

## Synthesis and characterization of nano ZnO and MgO powder by low temperature solution combustion method: studies concerning electrochemical and photocatalytic behavior

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The objective of the research was mainly focused on the synthesis of ZnO and MgO nanoparticle by low temperature solution combustion method using Urea as fuel. The accurate size and morphology of the nanoparticles were studied from Transmission Electron Microscopy (TEM) to assess the structure of the ZnO and MgO particles. The phase composition of the Synthesized ZnO and MgO nanoparticles were confirmed from powder X-ray diffractometer (PXRD). The electrochemical impedance spectroscopy (EIS) shows the charge transfer capacity was more in the electrode with zinc oxide compared to magnesium oxide. Cyclic voltammetry studies were performed to ascertain the electrochemical reversibility of electrode. We evaluate the photocatalytic activity of nanoparticles shows rapid color removal and reduction in the concentration of dyes.

**Keywords:** Synthesis, ZnO, MgO, electrochemical and photo catalytic behavior.

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### 1. Introduction

The photocatalytic degradation efficiency and mineralization degree of dyes are limited because of the slow interfacial electron transfer. In recent years, the light-converting materials have attracted tremendous attention for photocatalysis and solar energy collection which can be easily absorbed by a given dye and thus effectively excite the dye to generate more electron-hole pairs, resulting in the improvement of the self-sensitized dye degradation. In this work, we report the photocatalytic degradation of Methylene Blue (MB) and Methyl Orange (MO) under visible light irradiation by using ZnO/MgO nanoparticles synthesized by a solution combustion method [1]. It was found that ZnO/MgO particles exhibited high enhancement of visible light photocatalytic performance in the degradation of MB and MO.

Currently, inorganic nano metal oxides (TiO<sub>2</sub>, MgO, CaO and ZnO) are attracting research interest due to their safety, stability and multifunctional properties [2]. Design of materials which can be efficiently trapped and transfer energy in the form of charges is a major challenge in photocatalysis, photoluminescence (PL) and solar energy conversion fields. However, less progress has been made for nanomaterials, which often exhibit their unique size dependent physical/chemical properties due to their large surface-to-volume ratio and quantum confinement effects. Zinc oxide finds a wide range of applications as photocatalyst, lasers, white light emitting diodes (WLEDs), sensors, antireflection coatings, antibacterial, antifungal, solar cell material, varistors, optical devices, piezoelectric devices, optoelectronic devices, photonics etc [3].

The aim of the work is the synthesis of ZnO and MgO Nanoparticle with Urea as a fuel by using low cost solution combustion method. The cyclic voltammetry and photocatalytic activity were carried out to predict the properties of prepared samples.

## 2. Experimental

### 2.1. Synthesis of ZnO/MgO nano particles

In a synthesis, according to the stoichiometric ratio and molar mass of Zinc Nitrate ( $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ ), Magnesium Nitrate ( $\text{MgNO}_3 \cdot 6\text{H}_2\text{O}$ ) and Urea ( $\text{NH}_2\text{CONH}_2$ ) were dissolved in a small amount of distilled water. Then, the solution was heated in a furnace 10 to 15 minutes at  $450^\circ\text{C}$ . After the reaction was complete, the resulting white product was crushed into a fine powder. Then, the as-synthesized products were calcined at  $500^\circ\text{C}$  for 4 h in air to obtain ZnO/MgO nanoparticles [4]. Stoichiometric compositions of the metals nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valences of the components which serve as numerical coefficients for stoichiometric balances.



### 2.2. Characterization

X-Ray diffraction analyses were carried out using a high resolution X-ray Diffractometer Maxima-7000 (Shimadzu) at a scanning rate of  $2^\circ\text{min}^{-1}$  using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) operating at 40 kV and 30 mA. TEM was used to study the accurate size and morphology of the ZnO/MgO. TEM images of the ZnO/MgO were obtained at 80 kV under high resolution TEM instrument (JEOL, Japan, and JEM-1011). Cyclic voltammetry and electrochemical impedance were measured by Electrochemical workstation CHI604E. The samples were analyzed by recording UV-vis spectra of MB and MO, using a Spectra treats 3.11.01 Release 2A UV-vis spectrophotometer.

## 3. Result and discussion

### 3.1. X-Ray diffraction

The average crystalline size, structure and phase of sample were determined using XRD in the  $2\theta$  range from  $20 - 700$  at a scanning rate of  $2^\circ\text{min}^{-1}$ . Using the peak width at half maximum height and peak position ( $2\theta$ ) in the XRD spectra, the inter layer space can be calculated utilizing Bragg's law:

$$n\lambda = 2d \sin \theta, \quad (3)$$

where  $\lambda$  is wave length of X-ray radiation used in the diffraction experiments,  $d$  is the space between layers in the clay lattice and  $\theta$  is the measured diffraction angle.

The XRD form of ZnO/MgO nanoparticles obtained from solution combustion synthesis were as shown in Figs. 1(a) and 1(b). The peaks at  $2\theta$  values of  $31.71, 34.41, 36.21, 47.46, 56.57, 62.76$  and  $67.94^\circ$  corresponded to the crystal planes of (100), (002), (101), (102), (110), (103) and (112) of zinc oxide nano particles. The diffraction peaks could be referring to the spherical phase, which was evaluated with the data from JCPDS card No. 89-7102. The strong and narrow peak denotes that the product particles have a well-formed crystalline nature. The particle average size was calculated by the Scherrer formula and found to be in the range of 38 nm. In Fig. 1(b), the XRD results of MgO revealed that the structure was in cubic structure and these results were matched with JCPDS card number 75-1525. Peaks were absorbed at  $36.8, 42.8, 62.1, 74.6$  and  $78.5^\circ$  along with miller indices values (111), (200), (220), (311) and (222) respectively. As the width of the peak increases, the size of particle size decreases, which appears to make the present material in the nano range. The average crystallite size was measured as 40 nm.

### 3.2. Transmission electron microscopy

Transmission Electron Microscopy (TEM) is useful to understand if amorphous or crystalline sized particles are smaller. The TEM images of ZnO and MgO nano particles were shown in the Figs. 2(a) and 2(b) respectively. From Fig. 1(a), it is clearly shown that, ZnO exhibits nearly circular/spherical like structure and Fig. 1(b) indicating MgO exhibits the hexagonal shape and very homogeneous crystal structures without any observable pores.

### 3.3. Cyclic voltammetry studies

Cyclic voltammetry (CV) and electrochemical impedance measurements were carried out using CHI604E electrochemical workstation. For cyclic voltammetry studies, the test electrode was prepared by grinding the combination of 20 % prepared ZnO/MgO Nano powder, 70 % graphite powder and 10 % silicone oil used as binder and resulting pasted on a disk electrode. A platinum foil was used as a counter electrode; Ag-AgCl electrode as a reference electrode and 0.5 M  $\text{Na}_2\text{SO}_4$  solution as electrolyte. All measurements were carried out at room temperature. The representative CV curves for ZnO/MgO are shown in Figs. 3(a,c,d) with different scan

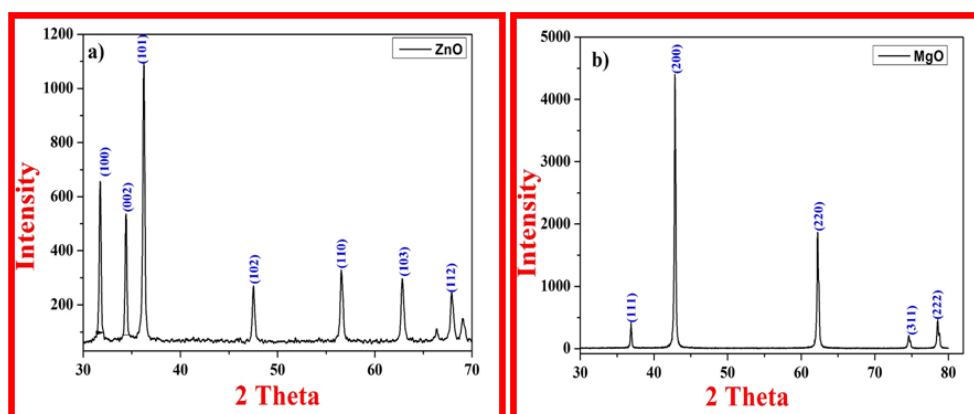


FIG. 1. XRD images of ZnO and MgO nano particles

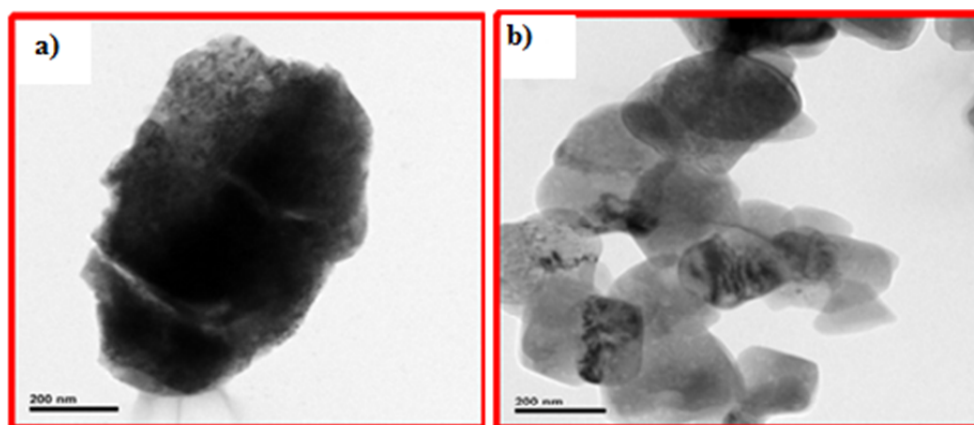


FIG. 2. TEM images of ZnO and MgO nano particles

TABLE 1. Electrochemical reversibility and EIS of ZnO/MgO Electrodes

Electrode	Electrolyte	$E_0$ (V)	$E_R$ (V)	$E_0 - E_R$	$R_{ct}(\Omega)$	$C(F) \times 10^{-5}$
ZnO	$Na_2SO_4$	0.2988	0.2739	0.0249	12.01	2.801
MgO	$Na_2SO_4$	0.2986	0.2639	0.0347	16.09	0.0326

rates. Increasing the scan rate from 10 mv to 50 mv, increases the oxidation and reduction of peaks for ZnO/MgO samples. The comparative CV results of electrodes ZnO/MgO at a scan rate of 0.01 V/s are tabulated in Table 1. The data there confirm that the electrochemical reversibility of ZnO is superior than that of MgO. Therefore, ZnO is more suitable for electro and photo catalytic activity applications. These results indicate that the charge and discharge process of the ZnO pasted electrode shows better electro chemical reversibility than MgO pasted electrodes. Fig. 3(b) represents the electrochemical impedance spectra (EIS) of the ZnO/MgO pasted electrodes. The impedance spectra of all these electrodes display a depressed semicircle considerable from charge transfer resistance ( $R_{ct}$ ) in the high-frequency region, corresponding to  $R_{ct}$  in parallel connection with the capacitance ( $C$ ) and the line at low frequency regions corresponds to Warburg impedance ( $W$ ) of proton diffusion. A decrease in the charge transfer resistance and an increase in the capacitance indicate that ZnO-paste electrode shows more surface electrochemical activity than that of MgO-paste electrode.

### 3.4. Photocatalytic studies

In the current work, Methylene blue (MB) and Methyl orange (MO) dyes were used as pollutants in our models to assess the photocatalytic activity of ZnO/MgO under UV light irradiation. 60 mg of ZnO/MgO was spread in 250 ml MB (20 ppm). The mixed suspensions were first magnetically stirred in the dark for 30 min

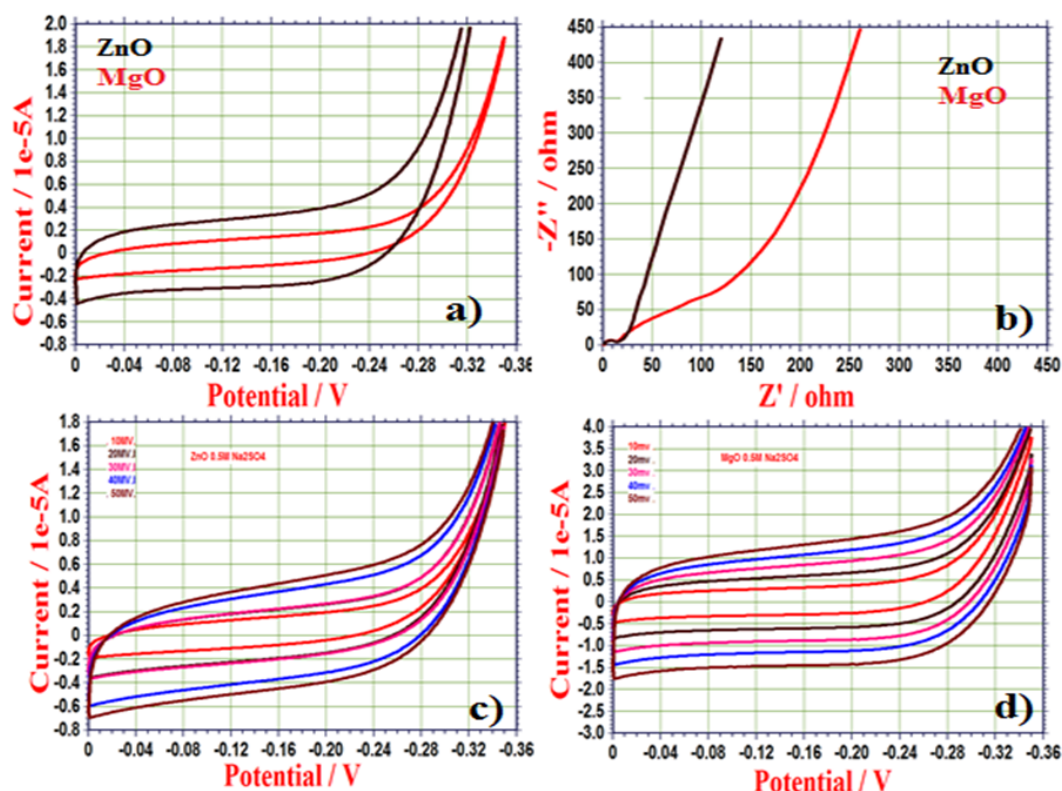


FIG. 3. Cyclic voltammograms and EIS of a) ZnO b) MgO with different scan rate

to reach the adsorption-desorption equilibrium. Under the ambient conditions and stirring, the mixed suspensions were open to visible light irradiation created by a 400 W metal Philips lamp (wavelength: 254 nm). At certain time intervals, 5 ml aliquots of the mixed suspensions was extracted. The filtrates were analyzed by recording UV-vis spectra of MB and MO using a Spectratreats 3.11.01 Release 2A UV-vis spectrophotometer. In UV light, RGO/ZnO can absorb UV light (254 nm) and generate electron-hole pairs. These photo-produced electron and hole pairs can travel into the catalyst surface and react with surface adsorbed  $\text{O}_2$  to form active oxygen species. Photo degradation of MB and MO by ZnO/MgO nanoparticles was studied. In Figs. 4(a) to (b) show the UV-vis absorption spectra of MB and MO as a function of the catalytic reaction time. Both MB and MO solutions turns colorless after 60 min that specifies that complete degradation of the dye molecules by ZnO/MgO. After 60 min of reaction, the ZnO/MgO, Showed a good catalytic degradation of MO. It was observed that by using prepared composite material, the MB solution with concentration of 60 mg/L can be degraded up to 93 % in 60 minutes, whereas the MO was degraded up to 76 % using ZnO particle. Additionally, 98 % and 91 % of MB and MO respectively were degraded using MgO nanoparticles.

#### 4. Conclusion

In the present work, ZnO and MgO were prepared by simple and low cost solution combustion method at low temperatures (400 °C). The average grain sizes of ZnO and MgO nanoparticles were found to be 38 nm and 40 nm, which are confirmed by XRD results. The ZnO pasted electrode showed better electro chemical reversibility than the MgO pasted electrode. A decrease in the charge transfer resistance and an increase in the capacitance indicate that ZnO pasted electrode shows more surface electrochemical activity than that of MgO pasted electrode. The photocatalytic activity of ZnO/MgO nanoparticles showed a good catalytic degradation of MB and MO. This indicates that using as-prepared composite material, the MB and MO solution with concentration 60 mg/L can be degraded up to 98 % and 93 %, MO degraded up to 91 % and 76 % in 60 minutes using ZnO and MgO particles.

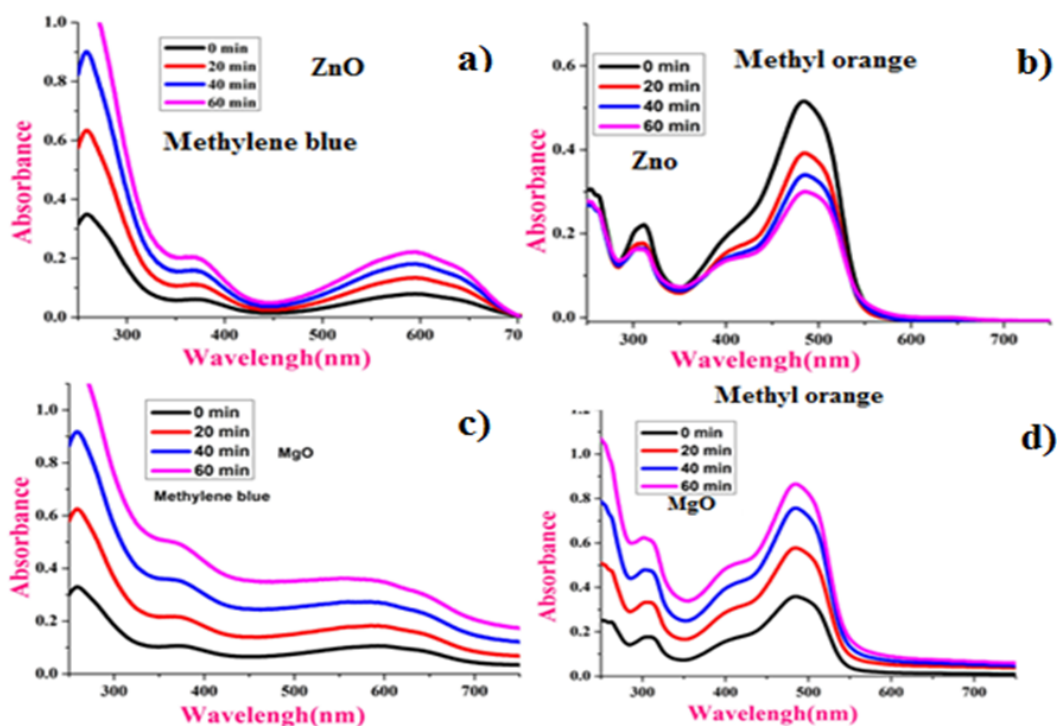


FIG. 4. UV-visible absorption spectra of MB and MO catalysed by ZnO and MgO

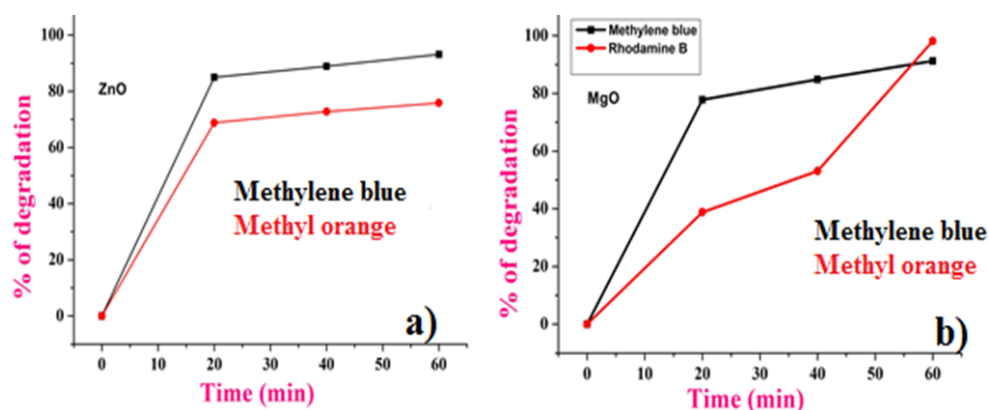


FIG. 5. Effect of Degradation of MB and MO by ZnO and MgO

## References

- [1] Park J.Y., Lee Y.J., et al. Chemical synthesis and characterization of highly oil dispersed MgO nanoparticles. *J. Ind. Eng. Chem.*, 2006, **12**, P. 882–887.
- [2] Naik R., Prashantha S.C., et al. Low temperature synthesis and photoluminescence properties of red emitting  $\text{Mg}_2\text{SiO}_4: \text{Eu}^{3+}$  nanophosphor for near UV light emitting diodes. *Sensors Actuators B*, 2014, **195**, P. 140–149.
- [3] Anilkumar M.R., Nagaswarupa H.P., et al. Bio-inspired route for the synthesis of spherical shaped  $\text{MgO:Fe}^{3+}$  nanoparticles: Structural, photoluminescence and photocatalytic investigation. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2015, **149**, P. 703–713.
- [4] Patil K.C., Hegde M.S., Tanu Rattan, Aruna S.T. *Chemistry of Nanocrystalline Oxide Materials, Combustion Synthesis, Properties and Applications*. World Scientific Publishing Co. Pt. Ltd., UK, 2008.