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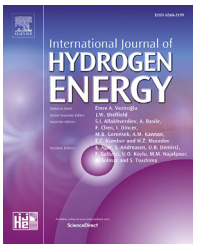

Ionothermal synthesis of TiO_2 nanoparticles for enhanced photocatalytic H_2 generation

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ABSTRACT

Photocatalytic hydrogen generation is one of the most promising solutions to convert light energy into green chemical energy. In the present work, methoxy ethyl methyl imidazolium methyl sulphonate ionic liquid is used for the synthesis of i-TiO_2 nanoparticles via ionothermal method at 120 °C. The obtained products were characterized by various spectroscopic techniques like XRD, FTIR, Raman, UV–visible, DRS, TEM and TG-DSC analysis. XRD pattern confirmed the anatase phase with minor rutile phase having average crystallite size of 5 nm. From the FTIR spectrum, the band appeared at ~547 cm^{-1} confirmed the Ti–O–Ti stretching and also few bands of ionic liquid. UV–vis spectrum clearly reveals the blue shift due to size effect of TiO_2. The spherical surface structure and particle size (15–30 nm) have been studied in detail using TEM images. Finally, the practical applicability of the as synthesized i-TiO_2 nanoparticles is shown by using it as a photocatalyst towards the generation of H_2 through water splitting reaction and it is found to be 462 μmol $h^{-1}g^{-1}$.

Introduction

Hydrogen gas has been recognised as an alternative fuel for the next generation. Wind and solar energies are the renewable and efficient sources for hydrogen gas production. Presently there is only 5% production of the H_2 from the renewable sources and 95% of H_2 is produced from fossil fuels. Because of the high cost, renewable H_2 production is not popular as non-renewable H_2 production. Currently, global H_2 production from coal, oil and natural gas is 18, 30 and 48% respectively [1–3]. These three methods produce CO_2 as by-product, which is again hazardous to the environment. These methods are not eco-friendly and lead to the global warming and ozone layer depletion. But only 4% of H_2 is produced from the water and it is eco-friendly. Therefore it can be used as an alternative power source for laptops and vehicles [4,5]. Recently, space-shuttles and space-ships have started to use H_2 as a fuel. Scientists show much interest towards metal oxide nanoparticles (Nps) for energy related applications due to their unique properties [6–10]. Semiconductor nanomaterials achieved a significant progress towards the production of H_2 from water splitting reaction [11]. According to the available literature, the physical and chemical properties of TiO_2 can be modified by changing the particle size, surface morphology, crystalline phase etc., [12,13]. Therefore, the preparation of

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nanostructural TiO_2 of reduced crystallite size with large surface area is of very important for novel application. TiO_2 is chemically stable, green, economic and available abundantly; therefore it used widely as photocatalyst for water splitting reaction in pure, doped/modified and composite forms [14–32]. Various methods such as hydrothermal, solvothermal, sonochemical, sol-gel, chemical vapour deposition etc., are employed for the synthesis of TiO_2 nanomaterials [33,34]. Recently ionic liquids (ILs) significantly attracted the attention for the preparation of metal oxide nanomaterials due to their outstanding properties like high thermal stability, large electrochemical window, high ionic conductivity, large liquidus range, best polar solvents and vapour pressure at negligible level. In addition to these, ILs are low melting organic salts and acts as solvent for the reaction media for more number of applications. Because of these reasons, ILs are popular as designer-solvent [35]. The most attractive property of ILs for the synthesis of TiO_2 Nps is the surfactant-like nature, which inhibits the aggregation of the resultant Nps. With proper selection of cation and anion of the ILs, it is possible to tune the physical and chemical properties of the TiO_2 Nps [14]. Ionic liquids were primarily used to synthesis organic molecules. But now a days, many of the research papers have come out towards synthesis of inorganic materials using ionic liquids. Zhou et al. has reported the synthesis of TiO_2 nanocrystals using $TiCl_4$ with [BMim] [BF_4] mixture at 80 °C [36]. Dionysiou et al. have synthesized the mesoporous TiO_2 using [BMim] [PF_6] and $Ti(OBu)_4$ [37]. Macroporous TiO_2 was fabricated by the spontaneous self-assembly of Ti (i-OPr)$_4$–[TF_2N] [C_4Mim] by Zhou et al. [38]. Nakashima et al. have prepared the hollow TiO_2 microspheres using a mixture of $Ti(OBu)_4$–[PF_6] [BMim] [39]. Recently, functionalized ILs have been used to attempt the incorporation of functional groups as a part of anion or cation for specific applications [40]. At present, there is a leaning in the direction of photocatalytic water splitting into H_2 and O_2 by the usage of semiconductor oxide nanomaterials. In this report, we have used methoxy ethyl methyl imidazolium methyl sulphonate (MOEMIMS) ionic liquid as the solvent/surfactant to prepare TiO_2 Nps for photocatalytic water splitting reaction.

Experimental

Preparation of Methoxy ethyl methyl imidazolium methane sulphonate (MOEMIMS)

5.38 g of 2-Methoxyethyl methane sulphonate (32 mmol) was mixed with 2.62 g of 1-methyl imidazole (32 mmol) and the reaction mixture was heated to 60 °C for 30 h [41]. The resultant liquid was washed twice with ethyl acetate (5 mL) and dried under vacuum, the obtained liquid (MOEMIMS) was hygroscopic, transparent and was used for the preparation of TiO_2 Nps and the structure of MOEMIMS is shown in Fig. 1.

Preparation of TiO_2

5 mL MOEMIMS ionic liquid was added to 10 mL Teflon tube with constant stirring. 0.5 mL of $TiCl_4$ was added slowly to the above IL followed by the addition of 1 mL of water. The resulting mixture was stirred well until the complete removal of HCl. The obtained reaction mixture was kept in hot air oven for a day at 120 °C. Later, the autoclave was cooled naturally to room temperature. The resulting product was washed with water followed by methanol and acetonitrile to remove ILs. The resulting product named as i-TiO_2 throughout the manuscript. The obtained powder was calcined at 400 °C for 3 h to remove impurities and used for characterizations and applications.

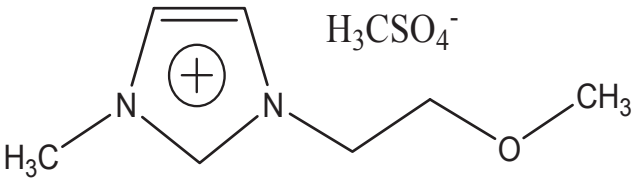

Fig. 1 – Structure of Methoxy ethyl methyl imidazolium methyl sulphonate.

Characterization

Siemens-Bruker-AXS D-5000 X-ray diffractometer operating at 40 kV, 25 mA, Cu-Kα radiation was used to get the phase and purity of the i-TiO_2 Nps. Morphology was examined by FEI Tecnai G2 S-Twin Transmission electron microscopy (TEM) operating at 200 kV. UV–Visible spectrum was recorded by Shimadzu UV-1800 UV–vis spectrophotometer and Perkin Elmer UV–Vis diffuse reflectance spectrophotometer. Stretching frequencies of the material were recorded with Bruker-alpha Fourier Transformer Infrared (FTIR) spectrophotometer. The Raman spectrum was recorded by i-Raman-plus portable Raman spectrometer. Weight loss was measured by TG-DSC technique using Seiko Instruments Inc. EXSTAR6000 TG/DSC Thermo-Gravimetric/Differential Thermal Analyzer. Evolved H_2 gas was measured by Agilent 6820 GC Chromatograph furnished with a thermal conductivity detector (TCD).

Photocatalytic hydrogen production experiments

Photocatalytic activity of ionothermally synthesized i-TiO_2 Nps was studied by determining the amount of H_2 liberated using gas chromatography at ambient temperature. Pool of water-ethanol system was used for the hydrogen production. Inner irradiation type reactor with closed gas circulating system was used for the production of hydrogen. 4 mg of i-TiO_2 Nps was dispersed in 6 mL of aqueous solution and sonicated for 20 min for complete dispersion and 2 mL of ethanol (sacrificial agent) was added. Before irradiation, the system was degased followed by argon bubbling for 15 min to remove the oxygen content. Reaction temperature was maintained at 25 °C throughout the experiment. Outer jacket of the reactor was cooled by supplying water to remove the IR radiation. 300 W xenon lamp was used as a light source for the H_2 generation. The evolved hydrogen gas was measured using gas chromatographic technique with argon as carrier gas. Using a micro syringe, the produced gas was injected at 30 min time interval to measure the amount of H_2 produced per gram.

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