Chitosan Stabilised Iron Containing Nanoparticles For Photocatalytic Hydrogen Generation

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Abstract:

Metal nonoparticles stabilized by polymers is emerging as a new class of materials having entirely new physico-chemical properties as that of bulk and atom both. Stabilizers play important role in protecting the nanoparticles and also contributes in improvising the overall surface area. Chitosan, a natural polymer is selected as a stabilizer for the synthesis of iron containing nanoparticles. These nonoparticles are thoroughly characterized by using BET-surface area, FTIR, TEM and XPS. TEM image is showing well dispersed nanofibers with average size of 13nm. XPS data supports the formation of Fe_2O_3 type structure with O1s binding energy at 534.5 eV and Fe $2P_{3/2}$ and Fe $2P_{1/2}$ binding energies at 712eV and 723.2 eV. BET Surface area value is 36.72m^2/g with pore size of 145.16 and pore volume of 0.1332 cm^3/g. This synthesized nanomaterial was evaluated for photocatalytic hydrogen generation via water splitting reaction. Iron containing nanoparticles are showing excellent photocatalytic activity with hydrogen generation yield of 55.5 mmoles $h^{-1}g^{-1}$ of photocatalyst. The nanoparticles are magnetically retrievable and hence can be separated effectively from heterogeneous system.

Keywords: metal nanoparticles; photocatalysis; hydrogen generation; water splitting

1. Introduction:

World is moving towards carbon neutral emissions and non carbon based fuels where hydrogen is promising candidate with combustion product as steam and heat. Harnessing solar energy and utilizing water as a source of hydrogen is a sustainable option for fuel generation. However photocaralytic approach of hydrogen generation often traces the importance of a semiconductor photocatalyst which mediates the reaction. Visible light active, stable semiconductor is a need of the hour. Chemical properties of materials are shape and size sensitive, as we change size from bulk to nano, properties of material changes [1]. This highlights the nanoparticle synthesis and its applications in various fields such as catalysis, photocatalysis [2], metal sensors [3] biosensors [4] and optical applications [5]. TiO_2 being more promising candidate is widely studied however, ultra violet light activity and fast electron-hole recombination reaction are the major drawbacks of it. Iron oxide being visible light active semiconductor (band gap ~2.2eV), is a probable candidate for harnessing major portion of solar radiation [ref]. Iron /Iron oxide nanoprticles synthesis by different routes and its applications mainly in the biological field are widely reported [6-7].

Nanoparticles synthesis majorly involves two things, selection of stabilizing agent and targeted size of material. Improved photocatalytic activity is observed with smaller size of nanoparticles. Nanoparticles with size below 20nm are found to be catalytically more active [8-9]. Often a support for nanoparticles synthesis plays a vital role in controlling the size of nanoparicles, separation, as well as its stabilization. Support offering less agglomeration or well separation with great stabilization is in more demand. Various supports are identified which ranges from inorganic materials such as Silica gel, fly ash, zeolite, clay to biological supports such as lignin, seaweeds, agricultural waste. Chitosan with highest chealating capacity against any natural support [10] works as an efficient binder. Chitosan is a biopolymer obtained from Chitin, N-acetylated chitin is known as chitosan (n-acetyl D-glucosamine –co-D glucosamine).

There are various reports available on iron nanopartcles, in 1940's and 1950's iron nanoparticles were synthesized by dispersing them in mercury however this method is replaced by many other methods due to mercury toxicity[11]. Reduction of iron salts and oxides is the preferred technique using wet chemical methods. The industrial process mostly involves formation of iron hydroxide and then reduction by using Hydrogen gas [12]. B. Baruwati et-al [13] reported bulk synthesis of metal doped γ-Fe_2O_3 nanoparticles at water organic interphase by microwave radiation technique with particle size between 5-10nm.These molecules are also functionalized with organic moiety. S. T. Navale et-al [7] synthesized iron nanoparticles of size around 40nm by using sol-gel method and extended its application for nitrogen dioxide sensing auto 200ºC. Polysaccharides as a template were used for synthesis of iron nanoparticles by where chitosan, starch and alginate were tested as a template [14, 15]. Where author mentions use of suitable template prevents aggregation of particles and yields stable homogeneous nanomaterials.

H. Lu (2014) [16] reported synthesis of chitosan stabilized zero valent iron nanoparticles and employed it for catalytic reduction of p-nitrophenol. Recently M. Ottonelli (2020) reported use of chitosan as a stabilizing agent for synthesis of metal nanoparticles. Here they investigated Chitosan as a shape direction agent. They further reports that size and shape of nanoparticles depends upon the type of polysaccharide selected, by comparing two type of chitosan of different origin [17]. Iryna Khamara (2019) reported synthesis of chitosan stabilized iron nanoparticles for MRI application [18]. Xiulan Weng (2013) synthesized Chitosan stabilized bimetallic Fe/Ni nanoparticles and applied for removal of amoxicillin and Cd (II) from waste water via adsorption [19]. However 68.9% and 81.3% removal was observed for amoxicillin and Cd (II) co-existance and 93.0% and 90.9% at individual level with 60mg/L as an initial concentration for 60min. Simillar studies were also carried out by Andressa Aparecida Gonçalves (2018) for removal of Nimesulide by using chitosan stabilized Fe / Ni bimetallic nanoparticles [20]. Heavy metal removal is the another area of interest where chitosan stabilized nanoparticles works effectively [21-22].

Green approach has also been attempted, J. C. Tarafdar, (2013) biosynthesized eco friendly iron nanoparticles using Aspergillus oryzae TFR9 with resulted particle size between 10 to 24.6 nm.[23]. Alovera as a stabilizing agent was reported by E Vélez et-al for synthesis of fe_2O_3 and α Fe_2O_3 by using NaOH as a precipitating agent. The nanopartcles around 100nm found effective up to 70% mercury removal from wastewater. [24]

With this background we have synthesized iron containing nanoparticles by using sodium borohydride as a typical reducing agent and chitosan as a stabilizer. The synthesized photocatalyst was employed for photocatalytic activity by using water splitting reaction and the photocatalyst was found very much active with hydrogen yield of 55.5 mmoles h^{-1} g^{-1} of photocatalyst

2. Material and Method:

2.1 Materials:

Chitosan with deacetylation degree (DD) of 95% and the molecular weight (MW) of 360 kDa was purchased from chemchito India Limited, Chennai., India, Sodium borohydride, Acetic acid, $FeSO_4.7H_2O$, Chloroplatinic acid, ethanol were procured from Merck, India Ltd. Tungsten lamps of 100, 200, and 500W were procured from Philips India Ltd, Mumbai. All reagents are AR grade and used without further purification.

2.2 Synthesis of iron nanoparticles:

3 g of chitosan flakes were dissolved in 150mL, 0.05 M nitric acid solution and stirred for 3 h. Iron solution was prepared by dissolving 9.93 gm of $FeSO_4.7H_2O$ in 333.3 mL de-ionized water and added to chitosan solution to form chitosan- iron solution. The stirring was done for 30 min in nitrogen environment. This chitosan- iron solution was added drop wise to $NaBH_4$ solution. The concentration of Sodium borohydride was kept six times higher than concentration of Iron to ensure complete reduction into size. Black precipitate formed was collected and washed by deoxygenated water to form chitosan stabilized iron containing nanoparticles

(CSINP) as published in elsewhere [25-26]. Synthesized catalyst was stored in vacuum desiccator till further use.

2.3 Characterization of Iron nanoparticles:

As-synthesized nanoparticles were subjected to various characterization techniques, specific surface area of CSINP was measured by Nitrogen adsorption/desorption at 77 K as per BET (Brunauer, Emmet and Teller) method using a micromeritics ASAP 2010 volumetric adsorption analyzer. Pore size and pore volume was carried out at Micrometics USA ASAP 2000 specific surface area analyzer. Transmission electron microscopy (TEM) of CSINP was performed on Philips TEM-CM200 with resolution of 0.23nm and voltage of 200kV. X-ray photoemission spectroscopy of powdered sample was carried out at VG Microtech ESCA 3000 instrument at a pressure of >1 _ 10_9 Torr. FTIR spectra of Chitosan and CSINP were recorded on Bruker Vertex- 70 using diffused reflectance accessory technique.

2.4 Experimental method for photocatalytic hydrogen generation:

Photocatalytic water splitting was carried out in 10mL borosilicate vial equipped with aluminum crimp cap with gas tight septum. Known amount of photocatalyst was carefully weighed and transferred to vial followed by deoxygenated water –ethanol mixture (20:1). Small amount of platinum (IV) chloride solution was added in vial. Magnetic needle of definite size was also placed in a vial. The vial was crimped with aluminum cap with help of crimper and the system is the evacuated with the aid of vacuum pump in order to remove any oxygen present in the vial. The vial is then placed in photocatalytic reaction chamber which is equipped stirrer and with two tungsten filament lamp of each capacity of 200W. Vial is allowed to illuminate for definite time under constant stirring.

Generated hydrogen is the evaluated on gas chromatograph (Perkin Elmer Gas Chromatograph Clarus 500) equipped with thermal conductivity detector and molecular sieve 5A column. Nitrogen (99.99%) was used as carrier gas.

3. Results and discussion

3.1 Characterization of Chitosan stabilized Iron containing nanoparticles (CSINP):

X-ray Photo emission Spectroscopy: XPS Data reveals presence of Iron, Oxygen, Carbon and Nitrogen elements in the synthesized photocatalyst. Fig: 1 shows XPS spectra for Iron nanoparticles (CSINP), Fe2P, O1s and N1s and C1s. In case of Fe2p spectra characteristic binding energies for Fe $2P_{3/2}$ and Fe $2P_{1/2}$ are at 712eV and 723.2 eV the values are in good agreement with Fe_2O_3 indicating presence of Fe $^{3+}$ state of iron [27]. The slight shift in the binding energies may be due to presence of chitosan substrate. N1s spectra shows presence of two strong peaks around 402.1 and 402.9 eV. Specific peak for $–NH_2$ group around 398eV was not seen which indicates chelation between Nitrogen from amino group and Iron atom (Fe-NH_2) [28]. O1s spectra shows peak at 534.5 eV which indicated presence of lattice oxygen [29]. C1s spectra shows presence of only one peak at 288.1eV which may be due to presence of C=O group.

Other characterizations of CSINP: Transmission electron microscopic image shows formation of nanofibers of average diameter 13.02nm. BET Surface Area for Iron Nanoparticles was found to be 36.7283 (m^2/g), pore size 145.1610 (Å) and pore volume 0.133288 (cm^3/g). FTIR Spectra shows shift in peak around 691.36cm^{-1} which may be due to Fe-NH bonding, in case of for synthesized photocatalyst [25].

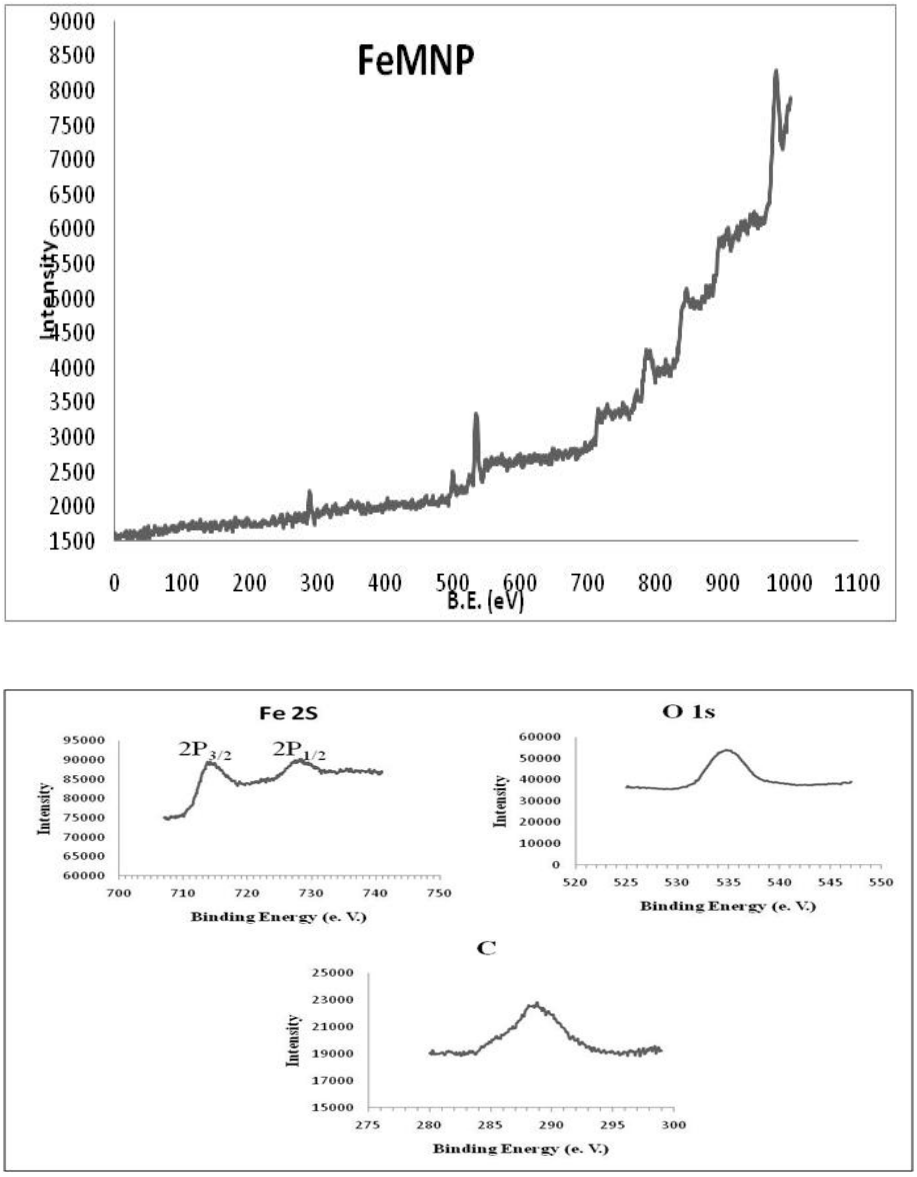

Fig. 1: XPS spectra of Chitosan stabilized Iron containing nanoparticles.

3.2 Photocatalytic Hydrogen generation by using Chitosan stabilized Iron containing nanoparticles:

As synthesized photocatalyst was subjected to photocatalytic hydrogen generation by using water-ethanol system and studied for two operational parameters.

3.2.1 Effect of photocatalyst dose:

Photocatalyst dose was varied from 1to 5mg and subjected for photocatalytic water splitting reaction keeping illumination intensity 400W and time 2h constant. Fig.2 shows that 1mg yields highest hydrogen yield that of 55.5mmoles $h^{-1}g^{-1}$ of photocatalyst of dose 1mg followed by 25.250, 11.78 and 4.26 and 4 mmoles $h^{-1}g^{-1}$ for 2,3,4 and 5 mg. As we increase dose from 1to 3 mg there is gradual decrease in hydrogen yield however further increase in photocatalyst dose yield remains almost constant. This may be due to the fact that increase in the photocatalyst dose decreases the opacity of solution which in turn decreases penetration of light in the reaction mixture. Therefore optimum dose for CSINP is 1mg for 10mL of water-ethanol solution under given sets of conditions.

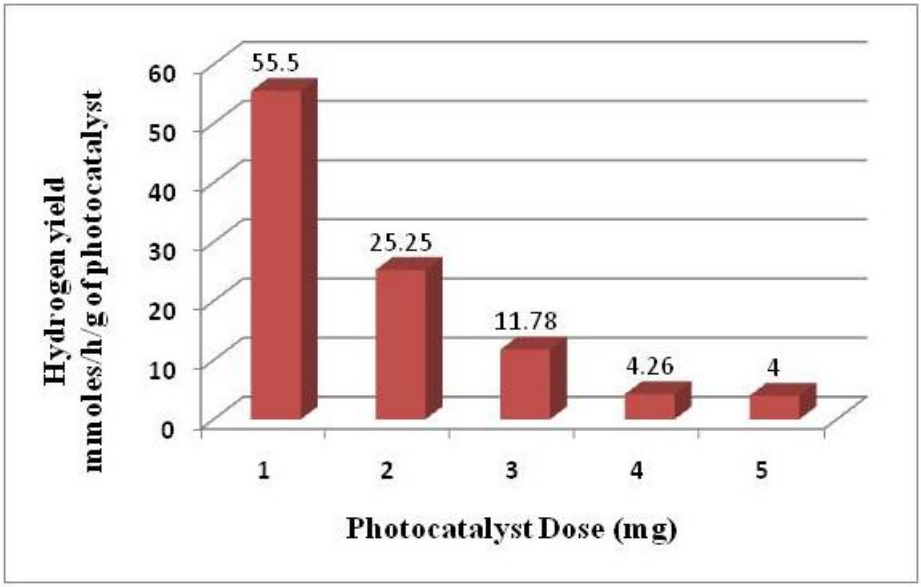

Fig.2: Effect of photocatalytic dose on hydrogen yield via water splitting reaction.

3.2.2 Effect of illumination time:

Effect of illumination time on photocatalytic hydrogen generation was studied by increasing illumination time from 1-4h. Fig.3 shows that with increase in illumination time from 1 to 2h there is increase in hydrogen yield from 29.20 to 55.50 mmoles $h^{-1}g^{-1}$ however further increase in illumination time there is marginal increase in hydrogen yield and then yield remains almost constant i.e. hydrogen yield 54.57 and 55.18 mmoles $h^{-1}g^{-1}$ of photocatalyst for 3 and 4h respectively. This is attributed to exhaustion of sacrificial donor.

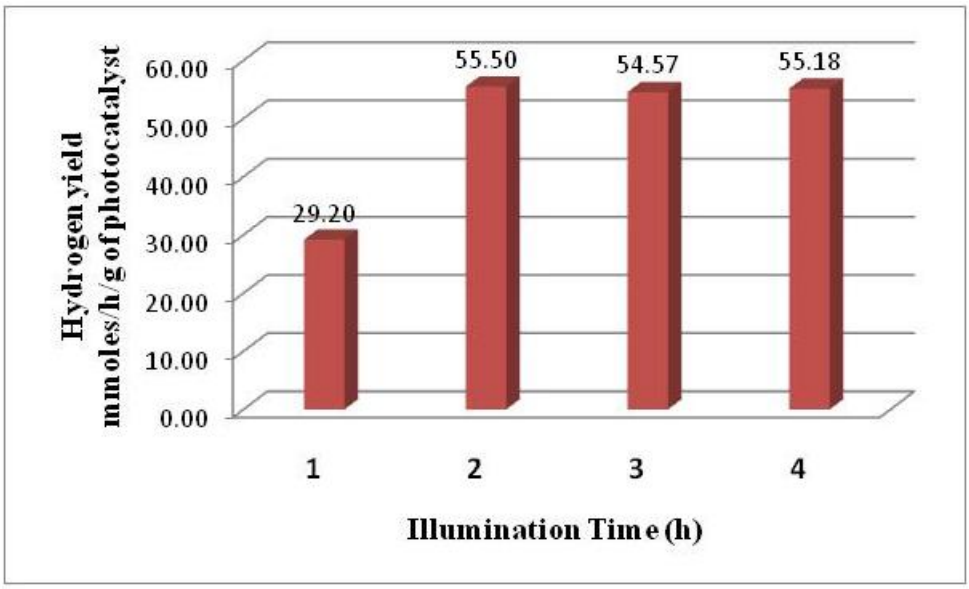

Fig.3: Effect of illumination time on hydrogen yield via water splitting reaction.

3.3 Possible mechanism:

XPS data supports the presence of Fe_2O_3 type nanoparticles therefore possible mechanism as depicted in Fig.4. may be as follows:

- Fe_2O_3 being visibly active will absorb light in visible region from tungsten filament lamp. Absorption of light leads to excitation of electrons from valence band to conduction band.

- Co-catalyst Pt (IV) chloride in the form of Pt may get photodeposited on the surface of nano Fe_2O_3 in the due course of time and effectively separate electron from conduction band [30].
- This Pt may provide site for efficient photoreduction of water into hydrogen.
- Ethanol as a hole scavenger continues the chain of electron from valence band to conduction band and the further towards Pt.
- Exceptionally high hydrogen yield may be attributed to nanosize of synthesized photocatalyst.

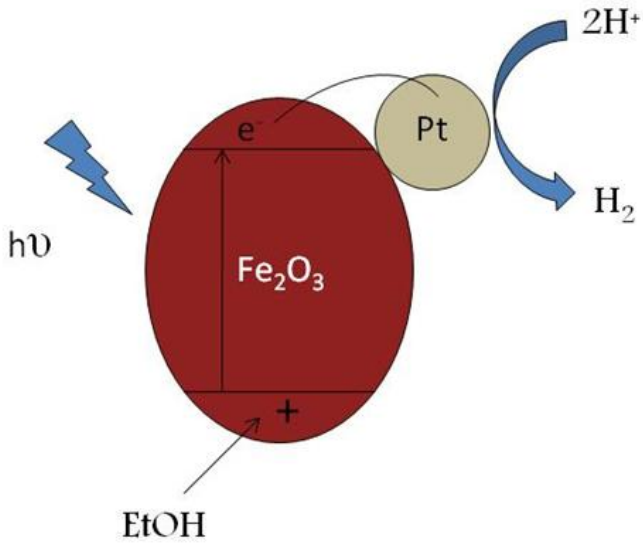

Fig .4 Possible mechanism for hydrogen generation by CSIN using water splitting reaction.

4. Conclusion:

Iron containing nanoparticles were synthesized and stabilized by using biopolymer chitosan. The synthesized photocatalyst was characterized in detail with characterization tools such as BET-SA, pore size, pore volume, TEM, XPS and FTIR. TEM image reveals the presence of nice nanofibers of diameter 13.02nm. FTIR data gives evidence for presence of Fe-NH_2 interaction indicating stabilization of Fe Nanoparticles by chitosan

framework. XPS data confirms the presence of Fe in Fe^{3+} state as in Fe_2O_3. Presence of Nitrogen and Carbon was also seen in XPS spectra. Presence of nitrogen confirms chelation of Fe with $–NH_2$ group of chitosan. Synthesized nanoparticles were evaluated for photocatalytic hydrogen generation by using water splitting reaction under visible radiations. Excellent photocatalytic activity was shown by nanoparticles with hydrogen yield of about 55.5mmoles $h^{-1}g^{-1}$ of photocatalyst under optimum photocatalyst dose of 1 mg and illumination time of 2h. Synthesized photocatalyst is also magnetically active and can be easily separated from water by using magnetic retriever. Hence isolation and reuse is also possible.

5. Acknowledgement:

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Conflict of interest:

There is no conflict of interest.

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