Synthesis and Characterization of Coupled ZnO/Ag/CuO Nanomaterials for Photocatalytic Degradation of Organic Dye under UV Irradiation

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Abstract: **Coupled ZnO/Ag/CuO nanophotocatalyst was prepared by thermal decomposition method. Also ZnO, Ag, CuO were separately synthesized by the same method under similar conditions, for comparative studies. The synthesized ZnO/Ag/CuO was annealed at various temperatures. The structure and the crystallinity of all the samples were confirmed by powder X-ray diffraction. The crystallite sizes were found to be in the range from 9 nm to 49 nm for different samples. The surface morphology and elemental composition were analyzed with FE-SEM and EDX Spectrometer. Optical properties of the samples were investigated with UV-Vis DRS spectrometer and the band gaps of the samples were estimated. Then the coupled nanophotocatalysts, treated at different temperatures, were employed to degrade the methylene blue dye under UV irradiation and the degradation efficiencies were studied. The nanophotocatalyst annealed at 400 ^{0}C exhibited the highest photocatalytic degradation efficiency.**

Keywords: **nanophotocatalysts; photocatalytic degradation; ZnO/Ag/CuO; nanomaterial; organic dye**

I. INTRODUCTION

Photocatalysis has its origins in early research effort into photo-electrochemical systems for solar to chemical energy conversion. In 1972, Fujishima and Honda in their landmark study found that TiO_2 could be used as catalytic electrode in photo-electrolysis cell to decompose water into H_2 and O_2, without applying an external voltage [1]. Soon it was realized that this micro-cells, consisting TiO_2 particles with deposit of Pt on them, was also able to work as photocatalysis for splitting H_2O. This led to much active research to use TiO_2, and then ZnO as an alternative to TiO_2 for photo-assisted degradation of organic compounds and reduction of inorganic compounds [2-4].

As a semiconductor oxide with wide-band gap in the order of 3.2 - 3.4 eV [2, 5, 6], ZnO is easy to be irradiated especially by UV light to create the excited electron–hole pairs which could separate and the resulting charge carriers might migrate to the surface where they react with adsorbed water and oxygen to produce radical species. These radicals strike any adsorbed organic molecules, resulting in complete or selective decomposition.

Several studies have been reported on the photocatalytic degradation of textile dyes by TiO_2 and ZnO and binary nanocomposites based on these materials. The efficient photo generation of electron - hole pairs and the prevention of recombination of them are two key factors in increasing the efficiency of photocatalytic activity. The specific surface area presented by a catalyst also plays a significant role in increasing the efficiency of photocatalytic activity. Several researches proved that the recombination is prevented by semiconductor-metal composites or by employing two different semiconductors [7-11]. Modification of semiconductors with noble metals too fascinated researchers as they play a role in enhancing the reduction process and thereby the photocatalytic degradation process[12].

In this study, an attempt was made to synthesize coupled ZnO / Ag / CuO at a chosen weight ratio and study the effect of annealing temperature on the efficiency of photocatalytic activity by the degradation of a model textile dye, methylene blue (MB), which belongs to azo dye family.

II. PREPARATION OF SAMPLES

A. Materials

The three precursors, zinc acetate dihydrate, silver acetate (anhydrous) and copper acetate (hydrate), and the methylene blue used in the present study were of analytical reagent grade. All the chemicals were used as received without further purification. Throughout the experiment all aqueous solution were prepared using double distilled water.

B. Synthesis of ZnO, Ag and CuO

ZnO, Ag and CuO were synthesized via thermal decomposition method as follows: zinc acetate, silver acetate and copper acetate were taken separately and subjected to heat treatment in alumina crucibles by increasing the temperature up to 300 ^{0}C in steps of 4 ^{0}C / min. to undergo complete thermal decomposition to form the ZnO, Ag, and CuO nanoparticles. Then the samples were annealed at 300 ^{0}C for 3 hours to refine the structure. After the heat treatments, the samples were allowed to cool to the room temperature naturally.

C. Synthesis of Coupled ZnO/Ag/CuO

The coupled ZnO/Ag/CuO was prepared by simple thermal decomposition method. Zinc acetate, silver acetate and copper acetate, taken in the weight ratio of 75:15:10 were mixed and ground well for 3 hours[13, 14]. Then the mixture was subjected to heat treatment in alumina crucible by raising the temperature up to 300 ^{0}C in steps of 4 ^{0}C / min. to undergo thermal decomposition to form the coupled ZnO/Ag/CuO. Then the samples were annealed at three different temperatures 300 ^{0}C, 400 ^{0}C, and 500 ^{0}C for 3 hours to refine the structure. After heat treatments, the samples were allowed to cool to the room temperature naturally. Samples were treated at three different temperatures to study the effect of temperature dependent morphological changes on the efficiency of the photocatalysts.

III. CHARACTERIZATION, RESULTS AND DISCUSSIONS

A. Phase and Structure Confirmation

The ZnO, CuO, Ag and the coupled ZnO/Ag/CuO composite are prepared at three different temperatures and characterized by powder X-ray diffraction technique to study their crystal structure, phase purity and crystallite size. The powder X-ray diffraction patterns of the ZnO, Ag, and CuO, and that of coupled ZnO/Ag/CuO composite annealed at 300 ^{0}C, 400 ^{0}C and 500 ^{0}C were shown in Fig. 1.

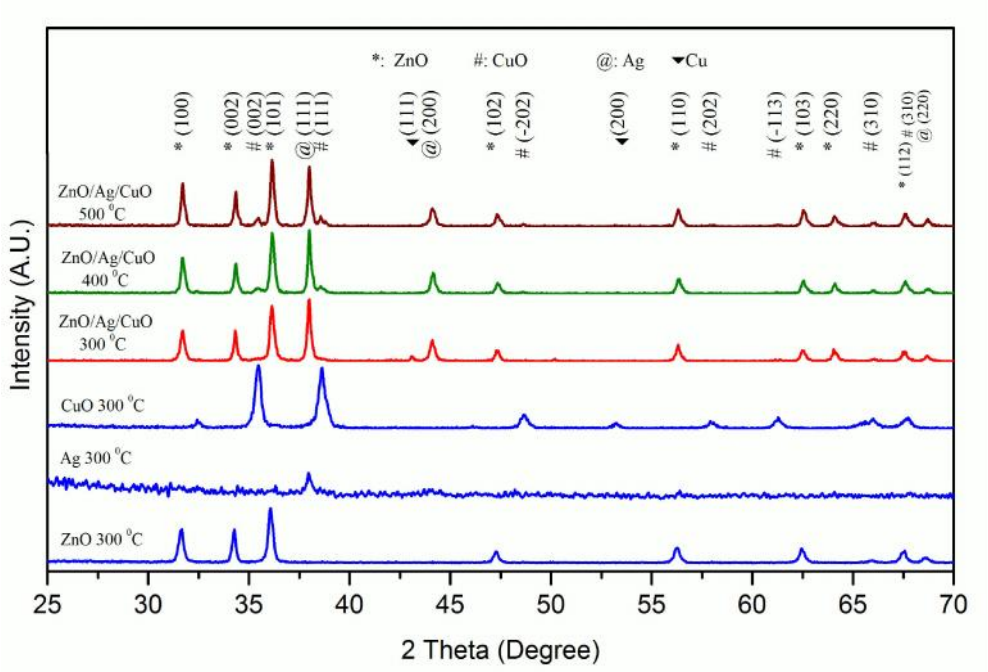

Figure 1: XRD patterns for ZnO, Ag, CuO and ZnO/Ag/CuO annealed at different temperatures

The diffraction peaks corresponds to (100), (002), (101), (102), (110), (103), (220) and (112) lattice planes exhibits hexagonal structure of pure ZnO as well the ZnO phase present in the nanophotocatalysts (ZnO/Ag/CuO) at three different temperatures (300 ^{0}C, 400 ^{0}C, 500 ^{0}C) which are well match with standard JCPDS card no: 79-0208. The diffraction peaks corresponds to (111), (200) and (220) crystal planes are found to agree well with the cubic structure of pure silver metal as well the silver metal phase present in nanophotocatalysts at all three temperatures with reference to the JCPDS card no: 03-0921. All of the x-ray diffraction peaks corresponds to (002), (111), (2$\bar{1}$02), (310) and (310) lattice planes represent the monoclinic structure of pure CuO and CuO phase in nanophotocatalysts at the above mentioned temperatures which are well satisfied with JCPDS card no: 89-2531.

The additional diffraction peaks corresponds to (111) and (200) crystal planes in the sample annealed at 300 ^{0}C indicates the presence of impurity phase of copper metal that match well with JCPDS card no: 03-1005. This impurity phase may be due to non-availability of sufficient oxygen to the precursor trapped at the bottom of

the crucible during the decomposition process at 300 ^{0}C, which is just around the critical point of complete decomposition of the copper acetate. However this impurity phase was not found in the other two samples annealed at 400 ^{0}C and 500 ^{0}C.

B. Lattice Parameters and Mean Crystallite Sizes

Table 1: Lattice parameters values for all prepared samples

Samples	ZnO (79-0208) Hexagonal		Ag (03-0921) Cubic	CuO (89-2531) Monoclinic			Cu (03-1005) Cubic
	a (Å)	c (Å)	a (Å)	a (Å)	b (Å)	c (Å)	a (Å)
ZnO (300 ^{0}C /3h)	3.269	5.229					
Ag (300 ^{0}C /3h)			3.914				
CuO (300 ^{0}C /3h)				4.706	3.438	5.129	
ZnO/Ag/CuO (300 ^{0}C /3h)	3.270	5.220	3.925	4.750	3.388	5.117	3.632
ZnO/Ag/CuO (400 ^{0}C /3h)	3.269	5.216	3.929	4.714	3.437	5.131	
ZnO/Ag/CuO (500 ^{0}C /3h)	3.269	5.217	3.941	4.698	3.480	5.126	

Lattice parameters of the prepared samples are shown in the Table 1. No significant deviation of lattice parameters of ZnO/Ag/CuO annealed at three different temperatures from that of individual ZnO, Ag and CuO were observed, and it suggests the formation of coupled ZnO/Ag/CuO. Intra-granular coupling provides close contact between all the three phases.

The crystallite sizes were estimated, using on Scherrer's formula, for the maximum intensity peaks are given in Table 2.

Table 2: Calculated mean crystallite sizes for all the samples

Samples	Crystallite Size (nm)		
	ZnO	Ag	CuO
ZnO (400 ^{0}C /3h)	37		
Ag (400 ^{0}C /3h)		28	
CuO (400 ^{0}C /3h)			28
ZnO/Ag/CuO (300 ^{0}C /3h)	35	44	9
ZnO/Ag/CuO (400 ^{0}C /3h)	36	49	22
ZnO/Ag/CuO (500 ^{0}C /3h)	40	43	25

C. Morphology

The Field Emission Scanning Electron Microscopy (FESEM) images of coupled ZnO/Ag/CuO prepared by thermal decomposition method and annealed at three different temperatures for 3 hours are shown in the Fig. 2. Fig. 2(a) shows the presence of randomly distributed nanorods among the spherically shaped nanoparticles. The

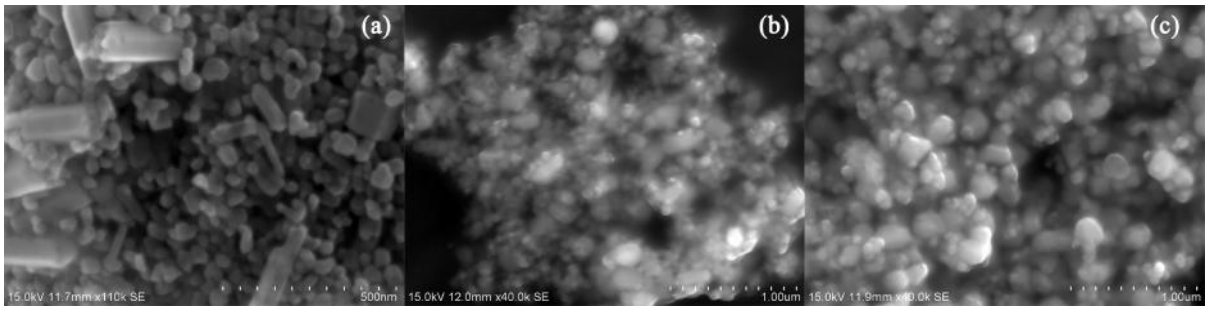

Figure 2: FE-SEM images of (a) ZnO/Ag/CuO - 300 ^{0}C (b) ZnO/Ag/CuO - 400 ^{0}C (c) ZnO/Ag/CuO - 500 ^{0}C

presence of an impurity phase of copper in its metallic form was revealed in the x-ray diffraction pattern taken for the same sample, and therefore the nanorods could be recognized as that of copper metal phase. The EDX spectra

taken over these regions confirm the presence copper. Figures 2 (b) & (c) show only the presence of agglomerated spherically shaped nanoparticles. This indicates the absence of impurity Cu metal phase in the samples annealed at higher temperatures. Better diffusion chances in the given environment might have facilitated the complete oxidization of Cu metal.

D. UV-Vis Diffuse Reflectance Spectra

The optical properties of the prepared samples were studied with UV-Vis Diffused Reflectance Spectroscopy (DRS) and the results are shown in the Fig. 3. The sharp absorption edges in the UV-Vis reflectance spectrum for ZnO and also those of ZnO/Ag/CuO (300 ^{0}C), ZnO/Ag/CuO (400 ^{0}C) and ZnO/Ag/CuO (500 ^{0}C) are all in the UV region and these properties suggest photocatalytic activity under UV light irradiation.

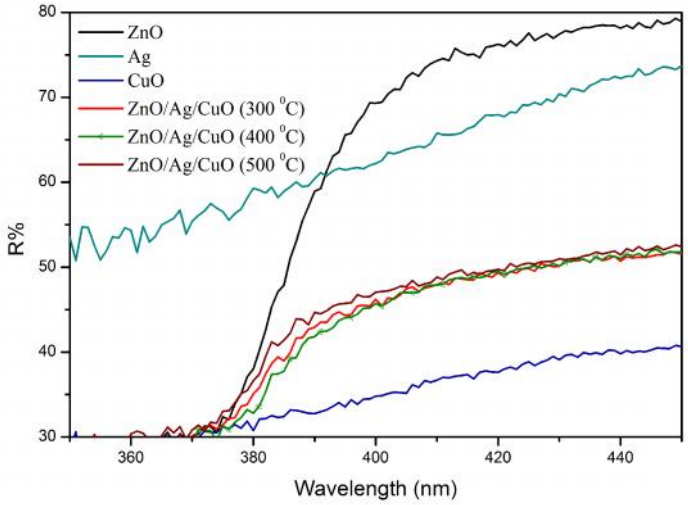

Figure 3: Diffuse Reflectance spectrum of all prepared samples

Further the optical band gap energy of pure ZnO as well as that of coupled ZnO/Ag/CuO synthesized at three different temperatures were estimated using Kubelka Munk equation. The absorption coefficient, ~, and the Kubelka Munk equation[15-17] can be related as follows.

$$\sim = F(R) = (1 - R)^2 / (2R) \qquad \text{where } R \text{ is reflectance}$$

The band gap energies of the prepared samples were estimated from the linearly fitted slope in the graph plotted between $(\alpha h\nu)^2$ and E (eV) as shown in Fig. 4. Table 3 gives the estimated band gap energies.

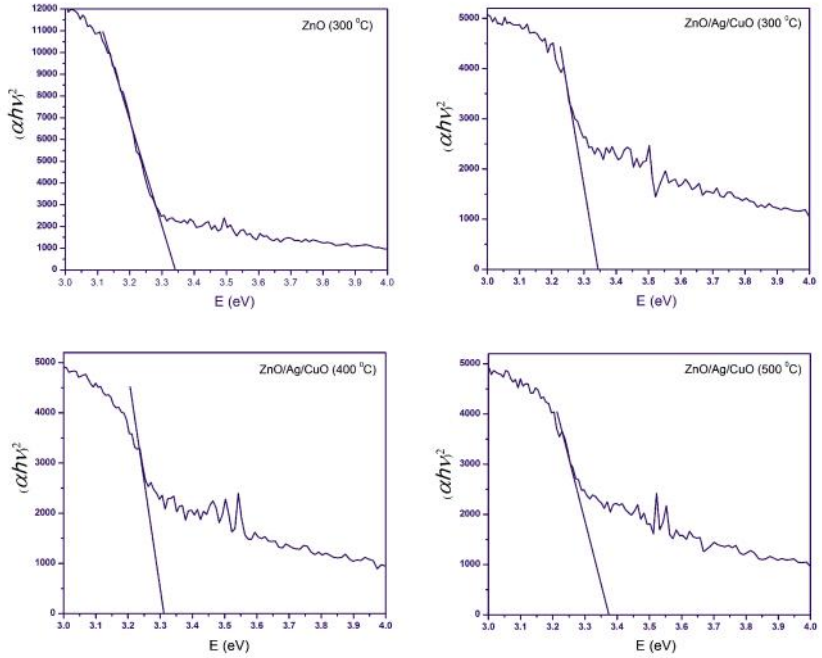

Figure 4: Estimation of Band Gap Energies

Table 3: Optical band gap energies for the three nanophotocatalysts and ZnO

Sample	Band gap energy (eV)
ZnO	3.35
ZnO/Ag/CuO (300 ^{0}C)	3.34
ZnO/Ag/CuO (400 ^{0}C)	3.31
ZnO/Ag/CuO (500 ^{0}C)	3.37

IV. PHOTOCATALYTIC DEGRADATION EXPERIMENT, RESULTS AND DISCUSSIONS

Reaction suspensions to carry out the photocatalytic activity were prepared by adding the required amount of photocatalysts (100 mg) into 100 ml of methylene blue (MB) solution taken with an initial concentration of 3.6 x 10^{-5} moles/liter . MB belongs to the family of azo dyes. The adsorption equilibrium between dye and surface of catalyst was maintained by stirring in dark condition for about 20 minutes before exposed to UV light. Then the suspension was irradiated with UV light and the suspension was continuously stirred to obtain uniform mixture of particles throughout all experiments. During irradiation, degraded MB solution was syringed at regular intervals of time and centrifuged to wipe out the catalysts. The amount of colour degradation at the said intervals was studied with UV-VIS spectroscopy. The absorptions by the syringed solutions were measured by a UV-VIS spectrophotometer at the peak absorption wavelength of 664 nm.

The experiment was carried out in a photocatalysis chamber integrated with an 8W mercury vapour lamp positioned at horizontal to the vessel, which is placed on a magnetic stirrer. Degradation efficiencies were calculated using following equation:

$$\eta\,(\%) = (1 - C_t/C_0) \times 100$$

where, C_0 is the initial absorbance by the MB before illumination (at t = 0) and C_t is the amount of absorbance by the MB at regular intervals of time (at t = 30, 60, 90, 120 minutes) during the irradiation. The obtained degradation profile of MB is shown in Fig. 5.

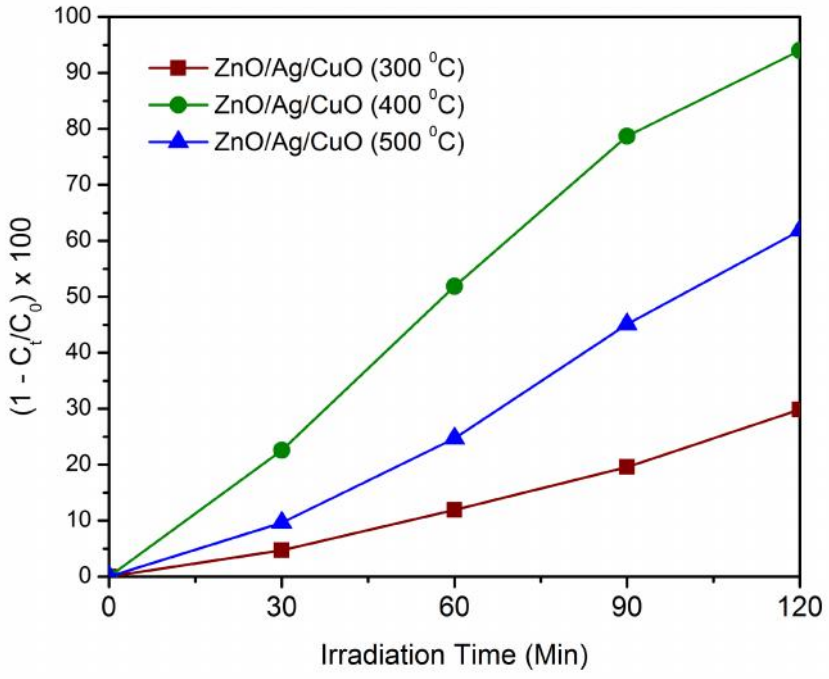

Figure 5: Degradation profile of Methylene Blue

The results indicate significant variation of photocatalytic degradation activity with the annealing temperature. The highest photocatalytic activity was shown by the coupled ZnO/Ag/CuO photocatalyst annealed at 400 ^{0}C. This could be attributed to reduced bandgap, as it was revealed by the UV-Vis diffused reflectance spectroscopy study and also to comparatively uniform distribution of spherically shaped smaller particles, as it was revealed by the FESEM micrographs.

The ZnO/Ag/CuO catalyst annealed at 300 ^{0}C has given the least efficiency among the prepared catalysts. Though the particle sizes were comparatively small, the presence of Cu metal phase, especially in the nanorods form, might have contributed to its least performance. Comparatively larger spherically shaped particles and intense agglomeration might have contributed to its reduced photocatalytic degradation performance of the ZnO/Ag/CuO catalyst annealed at 500 ^{0}C.

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