$ZnFe_2O_4$ Doped TiO_2 Photocatalyst Synthesis and Characterization with Effect of Different Coupling Ratios on Band Gap

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Summary: In this work the effect of different coupling ratios of $ZnFe_2O_4$ and TiO_2 on the band gap was investigated, to convert TiO_2 as a visible light driven photocatalyst $ZnFe_2O_4$. In this work, $ZnFe_2O_4$ was synthesized utilizing sol-gel technique and calcining under normal atmosphere at 900 °C. Thereafter, $ZnFe_2O_4$ was coupled with TiO_2 by mixing in 50 ml water in three different coupling w/w ratios (1:1, 1:2 and 2:1) followed by the calcination of coupled catalyst under nitrogen environment at 500 °C. XRD, XPS, FESEM-EDS imaging, TGA, UV-Vis, and FTIR were performed to characterize the catalyst. Crystal phase identification could be confirmed through XRD analysis with homogenous distribution of metal constituents through color mapping and surface charge transitions from XPS analysis for a better electron hole generation. Thermogravimetric analysis (TGA) confirmed that the pure $ZnFe_2O_4$ obtained at 900 °C, while FTIR verified the presence of desired functional group in $ZnFe_2O_4$. Moreover, Fourier Transformation Infrared Spectroscopy (FTIR) illustrated two major peaks and no extra major impurity was detected. $ZnFe_2O_4$ is visible light driven photocatalyst and TiO_2 can work only under UV light. So, the effect of different coupling ratios of $ZnFe_2O_4$ with TiO_2 was examined by UV-Vis characterization. The band gap is given by 1:1 was 2.8, 2:1 was 3.17 and 1:2 was 3.02. It was observed that the most optimum coupling ratio is 1:1 and the band-gap fall under visible region. The findings of this work could be supportive significantly for the selection of suitable coupling ratio to convert UV-driven photocatalyst into visible region active photocatalyst.

Keywords: TiO_2; $ZnFe_2O_4$; TGA; UV-VIS; FTIR and ratio.

Introduction

IN the current times global warming has become an important issue to scientists. The emission from automobiles and industries is the biggest source of global warming. The ultimate and promising aspect to reduce these greenhouse gases (GHGs) is to convert them in to high value chemical and fuels using a sustainable pathway *i.e*. the visible light transformation of gaseous product CO_2 into liquid fuel (methanol) [1, 2].

Visible lights make up approximately 47% of the solar radiations from Sun and only 4 to 5 % of it is comprised of UV light. Due to the constraints that the solar energy is not able to transform CO_2 into valuable fuels due to the energy barrier or endothermic nature of the reaction, an external energy source is required which can be fulfilled by using a photocatalyst in order to overcome this energy barrier [3]. A vast majority of photocatalyst materials offer high band gap values and are active under the UV region of the solar radiation. The obvious distinction which determines either the photocatalyst is visible or UV light-driven depending upon its band gap. A photocatalyst will work visible light driven if its band gap less than 2 eV.

Metal ferrites have emerged as an excellent alternative to this problem as photocatalyst materials owing to the low values of band gap and capacity to utilize the solar radiation visible region [4-6]. The problem with using photocatalyst with low band gap value is the potential of high electron hole recombination rate. Doping of various materials have been conducted in order to decelerate the electron hole recombination process while allowing the photocatalyst material to complete the reaction cycle to synthesize liquid products [7-10].The following characteristic should be portrayed by a photocatalyst through semiconductor-semiconductor coupling technique, the conduction band position of small band gap semiconductor should be more negative [11, 12]. As suggested by literature review, $ZnFe_2O_4$ is a promising candidate as a visible light driven photocatalyst material having a small band gap value [4]. TiO_2 doped $ZnFe_2O_4$ material has the capability to sensitize the TiO_2 counterpart thus inducing visible

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light activity and charge transfer characteristic making this heterojunction material a very active visible light photocatalyst. Formation of heterojunction helps to slow down the charge recombination.

Experimental

Materials

All the chemicals which were bought, consumed deprived of any cleansing. Nitric acid (HNO_3), iron nitrate ($Fe(NO_3)_3.9H_2O$) (99.5%), Zinc nitrate ($Zn(NO_3)_2.6H_2O$) (99.5%), commercialized TiO_2 and Agar had been utilized to synthesize the photocatalyst material $ZnFe_2O_4/TiO_2$. The water had a resistivity of $>10^{18}$ MΩ cm^{-1}. All the chemicals were reagent grade.

Synthesis

The synthesis of the photocatalyst material $ZnFe_2O_4$ was made possible by employing the sol-gel technique as has been outlined earlier [13, 14]. Calcination of $ZnFe_2O_4$ was performed at 900 °C. The calcined material was then doped with the TiO_2 counterpart applying the sol-gel technique. The commercialized TiO_2 with $ZnFe_2O_4$ were mixed in distilled water (50 ml) having the mentioned w/w (1:1, 1:2, 2:1) ratio. The resulting mixture was then kept for ultrasonication for 1 h and afterwards was placed in an oven for 12 h at a temperature of 100 °C for drying. Lastly, the dried doped photocatalyst material was calcined under the presence of nitrogen gas in a tubular furnace at 500 °C [15].

Characterization

The synthesized photocatalyst material $ZnFe_2O_4$ was characterized with the help of Ultraviolet Visible light (UV-Vis) spectroscopy, for visible light activity, Fourier Transform Infrared (FTIR) analysis with Nicolet 6700, Thermo Scientific, USA in order to identify the existence of anticipated functional group and Thermogravimetric analysis (TGA) ASTA 6000, PerkinElmer, USA for the requisite calcination conditions in order to remove all the undesirable impurities. TGA of the sample was carried out heating at a rate of 10°C/ min for appropriate calcination temperature identification. X-ray photoelectron spectroscopy (XPS) analysis employing Thermo Fisher Scientific K-Alpha system with a mono-chromatic Al Kα1source (1593 eV) of the synthesized samples was performed for the surface elemental presence of all the metals in the composite photocatalyst material. X-ray Diffraction (XRD) patterns in the 2 theta domain from 10° till 80° with Bruker diffractometer with Cu Kα radiation (λ=0.154 nm) with an accelerating potential of 40 kV for the confirmation of the composite photocatalyst were also performed. The surface morphology was studied with FESEM-EDX colour mapping was performed with a Zeiss Supra 55 VP for surface morphology determination. In the end, the TiO_2 and $ZnFe_2O_4$ doped material having w/w ratio (1:1, 1:2, 2:1) respectively was subjected to absorbance study by employing UV-Vis spectroscopy by DR-UVS K Series spectrophotometer within a range of 200 nm to 800 nm to determine the consequence of doping ratios on band gap and absorbance.

Results and Discussion

FTIR

The FTIR analysis is provided in **Error! Reference source not found.** The spectrum reveals a similar behavior as compared to earlier reported [16]. The evident sharp decrease at 538 and 421 cm^{-1} respectively signifies the Zn^{2+} and Fe^{3+} states in the sample [16, 17]. Correspondingly, the sharp depression at 1456 cm^{-1} and 1649 cm^{-1} can be attributed to the presence of bending vibrations of water [18] portraying less concentration of OH ions of water. The comprehensive 1123 cm^{-1} band might be ascertained to the vibrational stretchings of Zn–O [17].

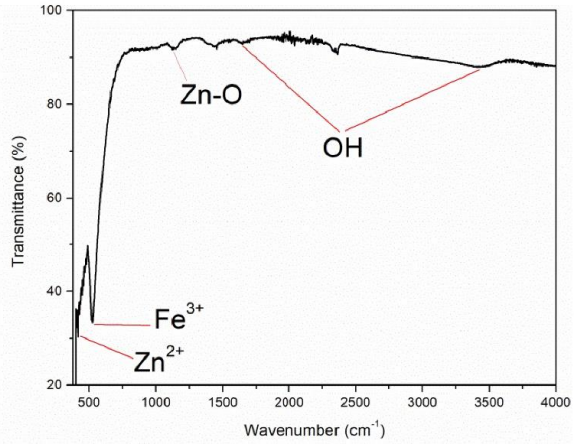

Fig. 1: FTIR Spectra of $ZnFe_2O_4$

XRD

The XRD analysis is provided in Fig.. And it can be seen that the composite photocatalyst material confirmed the synthesis of the photocatalyst material $ZnFe_2O_4/TiO_2$. The

synthesized structure shows complete crystal formation and no amorphous phase presence and the findings are consistent with literature [6] as well.

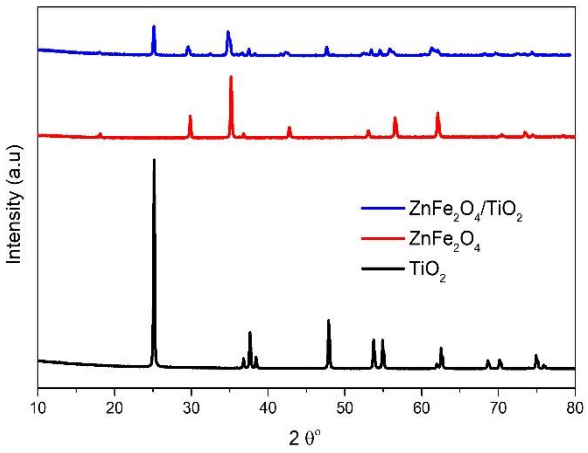

Fig. 2: XRD analysis of $ZnFe_2O_4$, TiO_2 and $ZnFe_2O_4/TiO_2$.

XPS

The XPS analysis is provided in Fig.. Which provides the surface metal presence over the synthesized materials. It is very obvious that no Ti can be observed in the $ZnFe_2O_4$ sample and no Zn and Fe could be found over the surface of TiO_2 material. The coupling of $ZnFe_2O_4$ with TiO_2 resulted in composite material with all the elements detected by in the survey of the $ZnFe_2O_4/TiO_2$ photocatalyst material as depicted in the Fig 3 as well. The XPS confirms the formation of the target material along with the XRD analysis.

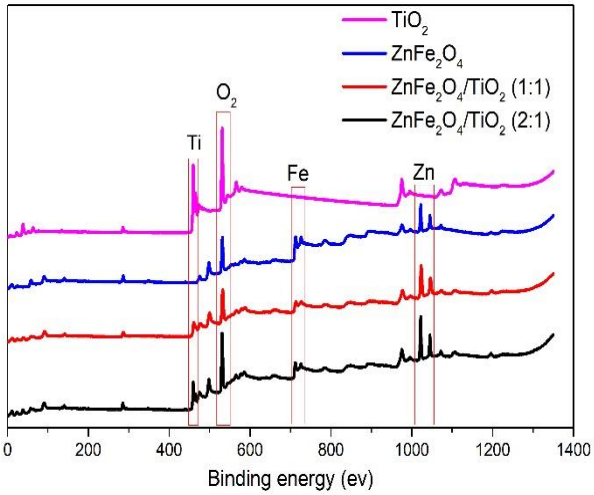

Fig. 3: XPS analysis of $ZnFe_2O_4$, TiO_2 and $ZnFe_2O_4/TiO_2$.

FESEM and Colour Mapping

The FESEM image analysis for the surface morphology is given in Fig. (a – c) respectively for $ZnFe_2O_4$, TiO_2 and $ZnFe_2O_4/TiO_2$ samples.

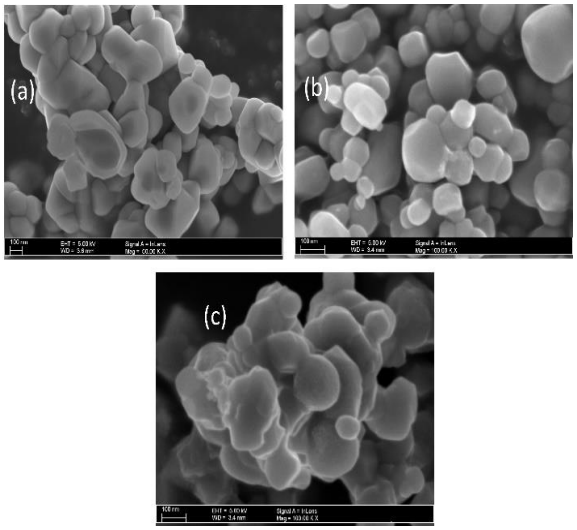

Fig. 4: FESEM images of (a)ZnFe2O4, (b)TiO2 and (c) $ZnFe_2O_4/TiO_2$.

The colour mapping is also presented in Fig. 5 for $ZnFe_2O_4$, and in Fig. 6 for TiO_2 and Fig. 7 for $ZnFe_2O_4/TiO_2$ samples. The colour mapping also verifies the formation of the target molecules.

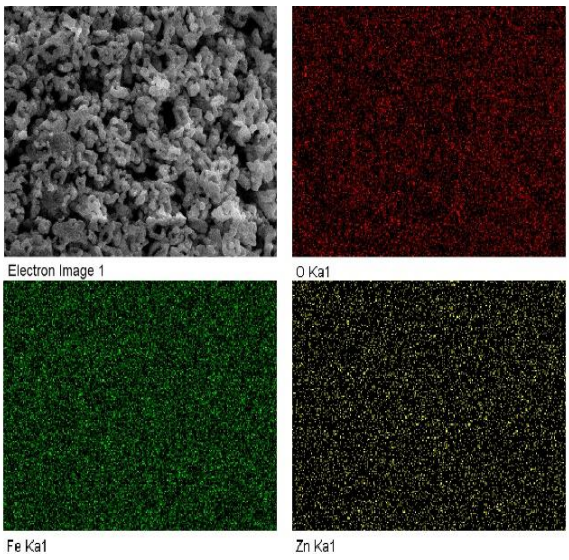

Fig. 5: Color Map images of $ZnFe_2O_4$.

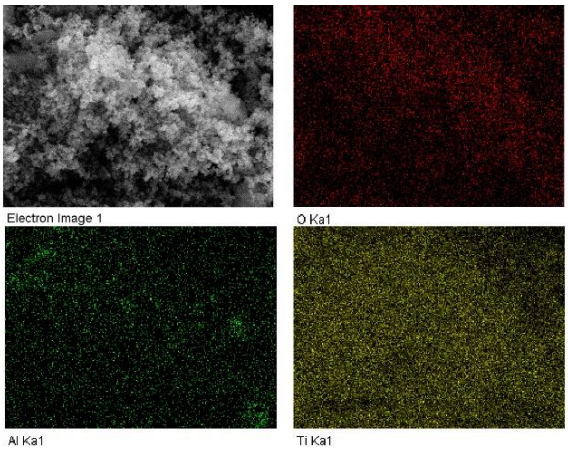

Fig. 6: Colour Map images of TiO_2.

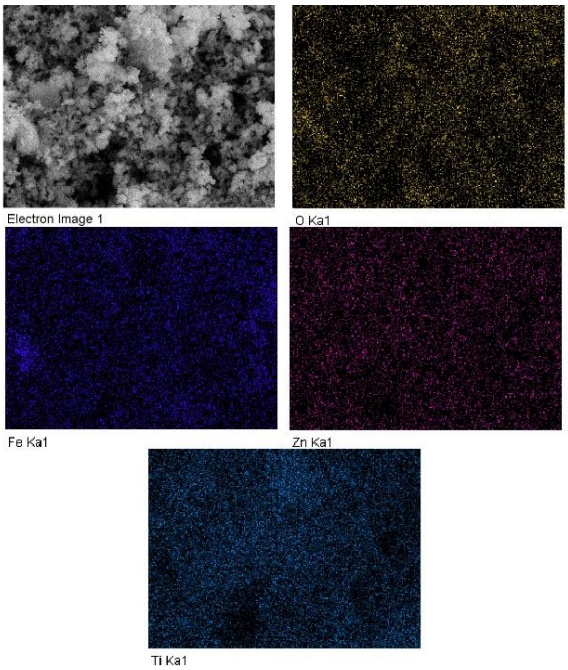

Fig. 7: Colour Map images of $ZnFe_2O_4/TiO_2$.

TGA

The TGA analysis is given in

Fig. which portrays the derivative profiles of $ZnFe_2O_4$ mass loss relating to temperature. TGA was conducted prior to calcination in order to conclude the catalyst stability with respect to increasing temperatures. The TGA of the un-calcined catalyst material sample was in agreement with our earlier work having slight disparity. In earlier work reported the 50-200 °C weight loss amounted to 10% conversely, in the current work, a 20% weight loss had been detected between the same temperature intervals. Likewise, our earlier work represented a 20% weight loss within 200-600 °C owing to the elimination of ZnO but in this study 25% weight loss was detected that can be attributed to the presence of interlayer water molecules [13]. The presence of large amount of water molecules resulted in additional time required for complete drying of the moisture content. The observed weight loss between 600 – 900 °C, was not significant. Results of this study are in agreement with the earlier reported study [4]. From the TGA analysis of samples the calcination temperature in this study was fixed at 900 ^oC.

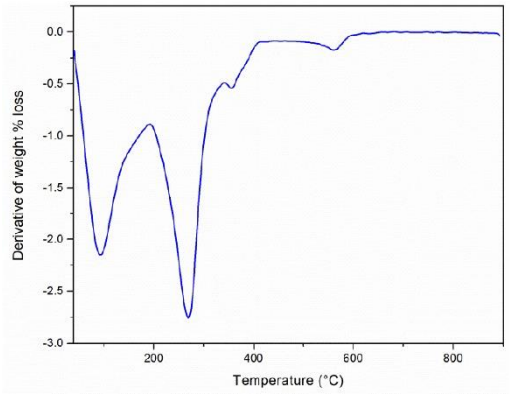

Fig. 8: DTGA curve of $ZnFe_2O_4$.

UV-Visible Study

The UV-Visible analysis of the synthesized photocatalyst materials TiO_2 (700 °C calcination temperature) doped with $ZnFe_2O_4$ (900°C calcination temperature) having a (1:1, 1:2, 2:1) w/w ratio was analyzed from 200-800 nm is presented in

Fig.. The coupling of TiO_2 with $ZnFe_2O_4$ demonstrates a definite absorbance in the visible region *i.e*. 400-800 nm. All the synthesized samples depicted visible region absorbance nonetheless the 1:1 w/w ratio sample showed considerably greater absorbance in comparison with other ratios. 1:1 coupling ratio portrayed a promising alteration of TiO_2 band gap from UV region to the visible portion.

$ZnFe_2O_4$ does not simply alter the TiO_2 band gap becoming visible light active but also decreased the band gap value. From the analysis the photocatalyst with a w/w/ ratio of 1:1 was found to be most promising among the ratios effectively decreasing the band gap of the photocatalyst and presented largest absorption within visible region. The 1:1 w/w ratio doped catalyst at 760 nm displays highest band energy and can be attributed to the electron transition to the Conduction band of $ZnFe_2O_4$ from the $ZnFe_2O_4$ Valence band.

Correspondingly, the absorption at 446 nm might be ascertained to the electron transition from $ZnFe_2O_4$ Valance band to TiO_2 conduction band. The $ZnFe_2O_4$ Band-gap structure can be corresponding to the valence band (O-2p orbital) and conduction band (Fe-3d orbital) [19, 20]. The *hv* value was deliberate employing Equation 1.

$$hv = 1240/\lambda \quad (1)$$

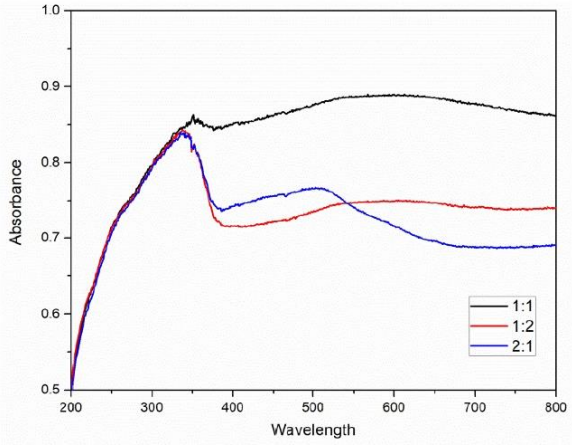

Fig. 9: Absorption spectrum of synthesized photocatalyst materials $ZnFe_2O_4/TiO_2$ (1:1), $ZnFe_2O_4/TiO_2$ (1:2) and $ZnFe_2O_4/TiO_2$ (2:1) under UV-Visible light irradiation.

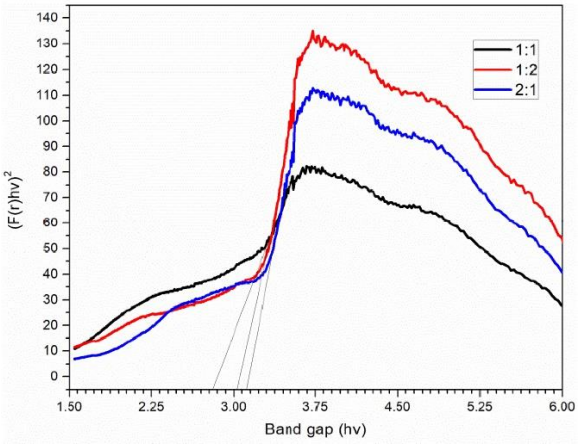

Fig. 10: Calculation of Band gap energy of synthesized catalyst.

The calculation of band-gap was made possible by plotting the tauc plot relation. The graph plotted between *hv* and $(F(R).hv)^2$ is demonstrated in Fig.. The extrapolation of the steep linear portion of the graph to the X-axis results in the value of band gap of the photocatalyst which in turns identify the activity of photocatalyst in UV or Visible region. The band gap values of the synthesized samples in (1:1, 1:2, 2:1) w/w proportions were relatively found to be 2.8, 3.02 and 3.10. The TiO_2 doping with the $ZnFe_2O_4$ in suitable proportion relocated the TiO_2 band gap of from UV region in to the visible light region. This visible light active photocatalyst can be exploited effectively for redox reaction studies under visible light.

Conclusion

In the current study $ZnFe_2O_4/TiO_2$ hetero-junctions photocatalyst material was synthesized employing the sol-gel technique which portrayed absorbance in the visible light region of the solar spectrum. The Band gap analysis shows that the 1:1 w/w ratio is the most promising among the other ratios namely 1:2 and 2:1 for the conversion of CO_2 to hydrocarbons and valuable fuels. The XRD and XPS study also confirmed the formation of the target hetero-junction material. The FESEM and EDS image analysis further evidenced its formation. The electron hole recombination will also be altered due to heterojunction formation. Successful reduction of CO_2 into methanol could be observed from the synthesized $ZnFe_2O_4/TiO_2$ photocatalyst under the visible light region of solar spectrum.

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