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ENHANCED PHOTO-DEGRADATION ACTIVITY OF HYBRID $ZnMgTiO_2$ NANOCOMPOSITES AGAINST METHYL ORANGE DYE UNDER UV IRRADIATION

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The main focus of this research is to study the role and effect of magnesium, titanium composites on the optical, morphological and structural properties of ZnO nanoparticles. Hybrid nanocomposites of ZnO has been successfully synthesized by soft chemical method using zinc nitrate hexahydrate, magnesium nitrate hexahydrate, titanium isopropoxide and sodium hydroxide. The structural characterizations were done by powder XRD and FT-IR shows the ZnO nanoparticles are polycrystalline with a standard hexagonal ZnO wurtzite crystal structure and the respective decrease in particles size shows that increases the percentage of TiO in the ZnO crystal lattice. The morphology of the composite ZnO nanoparticles has been determined by SEM. The UV-VIS absorption analysis depicted that all the samples exhibit the absorption in the visible region also increases with change in concentration of the dopants. In addition with this the Photo-degradation activity of all the synthesized hybrid nanocomposites were tested against methyl orange dye. The $ZnMgTiO_2$ was emerged as a better Photo-degradation activity when compared to pure ZnO and Mg doped ZnO samples.

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1. Introduction

New technologies often create new challenges to science in addition to their benefits, raise concerns about health and various environmental problems. Recent nanotechnology holds a promise and a broad aspect towards wide applications of nanoparticles in a multiple way of emerging fields of science and technology. Nanosized materials have already been comprehensively studied by the researchers worldwide, because of their unique physical properties like band gap, refractive index, mechanical and magnetic properties and chemical properties compared with their bulk materials [1].

The metal oxide nanoparticles have various functions which are not observed in bulk phase [2, 3]. All these are already been studied broadly due to their exclusive electronic, magnetic, optical, catalytic and antimicrobial properties of metal oxide nanoparticles [4, 5]. The metal nanoparticles have the surface plasmon resonance absorption in the UV–visible region [6]. Over the past few decades, the structure of inorganic nanoparticles exhibit appreciable, drastic, novel and highly improved physical, chemical and biological properties with well recognized function due to their nano scale size. Different types of specific applications can be used for synthesis of metal oxide nanoparticles as major components like light emitting diode, sensors, solar cells, bio sensor, UV light emitter, spintronic devices, pigments and various medical materials [7]. Large efforts have been promoted on wide-band gap semiconductors because of the intense interest in blue and ultra violet light emitters and detectors. Zinc oxide is currently listed as generally regarded as safe (GRAS) by the US Food and Drug Administration. ZnO is an attractive II-VI compound semiconductor has a direct wide band gap (~3.37 eV) at room temperature [8]. It is

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piezoelectric and optically transparent with a large exciton binding energy of 60 MeV. In tetrahedral bonded structure semiconductors, it has been stated that ZnO has the maximum piezoelectric tensor.

Most of the researches have underlined the enhanced activity of ZnO on photo-degradation of some organic compounds [9]. In addition, Nano sized ZnO has major role than compared TiO_2 [10] and latest study has most significant role of ZnO can also be used in the acidic and basic conditions through the waste water management [11]. Therefore, the study of ZnO is necessary and quite essential. Titanium dioxide (TiO_2) has been also attracted significant attention due to their broad-spectrum and effective applications particularly in photocatalysis, catalyst support, antibacterial, environmental remediation, and air purification [12,13]. This is owing to its non-toxicity, low cost and environmentally being nature. The TiO_2 occurs in nature as three distinct crystallographic phases namely anatase, rutile and brookite. Among the three crystalline phases, anatase TiO_2 had promising photocatalytic activity, especially anatase nanoparticles (<14 nm) is more dominant for photocatalysis due to its high surface area. In general, the photocatalytic activity of the TiO_2 depends on several factors such as crystalline phase, crystal size and specific surface area as well as depends on other factors such as production capacity of electron–hole pair, separation efficiency of the photo generated charge pair and the transfer efficiency to compounds adsorbed on the TiO_2 surface [14]. ZnO is n-type semiconductor and has the similar band gap as TiO_2 (ZnO - 3.37 eV and TiO_2 - 3.2 eV). The added advantage of ZnO, MgO over TiO_2 is that, it absorbs over a larger fraction of the UV spectrum having threshold wavelength of 387 nm. Therefore, it is interesting to prepared $ZnMgTiO_2$ nanocomposite. The present work aimed to prepare$ZnMgTiO_2$ nanocomposites by soft chemical method. The structural, morphological and optical property of the prepared nanocomposites was investigated and the results are discussed on the light to use these composites for photo-degradation activity.

2. Materials and methods

2.1 Materials used

Reagent-grade Zinc nitrate hexahydrate ($ZnN_2O_6.6H_2O$), Magnesium nitrate hexahydrate (Mg $(NO_3)_2.6H_2O$), Titanium (IV) isopropoxide, sodium hydroxide (NaOH) and deionized water (90.0% pure) were used as precursors without any pretreatment.

2.2 Synthesis procedure

The soft chemical method was used for the synthesis of composite ZnO. Zinc nitrate, Magnesium nitrate, Titanium isopropoxide and sodium hydroxide were used as the precursors without further purification. For the preparation of $ZnMgTiO_2$nano composite, Zinc nitrate (0.08M),Magnesium nitrate (0.01M) and Titanium isopropoxide (0.01M)were dissolved in 50ml double distilled water and kept in magnetic stirrer for 5hrs under vigorous stirring. A separate buffer solution was prepared by dissolving 0.2M of sodium hydroxide in 50 ml double distilled water. Buffer solution was then added drop wise to the initial solution under constant string at room temperature to produce a white precipitate. The white precipitates were filtered and washed with double distilled water and ethanol many times. The final precipitates were dried in oven at 80^0C for 4hrs. The dried precipitates were collected and ground in an agate mortar. Finally, the collected powder was annealed at 500^0C under argon atmosphere for 5 hrs followed by furnace. The final products were collected for further characterization studies. The same procedure was repeated with different concentration [x= .015, 0.01and 0.005; y=0.015, 0.01 and 0.005].

2.3 Characterization techniques

The synthesized $ZnMgTiO_2$ nanocomposites were primarily characterized by XRay diffractometer (X'Pert-PRO, Alagappa University, Karaikudi). The high resolution on XRD patterns were measured at 3 KW with Cu target using a scintillation counter (λ=1.5406Å) at 40 kV and 40 mA were recorded in the range of $2\theta=5^{\circ}$ to 80°. The changes in the surface chemical bonding and surface composition were characterized by using Fourier Transform Infrared (FT-IR) Spectroscopy (Nicolet Avatar series 330, Annamalai University). UV-Visible spectroscopy, which

has proved to be a very useful technique for the analysis of nanoparticles. UV-Visible spectra were obtained using aShimadzu UV-1650pc Spectrophotometer (CSIL, Annamalai University). Scanning Electron Microscopy (SEM) was used to identify the shape by FEI Quanta 200.

2.4 Photo-degradation analysis

For photo-degradation analysis, 50 mg/L of Methyl orange dye (MO) was dissolved in 50 ml of double distilled water. Then, each 30 mg $ZnMgTiO_2$ NPs samples were dispersed in dye solution and stirred. The catalytic solutions were placed under UV irradiation for degradation of dye with different irradiation time (0, 30, 60, 90 and 120 minutes). The decomposition effect was measured by UV-absorption measurement. The effect of ultra violet light sources on Photo-degradation of Methyl orange dye was carried out with a 30 W (UV-C, 254 nm) mercury lamp (Philips). The distance between dye solution and violet light sources was 25 cm.

3. Results and discussion

3.1 Structural analysis (XRD)

The XRD spectra of the ZnO nanocomposites with various concentrations are shown in Fig. 1. All samples exhibit sharp diffraction peaks conforming (100), (002), (101), (111),(102), (110) and (200) planes of wurtzite hexagonal ZnO structure inconformity with the database of the JCPDS Card No: 36-1451. XRD peaks (101) and (220) exhibited the anatase phase $TiO_2$and Mg in conformity with the database of the JCPDS Card No: 21-1272 and 4-0829 respectively. It is confirms that only one crystalline phase was formed during the synthesis process. No traces of secondary phases such as rutile or brookite were observed. This fact indicates that the nanocomposites are not a single phase but a composite. The sharp intense peaks of ZnO confirm the good crystalline nature of ZnO and MgO peaks can be well indexed to the cubic lattice. The calculated average grain size for sample A=42.71nm, B= 36.97 and C=37.87 respectively. The crystalline size of various concentration of $ZnMgTiO_2$ nanocomposite was calculated using Scherrer's formula [15],

$$D = \frac{0.9\,\lambda}{\beta \operatorname{Cos}\,\theta} \tag{1}$$

where the λ is wavelength of X-Rays, θ is Bragg's angle, β is the full width at half maximum.

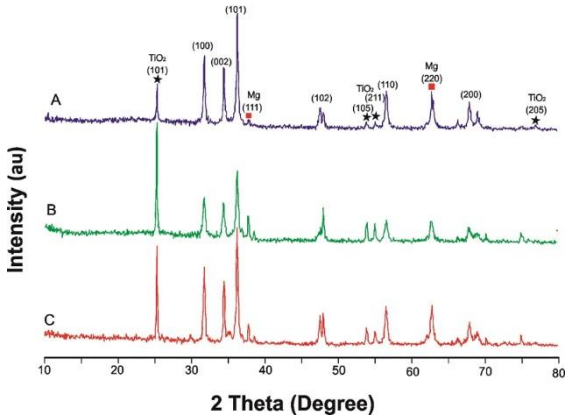

Fig. 1. XRD spectra of $ZnMgTiO_2$ nanocomposites (A) $Zn_{0.08}Mg_{0.01}TiO_{0.01}$, (B) $Zn_{0.08}Mg_{0.005}TiO_{0.015}$, (C) $Zn_{0.08}Mg_{0.015}TiO_{0.005}$.

3.2 Spectral studies (FT-IR)

Fig. 2 shows the FTIR spectra of synthesized nano composite ZnO nanoparticles. The spectral bands observed at 481 cm^{-1} and 510 cm^{-1} for ZnO are correlated to metal oxide bond and distinctly show the presence of ZnO as reported. It is well known that the peaks range of 410 – 735 cm^{-1} corresponds to ZnO stretching mode as reported by [19]. Bonds at 1411, 1491, 1422 cm^{-1} for

A, B and C are attributed to the bending frequency of oxygen stretching mode. The presence of peak around 2955 cm^{-1} is due to C-H stretch frequency and the peak 3456 cm^{-1} is due to O-H stretching vibrations. The Zn-O-Zn network is disturbed by the existence of TiO in its environment. This disruption explains the shift in the peak position of the ZnO absorption bands observed by the XRD analysis.

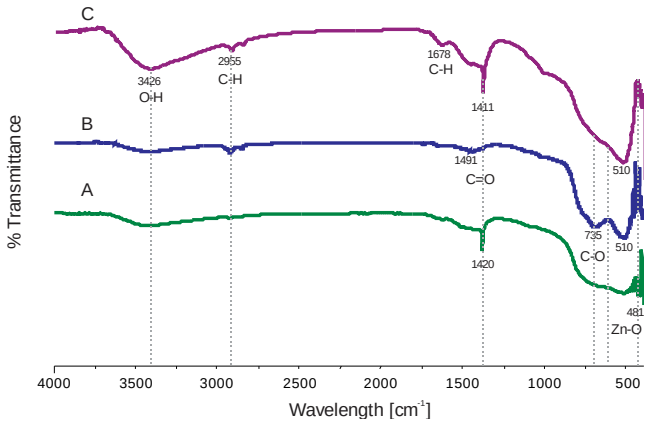

Fig. 2. FTIR spectra of nanocomposites (A) $Zn_{0.08}Mg_{0.01}TiO_{0.01}$, (B) $Zn_{0.08}Mg_{0.005}TiO_{0.015}$, (C) $Zn_{0.08}Mg_{0.015}TiO_{0.005}$

3.3 Optical studies (UV-Vis.)

Fig. 3 shows UV-Vis absorption spectra of $ZnMgTiO_2$ nanocomposites with three different concentration ratios. The spectra were recorded at room temperature in the range of 200-800nm. This nanocomposite absorbs more visible light and therefore can be used as an efficient photocatalyst. The increase in the absorption intensity in the blue region can be attributed to more pronounce doping of ZnO with MgO and TiO_2 ion. The absorption edge is found to shift in a systematic manner to longer wavelength with increasing content of doping in composite. The fundamental absorption edge of$ZnMgTiO_2$ appeared in the visible region at about 250-500 nm in the electromagnetic spectrum. The absorption in the visible region also increases with change in concentration of the dopants.

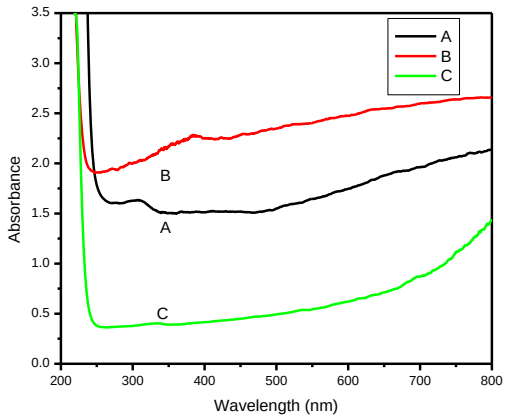

Fig. 3. UV-Visible spectra of $ZnMgTiO_2$ nanocomposites (A)$Zn_{0.08}Mg_{0.01}TiO_{0.01}$, (B) $Zn_{0.08}Mg_{0.005}TiO_{0.015}$, (C) $Zn_{0.08}Mg_{0.015}TiO_{0.005}$.

3.4 Microscopic studies (SEM)

The surface morphologies of the synthesized nanocomposites were characterized by SEM, as depicted in figure. The SEM image obviously showed different morphologies of different concentrations of $ZnMgTiO_2$ NPs. The SEM results showed the presence of agglomerated NPs.

Fig. 4(a) shows the sphere like $ZnMgTiO_2$ nanocomposites and fibrous agglomeration was found in Fig. 4(b). The $ZnMgTiO_2$ nanoflower (or) nanoflake was observed in Fig. 4(c). Nanoflakes agglomerated have been observed a closer view reveals that most of the nanoflakes have uniform thickness and length. There is a significant change in morphology and the thickness of the nanoflakes, accompanied with change in length. It is noticed that the crystallite sizes of the NPs decreases from 42.71 and 37.87 to 36.97 with the increases in dopant level of TiO. It can be deduced that TiO doping slightly influenced the surface morphology and the particle size depending on the dopant level.

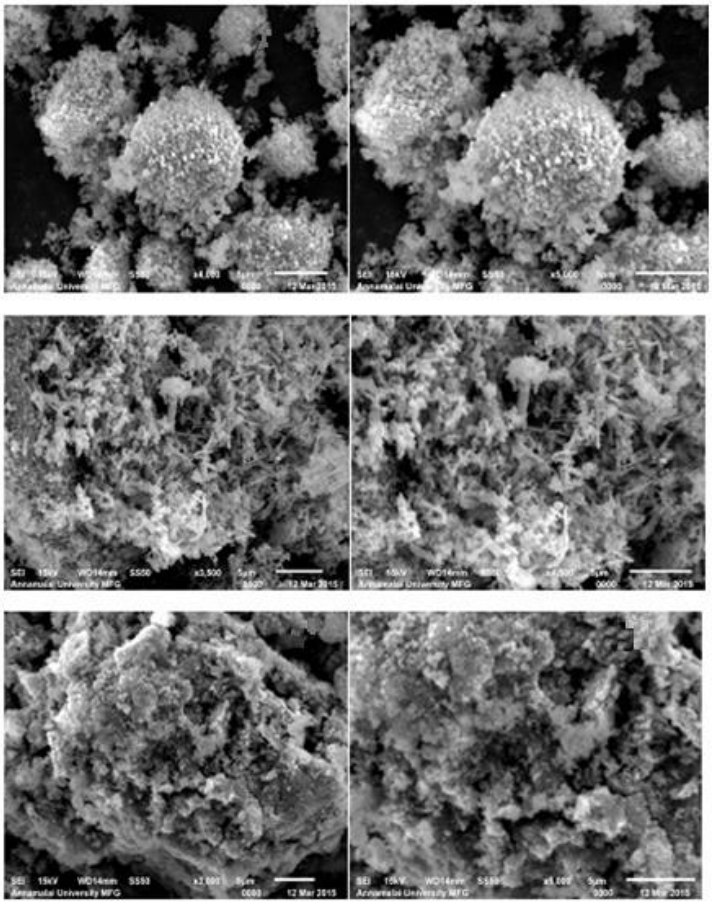

Fig. 4. SEM morphological images of $Zn_{0.08}Mg_{0.01}TiO_{0.01}$, $Zn_{0.08}Mg_{0.005}TiO_{0.015}$, & $Zn_{0.08}Mg_{0.015}TiO_{0.005}$ nanocomposite.

3.5 Photo-degradation analysis

The photo-degradation efficiency of the $ZnMgTiO_2$ nanocomposites was estimated by the photo-degradation of MO aqueous solution under UV irradiation and the results are given in Fig 5.1 A, B, and C.

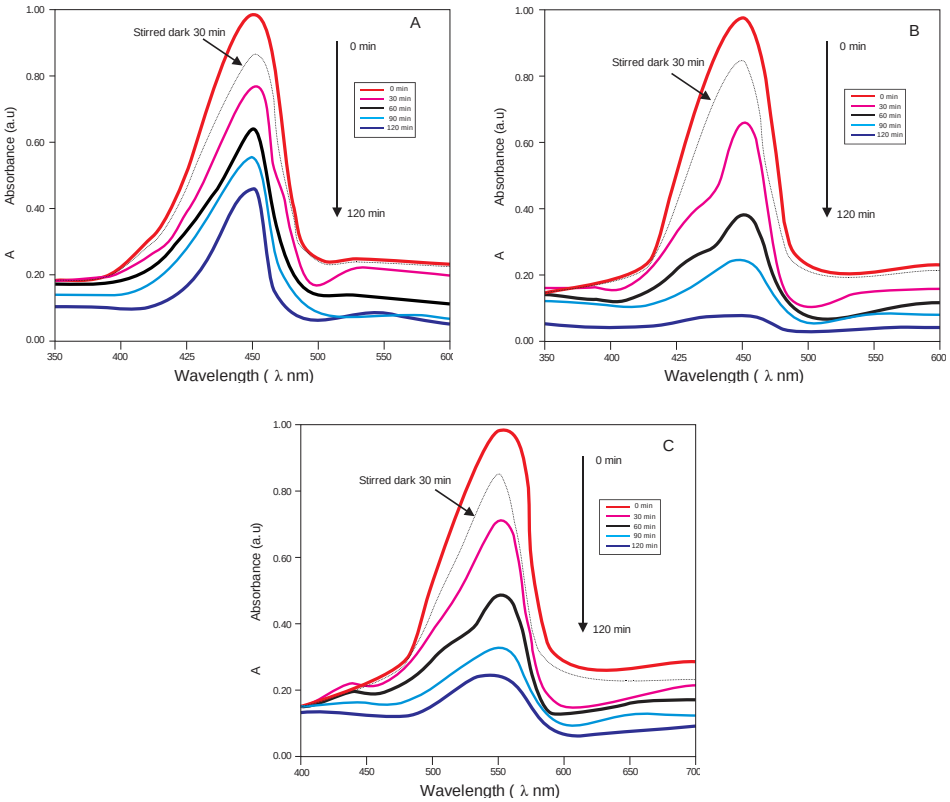

Fig. 5.1. UV-Vis absorption spectra of $ZnMgTiO_2$ nanocomposites (A) $Zn_{0.08}$ $Mg_{0.01}TiO_{0.01}$, (B) $Zn_{0.08}$ $Mg_{0.005}TiO_{0.015}$, (C) $Zn_{0.08}$ $Mg_{0.015}TiO_{0.005}$.

Before to the UV- irradiation, MO aqueous solution in the dark place for 30 min led to the adsorption of MO molecules on the $ZnMgTiO_2$ nanocomposite as shown dotted line in Fig. 5.1. The absorption peaks of MO around 452 nm gradually decreased under UV-irradiation in the presence of the $ZnMgTiO_2$ nanocomposites. Meanwhile, due the decolorization of the MO aqueous solution gradually decreased, it shows that the decomposed the chromophoric group structure of MO. Therefore, the figure shows that the UV photo-degradation activity of the $ZnMgTiO_2$ nanocomposites was high in the sample - B. To compare the estimation of the photo-degradation efficiency of other samples (A and C) were well performed to maintain the same experimental setup as mentioned above. For comparison, photo-degradation efficiency of MO was about 57.21, 92.30 and 77.66% for sample A, B and C after 120 min, respectively. It was impressive that around 92.30% of MO was photo-degradation by the sample B after UV-irradiation for 120 min. Meanwhile, it was noted that the $ZnMgTiO_2$ nanocomposites exhibited extraordinarily photo-degradation efficiency to their counterparts of TiO_2 and ZnO particles. Especially, the irradiation time for an entire process of decolorization of MO over the $ZnMgTiO_2$ nanocomposites was about 120 min, which was to a great extent shorter than the degradation time of other $ZnMgTiO_2$ nanocomposites as shown in Table 5.1.

Table 5.1. The Photo-degradation efficiency of $ZnMgTiO_2$ nanocomposites.

Nanocomposites	**Decolorization under UV irradiation time (after 120 min)**
$Zn_{0.08}$ $Mg_{0.01}TiO_{0.01}$ (A)	57.21%
$Zn_{0.08}$ $Mg_{0.005}TiO_{0.015}$ (B)	92.30%
$Zn_{0.08}$ $Mg_{0.015}TiO_{0.005}$ (C)	77.66%

The photo-degradation reaction can be explained as follows:

$$h\upsilon + (TiO_2 – ZnO) \rightarrow e^- (TiO_2) + h^+ (ZnO) \quad (1)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \text{ (superoxide radical anions)} \quad (2)$$

$$h^+ + OH \rightarrow OH^{\bullet} \quad (3)$$

$$O_2^{\bullet -} + H_2O \rightarrow HO_2^{\bullet} + OH \quad (4)$$

$$HO_2^{\bullet} + H_2O \rightarrow H_2O_2 + OH^{\bullet} \quad (5)$$

$$H_2O_2 \rightarrow 2OH^{\bullet} \quad (6)$$

$$OH^{\bullet} + MO \rightarrow CO_2 + H_2O \quad (7)$$

The chemical reaction of the photo-degradation efficiency over the $ZnMgTiO_2$ nanocomposites can be explained in Fig. 5.1. The energy band gap of ZnO and TiO_2 nearly same (3.37 vs. 3.2 eV). When UV irradiation (photon) is applied to ZnO is to exceed its band gap energy, electrons are excited to the VB to the CB, and then electrons transfer to the CB of TiO_2 on account of the potential difference between them. Due to thermal equilibrium, the holes transfer from the VB of TiO_2 to the VB of ZnO under UV excitation [16].

The photo-degradation process can be explained as due to UV irradiation, the photo-generated electrons penetrate through ZnO region to TiO_2 region and photo-generated holes penetrate through TiO_2 region to ZnO region. As result, conduction band electron and valence band holes to make the recombination of electron–hole pair takes place, it is markedly reduced. As a result the electron reacts with dissolved oxygen molecule to generate superoxide radical anions ($O_2^{\bullet -}$). The holes are reacts with hydroxyl groups on the surface of the photocatalyst to generate $OH^{\bullet}$ radicals. The hydroxyl radicals ($OH^{\bullet}$) and hydroperoxy ($HO_2^{\bullet}$) radicals are generated by the $O_2^{\bullet -}$. Meanwhile, protonation of $O_2^{\bullet -}$ are generated highly reactive H_2O_2 molecules. After that, $OH^{\bullet}$ radicals are also quickly generated by the decomposition of H_2O_2 molecules. In finally, all these OH radicals act as a powerful oxidizing agent to oxidize the dye (MO) in the form H_2O and CO_2. It is clearly shows that the mutual effects led to the enhanced photo-degradation activity. Figure 5.2 shows that the structure of the ZnO-TiO_2 junction and the propose charge transfer and the separation process of $ZnMgTiO_2$ nanocomposites under UV irradiation.

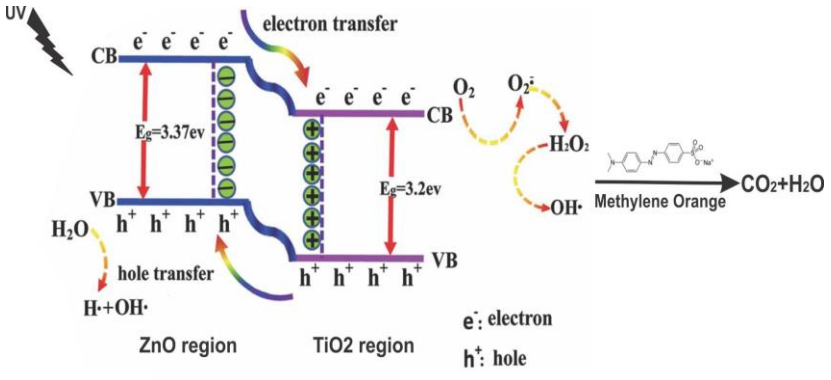

Fig. 5.2. Structure of the ZnO-TiO_2 junction.

The photo-degradation effect was estimated the following formula [17],

$$D\ (\%) = (A_0 – A_t) / (A_0) \times 100 \quad (8)$$

where, D is the degradation efficiency (in %). A_0 is the UV absorption of dye with sun light irradiation time (0 min) and A_t is the UV absorption of dye after UV-light irradiation (t-min).

The UV-Vis absorption spectra of MO dye solution in the presence of $ZnMgTiO_2$ nanocomposites with UV irradiation for different irradiation time intervals were shown in Fig. 5.3. The photo-degradation spectrum was drawn between UV irradiation time and absorption intensity. The photo-degradation efficiency of sample (B) was estimated as 93.30%. This route could be apt to treat the industrial and sewage water treatment.

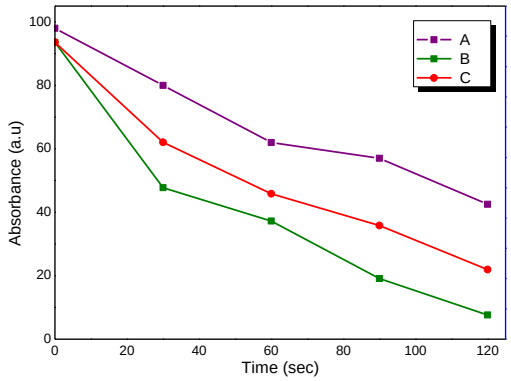

Fig. 5.3. Photocatalytic degradation of MO over the $ZnMgTiO_2$ nanocomposites (A) $Zn_{0.08}Mg_{0.01}TiO_{0.01}$, (B) $Zn_{0.08}Mg_{0.005}TiO_{0.015}$, (C) $Zn_{0.08}Mg_{0.015}TiO_{0.005}$

4. Conclusions

The $ZnMgTiO_2$ nanocomposites were prepared in three different concentrations by soft chemical method. The powder XRD results revealed that the ZnO were in good agreement with standard JCPDS card. The XRD results clearly showed in incorporation of Mg and TiO_2 ions into ZnO lattice. The calculated crystallite size depicted that all the synthesized samples are in nano dimensional range. FTIR spectra predicted the presence of essential functional groups present in the proposed nano composites with metal oxygen bond in all the samples. Optical studies of the synthesized nanocomposites were observed by UV-Vis spectroscopy. The SEM micrographs demonstrated the produced surface morphology of the prepared $ZnMgTiO_2$ nanocomposites.

Photo-degradation activity of hybrid $ZnMgTiO_2$ nanocomposites were demonstrated against methyl orange dye. The dye degradation rate D (%) was estimated as 93.30% for $ZnMgTiO_2$ nanoparticles. An enhanced degradation effect was observed from the $ZnMgTiO_2$ nanoparticles against Methyl orange dye under UV-irradiation. The result was observed photo-degradation effect of the prepared sample $Zn_{0.08}$ $Mg_{0.005}TiO_{0.015}$ (B) nanocomposites was against MO. under UV irradiation (120 min) enhanced effectiveness than the other samples for industrial waste water treatment for removal of hazards chemicals like in environmental remediation.

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