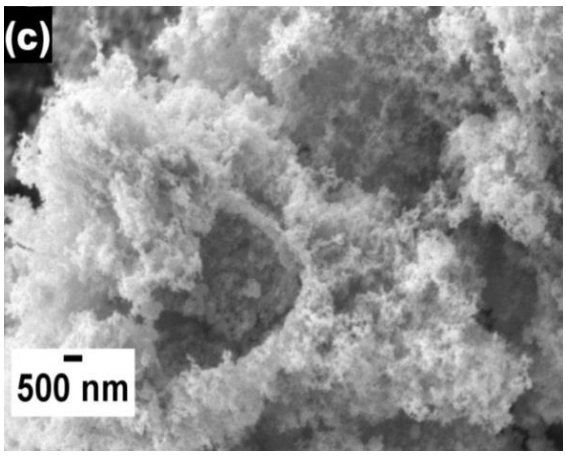


Figure 4: SEM images of (a) IG(0) (b) IG(0.05) (c) IG(0.1)

Fig. 4(a), (b), (c) shows the SEM images of the Copper oxide nano materials. Fig. 4(a) clearly reveals that IG(0) has the particle like morphology with smooth surface. Sponge like morphology was obtained for the materials IG (0.05) and IG (0.1) are displayed in Fig 4(b) and (c) respectively. From the different morphologies of the synthesized materials it can be concluded that Igepal can acts as a template and changes the morphology of the material for the current experimental conditions



B. Photo degradation analysis

Mechanism of photo degradation says that electron hole pairs are produced by excited state of CuO which is produced by absorbing photons from the solar energy. These electrons and holes react with surface bound water and oxygen and produce hydroxyl ions. These hydroxyl ions are the responsible for the oxidation of organic dye molecules.

Dye compounds + OH^- → (intermediate compounds) → CO_2+H_2O [12].

The effect of synthesized materials (IG(0), IG(0.05) and IG(0.1)) on the absorption spectral changes of the Congo red dye under the sunlight was shown in Fig. 5(a), (b) and (c) respectively. Fig. 5(a) shows that Congo red has two absorption peaks around 490 nm (peak 1) and 340 nm (peak 2). Spectral intensity of peak 1 decreases continuously with increase in time, but peak 2 increases progressively. Decrement of peak 1 indicates the degradation of the dye compound where as the increment of peak 2 indicate the formation of the intermediate compounds which absorbs light around 340 nm [13]. Analysis of absorption data of IG (0) sample at various time informed that after 4^{th} hour peak 2 attain high intensity. This shows the dye material was completely changed into intermediate compounds after 4 hours. Similarly dye was completely degraded into intermediate compounds by IG (0.05) and IG (0.1) after 3^{rd} and 2^{nd} hour respectively which is shown in Fig. 5(b) and 5(c) respectively. After reaching the high intensity, peak 2 started to decrease which indicates the degradation of intermediate compounds into CO_2 and H_2O. Thus the analysis of data informed not only the degradation ability of the material, but also confirms the mechanism of dye degradation.

The degradation percentage of the dye, in the presence and absence of catalyst was calculated using the relation $Degradation\,\% = \left(1 - \frac{A_t}{A_0}\right) \times 100$ Where A_0 is initial absorption, A_t is absorption after t hours [14].

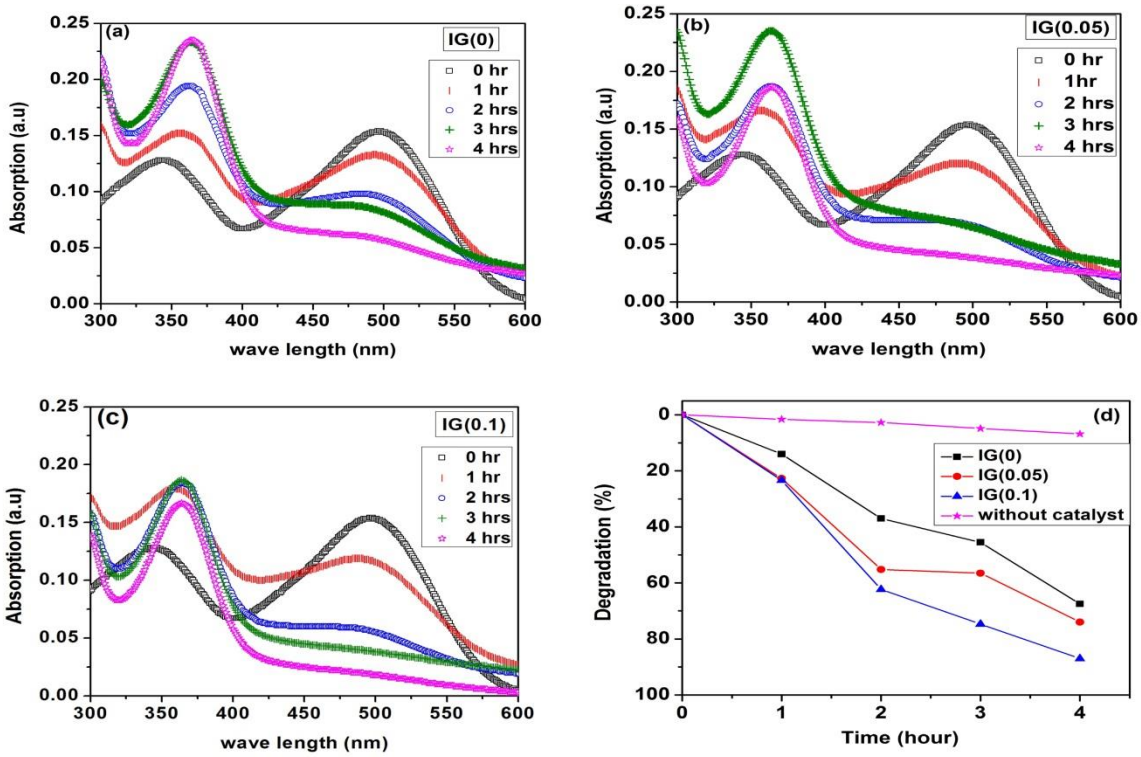


Figure 5: Time dependent absorption spectra of (a) IG (0) (b) IG (0.05) (c) IG(0.1), (d) Comparison of photo degradation ability of the photo catalysts

Fig. 5(d) reveals that, only 7% degradation occurred in the absence of the catalyst while in the presence of IG (0), IG(0.05) and IG(0.1) percentage of degradation is 67%, 74% and 87% respectively. In this, IG (0.1) has relatively more ability to degrade the Congo red dye. Reason for the enhanced photo catalytic activity of IG (0.1) is its smaller particle size and high surface area. High surface area of the nano materials reducing the possibility of recombination materials increases the photo catalytic ability by charge carriers [15]. Secondly, nano sponge is adsorbed the dye and so the hydroxyl ions can act on the dye more efficiently than nano particle morphology.

IV. CONCLUSIONS

Copper oxide nanomaterials (IG (0), IG (0.05), and IG (0.1)) were synthesized using Igepal as a surfactant. Particle size, surface area and band gap of the materials were affected by the surfactant. Igepal surfactant changes the morphology of the material to nanosponge from nanoparticle. Sunlight driven photo catalytic properties of synthesized materials were studied using Congo red as model dye. IG (0.1) degraded the dye solution up to 87% in four hours and shows better photo catalytic properties. The present results elucidated that morphology controlled synthesis of nanomaterials is a novel technique to design better performance sunlight driven photo catalyst.

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