Ag-ZnO NANOCOMPOSITES: SYNTHESIS, CHARACTERISATION AND PHOTOCATALYTIC STUDIES

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Abstract: *Zinc oxide nanoparticles have semiconducting and photocatalytic properties and are finding application in transparent electronics, chemical sensors and spin electronics. Silver is a good candidate for forming shallow acceptor level in ZnO, which improves the suitaility for various optical and photocatalytic applications. Besides Ag doping in ZnO improves the surface charge distribution and discarded recombination of photo generated electron-hole. The photocatalytic activity is further enhanced by the incorporation of ZnO/Ag nanoparticles into a polymer matrix. In this research work, we have synthesised three PoPD(poly o-phenylene diamine) /Ag-ZnO nanocomposites. The nanoparticles and PoPD/Ag-ZnO nanocomposites were characterized by FTIR, XRD, FESEM and UV- visible spectroscopy.*

Key words: **Nanoparticles, Nanocomposites, Photocatalytic studies.**

1) Introduction

Nanotechnology refers to an emerging field of science that includes synthesis and development of various nanomaterials. Nanoparticles can be defined as objects ranging in size from 1-100 nm. Presently, different nanomaterials are being produced using copper, zinc, titanium, magnesium, gold and silver. Nanoparticles are being used in the fields of medicine and industry [1].

In general, nanomaterials exhibit significantly different properties from their bulk counterparts. The physico-chemical and opto-electronic properties of nanomaterials are influenced by their size, shape, surface and nature of material (metallic/semiconducting) [2]. The opto-electronic properties can be tailored by simple changes in nanoparticle dimensions [3]. Physical properties such as surface area also vary due to the availability of more interfaces in the small range. The surface to volume ratio is more in nanostate than in bulk. The band gap in semiconductor particles also increases when the particle size decreases due to the loss of in-between energy levels during the size reduction.

2. Results and Discussion

The different concentrations of Ag-ZnO nanoparticles doped PoPD/Ag-ZnO nanocomposites were synthesized by insitu oxidative polymerization method. The synthesized PoPD/Ag-ZnO nanocomposites were characterized by FTIR, XRD, FESEM, UV- visible and photoluminescence spectroscopy.

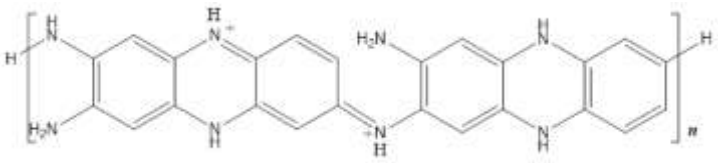

Fig.1. Structure of poly(o-phenylenediamine)

2.1. FTIR Spectrum

The FTIR spectrum of PoPD is shown in Figure 2. The two broad bands appeared at 3326 and 3151 cm^{-1} are due to stretching vibration of -NH- and $-NH_2$ groups. The aromatic C-H stretching frequency appeared at 3045 cm^{-1} [6]. The peaks at 1614 and 1514 cm^{-1} are assigned to the C=C bonds of quinonoid

and benzenoid rings respectively. The absorption peak at 1345 cm^{-1} can be assigned to the C-N stretching vibration of quinonoid rings, while the peak at 1239 cm^{-1} is attributed to C-N stretching vibration of the benzenoid rings. The characteristic peak at 1107 cm^{-1} is ascribed to C-H in-plane bending vibrations and C-H out-of- plane bending vibrations are appeared at 758 and 619 cm^{-1} which confirmed the presence of 1,2,4-trisubstituted benzene rings in the PoPD. From this study, we confirmed the chemical structure of PoPD, which is also consistent with previous report [7].

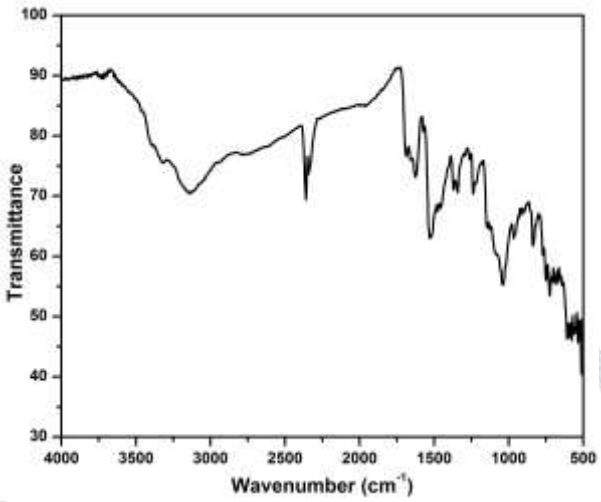

Fig.2. FTIR spectrum of PoPD

2.2. X-ray diffraction

The XRD pattern of Ag doped ZnO nanoparticles and PoPD/Ag-ZnO nanocomposites are shown in Figure 3. The nanoparticles diffraction peaks of Ag/ZnO nanoparticle angles 2θ of 34.4, 36.2, 47.6, 56.5, 62.9, 66.5, 68.04, 72.6 and 76.6 correspond to the reflection from (100), (002), (101), (102), (110), (103), (200), (201) (004) and crystal planes of the hexagonal wurtzite zinc oxide structure . No additional peaks corresponding to the secondary phases of silver doped zinc oxide were obtained for x = 0.01-0.05 at 600 ºC, which indicates that the wurtzite structure is not disturbed by doping of Ag and all the diffraction peaks agreed with the reported JCPDS card no. 80-0075. The XRD pattern of PoPD/Ag-ZnO nanocomposites has characteristics peaks of Ag-ZnO nanoparticles which revealed that the nanoparticles are incorporated in PoPD matrix. The crystalline nature of PoPD/Ag-ZnO nanocomposites increases with increase in Ag-ZnO nanoparticles concentration. The results revealed interaction between PoPD and Ag-ZnO nanoparticles.

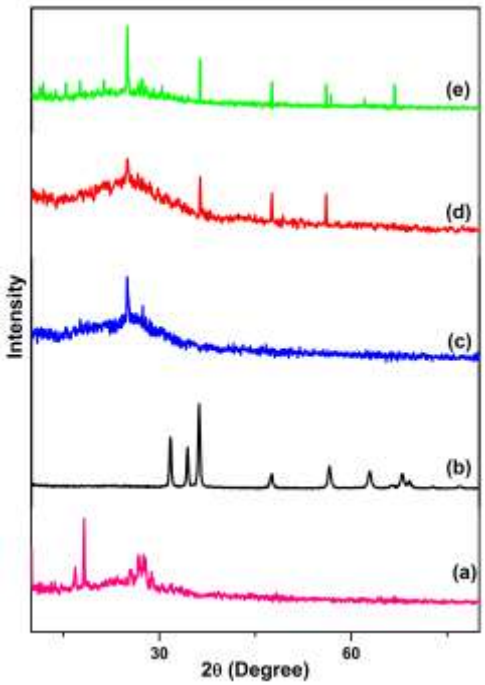

Fig. 3. XRD pattern of (a) PoPD, (b) Ag-ZnO, (c) PAZ1, PAZ2 and PAZ3

2.3. FESEM analysis

The morphology and crystalline size of Ag silver doped nanoparticles were analyzed through scanning electron microscope. The FESEM images of PAZ1, PAZ2 and PAZ3 are shown in Figure 4. The flakes and hollow sphere like morphology are observed from FESEM images of PoPD. The Ag doped ZnO nanoparticles have cauliflower like morphology and also indicated agglomeration of nanoparticles [8]. The morphology of PoPD/Ag-ZnO nanocomposites varies from the morphology of PoPD and Ag-ZnO nanoparticles. The FESEM images of PAZ2 and PAZ3 shown flakes like morphology. The spherical morphology of PoPD is completely modified by the incorporation Ag-ZnO nanoparticles. The FESEM results revealed the incorporation of Ag-ZnO nanoparticles in PoPD matrix.

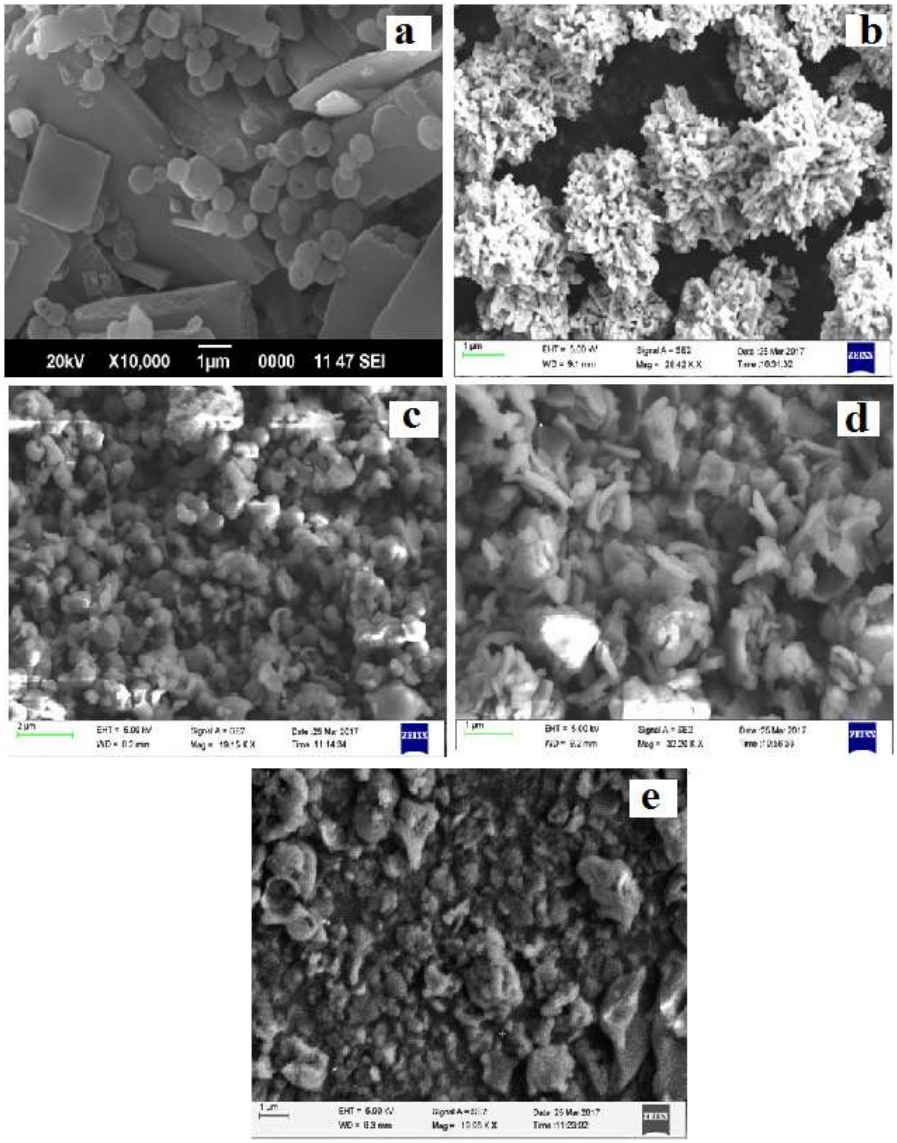

Fig. 4. FESEM images of (a) PoPD, (b) Ag-ZnO, (C) PAZ1, (d) PAZ2, (e) PAZ3

2.4. UV-visible spectrum

The optical absorption spectra of PAZ1, PAZ2 and PZA3 by UV-Vis spectrometer in the range 200-900 nm are presented in Figure 5. The spectrum illustrates the major absorption bands of 229 and 417 nm. The bands appeared at 232 is mainly due to $\pi \rightarrow \pi^*$ transitions of aromatic ring. The broad band at 432 nm is attributed to the charge transformation of conjugated benzenoid fragmentation to quinonoid one. The optical band gap is calculated using the Tauc relation [9, 10].

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where α is the absorption coefficient, A is constant, E_g is the optical band gap of the material and n is an index, which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of electronic transition, n = 1/2 for direct band gap of semiconductors. The extrapolation of the linear region of plot $(\alpha h\nu)^2$ vs $h\nu$ gives the value of the optical band gap Eg. The band gap of PAZ1 is 1.86 eV and PAZ2, PAZ3 is 1.79eV and 1.78 eV respectively. When the concentration of Ag-ZnO increases in PoPD/Ag-ZnO nanocomposites, there is a decrease in band gap continuously.

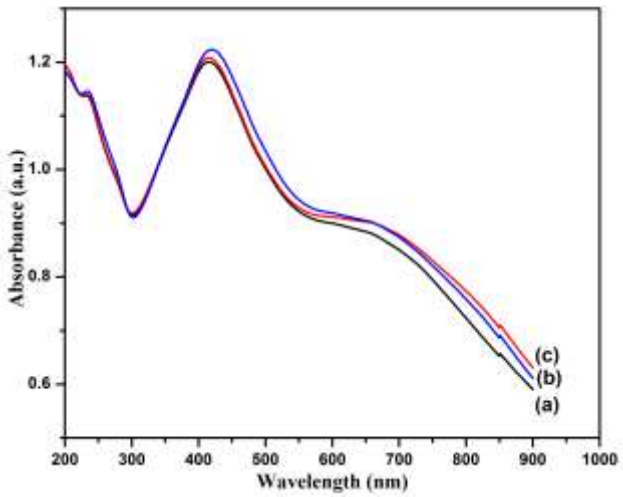

Fig.5. UV spectrum of (a) PAZ1, (b) PAZ2, (c) PAZ3

2.5. Photocatalytic activities

The photo catalytic study of MB (Methylene Blue) dye was done in presence of PAZ3 under UV radiation. UV spectroscopy has been used to monitor the degradation process. The change in intensity absorption maximum MB with respect to time with PAZ3 is shown in Figure 6. The observations were taken at various time intervals after the solution was exposed to the UV radiation. It is observed that the intensity of the absorption maximum decreases with increase in exposure time from 0 to 180 min. The intensity of absorption peak of the solution decreases due to degradation of the MB dye. Decolourization efficiency was calculated from the formula [11, 12],

$$\text{Decolourization efficiency (\%)} = \frac{(A)_o - (A)_t}{(A)_o} \times 100$$

Where $(A)_o$ is the absorbance before irradiation and $(A)_t$ is the absorbance at time t. Figure 7 gives percentage degradation in concentration of MB dye with respect to time. After 4 hrs of UV radiation 96 % of MB dye disappears from the dye-water. The photocatalytic activity of the photocatalyst depends on the adsorption quantity of dye molecules on the surface of the photocatalyst [13].

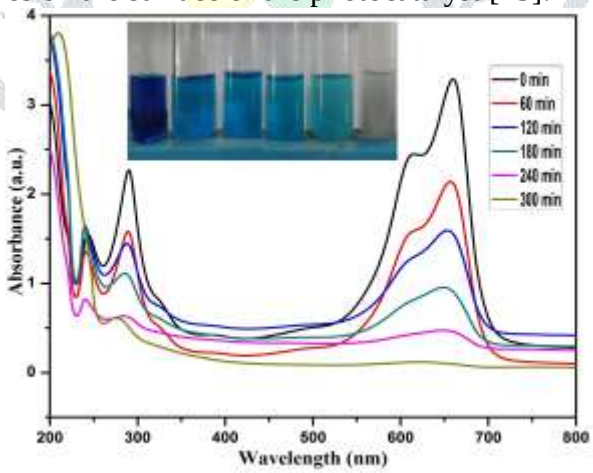

Fig.6 Change in absorption intensity of MB/PAZ3 with respect to time

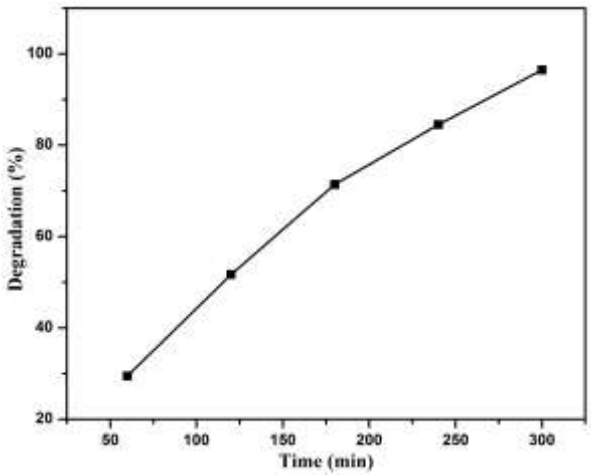

Fig. 7 Percentage degradation of MB dye with respect to time

2.5.1. Photocatalytic degradation of methylene blue (MB) dye

The photo degradation mechanism of the MB dye using Ag-doped ZnO NPs is shown in Figure 8, which describe the effect of silver addition in ZnO for improving photocatalytic activity. In this mechanism, when the sample is irradiated with UV light, the electrons are excited from valance band to conduction band. Silver (Ag^+) traps the electrons from CB and after that silver (Ag) is oxidized by the absorption of oxygen to produce reactive oxygen species (O_2^-). The reactive oxygen species (O_2^-) is then further reduced to form hydroxyl ($^{\bullet}OH$) radical. On the other hand, the holes combine with water to form hydroxyl ($^{\bullet}OH$) radical and these hydroxyl ($^{\bullet}OH$) radicals break down the dye molecules in order to degrade the dye. In this way, the silver addition in ZnO accelerates the transfer of electrons from conduction band to oxygen molecule thus avoid recombination with holes and therefore enhances photo activity. Therefore, the presence of large number of electron (e^-) and holes (h^+) induces redox reactions that generate more reactive oxygen spices for photo-catalytical degradation of MB dye in aqueous solution.

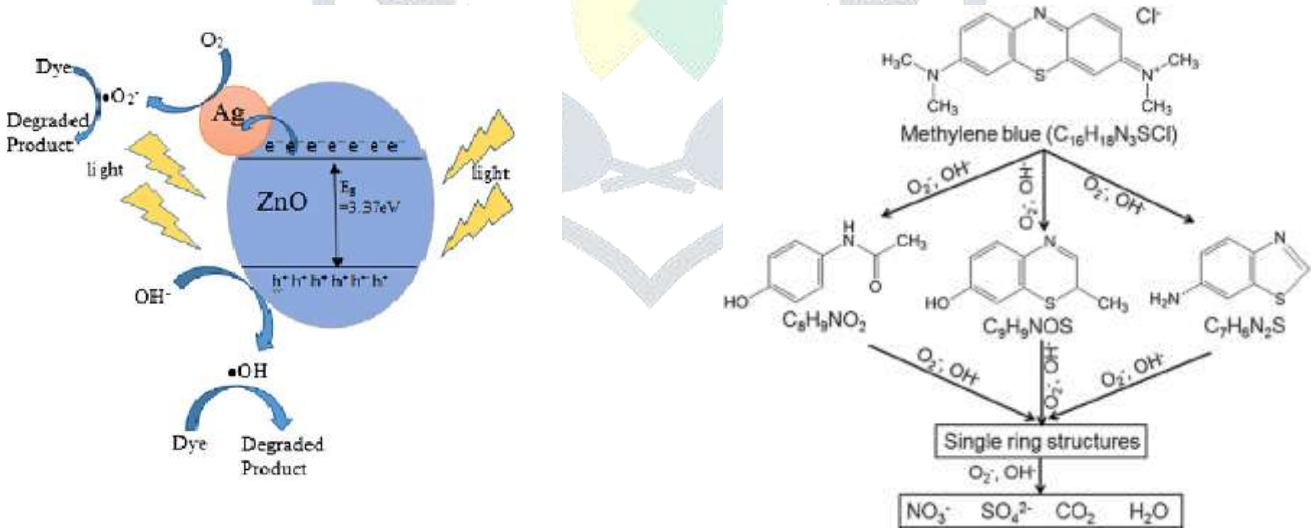

Fig.8 Photo degradation mechanism of the MB dye in presence of Ag-doped ZnO NPs

3) Experimental methods

3.1. Synthesis of silver doped ZnO nanoparticles

The silver doped Zinc oxide nanoparticles were synthesized through microwave method. In this method, 0.1 mole of zinc nitrate was dissolved in distilled water and to this 0.01 mole of aqueous solution of silver nitrate was added with constant stirring. Then 0.1 mole of NaOH was added into reaction mixture. After that, the reaction mixture was irradiated with microwave energy (700 W) for 15 min. The solution was allowed to settle overnight and the supernatant solution was then discarded carefully. The remaining solution was filtered and washed several times with distilled water. The precipitate was dried in oven at 110 ºC for 2 hrs and thoroughly ground and then calcined at 600 ºC for 3 hrs. Here, $Zn(OH)_2$ is converted to ZnO.

3.2. Synthesis of PoPD/Ag doped ZnO nanocomposites

Poly(*o*-phenylenediamine) was prepared by chemical oxidative polymerization method. The *o*-phenylenediamine (0.01 mol) was dissolved in distilled water and previously synthesized Ag doped ZnO nanoparticle was added in to it with constant stirring. Then, the equimolar ratio of ammonium persulphate was also added to that. The reaction mixture was kept in the microwave oven and irradiated with microwave energy (120 watt) for 20 min. The formed precipitate was filtered, washed with hot water and dried under vacuum. The same procedure was followed for fabricating the nanocomposites with various concentrations. The composition details of synthesized samples are shown in Table 1.

Table 1.

The composition details of PoPD/Ag doped ZnO nanocomposites

S.No	Samples	Code	PoPD/Ag-ZnO (w/w)%
1	Poly(*o*-Phenylenedimine)	PoPD	100
2	PoPD/Ag-ZnO	PAZ1	90:10
3	PoPD/Ag-ZnO	PAZ2	80:20
4	PoPD/Ag-ZnO	PAZ3	70:30

3.3 Photocatalytic activities of PoPD/ Ag doped ZnO nanoparticles

A specially designed photocatalytic reactor system made of double walled reaction chamber of glass tubes was used for photodegradation experiments. A UV lamp of 125 W was used for the experiment. The solution for photodegradation measurement was prepared by adding 5 mol% Ag doped ZnO (1 g/l) to 50 ml aqueous solution of methylene blue (10 ppm MB 50 ml). In order to ensure the catalyst powder dispersed in the MB solution, the mixture was stirred for 10 min, and then kept in dark for an hour to achieve adsorption equilibrium. The sample was then transferred into the photoreactor for UV exposure and the lamp was turned on and approximately 5 ml mixture of catalyst and MB solution was sampled from the photoreactor after fixed time interval. The concentration of MB in the solutions was ascertained by referring to an absorption-concentration standard curve that was established by measuring the optical absorption of methylene blue at 657 nm by UV-Vis spectrometer.

5. Conclusion:

Silver doped ZnO nanoparticles were prepared through microwave assisted method. The synthesized Ag-ZnO nanoparticles were confirmed through XRD pattern. PoPD/Ag-ZnO nanocomposites were synthesized by insitu oxidative polymerization method. The formation of PoPD/Ag-ZnO nanocomposites was confirmed through XRD pattern and SEM analysis. The crystalline nature of

PoPD/Ag-ZnO nanocomposites increases with increase in concentration of Ag-ZnO nanoparticles. FESEM images of PoPD is revealed sphere like morphology.In PoPD/Ag-ZnO nanocomposites, spherical morphology of PoPD is completely modified by Ag-ZnO nanoparticles. In photoluminescence spectrum of PAZ3, the emission peak appears in green region. Within 5 hrs 96% of MB dye is degraded by PAZ3.

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7. REFERENCES

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