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Enhanced photocatalytic hydrogen production from Y₂O₃/TiO₂ nanocomposites: A comparative study on hydrothermal synthesis with and without ionic liquid

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Abstract

Hetero-junction Y_2O_3/TiO_2 nano-composite (NC) photocatalysts were synthesized by conventional hydrothermal method (Y_2O_3/TiO_2 NC_(HM)) and by ionic liquid assisted hydrothermal method (Y_2O_3/TiO_2 NC_(ILAHM)). The composite nature and physico-chemical properties of the photocatalysts prepared by both routes as a function of thermal treatment were investigated via thorough characterizations. A comparison of the photocatalytic hydrogen production via water splitting is provided. It was found that the concentration of Y_2O_3 in TiO₂ matrix and post thermal treatment have an obvious effects on the hydrogen production activity that were fine-tuned for the enhancement. The synergy between Y_2O_3 and TiO₂ has an optimum for concentration of 25 wt% of Y_2O_3 in TiO₂ matrix prepared at 400°C for 1 h. The optimized NC i.e 25 wt % Y_2O_3/TiO_2 NC_(ILAHM) has produced promising hydrogen evolution of *1380 µ mol/g* that was almost 2–fold the production from 25 wt % Y_2O_3/TiO_2 NC_(HM). The enhancement was attributed to porous like surface morphology, higher surface area and quantum yield of the NC prepared by ionic liquid assisted hydrothermal method.

Keywords: Ionic liquid assisted hydrothermal method, Y_2O_3 modified TiO₂ nano-composites, hydrogen evolution via water splitting, thermal treatment, photocatalysis.

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1. Introduction

Recently, renewable techniques to harvest energy have been emerged as research hot topic since the conventionally used fossil fuels are costly and present environmental limitations [1-3]. In this regard, photocatalytic and photoelectrochemical hydrogen production via water splitting posses enormous potential for sustainable development of society [4-6]. Several semiconductors have been utilized for photocatalytic hydrogen production [7-9]. Amongst these; TiO₂ has been widely used as a photocatalyst for hydrogen generation via water splitting [10-12]. Numerous methodologies have been employed to fine tune the properties of TiO₂ for improved photocatalytic activity [13-14]. Hetero-junctioning the TiO₂ with oxide semiconductors has proven to enhance hydrogen production compare to bare TiO₂ nanomaterials. Nanocomposites (NCs) of Y_2O_3/TiO_2 are promising candidates as photocatalysts [15-16]. In Y_2O_3/TiO_2 NC; the Y_2O_3 acts as electrons drain and minimizes the recombination of electron/hole pairs [17-18].

Various preparation methods such as, sol-gel, co-precipitation and combustion have been used for the syntheses of Y₂O₃/TiO₂ NCs [19-20]. Room temperature ionic liquids (RTILs) hydrothermal method has received extensive attention for both academic research and industrial investigations over the past two decades for the syntheses of oxide materials [13, 21, 22] RTILs possess unique properties such as wide liquid temperature range, high thermal stability, high ionic conductivity and wide electrochemical window [23]. An important aspect of the interaction of RTILs with nanoparticle (NP) precursors involves the nucleation and growth of NPs that helps to control the morphology of the NPs [24]. Ionic liquids possess following special physical properties that render them interesting as potential solvents for inorganic synthesis; (1) they are good solvents for a wide range of inorganic materials and they can help bring the unusual combinations of reagents into the same phase, (2) their compositions of poorly coordinated ions

make them highly polar yet non coordinating solvents and (3) they are nonvolatile having low vapor pressure so that they may be used in high-vacuum systems [25-26]. With these tremendous properties; the ILs are very attractive to be used as additional solvent and surface directing agents for the hydrothermal synthesis of many other materials [21,22]. However, to date, there is no report on the syntheses of Y_2O_3/TiO_2 NCs employing RTIL hydrothermal method.

Herein, we have proposed for the first time a simple single step RTIL assisted hydrothermal method to synthesize Y_2O_3/TiO_2 NCs. For the sake of comparison, a conventional hydrothermal method without ionic liquids is applied for the synthesis of the photocatalysts. The NCs are optimized by thermal treatment and by varying the concentration of Y_2O_3 for improved photocatalytic hydrogen production via water splitting.

2. Materials

Titanium tetrachloride (TiCl₄) and Yttrium nitrate (Y(NO₃)₃ .6H₂O) were purchased from Sigma Aldrich, Sodium hydroxide (NaOH) was purchased from Merck, India.1-(2-methoxyethyl)-3methylimidazolium methanesulfonate ionic liquid was prepared by previously developed method [27]. Double distilled water was used throughout the experiments.

3. Experimental section and instrumentation

3.1. Ionic liquid assisted hydrothermally derived photocatalysts

For the syntheses of pristine Y_2O_3 and TiO_2 nanoparticles (NPs), 0.05 M Y(NO₃)₃.6H₂O and 5.5 mL of TiCl₄, respectively were used as precursors. In the first step, each precursor was added separately in Teflon tube having 2.5 mL 1-(2-methoxyethyl)-3-methylimidazolium methane sulfonate as IL and 3.5 mL of 0.1 M NaOH solution as mineralizer. The system was left for homogenization under a constant stirring and after that; 8 mL of water was added for the hydrolysis to occur. Furthermore, the precipitate in Teflon tube was put into the stainless

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autoclave followed by hydrothermal treatment at 130 °C for one day. After the reaction, the system was cooled to room temperature naturally. In the second step, the obtained product was mixed with acetonitrile and stirred overnight to remove the IL's residue. Finally, Y_2O_3 and TiO_2 nanoparticles were retrieved from centrifugation; thereby, post calcinations step was followed.

The Y_2O_3 incorporated TiO₂ NCs were prepared by following the similar procedures and post calcinations except for the first step once we mixed different concentrations (25, 50 and 75 wt %) of Yttrium nitrate with a fixed volume of Titanium tetrachloride (5.5 mL).

For the NCs synthesized by conventional hydrothermal method similar procedures were followed except for the addition of IL in the first step of the synthesis.

The NCs prepared by both techniques were post annealed at 400°–800°C for 1–3 hours of calcination times.

3.2. Photocatalytic H₂ production

Photocatalytic activities were evaluated by measuring hydrogen production using gas chromatography at room temperature in water ethanol system. The reaction was carried out in a closed gas circulating system in an inner irradiation type reactor. Different photocatalysts (10 mg) were sonicated for 20 min to disperse in 7.5 mL aqueous solution. After sonication, 2.5 mL ethanol was added as a sacrificial reagent. Prior to irradiation, the system was deaerated by bubbling argon for 10–15 min to reduce the oxygen content. During the entire experiment, the reaction temperature was kept at 25 °C by eliminating the contribution of IR radiation with the circulation of water in the outer jacket of the reactor. A 300 W Xenon/Mercury lamp has been used as light source. Analyses were conducted using Agilent 6820 GC Chromatograph equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve packed column with argon

as the carrier gas. Using a gastight syringe with a maximum volume of 50 μ L, the amount of hydrogen produced was measured at each 0.5 h intervals.

3.3. Determination of quantum yield

Quantum yield is a very important factor to evaluate the photocatalytic efficiency of the photocatalysts. The fluorescence quantum yield (Q) is the ratio of photons absorbed to photons emitted through fluorescence. The most reliable method for recording Q is the comparative method of Williams [28], which involves the use of well characterized standard sample (Quinine sulfite) whose Q value is already known and it was found to be 0.54 [29]. solutions of the standard and test samples with identical absorbance at the same excitation wavelength can be assumed to be absorbing the same number of photons. Hence, a simple ratio of the integrated fluorescence intensities of the two solutions (recorded under identical Conditions) will yield the ratio of the quantum yield values. Quantum yield of standard (Q_{known}) is known, it is trivial to calculate the quantum yield of test sample ($Q_{unknown}$) using following equation:

$$Q_{uknown} = \frac{Q_{known} \times (Slope)_{unknown} \times \eta_{unknown}^2}{(Slope)_{known} \times \eta_{known}^2}$$

Q is quantum yield; η is refractive index of solvent used. Brief procedure is discussed below

- (i) Prepare series of quinine sulfite solutions (0.01 to 0.06 M) in ethanol plus 0.01 % HCl, note down the absorbance of each solutions using UV-Vis spectrometer and also record the integrated fluorescence intensity of each solution using spectrofluorophotometer.
- (ii) Repeat step 1, for each of the test solutions (prepared photocatalysts) whose Q value has to be determined.

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(iii) Plot a graph with integrated fluorescence intensity vs absorbance of quinine sulfite and well as each test solutions and graph is straight line from this graph find out the slope from this slope and using equation 1, one can determined the Q of the photocatalysts.

3.4. Characterization

Powder X-ray diffraction data was recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu-K_{α} (1.5418 Å) radiation operated at 40 kV and 30 mA. X-ray photo electron spectroscopy (XPS) analysis was carried out on an ESCALAB 250 (Thermo-VG Scientific), using Al K_{α} as the excitation source. The binding energy (BE) from the advantageous carbon (284.6 eV) was used to calibrate the spectra. The absorption spectra of the samples were measured by dispersing the nanoparticles in water using Perkin Elmer Lambda-750 UV-Vis spectrometer helping to determine the band gap energy of the prepared photocatalyst using Kubalkamunk function. Integrated fluorescence intensity of the prepared materials was determined by using spectrofluorophotometer (Shimadzu, RF-5301PC Series) helping to determine the quantum yield of the prepared photocatalyts. The morphology was examined using table top Hitachi 3000 scanning electron microscopy (SEM). Samples were gold-coated prior to SEM analysis. The nanostructure of the product was observed by transmission electron microscopy (TEM) performed by JEOL JEM 1200 Ex operating at 100 kV. Samples for TEM were prepared by dropping the dispersion of 2-propanol metal oxide nanoparticle on a holey carbon grid and drying the grids under vacuum for 24 h. BET surface area i.e. N2 adsorptiondesorption measurements of the samples were measured using Tristar II, Micromeritics. The water/organic content present in the sample was investigated by thermo gravimetric analysis (TGA) using a SDT Q600 V20.9 thermo microbalance in N_2 atmosphere from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. For the sake of simplicity, the samples prepared by

ionic liquid assisted method are labeled adding subscript (ILAHM) whereas others without IL are labeled by (HM)

4. Results and discussion

4.1. Y₂O₃/TiO₂ NCs_(ILAHM)

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XRD is mainly used to know the phase composition and crystallite size of the prepared materials. Fig.1 showed the XRD patterns of the pristine photocatalysts, calcinated at 400°C for 1h. The diffractograms are in good agreement with JCPDS #s. 41-1105 and 2-387, that clearly confirm the formation of Y_2O_3 and TiO_2 , respectively. Once Y_2O_3 NPs were incorporated to TiO₂ NPs; the XRD patterns become broader and presence of tetragonal anatase TiO₂ and cubic Y_2O_3 phases can be clearly seen (Fig. 1). The relative intensity of the peak at $2\theta = 29.2$ related to (222) plane of cubic Y_2O_3 is increasing with concentration of Y_2O_3 . The crystallite size, BET surface area, band gap energy and quantum yield for 25, 50, 75 wt % Y2O3/ TiO2 NCs(ILAHM) and pristing NPs of TiO_{2(ILAHM)} and $Y_2O_{3(ILAHM)}$ are calculated and are shown in the Table 1. It can be seen that the NC materials present higher surface area compared to the pristine Y_2O_3 and TiO_2 NPs. In addition, 25 wt% $Y_2O_3/TiO_2 NC_{(ILAHM)}$ presents the highest surface area compared to all other photocatalysts. Furthermore, comparing the quantum yields of Y₂O₃/TiO₂ NCs_(ILAHM) and pristine nano-materials the NC materials seems to be more attractive for photolysis as compared to their pristine NPs (Table 1). The optical properties were characterized at room temperature using a UV–Vis spectrophotometer in the wavelength range between 200–800 nm and the band gap energies of the NCs were calculated from diffused reflectance spectra using Tauc plot function and the results are indicated in Table 1, corresponding UV-Vis spectra and Tauc Plot function for determination of band gap of different photocatalyts synthesized via ILAHM and HM are showed in supplementary file as Fig S1, Fig S2, Fig S3 and Fig S4, (S stands for

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supporting information). The band gap of pristine Y_2O_3 and TiO_2 were found to be 4.5 and 3.2 eV and upon hetero-junctioning the band gaps of the NCs were decreased. These results clearly show that light absorption of the hetero-junction NCs in increased



Fig. 1 XRD patterns of (a) pristine $Y_2O_{3(ILAHM)}$ NPs,(b) pristine $TiO_{2(ILAHM)}$ NPs, (c) 25 wt% (d) 50 wt% and (e) 75 wt% Y_2O_3 / TiO_2 NCs_(ILAHM), (A= Anatase TiO_2 and Y = Y_2O_3) and the samples are calcinated at 400°C for 1 h.

The pristine Y_2O_3 (ILAHM) & TiO₂ (ILAHM) NPs, and Y_2O_3/TiO_2 NCs (ILAHM) were subsequently applied for hydrogen evolution in water–ethanol system. Fig. 2 compares the gas chromatography results of the photocatalysts. It can be seen that the pristine NPs prepared in the current study have shown enhanced photoactivity compared to the commercially available powders that highlights the importance of the RTILs synthesis route. Furthermore, the photocatalytic activity of NC materials is better than the pristine Y_2O_3 (ILAHM) and TiO₂(ILAHM) NPs presenting NC as promising photocatalysts. For the Y_2O_3/TiO_2 NCs_(ILAHM), the

concentration of Y_2O_3 in TiO₂ matrix has an obvious effect on the H₂ evolution activity that has an optimum for 25 wt% concentration of Y_2O_3 evolving 1380 μ mol/g of H₂. On the other hand, the H₂ evolution rate dropped to 890 μ mol/g for 75 wt% Y_2O_3 /TiO₂ NC_(ILAHM).

Table 1 Crystalline size, BET surface area, quantum yield and band gap energies of the differentphotocatalysts synthesized via ionic liquid assisted hydrothermal method (ILAHM) and hydrothermal method (HM).

Samples	Y ₂ O ₃ content (wt %)	Crystalline size (nm)		BET surface area (m ² /g)		Quantum yield	1	Band gap (eV)		
		ILAHM	HM	ILAHM	НМ	ILAHM	HM	ILAHM	НМ	
TiO ₂ NPs	0	33.3 for (101)	32.7	32.1	29.4	0.21	0.20	3.34	3.32	
Y ₂ O ₃ /TiO ₂ NCs	25	41.3 for (101)		50.6	40.6	0.51	0.41	2.10	2.15	
	50	42.1 for (101)		35.7	33.7	0.45	0.35	2.00	2.07	
	75	42.6 for (101)		32.8	30.3	0.41	0.31	1.97	1.99	
Y ₂ O ₃ NPs	100	28.6	29.8	20.4	18.4	0.09	0.08	4.50	4.50	

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The enhanced photocatalytic activity of Y_2O_3/TiO_2 NCs _(ILAHM) can be explained as follow; water splitting is an uphill reaction that needs the standard Gibbs free energy change of ΔG° of 237 kJ/mol or 1.23 eV. Therefore, the band gap energy (E_g) of the photocatalyst should straddle the water redox potentials and it should be between 1.23 eV < E_g < 3.26 eV [30,31].

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Fig. 2 Hydrogen generation of different photocatalysts synthesized via ILAHM and commercial TiO₂ (Degussa P-25).

In addition, the photocatalyst should be efficient enough to separate the photogenerated carriers and to transport them to their reactive sites in order to decrease the electron-hole pair recombination. In hetero-junction photocatalysts that possess appropriate band gap energetics the CB electrons of one semiconductor are injected to other thereby; achieving a wide electron-hole separation (Fig. 3) [33]. The CB of TiO₂ and Y₂O₃ are positioned at ca. – 0.7 and – 0.35 V, respectively more negative than that of water reduction potential and VB of TiO₂ lies closed to the water oxidation potential compared to the VB of Y₂O₃ [33,34].

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Fig. 3 Electron transportation in Y_2O_3 / TiO₂ NCs for photocatalytic hydrogen generation.

Therefore, owing the advantage of hetero-junctioning of Y_2O_3 and TiO_2 , under illumination; electrons are excited from VB to CB of TiO₂, thereof transferred to the CB of Y_2O_3 , thereby; reducing water to hydrogen. On the other hand holes from the VB of TiO₂ oxidize water. Therefore, the hetero-junction formed between TiO₂ and Y_2O_3 efficiently separates the photoexcited electron-hole pairs, and thus hinders the charge recombination and improve the photocatalytic performance of NC materials compared to the pristine Y_2O_3 and TiO₂ NPs. Since we are changing the concentration of Y_2O_3 that evidently affects the capture of photoexcited electrons from the CB of TiO₂. If concentration of Y_2O_3 is large, the light absorption from TiO₂;

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will be small thereby inhibiting the generation of electron-hole pairs in TiO₂ that is the main reason of decreasing H₂ evolution rate of high content incorporation of Y_2O_3 such as that 75 wt% of Y_2O_3 in TiO₂ matrix [16]. In the absence of Y_2O_3 , most of these charges tend to recombine rapidly as the pristine TiO₂ NPs present lower photocatalytic hydrogen generation. Therefore, the synergy for improved photocatalytic activity can be obtained only for a certain concentration of Y_2O_3 in TiO₂ matrix. In the current work that synergy is achieved for the 25 wt% Y_2O_3/TiO_2 NC. Therefore, the optimum concentration of Y_2O_3 in TiO₂ matrix not only optimize the light absorption but also increase the BET surface area and quantum yield (Table 1) which than synergize 25 wt% Y_2O_3/TiO_2 NC for enhanced photocatalytic activity compared to all other samples.

4.2. Y₂O₃/TiO_{2(HM)}

For the sake of comparison, the $Y_2O_3/TiO_2 NCs_{(HM)}$ were prepared by hydrothermal method without the presence of IL. Fig.4 shows the XRD patterns of different photocatalysts, calcinated at 400 °C for 1h. The diffractograms of the pristine photocatalysts are in good agreement with JCPDS #s. 41-1105 and 2-387, that clearly confirm the formation of Y_2O_3 and TiO₂, respectively. Once $Y_2O_{3(HM)}$ NPs were incorporated to TiO_{2(HM)} NPs; the XRD patterns become broader compared to those observed for NCs prepared by ILAHM (Fig. 1). These results suggest the presence of amorphism in the NC_(HM) matrix; therefore it is hard to determine the crystalline grain from the Scherre's equation. On the other hand, in case of ILAHM synthesis, well defined peaks can be observed these results clearly indicate that the presence of ionic liquid in the hydrothermal synthesis helps to improve the crystalline structure of the photocatalysts. As compared to pristine $Y_2O_{3(HM)}$ and TiO_{2(HM)} NPs the NCs_(HM) present higher surface area (Table 1). In addition, 25 wt% $Y_2O_3/TiO_2 NC_{(HM)}$ present the highest surface area and quantum yield

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compared to all other photocatalysts. Interestingly, same sample when prepared by the ILAHM has presented the highest surface area as well as the quantum yield when compared to other samples (Table 1). These results show that the concentration of $Y_2O_{3(HM)}$ in TiO_{2(HM)} is a critical factor for higher surface area that has an optimum of 25 wt % in the current study. The band gap energies (Table 1) obtained from the absorption spectra presented the similar trend as observed for different concentration of Y_2O_3 prepared by ILAHM



Fig. 4 XRD patterns of (a) pristine $Y_2O_{3(HM)}$ NPs,(b) pristine $TiO_{2(HM)}$ NPs, (c) 25 wt% (d) 50 wt% and (e) 75 wt% Y_2O_3 / $TiO_2 NCs_{(HM)}$, (A= Anatase TiO_2 and $Y = Y_2O_3$) and the samples are calcinated at 400°C for 1 h.

Fig. 5 compares the gas chromatography results of the prepared photocatalysts. The photocatalytic hydrogen production for $NCs_{(HM)}$ materials is far better than the pristine $Y_2O_{3(HM)}$ and $TiO_{2(HM)}$ NPs. The highest hydrogen production (890 µmol /h/g) was observed for 25 wt%

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 Y_2O_3 / TiO₂ NC_(HM). However, all of the NCs prepared by ILHAM (Fig. 2) have presented improve photocatalytic activity compare to the best NC prepared by HM. Comparing the samples prepared by two methods in Table 1; clearly the higher surface area and quantum yield can be observed for ILAHM synthesized NCs. These results show that the addition of ionic liquid in the hydrothermal synthesis not only results in improved crystalline structure but also other physicochemical properties that are vital for improved photocatalytic activity of the NCs.



Fig. 5 Hydrogen generation of different photocatalysts synthesized via HM and commercial TiO₂ (Degussa P-25).

4.3. Effect of temperature on photocatalytic hydrogen production

In the above discussion the samples were calcinated at 400°C for 1 h. Once we optimized the concentration of the Y_2O_3 in TiO₂ i.e.25 wt %, we further investigated the effect of thermal treatment on the photocatalytic performance of the NCs. Fig. 6 displays the XRD patterns of 25

wt% Y_2O_3 / TiO₂ NC_(ILAHM) calcinated at temperatures (from 500 – 800 °C) for 1 h. The presence of anatase phase of TiO₂ along with cubic Y_2O_3 can be seen up to 600°C. Further increasing temperature from 700°C and above, the intensity of anatase phase decreases and at 800 °C complete transformation to the rutile phase can be confirmed.



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Fig. 6 XRD patterns of 25 wt% Y_2O_3 / TiO₂ NC_(ILAHM), calcinated at different temperatures (A= Anatase TiO₂, R= Rutile TiO₂ and Y = Y₂O₃).

Usually, due to increase in the temperature the particles agglomerate thereby the surface area is decreased. The crystallite size for anatase phase of TiO₂ for (101) peak and BET surface area at different temperatures are calculated from Scherrer's equation and are shown in the *Table S1* the crystalline size gradually decreases with increasing the temperature. After heat treatment, the above photocatalysts were subjected to photocatalytic hydrogen production (*Fig. S5*). In the set of these samples the NC prepared at 500°C has shown improved photocatalytic activity (1280 μ mol/g) compared to other samples. However, compared to the sample prepared at 400°C (Fig. 2) the photocatalytic activity is clearly decreased. Once the rutile TiO₂ has found to decrease the

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photocatalytic performance of TiO_2 [35]; therefore, we suggest that the formation of rutile phase in the crystalline structure is the main reason to decrease the photocatalytic activity of the NC.

For 25 wt % Y_2O_3 / TiO₂ NC_(HM) prepared by HM without IL (Fig. 7) same thermal treatments were followed. The XRD patterns have followed the similar trend as that of Fig. 6. The BET surface area obtained at different thermal treatments is shown in the *Table S1*. It can be seen that the surface area decreases with increasing temperature that is clearly related to the agglomeration of the NCs as well as the formation of rutile phase of TiO₂.



Fig. 7 XRD patterns of 25 wt% Y_2O_3 / TiO₂ NC_(HM) calcinated at different temperatures (500 – 800 °C for 1h),(A= Anatase TiO₂, R= Rutile TiO₂ and Y = Y₂O₃).

After heat treatment, the above photocatalysts were applied to photocatalysis (Fig. S6) Comparing the photocatalytic activity of this set of samples one can observe that the sample prepared at 500°C has shown the best performance (470 μ mol/g). However, compared to the NC prepared at 400°C it has shown a phenomenal decrease in the photocatalytic activity that is

clearly related to the combined effect of higher crystallinity and surface area (Table 1) of the sample. The heat treatment results presented above have clearly shown that for the current study 400°C is an optimum temperature. To further investigate how time can affect the photocatalytic activity of the 25 wt% Y_2O_3 / TiO₂ NC_(ILAHM) is heat treated at 400°C for 1, 2 and 3 h duration. Comparing. *Fig. S7;* with Fig 2 it is clear that the best photocatalytic performance throughout the current study is observed for 25 wt% Y_2O_3 / TiO₂ NC_(ILAHM) prepared at 400 °C for 1h. It seems that the synergizing hetero-junction NCs the concentration of Y_2O_3 and thermal treatment are critical steps that not only affects the crystalline structure but also other physico-chemical properties of the photocatalysts.

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In above discussion we have comprehensively compared the photocatalytic activity of the samples prepared by ILAHM and HM and evidently the samples prepared by ILAHM have improved performances. Consider now the formation mechanism of the NCs employing hydrothermal method with and without adding IL. According to the literature when NPs are synthesized via HM; the important aggregation mechanisms to be considered are (1) Diffusion limited aggregation (DLA) and (2) Reaction limit aggregation (RLA) [36]. DLA occurs upon high collision between the NPs that traverse relatively low energy barrier due to the absence of structural directing agent. As a result the particles will be aggregated and morphology will not be controllable thereby the active surface area will decrease that is the case of HM synthesis without IL. The surface morphology of the prepared photocatalysts were analyzed using SEM. The SEM image of NC_(HM) in Fig. 8 (a) is evident to follow that mechanism due to the formation of irregular size agglomerates. On the other hand, in RLA the presence of self assembling template does not let the particles collide due to high energy barrier that let them to stay apart. Therefore, the morphology will be controllable and porous structure will be presented, thereby; the surface

area will increase [37]. In the literature, the mechanism to the formation of NPs prepared by ILAHM is not completely understood [38]. However, based on the self-assembling template nature of ionic liquid we suggest that in the current study the formation of $NC_{(II,AHM)}$ is prevailed by RLA. The anionic part of the IL i.e methanesulfonate possesses large hydrophilicity that will preferentially interact with water molecules in solution through hydrogen bonding. The cationic part of IL i.e 1-(2-methoxyethyl)-3-methylimidazolium ring will array in the opposite direction to pile up possibly by $\pi - \pi$ interactions or other non-covalent interactions (hydrogen bonding, van der Waals forces, and electrostatic forces) between imidazolium rings [39]. This implies that IL successfully participates in the reaction as a self-assembling template. Consequently, the titanium and yttrium precursors will be hydrolyzed and condensed around the self-assembled IL structure at a controlled rate thereby the collision between the particles will be constraint due to the presence of these templates, which leads to the formation of porous structure with high surface area. Fig. 8 (b) clearly indicates voluminous porous network with voids indicated by the arrows that will help to facilitate water adsorption, penetration and improved photocatalytic H_2 evolution. Scheme S1 presents the suggested mechanism to the formation of NCs via HM and ILAHM. Scheme S2 presents the structure of 1-(2-methoxyethyl)-3-methylimidazolium methanesulfonate (MOEMI.CH₃SO₃⁻¹).

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Fig. 8 SEM images of (a) 25 wt% Y_2O_3/TiO_2 NC synthesized via HM and (b) 25 wt% Y_2O_3/TiO_2 NC synthesized via ILAHM heat treated at 400°C for 1 h.

Being best in all aspects in the current study from now onwards we will characterize 25 wt% Y_2O_3 / TiO₂ NC _(ILAHM) comprehensively. Samples for TEM were prepared by dropping a dispersion of metal oxide nanoparticles in 2-propanol on a holey carbon grid and drying the grids under vacuum for 24 h. Fig. 9 (a) shows the TEM image, the average particle size was found to be 55 nm. The lattice spaces of 0.35 nm, 0.30 nm and 0.53 nm can be observed in HRTEM image (Fig. 9 (b)), that are in good agreement with (101) plane for anatase TiO₂, (222) and (200) planes for cubic Y₂O₃. The corresponding SAED spectrum is shown in Fig. 9 (c) that further indicates the presence of Y₂O₃ and TiO₂.

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Fig. 9 (a) TEM image, (b) HRTEM image and (c) SAED pattern of the 25 wt% $Y_2O_3/TiO_2 NC$ synthesized via ILAHM.

The surface chemical composition and the oxidation state for the synthesized samples are investigated by XPS measurements. From the survey spectrum (not shown) the presence of C, S, Ti, Y and O elements was recorded. The high resolution deconvoluted XPS spectra of O 1s, Ti 2p, Y 3d and S 2p regions are displayed in Fig 10. In Ti 2p region (Fig. 10 (a)) the binding energies of 458.6 and 464.1 eV are indicative of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ which correspond to Ti⁴⁺ [40]. In O 1s region (Fig.10 (b)) the peak centered at 529.6 eV is related to the oxygen in TiO₂ and Y₂O₃ lattice. However, the adjacent peak at 531.4 eV can be regarded as the presence of

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surface hydroxide species that were found to be advantageous for improved hydrogen generation [41], in Y 3d region (Fig. 10 (c)), the binding energies for Y $3d_{5/2}$ and Y $3d_{3/2}$ are observed at ca. 155.82 and 158 eV, respectively, with a spin-orbit splitting of 1.74 eV. These results match with the previous reports on Y₂O₃ [42]. In addition, another peak in the middle of Y $3d_{5/2}$ and Y $3d_{3/2}$ was also observed that might be related to some lower oxidation state of Y. A nominal amount of sulphur was registered in the XPS spectra and the corresponding S $2p_{3/2}$ and S $2p_{1/2}$ peaks are centered at 166.80 and 168.30 eV, respectively (Fig. 10 (d)). The presence of sulphur in the NCs is related to the syntheses step itself as the source of that is the CH₃SO₄ anion in the ionic liquid [43].



Fig. 10 High resolution deconvoluted XPS spectra of (a) Ti 2p (b) O 1s, (c) Y 3d and (d) S 2p regions in 25 wt% Y_2O_3 / TiO₂ NC synthesized via ILAHM.

Furthermore, EDS was used to identify the elements present in the prepared materials (*Fig. S8*). In case of both of the pristine $Y_2O_{3(ILAHM)}$ and $TiO_{2(ILAHM)}$ NPs, O was found along with their corresponding Y and Ti elements (*Fig. S8 (a & b)*). However, 25 wt% Y_2O_3 / TiO₂ NC_(ILAHM); the presence of all of three elements can be observed in *Fig. S4 (c)*, confirming the existence of Y_2O_3 content in the TiO₂ matrix.

FT-IR spectroscopy is mainly used to check the presence of functional groups present in the synthesized nanomaterial, *Fig.S9* contrasts the FT-IR spectra of pristine Y_2O_3 , TiO₂ NPs and 25 wt% Y_2O_3 / TiO₂ NC_(ILAHM). The significant characteristic peak for Y_2O_3 is observed at ca. 421cm⁻¹ (*Fig.S9 (a)*) that can be assigned to stretching vibration modes of Y-O [44], and spectral region centered at ca. 3500 cm⁻¹ can be assigned to vibrational modes of H₂O molecules on the surface of Y_2O_3/TiO_2 NC [45]. *Fig. S9 (b)* shows the significant characteristic peak at ca. 400 cm⁻¹ due to the Ti-O stretching vibration modes in TiO₂ [46]. For 25 wt% Y_2O_3/TiO_2 NC (ILAHM), these peaks can be observed at ca. 478 cm⁻¹ and ca. 668 cm⁻¹ i.e shifted to higher wavenumber compared to pristine Y_2O_3 & TiO₂ NPs (*Fig.S9 (c)*), from these analyses, the formation of Y_2O_3/TiO_2 NC can be confirmed and the shift in the wavenumber in Y_2O_3/TiO_2 NC compared to Y_2O_3 and TiO₂ may be related to the composite nature of the material.

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TG analysis was employed to determine the thermal stability of the as-prepared materials. Thermal stability of the *as prepared* 25 wt% Y_2O_3 / TiO₂ NC _(ILAHM) was studied by TGA analysis (Fig. 11). Two obvious weight loss stages can be observed. The first stage from room temperature to 100 °C and the second from 100 °C to 420 °C are attributed to the dehydration of water content and thermal decomposition of organic substances, respectively. Furthermore, beyond 420 °C there is no change in the shape of the curve (no weight loss) that indicates the prepared NC is thermally stable at high temperatures [47].

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Fig. 11 Thermo gravimetric analysis of 25 wt% Y₂O₃/ TiO₂ NC_(ILAHM).

5. Conclusions

We have successfully synthesized pristine Y_2O_3 and TiO_2 and Y_2O_3/TiO_2 NCs via simple ionic liquid assisted hydrothermal method for the first time. The photocatalytic activities of the NCs were compared to the samples prepared via hydrothermal methods in the absence of ionic liquid. Compared to the hydrothermal method the NCs prepared by ionic liquid assisted hydrothermal method have improved the photocatalytic hydrogen production from water splitting that highlights the importance of ionic liquid in the synthesis procedure. The hydrogen production was optimized via thermal treatment and the synergy for the enhanced was obtained for 25 wt% of Y_2O_3 /TiO_{2 (ILAHM)} calcinated at 400°C for 1 h. The same sample when prepared in the absence of ionic liquid has resulted into decrease in the photocatalytic activity. The enhancement can be understood from the largest BET surface area, highest quantum yield and adequate surface morphology of the sample. The methodology provided here clearly indicates the importance of

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ionic liquid assisted hydrothermal method for the syntheses of NCs. In the absence of IL the particles agglomerate due to diffusion limited aggregation. On the other hand, self-assembling template nature of IL prevails the reaction limit aggregation mechanism that helps to improve the physico-chemical preoperties of the NCs for enhanced hydrogen production.

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Enhanced photocatalytic hydrogen production from Y₂O₃/TiO₂ nanocomposites: A comparative study on hydrothermal synthesis with and without ionic liquid

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Syntheses of Y_2O_3/TiO_2 nano-composites via hydrothermal and ionic liquid assisted hydrothermal methods, for photocatalytic hydrogen production via water splitting reaction.