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# Synergistic Effect of Samarium doped Magnesium Zirconate Photocatalyst for the Degradation of Methylene Blue Dye via Efficient Charge Separation Pathway and its Photoluminescence Studies

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## ABSTRACT

In the present work, a well defined Samarium doped Magnesium Zirconate (MgZrO3:Sm3+) nanospheres were synthesized by facile solution combustion method. The prepared material was characterized by FTIR, PL and SEM. FTIR spectra showed broad peaks within 500 cm-1 indicating the presence of metal oxygen bonds. From the UV-Vis DRS results the band gap of MgZrO3:Sm3+ nanomaterials were evaluated and it is observed that, band gap decreases with the increase in concentration of Sm3+ and it was in the range of 5.89 eV-7.17 eV. From the SEM micrographs of the material with different concentration of Sm3+ it was evident that, in all the samples the particles are agglomerated and showed defined spherical morphology. The Photoluminescence studies of the material showed five bands at 360 nm, 397 nm, 442 nm, 487 nm and 535 nm, upon excitation at 290 nm. A detailed investigation on effect of Sm+3 on the PL intensity were studied and photocatalytic activity for the degradation of methylene blue was evaluated.

**Keywords :** Synergistic Effect, Photocatalysis, Degradation of Methylene Blue, Charge separation, Photoluminescence.

## I. INTRODUCTION

Ceramic supported photocatalysts have shown promising activity for air/water purification[1]. These materials are widely explored in the field of wastewater treatment, especially dyes, due to their low cost, recyclability, low toxicity, high thermal stability and the ability to process multi-electron exchange reactions[2]. Many photocatalysts have variable properties that can be modified by doping, size reduction, and so forth. Photocatalysis depends on the generation of charge carriers and the proficient transfer of a hole or electron. The effectiveness of a photocatalyst is primarily determined by the recombination rates of the photogenerated charge carriers. The recombination rates are generally much faster (nanoseconds) than the interfacial transfer rate (microseconds to milliseconds) where many charge carriers recombine releasing heat energy and reduces the overall quantum efficiency of the photocatalytic process.

Recently S. P. Ratnayake, et al. studied the photocatalytic activity of carbon quantum dots decorated nano zirconia as a highly efficient catalyst for the degradation of methylene blue in water[3]. Higher photocatalytic efficiency due to the coupling

of oxygen ion conduction with the photocatalysis was observed. The improved ionic conduction of oxygen ions at higher temperatures results in better separation of photogenerated charge carriers, thereby improving the overall efficiency of the photocatalytic process. Therefore, introduction of oxygen vacancies or increasing the density of oxygen vacancies at the surface of the photocatalyst can improve the photocatalytic process by effective inhibition of the recombination of electron–hole pairs. The oxygen can be bound to vacancies, which acts as an electron scavenger and can produce superoxide radicals[4], [5].

Zirconium oxide (ZrO2) and magnesium oxide (MgO) were widely used for catalysis [6]–[8] . The catalytic properties and oxide ion conductivity of zirconia originates from its phase and structure. These properties gives rise to oxygen vacancies. Further, ZrO2 has a band gap (3.2-5.0 eV) and works as a suitable photocatalyst [9]. When zirconia is doped elements like Mg, Ca and rare earth elements like dysprosium, europium and samarium, an improvement in photocatalytic activity was ascribed to an enhancement in the mobility of excitons, thus facilitating surface reactions [10]–[12].

## II. CHEMICALS AND INSTRUMENTS

Magnesium nitrate hexahydrate, zirconium oxynitrate, samarium oxide, neodymium oxide and urea were purchased from Merck chemicals and are of analytical reagent grade and used as received without further purification. FTIR spectra were recorded using Bruker spectrometer with specrtral grade KBr. The morphology and structure of the samples were inspected using Zeiss FESEM and Photoluminescent measurements were done using Agilent Cary eclipse Photoluminescent spectrofluoremeter equipped with xenon lamp as the source of radiation.

2.2. Synthesis of samarium doped magnesium zirconate photocatalyst

Samarium doped magnesium were prepared by simple solution combustion method. The precursor Mg(NO3)2.6H2O, ZrO(NO3)2.xH2O, were dissolved in a minimum quantity of water. The samarium oxide (Sm2O3) was digested in concentrated nitric acid then; the digested solution was mixed with the above solution followed by the addition of suitable amount of urea. The final solution obtained was mixed well to homogeneity. Then the solution was subjected to combustion in a preheated muffle furnace at 400$^{o}$C±10$^{o}$C, the reaction facilitated with the evolution of gases leaving behind white powder. Thus obtained powder was ground to fine and further calcinated at the same temperature for 3 h. Following the same procedure a series of 3, 5, 7 and 9 mol% of samarium doped magnesium zirconate (SMZ) were prepared and labeled as SMZ-3, SMZ-5, SMZ-7, SMZ-9 and SMZ-11 respectively..

## III. RESULTS AND DISCUSSION

### 1. Material characterization

FTIR spectra of the SMZ (1-9 mol %) are shown in Figure 1. The IR spectra of the SMZ exhibits a broad band observed at 3420 cm-1 and a small shoulder at 1115 cm-1, corresponding to the O–H stretching and bending vibration of physically absorbed water molecules. Two strong absorption peaks observed at 1520 and 1390 cm-1 are assigned to rocking and wagging vibration transitions of the O–H group. The appearance of a intense band at 500-700 cm-1 is assigned to the Sm–O stretching vibration mode revealing the formation of Sm2O3 nanoparticles, the data obtained was well in match with the literature reported.

SEM images of SMZ and NMZ nanoparticles are as shown in the Figure 5 and 6 respectively. The Figure 2a-2e shows FESEM images of SMZ (1-9 mol%) samples, as observed from the images, it is evident that the particles are of spherical morphology, porous natured and showed considerable

agglomeration, these properties are expected for the material processed via solution combustion reaction.

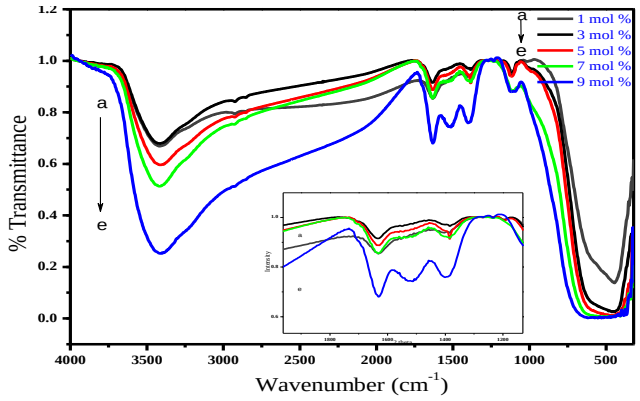


Figure 1: FTIR spectra of Samarium doped magnesium zirconate (1-9 mol %)

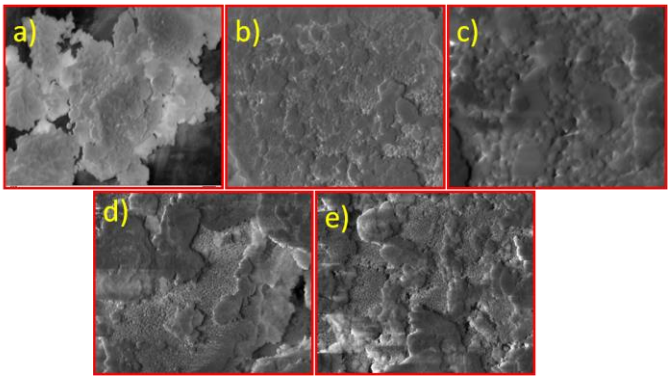


Figure 2: (a) to (e) FESEM images of SMZ samples (1-9 mol %)

## 2. Photoluminescence studies of samarium doped magnesium zirconate

Photoluminescence emission spectra of SMZ (1-9 mol %) samples were recorded at room temperature. As shown in the Figure 3, the material showed five bands at 360 nm, 397 nm, 442 nm, 487 nm and 535 nm, upon excitation at 290 nm. These transitions are attributed to the defect induced in ZrO2 due to oxygen vacancy defect.

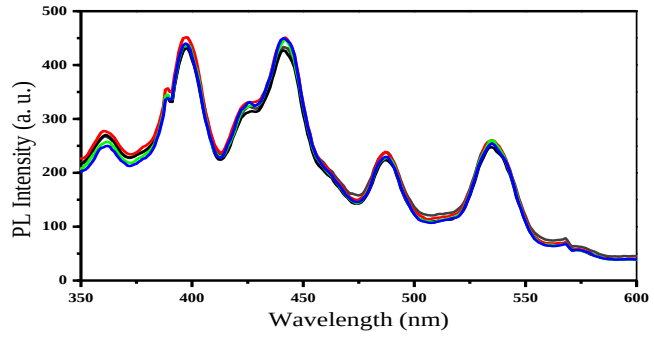


Figure 3: Photoluminescence spectra of SMZ nano particles (1-9 mol %)

## 3. Effect of photocatalyst dosage

The influence of photocatalyst amount towards methylene blue dye degradation efficiency is shown in Figure 4. It is observed that, increasing the amount of photocatalyst the number of active sites i.e., the available surface area for photocatalysis process increases significantly thereby enhancing the kinetics of dye degradation through the voluminous formation of $O_2^{\cdot}$ and $OH^{\cdot}$ reactive species. To study the optimum amount of samarium doped magnesium zirconate for the efficient dye degradation; a diverse range of photocatalyst quantity (10mg-30mg) was employed. The photocatalysts are equilibrated individually with 20 ppm of methylene blue dye solution (100mL) of pH 3.0. The figure denotes that >98% of dye degradation is achieved by using 30 mg within 2 hours of UV light irradiation. However, beyond 30 mg of the photocatalyst, the degradation efficiency decreases considerably, which is attributed to the excess of catalyst in the reaction medium eventually scatters the light entering into the reaction vessel, thus making it unavailable for dye photodegradation. Hence, 30 mg samarium doped magnesium zirconate photocatalyst was chosen as the appropriate amount for the methylene blue dye mineralization.

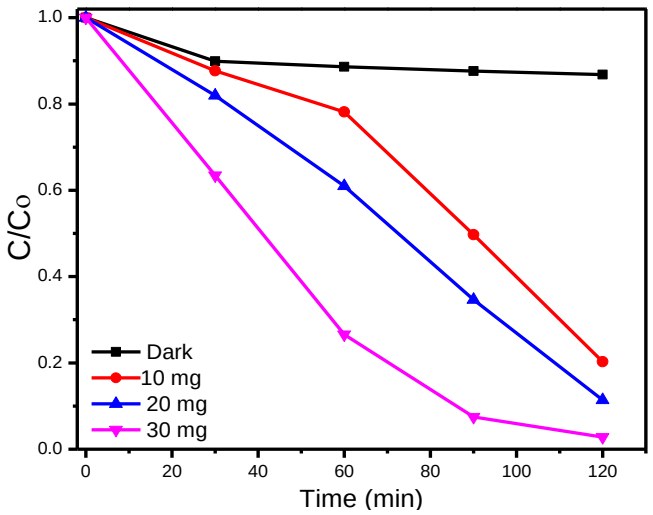


Figure 4: Effect of dosage of the catalyst on the photocatalytic degradation of methylene blue

## 4. Effect of dye concentration:

The influence of methylene blue dye concentration on the degradation kinetics is depicted in Figure 5.

The plot reveals a first-order kinetics for various concentrations of methylene blue dye solutions (100 mL) ranging from 5 to 25 ppm that are individually irradiated under optimum experimental conditions. In the case of 5 ppm of dye concentration, >99% of the dye molecules are degraded. However, for 10, 15, 20 and 25 ppm of dye concentrations, is noticed to achieve >90% dye degradation. This tendency is attributed to the greater availability of dye molecules in the reactive solution in comparison to surface of the photocatalyst at higher concentrations, which eventually hinders the photon absorption by the photocatalyst for dye degradation process. Furthermore, at higher dye concentrations, these dye molecules exerts shielding effect, hence the incident light suffers reduced path length through the solution medium that eventually leads to poor photocatalytic efficiency. Hence, as a matter of convenience, 20 ppm of methylene blue dye solution is used for photocatalytic studies.

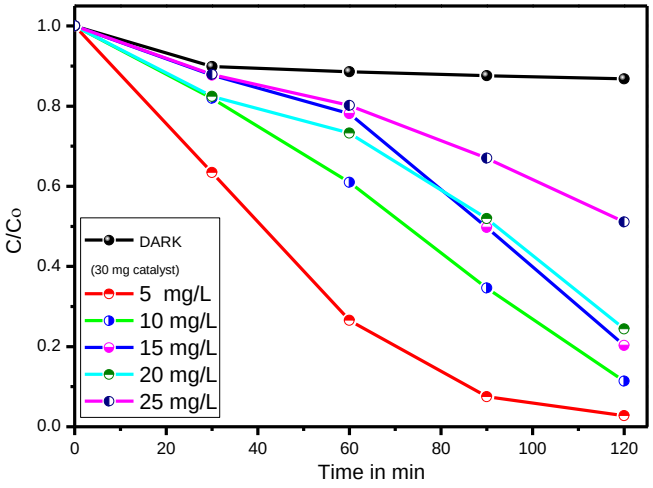


Figure 5: Effect of dye concentration on the photocatalytic degradation of methylene blue

## IV. CONCLUSION

The article reports on the facile solution combustion synthesis of structurally ordered sphere-like samarium doped magnesium zirconate with a stoichiometric intrusion of samarium as the dopant. The synthesized material was capable for inducing photocatalytic activity under UV light spectrum, with ultrafast dissipation response. From the dopant stoichiometric combinations, the use of 30 mg of catalyst was found to serve as the efficient photocatalyst material, which is confirmed by various instrumental and experimental parameters. The surface morphology and textural properties of the monolithic photocatalyst are characterized using SEM images, which reveal a highly ordered and continuous sphere-like structure of Mg-O-Zr network pattern. A detailed analytical investigation was performed to evaluate the photocatalytic properties of the synthesized catalyst. The studies reveal that, the photocatalyst materials exhibit excellent UV light induced photocatalytic activity towards rapid dissipation of organic textile dye (methylene blue).

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