

Ionothermal Synthesis of Anatase and Rutile TiO₂ Nanoparticles for Hydrogen Evolution

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Abstract- TiO₂ nanoparticles (NPs) have been synthesized at 120 °C for one day via ionothermal method using 1-carboxymethyl, methyl imidazolium tetra fluoro borate [CMMIM][BF₄] as a functionalized ionic liquid (IL). XRD pattern shows that the product is composed of tetragonal rutile phase. FTIR spectrum shows a band at ~405 cm⁻¹ which is due to Ti-O-Ti stretching mode. UV-Vis spectrum shows the high intense maximum absorbance at ~213 nm due to imidazolium moiety and a band at ~277 nm for TiO₂NPs. TEM images show that the sizes of the nanoparticles ranges from 20-40 nm. Furthermore rutile TiO₂NPs are a promising catalyst for hydrogen evolution.

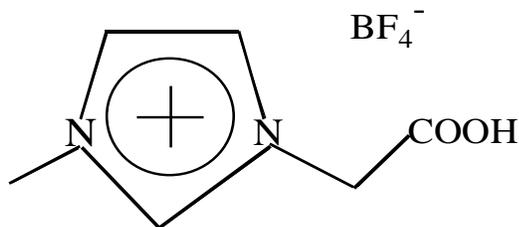
Key words: Anatase, Rutile, TiO₂ nanoparticles, ionothermal method, hydrogen evolution.

I. INTRODUCTION

Now-a-days, TiO₂ has been considered as one of the most commonly used metal oxide semiconductor materials due to its wide band gap (3.2eV), low cost, non-toxic nature, strong oxidizing power, high resistance to chemical or photo-induced corrosion etc. It has been widely used in photocatalysis, photovoltaics, solar energy conversion, sensors, textiles, paints, cosmetics, etc. [1-3]. It is used as promising photocatalysts in photo-degradations of most pollutants in water and air, has been extensively studied, mainly due to its superior ability to destroy organic contaminants [4,5]. TiO₂ has also been used as a good promising photocatalyst for hydrogen generation because harnessing and storing energy has been mankind's quest from time immemorial. This search for fuel had led to the discovery of fossil fuels, bio-fuels like gobar gas and secondary batteries. With increasing population and depleting natural sources, the necessity to find alternative fuel that would be both renewable and non-polluting becomes the need of the hour. In 1970s Fujishima and Honda [6] initiated the water

splitting reaction. This work involved photocatalysis to break down H₂O using an electrochemical cell with a TiO₂ electrode connected to a platinum electrode via an external circuit. Since this discovery there has been a proliferation of work conducted in the field of photocatalysis, using TiO₂ and other semiconductors, for the intention of hydrogen generation. Many methods are available to prepare TiO₂NPs, such as sol-gel, hydrothermal, solvothermal, sonochemical, chemical vapour deposition, electro-deposition, chemical/physical vapor deposition etc, [7]. As an alternative, ionothermal synthesis is one of the soft solution routes benefited from the other methods using ionic liquid (IL) as solvent. Over the past two decades, ILs have received extensive attention for both academic research and industrial investigations for the synthesis of inorganic nanomaterials. ILs possess unique properties such as negligible vapour pressure, wide liquid temperature range, high thermal stability, excellent solvent power for both organic and inorganic compounds, high ionic conductivity and wide electrochemical window etc, [8]. An important aspect of the interaction of ILs with nanoparticles precursor involves the nucleation and growth of NPs. ILs have been successfully used as a reaction media for the synthesis of TiO₂ nanomaterials. The most attractive property of ILs for the synthesis of TiO₂NPs is the surfactant-like nature, which inhibits the aggregation of the resultant NPs [9]. Furthermore, the fine-tuning ability of the reactants composition benefits the shape and size controlling over the TiO₂NPs. The above mentioned unique properties of ILs help in conducting the reaction in an open reactor. The term 'ionothermal' has been used to describe reactions that are conducted in ILs at high temperature with ambient pressures. As a result, ionothermal reactions avoid high pressure of hydrothermal or solvothermal reactions and eliminate safety problems related to high pressure [10]. Zhou et. al. [11] have synthesized TiO₂ nanocrystals using TiCl₄-[BMIM][BF₄] mixture to water at 80 °C. Nakashima et. al. [12] reported the synthesis of hollow TiO₂ microspheres by subjecting a mixture of [BMIM][PF₆], toluene and Ti(OBu)₄ to vigorous stirring. Zhou et. al [13] fabricated macroporous TiO₂ architectures via the spontaneous self assembly of

mixture of octadecene and 1-alkyl-3-methylimidazolium-based ionic liquid as the reaction medium. Dionysiou and coworkers [14] prepared mesoporous TiO₂ using aqueous solution of titanium tetra-isopropoxide and [BMIM][PF₆]. Herein we report the preparation of TiO₂NPs by an ionothermal method for hydrogen generation.



Scheme 1. 1-carboxy methyl, 3-methyl imidazolium tetra fluoro borate

II. EXPERIMENTAL

A. Synthesis and Structure of Ionic Liquid (1-Carboxymethyl, 3-Methyl Imidazolium Tetra-Fluoro-Borate)[CMMIM][BF₄]

The ionic liquid [CMMIM][BF₄] used in the synthesis of rutile and anatase TiO₂NPs has been prepared using the reported data [15,16].

B. Synthesis of TiO₂ Nanoparticles:

One mL titanium tetrachloride (TiCl₄) was transformed to 5 ml IL taken in Teflon tube under stirring. After homogenization of the mixture, 1 mL distilled water was added slowly to the above solution. Hydrolysis of TiCl₄ occurs immediately, as indicated by the effervescence of HCl fumes. This solution was subjected to ionothermal treatment (ITT) at 120°C for one day. When the reaction was complete, autoclave was cooled to room temperature naturally. The obtained product was washed with water and ethanol several times to remove IL and finally TiO₂ nanoparticles were separated by centrifugation. The final product was dried under vacuum for further characterization. Furthermore the structure of ionic liquid as shown in scheme.1

C. Photocatalytic H₂ Measurements:

Photocatalytic H₂ production reaction was carried out in a closed gas-circulating system in an inner irradiation-type reactor. TiO₂NPs were sonicated in 6 ml aqueous solution for 20 min to disperse the NPs and 2 ml ethanol was added as a sacrificial agent after sonication. Prior to irradiation, the system was de-aerated by bubbling argon for about 10-15 min. Photocatalytic activities of the TiO₂ NPs were evaluated by measuring H₂ production by gas chromatography at room temperature. During the entire experiment, the reaction temperature was kept at 25°C by eliminating the IR

radiation with the circulation of water in the water jacket of the reactor. Analysis were conducted on an Agilent 6820 GC Chromatograph equipped with a thermal conductivity detector and 0.5 Å molecular sieve packed column with argon as the carrier gas. Using a gastight syringe with a maximum volume of 50 µL, the amount of H₂ produced was measured at 0.5 h interval of time. The amount of gas liberated is plotted as a function of UV exposure time.

D. Characterization:

X-ray diffraction data was recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu-Kα (1.5418 Å) radiation. The fourier transform infrared spectrum of the sample was collected using Bruker (ALPHA) eco-ATRIR. The UV-Vis absorption spectrum of the sample was measured on a Shimadzu UV-Visible -1800 spectrophotometer. The morphology of the product was observed by transmission electron microscopy (TEM) which was performed with a Hitachi-H-8100 instrument (accelerating voltage up to 200 kV, LaB₆ filament) equipped with EDS (Kevex Sigma TM Quasar, USA).

III. RESULTS AND DISCUSSION

Wide angle PXRD pattern providing information on the crystalline nature of TiO₂ NPs is presented in the figure 1. The series of strong peaks in figure.1a were indexed to tetragonal rutile TiO₂ with the p42/mnm structure (space group 136 in the international tables for crystallography).

All the diffraction peaks are assigned to the (200), (111), (210), (211), (220) and main (110) reflection at 2θ=27.5° are indicating of the nano-crystalline rutile phase (JCPDS card no: 4-551, a=b= 4.594 Å, c=2.958 Å) and the shoulder peak of (101) reflection is due to nano-crystalline anatase phase. TiO₂ anatase over rutile ratio was calculated from [20]:

$$\text{Anatase content (A)} = \frac{1 (I)}{1 + 1.26 (I_R/I_A)}$$

Where I_A and I_R are the diffraction intensities of the (1 0 1) anatase and (1 1 0) rutile crystalline phases at 2θ= 25.3° and 27.5°, respectively. It should be noticed here that in case of the anatase over rutile ratio calculated according to Eq. (1). We found that the as-prepared sample contained the mixture of anatase and rutile phases are in the ratio of 36:64. The content of amorphous TiO₂ is not taken into consideration.

FTIR spectrum (figure.2) of IL-TiO₂NPs shows a band at 2925 cm⁻¹ is indexed to water. The bands at 1618 cm⁻¹ and 1445 cm⁻¹ are due to C-H stretching and in-plane vibrations of the imidazolium ring respectively [17]. The bands at 1156 cm⁻¹ and 1073 cm⁻¹ are the characteristic peaks of aliphatic

(organic compounds) in-plane vibrations. The band at $\sim 405\text{cm}^{-1}$ is due to the presence of Ti-O-Ti. In summary, however, IR spectroscopy suggests that even after extensive washing, some IL is adsorbed on the particles.

are as shown in the figure 4. From the DTA curve, it can be seen that an exothermic peak at below

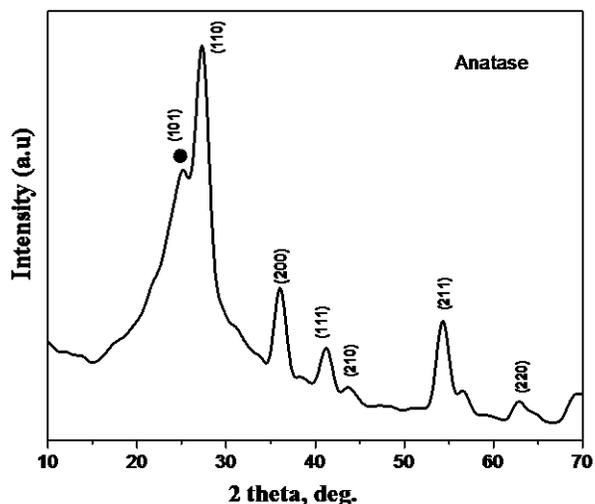


Fig. 1 PXRD pattern of as prepared TiO₂NPs

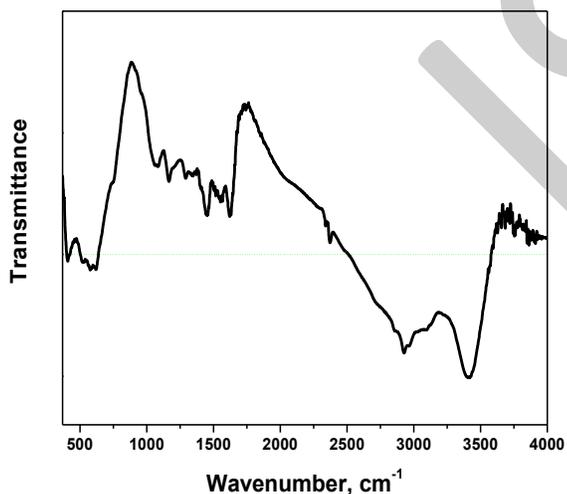


Fig. 2 FTIR spectrum of as prepared TiO₂NPs

Figure.3 shows the UV-Vis spectrum of IL-TiO₂ NPs. The absorption peak at $\sim 213\text{ nm}$ is due to presence of ionic liquid, which dominates the spectra, even after extensive washing [18] and at $\sim 277\text{ nm}$ due to titanium dioxide was blue shifted when compare to bulk material due to quantum confinement effect [19]. The TG-DTA curves of the as-prepared TiO₂ NPs

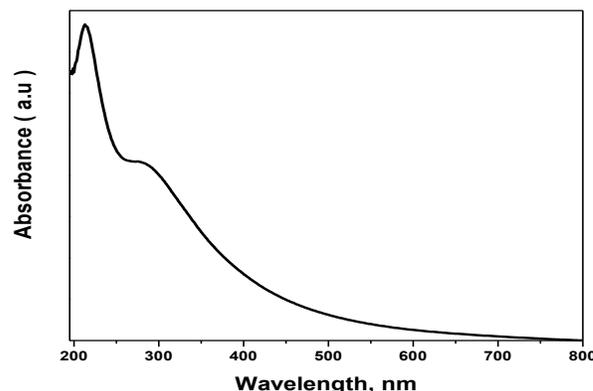


Fig. 3 UV-Vis spectrum of as-prepared TiO₂ NPs.

100 °C is due to the desorption of water and alcohol, Where as the first low intense exothermic peak at 338 °C and second very sharp high intense exothermic peak at 430 °C are assigned to the thermal decomposition of the organic substance as the evidence of weight loss ended at 430 °C. Since the TG curve shows that weight loss ended at 430 °C and total weight loss until this temperature was about 29 Wt%. It clearly indicates that 430 °C was sufficient temperature for complete removal of the organic substance from TiO₂ nanoparticles.

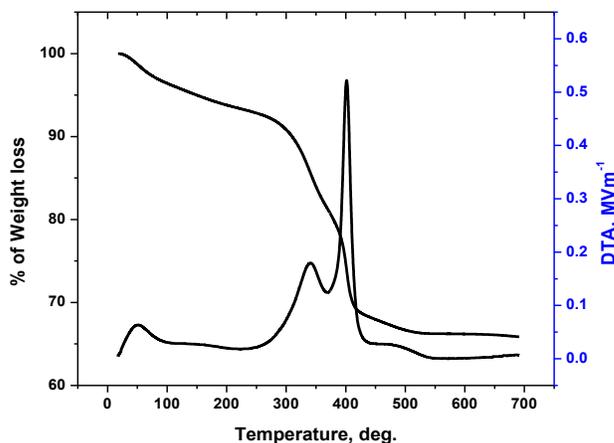


Fig.4 TGA-DTA of as prepared TiO₂ NPs

Figure.5 shows that TEM images of TiO₂ NPs prepared at 120 °C for 1 day using functionalized IL. It clearly indicates that the as-prepared compound (figure a) consists of cubic nanoparticles which are aggregated and looks like a chain

structure. Figure (b) clearly shows that obtained nanoparticles are cubic in shape at high magnification. The average diameters of the all cubic nanoparticles are in the range of ~20-40 nm.

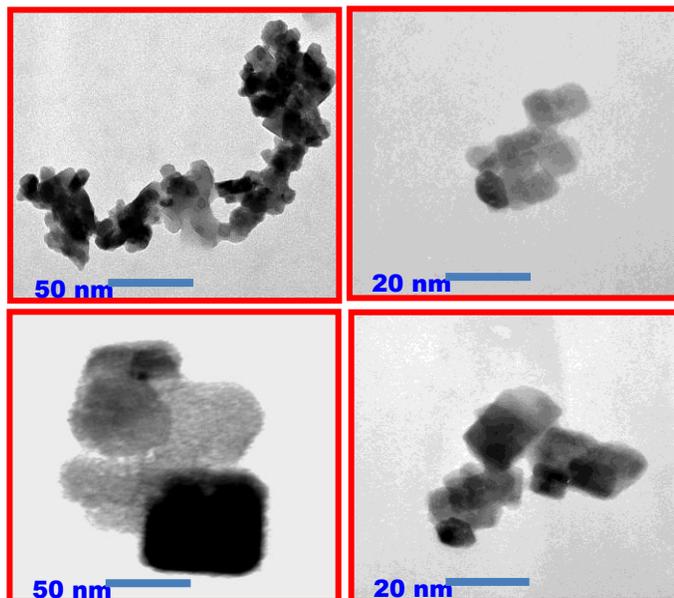


Figure.5 TEM images of TiO₂ NPs

IV. HYDROGEN GENERATION

The photocatalytic H₂ evolution activity was measured using as-prepared TiO₂NPs synthesized using functionalized IL. The rate of hydrogen evolution from UV photolysis of water as the solution in the presence TiO₂ was determined by gas chromatography as shown in the figure.6. The amount of gas liberated is plotted as the function of UV exposure time. We have observed that the evolution of H₂ production was 550 μ mol g⁻¹h⁻¹ of H₂ was liberated for 2.5 h, after this evolution of H₂ gas was stopped when the UV light was turned off and this indicated that H₂ evolution was induced by the UV irradiation, suggesting that it was a photo-electrochemical reaction.

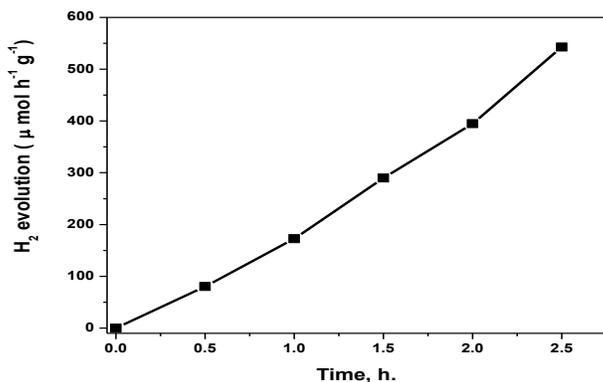


Figure .6 Hydrogen generation of TiO₂ NPs.

CONCLUSION

We have successfully synthesized anatase and rutile phases of TiO₂ NPs using functionalized ionic liquid via ionothermal method. XRD spectrum confirmed the existence of anatase and rutile phases of TiO₂ NPs and IR spectra indicates the presence of ionic liquid. In addition, the UV-Vis and TG-DTA show the presence of ionic liquid in the as prepared sample. The sizes of the TiO₂ NPs were in the range of ~20-40 nm. The obtained show good photocatalytic activity for hydrogen evolution i.e, it generates 550 μ mol g⁻¹h⁻¹ of H₂ as liberated for 2.5 h.

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