Impact of aqueous and alcoholic solvents mediated on the structural, optical, photocatalytic and antibacterial properties of ZnO-MgO nanocomposites via co-precipitation route

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Abstract

Aqueous and alcoholic solvents mediated Zinc oxide/Magnesium oxide (ZnO-MgO) nanocomposites (denoted as ZOMONC's) synthesized through co-precipitation process. The synthesized ZOMONC's exhibited the formation of hexagonal and cubic crystal structure which is authenticated by powder X-ray study. The synthesized ZOMONC's functional groups are scrutinized using FT-IR studies. Optical energy band gap and luminescence is identified by UV absorption and RT-PL studies. Spherical-like particles of various solvents mediated ZOMONC's are observed from the SEM analysis. Mixture solvents mediated ZOMONC's exhibited best in terms of size and morphology, which is subjected to TEM, Photocatalytic and antimicrobial studies. The synthesized ZOMONC's is exhibited good photocatalytic activity against Amido black 10B dye. The antibacterial activity of the synthesized water-methanol solvent mediated ZOMONC's sample against (a) *Escherichia coli* and (b) *Staphylococcus aureus* bacteria strain.

Keywords: Nanocomposites; Metal oxide; Co-precipitation; Optical features; Photocatalytic activity; Antimicrobial activity

1. Introduction

In recent past, many researchers focus on the fabricating semiconductor metal oxides [1-6] and metal sulfides [7-10], mixed binary semiconductor oxides [11-16], mixed binary

semiconductor sulfides [17,18], mixed ternary semiconductor oxides [19-23], mixed ternary semiconductor sulfides [24], ferrites and its nanocomposites [25-31], followed by extensively studied the photocatalysts for solving environmental problems. Among the materials, mixed semiconductor oxides compounds has been much attention in waste water treatment due to the reducing optical band gap, broad light absorption and emission bands in the visible portion, fast recombination of charge carrier and slow separation, high stability and non-toxic etc. [11-16]. Especially, photocatalytic behaviour of mixed binary oxide ZnO-MgO nanocomposite has been unique characteristic for waste water treatment [15-16, 32]. The different physico-chemical properties have been found in individual compound of ZnO and MgO material [33-36]. When mix the above said compounds together formation would be expect better photocatalytic properties, which lead to useful in waste water treatment. There are numerous reports available about waste water treatment process [25-31]. Among the process, photocatalytic process is advanced oxidative process, simple, low cost and easily degrade the chemicals. The other waste water treatment process has to do multiple processes for complete removing of dyes and unwanted residues.

Very limited works are reported the photocatalytic activity of ZOMONC's through different chemical routes by the scientists [15-16, 32]. The novelty of the present work, mixed solvent (water-methanol) mediated on the photocatalytic and antimicrobial properties of ZOMONC's. In addition, impact of aqueous and alcoholic solvents mediated on the structural behaviour, optical absorption & band gap, and RTPL emission bands of the ZOMONC's are elaborated in detail.

2. Experimental method of ZOMONC's

Under vigorous magnetic stirring, 2.19 g of $Zn(CH_3COO)_2.2H_2O$ and 2.14 g of $Mg(CH_3COO)_2.4H_2O$ were dissolved in 100 ml of aqueous solvent. By adding 0.8 g of NaOH to the above solution, precipitates were obtained. It was then heat-treated at 180 °C for 15 hrs to collect the intermediate compound ($Zn(OH)_2$/$Mg(OH)_2$). Finally, the nanocrystalline ZnO/MgO sample was obtained after calcined the precipitates at 450 °C for 2 hrs. The same method was used to synthesize ZOMONC's using alcoholic solvents like ethanol and methanol, as well as mixture solvent like water and methanol. The characterization of the prepared title compounds can be found in the supporting information.

3. Results and Discussion

The powder XRD patterns of the different solvents mediated ZOMONC's samples is displayed in Fig.1(a-d). The presence of diffraction patterns was well-matched with the previously reported diffraction peaks of the ZOMONC's nanocomposites, which confirmed the bi-phase crystal structure i.e. hexagonal crystal structure of ZnO (JCPDS File No. 80-0075) and cubic structure of MgO (JCPDS File No. 89-7746) [15]. Thus, nanostructured ZnO-MgO composite material was formed successfully via this current synthesis process and their average crystallite size was computed as using Debye-Scherrer's equation which is detailed in Table 1.

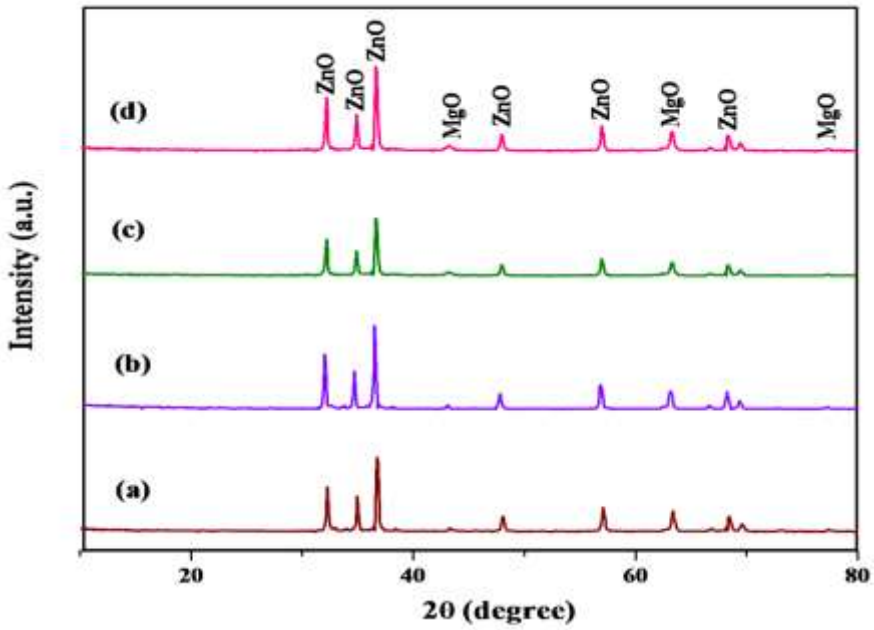

Fig.1 Powder X-ray diffraction patterns of (a) water (b) ethanol (c) methanol and (d) water-methanol mediated ZOMONC's

The FTIR spectra of various solvent-mediated intermediate compounds are exhibited in Fig.2(a-d). A wide band located at the wavenumber of ~3416 cm^{-1} attributed to surface hydroxyl groups (O-H) of water molecules from the functional group region (4000 to 1500 cm^{-1}). A broad band at wavenumber of ~1437 cm^{-1} indicated to O-H bending vibration of alcohol further in the finger print region (1500 to 450 cm^{-1}). Furthermore, the bands at wavenumber of ~524 and 459 cm^{-1} can be assigned to Zn-O and Mg-O, respectively [34,36], confirming the formation of the ZnO-MgO compound.

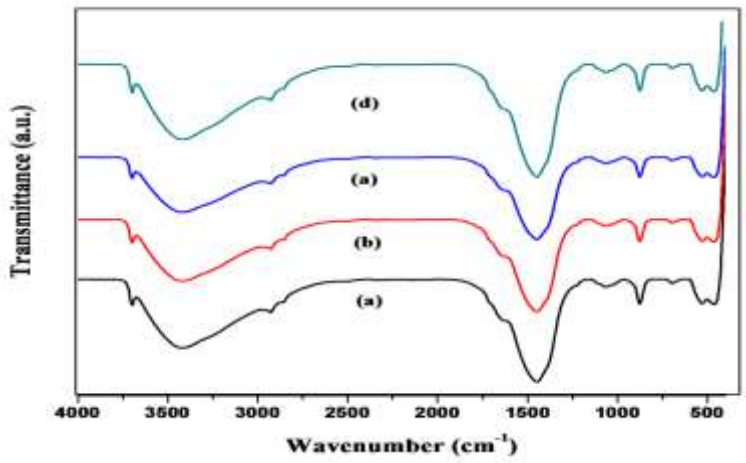

Fig. 2: FT-IR analysis of (a) water (b) ethanol (c) methanol and (d) water-methanol mediated intermediate compound.

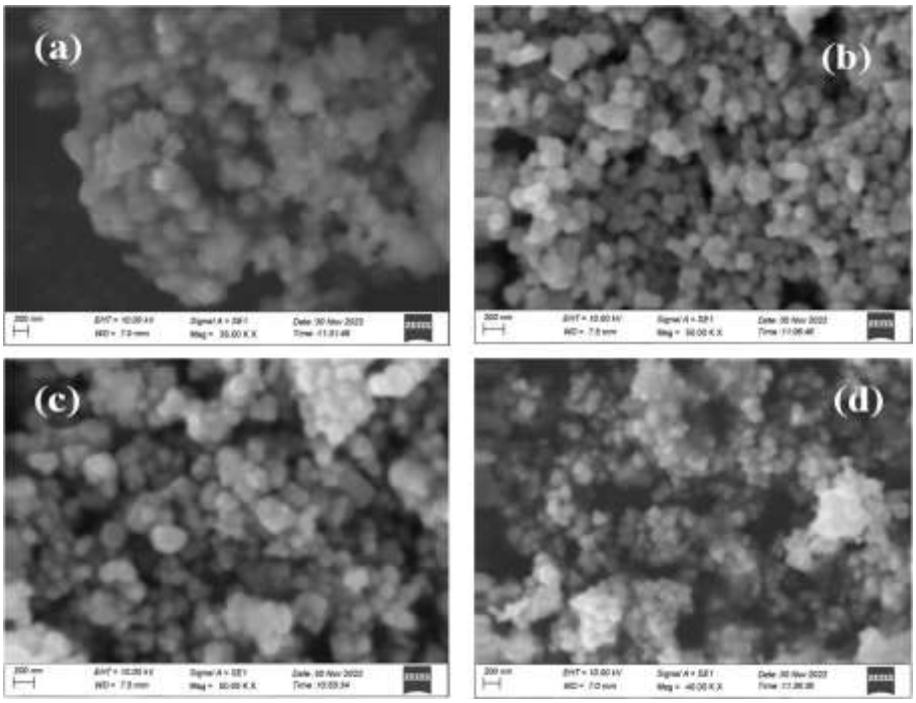

Fig.3: SEM photographs of (a) water (b) ethanol (c) methanol and (d) water-methanol mediated ZOMONC's.

Fig.3(a-d) shows the SEM images of aqueous and alcoholic solvents mediated ZOMONC's. Spherical-like well dispersed particles were observed from the SEM analysis. SEM image very clearly depicts the surface-morphology of the synthesized ZOMONC's with lesser aggregated particles due to solvents medium acted as a fine disperser.

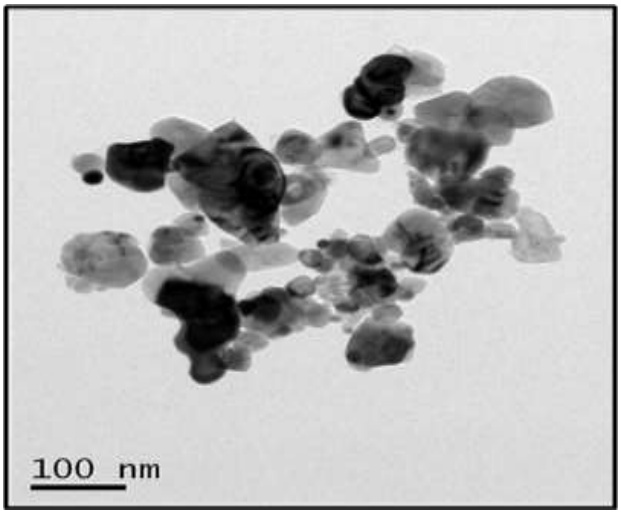

Fig.4: TEM picture of mixture solvents mediated ZOMONC's

Fig.4 shows the mixture solvent (water-methanol) mediated ZOMONC's. Spherical-like fine particles were observed from the TEM analysis. Mixture solvent played as not only as a

spacer but also modulate the distance between the metal particles (Zn-Mg) from the accumulation during the earlier process of organic removal. The average particle size was measured ranging from 15-25 nm.

The optical absorption spectra of various solvents-mediated ZOMONC's are shown in Fig. 5(a-d). A strong excitonic absorption band is identified, from which the absorption edges are estimated, and the band gap energies are measured, as shown in Table 1. Blue shift was observed in all samples from the optical absorption spectra due to the smaller particle size of ZOMONC's. Because of their improved optical behaviour, prepared ZOMONC's may be suitable for optoelectronic devices.

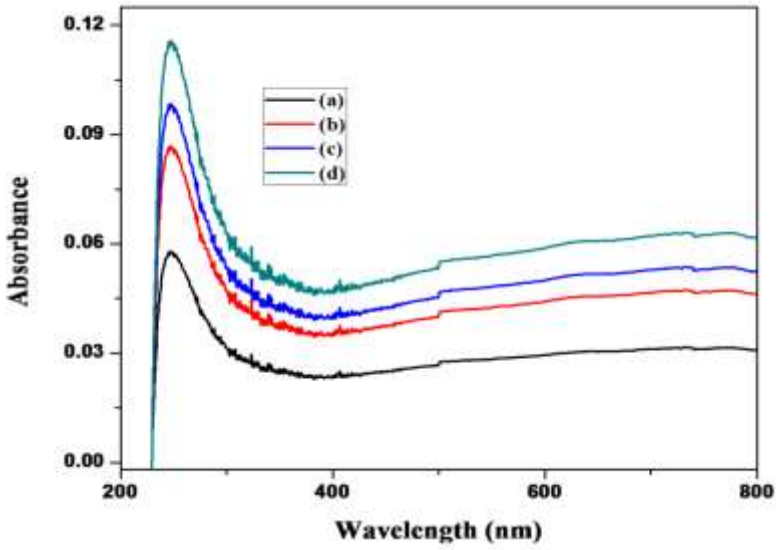

Fig.5: UV-vis absorption spectra images of (a) water (b) ethanol (c) methanol and (d) water-methanol mediated ZOMONC's

Table 1 summarizes the morphology, crystallite size and optical band gap energy of various solvents mediated ZOMONC's

Samples	Morphology	Crystallite size (nm)	Band gap energy (eV)
Water	Spherical	25.7	3.68
Ethanol	Spherical	23.4	3.71
Methanol	Spherical	22.8	3.79
Water-methanol	Spherical	20.5	3.87

The room temperature photoluminescence (RTPL) emission spectra of various solvents-mediated ZOMONC's are shown in Fig. 6. Only all of the samples had strong visible emission bands. The broad band at ~430 nm, as well as some low intensity shoulder peaks in all samples (Fig. 6 (a-d)), reveals that the appearance of oxygen vacancies and act as luminescence centres, demonstrating the better luminescence behaviour of prepared ZOMONC's [35].

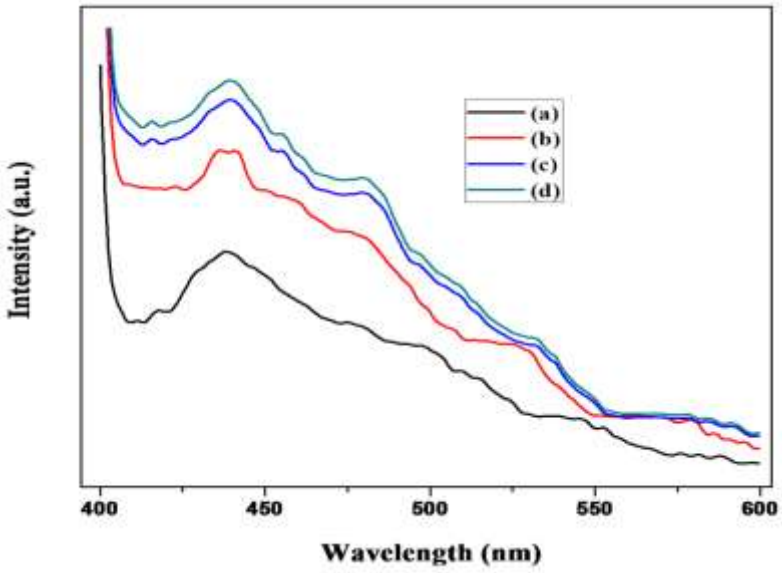

Fig.6: RT-PL spectra images of (a) water (b) ethanol (c) methanol and (d) water-methanol mediated ZOMONC's

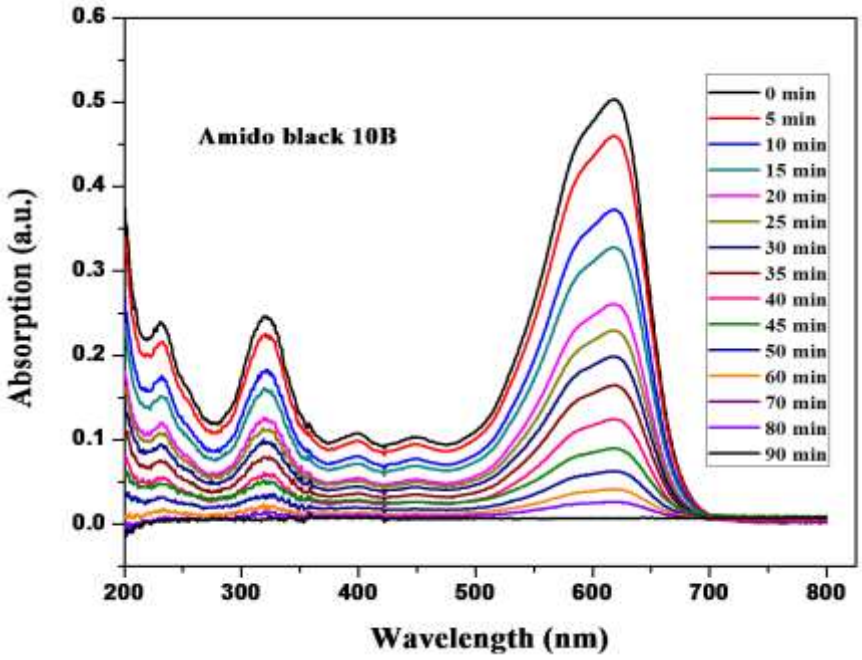

Fig. 7: Photocatalytic degradation of Amido black 10B dye using ZOMONC's photocatalyst

The UV-vis spectra of photocatalytic degradation of Amido black 10B (diazo type dye) using mixture solvent mediated by ZOMONC's photocatalyst are shown in Fig.7 The chromophore and aromatic parts of Amido black 10B have absorption wavelengths of 619 nm and 322 nm, respectively. Further, the chromophore and aromatic group decreased with increasing irradiation time under the effective activities of ZOMONC's sample at the end of 90 min irradiation time, indicating almost complete decolorization and degradation of the dye. The

photocatalytic activity of the ZOMONC's is estimated to be 99.145% efficient [34]. As a result, it is concluded that the ZOMONC's sample acted as a potential metal oxide nanocomposite photocatalyst.

Fig.8: Antimicrobial activity of the mixture solvent mediated ZOMONC's sample versus (a) *Escherichia coli* and (b) *Staphylococcus aureus*

The antimicrobial activity of the mixture solvent (water-methanol) assisted ZOMONC's is shown in Fig.8. Agar well diffusion process is used to examine the antibacterial efficacy of the ZOMONC's versus *S. aureus* (gram-positive) and *E. coli* (gram-negative) [37]. In the positive control (Streptomycin), the diameter of the zone of inhibition (DZI) was estimated to be 3.1 ± 0.2 cm for *E. coli* and 2.9 ± 0.2 cm for *S. aureus*, respectively. The negative control (distilled water) had no inhibitory zone. The presence of ZOMON's in the sample may be responsible for the bacteria's inhibitory effect. The release of Zn^{2+} and Mg^{2+} ions is responsible for the antibacterial activity against both strains. These ions form electrostatic bonds with the bacterial cell wall and rupture it. Excess free radicals produced by reactive oxygen species (ROS) damage and ultimately kill the bacterial cell's internal components. According to the findings, the synthesised ZOMONCs act as an effective antimicrobial agent.

4. Conclusion

Various solvents mediated ZOMONC's sample is successfully synthesized by co-precipitation route. The hexagonal and cubic crystal structure is confirmed by XRD analysis. The Zn-O and Mg-O vibration band are identified using FT-IR studies. Spherical-like morphologies are observed from SEM and TEM analysis. Due to the smaller crystallite size, the mixture solvent mediated sample is subjected to photocatalytic and antibacterial characterization analyses. The photocatalytic activity of the ZOMONC's is performed followed by photo degradation efficiency was computed to be 99.145%. From the antibacterial activity experiment, (DZI) was estimated to be 3.1 ± 0.2 cm for *E. coli* and 2.9 ± 0.2 cm for *S. aureus*, respectively.

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