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Photocatalytic water splitting is one of the most important renewable paths and a reliable hydrogen production system. In most successful molecular and supramolecular biomimetic hydrogen production methods, a photosensitizer and a catalyst were constructed where the photoexcited electron in the photosensitizer is transferred either inter- or intramolecularly to the catalytic centre. Similar to supramolecular complexes in a photocatalytic hydrogen production scheme, here we develop a redox system that contains Ti^{3+}/Ti^{2+} reduced states in TiO₂ which act as both visible light harvesting component as well as the catalytic site for the catalytic hydrogen production with visible-near infrared photons. The Ti^{3+}/Ti^{2+} states in TiO₂ produce hydrogen from pure water with a solar-to-hydrogen energy conversion efficiency of 0.89% and a quantum yield of 43% at 655 nm. The mechanism of hydrogen production by Ti^{3+}/Ti^{2+} reduced states in TiO₂ by the formation of an AlOOH layer surrounding the anatase and rutile particles. Once Ti^{3+} and Ti^{2+} states are generated, these states are continuously self-generated via absorption of visible-near infrared radiations where hydrogen is produced by the transfer of electrons from Ti^{3+}/Ti^{2+} to H^+ .

Introduction

The efficient combination of water and solar energy has an enormous capacity to fulfill the demands for energy by producing hydrogen fuel from photolysis of water. In photolysis, water is split into hydrogen and oxygen by using semiconductor photocatalysts in the presence of sunlight.¹⁻³ Low charge carrier mobility and narrow absorption range are the common limiting factors for efficient photocells.^{4, 5} TiO₂, Fe₂O₃, SnO₂, CdS and ZnO are the most common semiconductor materials used as photocatalysts.⁶⁻⁹ TiO₂ is the commonly used material in photocatalytic degradations, water splitting and environmental pollution removal owing to its high stability, low cost, and strong bonding.^{10, 11} Due to the high band gap energy of the TiO₂ which requires UV light to excite electrons from the valence band, photocatalytic water splitting by TiO₂ has an inferior solar to hydrogen quantum efficiency, as the solar spectrum

contains only 5% UV radiation. Additionally, rapid electron-hole pair recombination in TiO₂ is another common problem that limits the photocatalytic activity. In order to overcome these problems, remedies such as metal loading, metal ion doping, dye sensitization, composite semiconductors, anion doping and metal and metal ion implantation have been tested.¹²⁻¹⁸ During the past few decades, much effort has been devoted to making visible light active TiO₂ for better optical absorption through metal or non-metal doping. For example, a series of metal and non-metal elements have been introduced to partially replace titanium and oxygen atoms from the TiO₂ lattice.^{19, 20} All these efforts have enabled the absorption of TiO₂ from the visible light region and improved their photocatalytic activities marginally.

Chemical vapor deposition, high energy particle (laser, electron or Ar^+) bombardment and hydrogenation of TiO_2 have been employed as an effective approach in shifting the bandgap of TiO_2 to around 1.5 eV with an optical onset around 1.0 eV and it has triggered worldwide research interest in black TiO_2 nanomaterial.^{21, 22} Indeed, it is well known that heating TiO_2 under vacuum or in a reducing atmosphere leads to color changes where white color TiO_2 turns into yellow, blue or black due to the presence of Ti^{3+} or/and oxygen vacancies.²³⁻²⁶ The vacancy states localize at 0.75 to 1.18 eV below the conduction band minimum of the rutile phase of TiO_2 which is lower than the redox potential for hydrogen evolution.^{27, 28} Additionally, these reduced species are highly

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unstable and easily oxidized by air or dissolved oxygen in water, which limits their practical application.²⁹⁻³¹ Defective TiO₂ are containing e.g. oxygen vacancies, titanium interstitials can be considered as a class of new materials which are interesting for photocatalysis.^{21, 32, 33} High-energy facets of defective titanium dioxide nanomaterials are known catalytic sites for efficient oxygen reduction as well as proton reduction.^{29, 34, 35} Here in this report, we investigated the generation of reduced ${\rm TiO}_2$ with highly stable ${\rm Ti}^{3+}$ and ${\rm Ti}^{2+}$ states and their catalytic proton reduction reaction for the generation of hydrogen in the presence of water and visible/infrared (IR) photons. A remarkable 0.89% solar-tohydrogen conversion efficiency noted with the reduced TiO₂ could be assigned to the Ti^{3+}/Ti^{2+} states in TiO_2 in which they act as both light harvesting and catalytic sites for hydrogen production resembling to the proton reduction process in supramolecular devices.

Results and discussion

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Characterization of the catalyst: The photocatalyst (hereafter I- TiO_2/AI for the initial TiO_2 catalyst) was prepared by spray pyrolysis of a mixture containing a suspension of Degussa P25 TiO₂ in 1% I₂ (w/w%), 10% methanol in water and acetic acid on to the precleaned AI substrate at elevated temperature (see Supplementary Information for details on synthesis of the photocatalyst). During sintering process of the catalyst at 450°C, slightly blue colored reduced TiO₂ nanoparticles were formed due to reducing conditions prevailed during pyrolysis of TiO₂ on the heated Al surface (named I-TiO₂/Al in the following for the initial catalyst). As shown in Figure 1a, a dark blue color is formed once the I-TiO₂/Al catalyst in water is illuminated with solar radiation. The appearance in blue color in TiO₂ is due to the formation of reduced states in the TiO₂ lattice (hereafter R-TiO₂/Al for the reduced TiO₂ catalyst). Generally, the reduced states in TiO₂ are highly unstable and tend to oxidize rapidly under atmospheric conditions.³⁶ However the reduced blue colored TiO₂ nanoparticles formed on the Al surface was found to be highly stable in air.



Figure 1:(a) photograph of (I) I-TiO₂/Al catalyst, (II) and (III) I-TiO₂/Al catalyst in water after 30 and 60 minutes irradiation with solar simulator respectively. (b) The UV-Vis DRS spectrum of I-TiO₂/Al (green), and I-TiO₂/Al catalyst after 30 (blue) and 60 (purple) minutes irradiation with solar simulator respectively.

The blue color of TiO_2 arises upon illumination (Figure 1a-ii) and the blue color intensified upon further illumination and a very dark blue color appeared after 1 hour illumination (Figure 1a-iii). These

reduced states of titanium play a significant role in enhancing the light harvesting capability of TiO_2 which is evident by the UV-Vis DRS (diffuse reflectance spectra) of the initial (I-TiO₂/AI) and the reduced $TiO_2(R-TiO_2/AI)$ shown in Figure 1b, I-TiO₂/AI absorbs light below 400nm while R-TiO₂/AI catalyst absorbs light in the whole spectrum. As shown in Figure 1b, the bandgap of R-TiO₂/AI (3.25 eV) is slightly higher than that of I-TiO₂/AI and P-25 TiO₂ (3.10eV) and as a result, the blue color formation cannot be assigned to band gap narrowing. On the other hand, it is known that the formation of reduced states such as Ti^{3+}/Ti^{2+} below the conduction band in the TiO₂ lattice is responsible for the blue color and it can be assumed that the blue color in R-TiO₂/AI is due to formation of Ti^{3+}/Ti^{2+} in TiO₂.^{37, 38}



Figure 2: Ti 2P X-ray photoelectron spectra of: (a) surface region and (b) bulk of I-TiO₂/AI, (c) surface and (d) bulk of R-TiO₂/AI (60 minutes irradiated sample).

The origin of visible-NIR absorption of reduced TiO₂ can be explained as follows. Once Ti³⁺ and Ti²⁺ states are generated in the TiO₂ lattice, oxygen vacancies will form to maintain the electrostatic charge balance.^{32, 39, 40} It is known that the mid-gap energy level originated from oxygen vacancies is located at 0.75–1.18 eV below the conduction band of TiO₂ while the neighboring Ti atoms with the oxygen vacancy site form shallow donor states below the conduction band originated from Ti 3d states.^{28, 41} The electrons in these mid-gap states and shallow donor states get excited to the conduction band (CB) by the absorption of visible-NIR light, yielding a blue color in the reduced TiO₂. Especially, the absorption observed at 450–900 nm region corresponds to 1.37–2.75 eV and such a shoulder absorption is characteristic of TiO₂ with mid-gap impurity states.^{21, 42}

The presence of lower oxidation states of Ti³⁺, Ti²⁺ in the reduced TiO₂ catalyst was confirmed by X-ray photoelectron spectroscopy (XPS) measurements. The surface XP spectra and depth profiles of I-TiO₂/AI and R-TiO₂/AI are shown in Figure 2a,b and 2c,d respectively. In the case of the surface spectrum of the I-TiO₂/AI (Figure 2a), a peak of Ti2p_{3/2} is observed at 458.3, which corresponds to the Ti⁴⁺ state in TiO₂.^{43, 44} However in the surface

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spectrum of the R-TiO₂/Al catalyst, the corresponding peak is shifted to 457.9eV (Figure 2c), which may indicate the formation of oxygen vacancies in TiO₂ resulting in migration of electrons bound to oxygen and titanium ions towards oxygen vacancies.45-47 In contrast to the surface of R-TiO₂/Al, which only consists of Ti^{4+} species, a depth profile of $R-TiO_2/AI$ catalyst shows additional contribution of Ti³⁺(456.4 eV) and Ti²⁺(454.6 eV) oxidation states in the Ti 2p spectrum (Figure 2d).⁴⁸ Detailed quantification of the Ti 2p spectrum shows 51.6 at% of Ti⁴⁺, 24.3 at% of Ti³⁺ and 24.1 at% of Ti^{2+} . Considering that neither Ti^{3+} nor Ti^{2+} species were detected in the as-prepared sample after Ar pre-sputtering (Figure 2b), the reduction of TiO₂ in the conditions of the XPS experiment can be excluded. As mentioned earlier, a highly stable blue color in reduced TiO₂ could be assigned to the formation of stabilized Ti³⁺ and Ti²⁺ states in TiO₂ and the blue color changed only slightly (5-10% decrease in optical absorption of R-TiO₂/Al catalyst at 800 nm was noted) when kept in air for at least one year. However, the observation that the outermost layer of TiO₂ shows no peaks corresponding to reduced titanium is ruling out the presence of reduced states of Ti on the surface of the sample itself.



Figure 3: XRD patterns of $I-TiO_2/AI$ (green), and after irradiation of $I-TiO_2/AI$ catalyst for 24 (blue) and 48 (purple) hours respectively by the solar simulator in pH controlled at 5.5 aqueous solutions.

Existence of stabilized lower oxidation states which function as Vis-IR light harvesting centers such as Ti^{3+} and Ti^{2+} states in TiO_2 is one of the imperative requirements for the prolonged and enhanced Vis-IR photocatlytic activity. The stability of these reduced states could be due to the formation of a thin layer of aluminium hydroxide covering the TiO_2 nanoparticles leading to strong Al-O-Ti bonds.⁴⁹ In the following section, we explain how the formation of these Al-O-Ti type bonds and the stabilisation of Ti^{3+} states could happen. XRD patterns of the initial and the tested TiO_2/AI samples after 24 and 48 hours of hydrogen production reaction under pH controlled condition are shown in Figure 3. The XRD pattern for the I-TiO₂/AI sample correspondto both anatase and rutile TiO_2 phase. The diffraction peaks at 20 at 25.3, 38.6, 48.0, 55.3 can be indexed to the (101), (112), (200), and (211) crystal plane of anatase TiO_2 , respectively while peaks at 27.4, 44.5 and

55.1 can be indexed to the (110), (210) and (211) crystal plane of rutile TiO₂.⁵⁰ However, in the reacted sample, in addition to anatase and rutile diffraction patterns, formation of AlOOH is evident by the appearance of a weak diffraction peak at 20 at 14.4 (See Figure 3), corresponding to the Boehmite (γ -AlOOH) (020) reflection. As shown in Figure 3, the peak intensity of γ -AlOOH remains the same even after 48 hours of reaction suggesting that Al is not consumed continuously under pH controlled reaction medium at pH of 6.0.

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As shown in Figure 4a,b, AlOOH is found within the gaps of TiO₂ particles, as well as on top of the TiO₂ particles and in between the Al layer and the TiO₂ particles. This is caused by photocorrosion of Al to form AlOOH and its subsequent diffusion into the TiO₂ layer. As a result, the TiO₂ nanoparticles are covered by AlOOH. To analyze the oxidation states of Ti locally, electron enrgy loss spectroscopy (EELS) spectrum imaging was taken and shown in Figure 4c,d. By multivariate statistical analysis the chemical shift of the Ti-L₃ edge (see Fig. 4d) was evaluated.⁵¹ As shown in Fig. 4c, with respect to the Ti-L₃ edge position inside the particle, the Ti-L₃ edge on the surface of the particle shows a chemical shift towards lower energy loss. Such chemical shift is expected as Ti⁴⁺ is reduced to Ti^{3+, 52} Hence, we suggest that the presence of a AlOOH layer on the R-TiO₂/Al nanoparticles stabilizes the oxygen deficient Ti³⁺ species on the surface layer through the formation of stable Al-O bonds.



Figure 4 (a) Cross-sectional SEM and (b) STEM images of TiO₂ on Al after reaction (R-TiO₂/Al catalyst). A protective Pt layer is deposited on top of the specimen surface during the focused ion beam preparation. EDS elemental maps of Al, Ti, and O shows the distribution of AlOOH within the gaps of TiO₂ particles, as well as on top of the Al substrate and the TiO₂ particles. (c) EELS spectrum imaging of a TiO₂ particle with surrounding AlOOH and the map of the Ti-I₂ edge position showing reduction of Ti on the TiO₂ surface with (d) sample spectra from the bulk and the surface of TiO₂.

To gain further insight into the electronic structures, Mott–Schottky plots were collected at 1 kHz in the light and dark conditions and shown in Figure 5a. As expected, n-type semiconductor behavior is observed for TiO₂ and the flat band (FB) potential of I-TiO₂/Al has shifted negatively compared to the reported FB potential of TiO₂ (-0.1 eV)⁵³ while further negative shift in FB potential is noted for R-TiO₂/Al. Such a negative shift in FB has been reported for similar systems due to generation of extra charges (higher donor state densities N_d) in TiO₂ due to doping.^{13, 54-56} Mott-Schottky plots indicate comparatively a shallower slope in the R-TiO₂/Al catalyst

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than that of I-TiO₂/Al suggesting an increase of donor density due to generation of reduced states in R-TiO₂/Al catalyst. Interestingly, donor density of R-TiO₂/Al catalyst increases under visible light irradiation compared to dark condition indicating generation of extra charges under visible light. Calculated carrier densities of I-TiO₂/AI (dark), R-TiO₂/AI (dark) and R-TiO₂/AI (light) are 8.06 X 10²⁵ cm⁻³, 1.86 X 10^{26} cm⁻³ and 2.06 X 10^{26} cm⁻³ respectively from their corresponding slopes using $N_d = [2/e_0 \mathcal{E} \mathcal{E}_0]/[d(1/C^2)/dV]$, where the relative permittivity $\mathcal{E} = 170, \mathcal{E}_0$ is the permittivity in the vacuum, e is the elementary charge, C is the capacitance, and V is the potential from the Mott-Schottky plot .57 The observed N_d for P25-TiO₂ on Al substrate is comparatively higher than that of bare P25 TiO_2 (N_d, 1.11 X 10^{21} cm⁻³) ⁵⁸ which also indicates the formation of highly charged states in TiO₂. Hence, the increase in charge-carrier density in R-TiO₂/AI than that of the I-TiO₂/AI leads to an enhanced charge transport within the electrode. Additionally, the upward shift of Fermi level due to accumulation of charges may further facilitate the charge transfer kinetics at the interface. It should be noted that although the absolute donor density values calculated from a flatelectrode model may not be accurate, it provides a gualitative comparison of the slopes, considering the intact morphology and phase upon reduction.

(Figure 5b). The hydrogen production rate shown in Figure 5c is for the optimized catalyst (2µm thick TiO₂ film on Al substrate sintered at 450°C for 2hrs under air)under 1.5 AM one sun condition (250W Xenon lamp). For the same catalyst, no hydrogen formation was observed under dark conditions. Also, no hydrogen was observed either with Al substrate alone or TiO₂ alone under the same irradiation conditions, confirming light initiated hydrogen production in the R-TiO₂/Al catalyst. Hydrogen yields shown in Figure 5d are for the R-TiO₂/Al catalyst with a 150W halogen lamp light source (emits photons in the 500 – 900 nm range, 50 mW/cm²) and a 250W Xenon lamp light source (emits photons in the 300 -900 nm range, 100 mW/cm²). The normalized hydrogen yield against the light intensity indicated that the normalized hydrogen yield under halogen lamp is roughly 1.5 times higher than that of the Xenon lamp, a clear evidence for an enhanced visible light activity of the R-TiO₂/Al catalyst. Furthermore, the IPCE result of R-TiO₂/Al catalyst shown in Figure 6a has a broad response from 300-1000 nm region in the solar spectrum justifying the visible response and the enhanced charge carrier generation of the R-TiO₂/Al catalyst. On the other hand, before activation, the initial I-TiO₂/AI catalyst having the same TiO₂ thickness as the R-TiO₂/Al catalyst, exhibits weak response in the IPCE spectrum.





Figure 5: (a) Mott-Schottky plots of I-TiO₂/AI (dark, green), R-TiO₂/AI (dark, purple) and R-TiO₂/AI (light, blue) obtained in 0.5M Na₂SO₄ solution at pH 5.5. (b) image shows the formation of hydrogen on the reduced TiO₂ side of the R-TiO₂/AI catalyst, (c) hydrogen yields with R-TiO₂/AI catalyst, TiO₂ powder, AI plate and AI powder under irradiation with Xe lamp under AM1.5G and (d) hydrogen yield of the R-TiO₂/AI catalyst with Xe lamp (100 mW/cm², 300-900 nm region illumination), halogen lamp (50 mW/cm²500-900 nm region illumination).

Photocatalytic activity: Formation of highly stable reduced states is important in Vis-NIR active photocatalyst and it is known that reduced states of titanium play a significant role in the photocatalytic activity.^{38, 59-61} When the TiO₂/Al catalyst in pure water at neutral pH is exposed to solar radiation, the generation of hydrogen bubbles on the TiO₂ side is observed within few seconds

Figure 6: (a) IPCE spectra of R-TiO₂/Al and I-TiO₂/Al, (b) Transient photocurrent density of R-TiO₂/AL and I-TiO₂/Al over time without any external bias potential. The illumination was carried out with the halogen lamp (150 W) illumination (λ > 420 nm) and (c) hydrogen yield with time for R-TiO₂/Al catalyst under Xe simulated sunlight(AM 1.5G).

Similarly, as shown in Figure 6b, the transient photocurrent density of the R-TiO₂/Al catalyst is ~90 μ Acm⁻², which is much higher than that of the initial I-TiO₂/Al catalyst (10 μ A cm⁻²) under Vis-IR photons. The improved photocurrent density in the R-TiO₂/Al catalyst than that of I-TiO₂/Al catalyst indicates the production of greater number of excited electrons by Vis-IR light in the R-TiO₂/Al catalyst than that of I-TiO₂/Al catalyst. The enhanced photocurrent density in R-TiO₂/Al is mainly due to presence of a large number of

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 $Ti^{2+}/^{3+}$ states in R-TiO₂/AI that enables absorption of Vis-IR light while the TiO₂/AI contains comparatively a small number of Ti²⁺/³⁺ states such that the response to Vis-IR light is weak in the TiO₂/AI. The enhanced photocurrent density in R-TiO₂/AI indicates more electrons are produced and participate in the proton reduction reaction, which agrees well with the hydrogen yield of the catalysts. Importantly, the higher dark current observed for R-TiO₂/AI in Figure 6b also could be due to trapped electrons. As explained by XPS and EELS results, the origin of the visible light response of the R-TiO₂/AI catalyst is due to presence of Ti³⁺ and Ti²⁺ states and oxygen vacancies.

The photocatalytic activity of TiO₂/Al catalyst was optimized by the amount of TiO₂ on the Al sheet, pH of the reaction solution, sintering temperature and different light sources. Figure 6c shows the time variation of the hydrogen yield for the optimized catalyst $(TiO_2 - 3 mg/cm^2 \text{ of AI sheet, sintering temperature at 450°C and$ reaction solution pH of 6.0). Under the optimum reaction conditions, an apparent quantum yield of over 43% at 650 nm and an unprecedented solar-to-hydrogen (STH) conversion efficiency of ~0.89% were obtained under simulated 100 mW/cm² and AM 1.5G sunlight irradiation for the R-TiO₂/Al catalyst in pure water at neutral pH. The STH reported in this investigation with the R-TiO₂/Al catalyst with pure water without any external bias is one of the highest active visible light active photocatalysts for hydrogen production. It should be noted that during hydrogen production reaction, an increase in solution pH was observed resulting in decreasing the hydrogen generation rates which is contrary to the behavior of a normal semiconductor based photocatalytic system. The reported enahnced catalytic acitivity of a semiconductor based system with the solution pH value has been attribued to the negative shift in the FB potential of the semiconductor with the increase of the pH value. However, in the case of TiO₂/Al based photocatalytic system, the formation of AlOOH was noted under pH controlled reaction (pH of ~6) and by EELS spectroscopy, it was demonstrated that the presence of a AlOOH layer on the R-TiO₂/Al nanoparticles stabilizes the oxygen deficient Ti³⁺ species and has no net negaive effect on the photocatalytic activity. Despite that, as the pH of the reaction medicum increased, more AlOOH can be formed which can be diffused and covered the top of the TiO₂ particles hindering the photocatalytic activity and hence hydrogen yield. However, no noticeable decrease in hydrogen yield and hence a steady hydrogen production rate was obtained under pH controlled conditions when tested for 72 hours. On the other hand, one could argue that the hydrogen may possibly be produced by the aluminum-water reaction by scarifying the metallic AI.⁶² As we have noticed Al oxidation leading to the formation of AlOOH (Figure 3 and 4), the contribution to the hydrogen yield from Al-water reaction cannot be excluded, while the catalytic hydrogen production nature of the R-TiO₂/Al system explained in the following section justifies the

proposed catalytic mechanism. However, we believe further investigation of the reaction mechanism is imperative for a clear and definitive reaction mechanism.

For investigation of catalytic nature of the R-TiO₂/Al catalyst, the TiO₂ powder was deposited on 0.1 m² area AI foil and hydrogen yield was measured under the standard solar light as explained in experimental section. Under this experimental condition, a the constant hydrogen yield of ~60 ml/hr was observed for 10 hours and thereby the slow decrease in hydrogen yield was noted which could be due to blocking of active sites of TiO₂ by AlOOH. However, it was noticed that the hydrogen production was not completely ceased even after 48 hours of reaction. Hence, the system was reactivated after 10 hours of reaction by sintering of the R-TiO₂/AI catalyst at 400°C and hydrogen production was tested and the was repeated for roughly forty procedure times (thermodynamically Al³⁺ cannot be reduced to metallic Al by sintering at 400°C). The measured total hydrogen yield after forty cycles of reactions was ~ 24.0 L while the calculated theoretical hydrogen yield from Al-water reaction was found to be 6.7 L (details are given in SI) which gives supportive evidence for the catalytic nature of R-TiO₂/Al catalyst.

Based on the characterization properties and photocatalytic behavior of R-TiO₂/Al, the mechanism involved in the production of hydrogen on the R-TiO₂/Al catalyst is schematically illustrated in Figure 7. As an initial step, Ti^{3+} states were formed in TiO_2 by thermal as well as photochemical reaction (reaction 1). Once reduced, $Al^{3+}_{(Al)}-0-Ti^{3+}_{(TiO_{2-x})} \text{is formed at the surface of TiO}_2$ particles, and undergoes further reduction to form $Al_{(Al)}^{3+} - 0 Ti^{2+}_{(TiO_{2-v})}$ (reaction 2) as reduced $Al^{3+}_{(Al)} - 0 - Ti^{3+}_{(TiO_{2-v})}$ states with oxygen vacancy can harvest visible light efficiently. These photogenerated $Al^{3+}_{(Al)}-0-Ti^{2+}_{(TiO_{2-\kappa})} \ \ \, \text{species} \ \ \, \text{in} \ \ \, \text{TiO}_2 \ \ \, \text{can}$ efficiently react with \boldsymbol{H}^{*} to generate \boldsymbol{H}_{2} as the redox potential of Ti^{3+}/Ti^{2+} is -0.37 V with the oxidization of $Al^{3+}_{(Al)} - 0 - Ti^{2+}_{(Ti0_{2-x})}$ to form ${\rm Al}^{3+}_{(Al)} - 0 - {\rm Ti}^{3+}_{({\rm Ti}0_{2-\nu})}$ state (reaction 3) and the reaction cycle will be continued by harnessing the visible-IR photons by the $Al_{(Al)}^{3+} - 0 - Ti_{(TiO_{2-x})}^{3+}$ states. Due to the cyclic nature of the process, continuous hydrogen production was observed up to 72 hours reaction in the presence of Vis-IR light. The photogenerated holes can recombine with the reduced titanium species as well as can react with adsorbed OH or directly with water to produce OH radicals.^{63, 64} As formation of oxygen is not observed during hydrogen production reaction, a detailed mechanism should be investigated in order to fully understand the reaction mechanism. The cyclic catalytic process described in this investigation is similar to molecular and supramolecular bio-mimetic hydrogen production methods where a photosensitizer and a catalyst were constructed in which a photoexcited electron in the photosensitizer is transferred either inter- or intra-molecularly to the catalytic centre.



Figure 7: Schematic diagram of the prososed reaction mechansim.

Formation of reduced states of TiO₂ can take place according to:

$$Al_{(Al)}^{3+} - 0 - Ti_{(TiO_2)}^{4+} \xrightarrow{hv}{\rightarrow} Al_{(Al)}^{3+} - 0 - Ti_{(TiO_{2-x})}^{3+} + h^{+}$$
(1)

 $\label{eq:reduction} \mbox{Reduction of } Al^{3+}_{(Al)} - 0 - Ti^{3+}_{(TiO_{2-x})} \text{,}$

$$Al_{(Al)}^{3+} - 0 - Ti_{(TiO_{2-x})}^{3+} \stackrel{hv}{\rightarrow} Al_{(Al)}^{3+} - 0 - Ti_{(TiO_{2-x})}^{2+} + h^{+}$$
 (2)

Photocatalytic reaction:

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$$\begin{aligned} Al_{(Al)}^{3+} &= 0 - Ti_{(TiO_{2-x})}^{2+} + 2H_2O \xrightarrow{h\nu} Al_{(Al)}^{3+} - 0 - Ti_{(TiO_{2-x})}^{3+} + H_2 \\ &+ 2OH^- \qquad (3) \end{aligned}$$

$$h^+ + OH^- \to OH^o \qquad (4) \\ h^+ + Al \to Al_{(Al)}^{3+} \qquad (5) \end{aligned}$$

Conclusions

Air stable, highly reduced Ti^{3+}/Ti^{2+} states can be formed in TiO_2/AI catalyst and stability is owing to the passivation of Ti^{3+}/Ti^{2+} states by a thin AlOOH layer. These reduced Ti^{3+}/Ti^{2+} states in TiO_2/AI catalyst harvest solar energy efficiently producing hydrogen from pure water at neutral pH values. The observed long term stable hydrogen production was due to continuous self-generation of Ti^{3+} and Ti^{2+} states via absorption of visible-NIR radiations by the TiO_2/AI catalyst. The observed remarkable STH conversion efficiency is one of the highest reported STH efficiencies and the photocatalytic

system describes here is resemblance to that of a supramolecular photoctalytic hydrogen production scheme.

Experimental

Preparation of the catalyst. For the preparation of reduced TiO₂, a desired amount (3 mg of TiO₂ per 1cm² of substrate) of Degussa P25 TiO₂ was suspended in solution containing 1 w/w% l₂, 10% methanol in water and acetic acid. The suspension was sonicated for 30 minutes and spray pyrolysed on cleaned AI substrate. Prior to TiO₂ deposition, an AI foil was cut into samples measuring 50 mm × 100 mm and the surface was cleaned by electropolishing in 10% phosphoric acid electrolyte for 5 minutes. Finally, it was sintered at 450°C for 3 hours at a heating rate of 20°C/min and cooling rate of 5°C/min and finally cooled to room temperature in the furnace.

Characterization of the catalyst: The crystal structure of the various phases were studied using a SeifertX-ray diffractometer with Cobalt Kα (λ = 1.78897×10⁻¹⁰m) radiation. SEM measurements were done (Modular Cross Beam workstation or Gemini from Zeiss) to get morphological information. Scanning transmission electron microscopy (STEM) analyses were carried out on a FEI Titan Themis microscope operated at 300 kV using an aberration-corrected probe with a convergence semi-angle of 24 mrad and ~1 Å probe size. The high-angle annular dark field (HAADF) detector collect electrons with scattering angles of 73 - 352 mrad to form atomic weight contrast images. Electron energy loss spectroscopy (EELS) spectrum imaging was acquired using a Gatan Quantum ERS energy filter configured in the image-coupled mode to have a 35 mrad collection semiangle. Energy dispersive X-ray spectroscopy (EDS) spectrum imaging was acquired using a windowless, four quadrant silicondrift detector with a collection solid angle of > 0.7 sr. XPS (Quantera II, Physical Electronics, Chanhassen, MN, USA) was used to study the oxidation states of TiO₂ on a more global scale. Light absorption was measured by using diffuse reflectance UV-Visible spectroscopy (SHIMADZU UV-2450). Details of the methodology are given in the SL.

Photocatalytic activity of the catalyst: The reactor was prepared by using a 75cm³ gas test tube, filed with 25cm³ of distilled deionized water at 6.00 pH and the tube was sealed by using suba-sealed rubber septa by keeping 50cm³ of dead volume inside the test tube. 25 cm² of catalyst film was immersed in deionized distilled water and the produced gas was analyzed by using gas chromatography. Photoactivity of the catalyst was studied under different light sources (Xenon lamp and Halogen lamp) and different light condition including dark. Generated gas products were qualitatively as well as quantitatively analyzed using gas chromatography (SHIMADZU MODEL GC-9AM) with a steel column 12 feet in length packed with a charcoal column, 5A°Molecular sieves and a thermal conductivity detector (TCD) with Argon as the carrier gas. Details concerning the STH and QE calculations are given in the SI.

Electrochemical methods: Photoelectrochemical measurements were carried out using a Zahner Zannium electrochemical interface analysis instrument operated with the Thalas software in

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a standard three-electrode system with a Pt foil as counter 9. electrode, an Ag/AgCl electrode as the reference electrode and TiO₂/Al as the working electrode. A 350 W Xenon lamp (Newport, AAA solar simulator at 100 mW/cm²) coupled with an AM 1.5G filter was used as the simulated sunlight source and the intensity was measured with a standard Si-reference cell (Newport). The incident photon to current efficiency (IPCE) was measured with Bentham PVE300 unit with a TMc300 monochromator based IPCE with the Xenon arc lamp in the wavelength range in between 300-1200 nm range. Mott-Schottky analysis were performed with three component system in which platinum as counter, Ag/AgCl (0.01M), saturated KCl as reference electrode and TiO₂/Al as working electrode at 10 mV amplitude ac signal and 1KHz frequency by using Zahner Zannium universal electrochemical work station equipped with a frequency response analyzer (Thalas) at 10 mV amplitude ac signal and in the frequency range from 0.1 Hz to 1MHz under dark and illumination conditions. The transient photocurrent responses of the TiO₂/Al catalyst was tested under intermittent irradiation with Keithley 2400 source meter under one sun illumination using a solar simulator at AM1.5G (Newport AAA solar simulator at 100 mW/cm²) which intensity of light was calibrated with standard Si-reference cell.

Conflicts of interest

There are no conflicts to declare.

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Similar to supramolecular complexes in a photoctalytic hydrogen production scheme, here we develop a redox system that contains Ti^{3+}/Ti^{2+} reduced states in TiO_2 which act as both visible light harvesting component as well as the catalytic site for the catalytic hydrogen production with visible-near infrared photons.

