Supporting information

Superior solar-to-hydrogen energy conversion efficiency by visible light-driven hydrogen production via highly reduced Ti^{2+}/Ti^{3+} states in blue-titanium dioxide photocatalyst

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Synthesis of the catalyst

Reduced TiO_2 was synthesized by using 1% w/w I_2 mixed with the P_{25} TiO_2 solution. Al foil (99.96%), TiO_2 (Degussa, P_{25}) nanoparticles and all other chemicals used in this study were analytical grade from Sigma-Aldrich (USA). Distilled water was used for the preparation of all solutions and as a reaction medium. The solvent in the precursor solution was synthesized by mixing different amounts of acetic acid to the deionized distilled water and high purity ethanol to different ratios of water. pH of the final TiO_2 solution was the critical point of this synthesis and it was adjusted to 6.0 to 6.5 by using acetic acid to obtain a strong bond between metal and TiO_2. 99.96% purity Al 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. The mixture containing a suspension of Degussa P25 TiO_2 in 1% I_2 (w/w%), 10% methanol in water and acetic acid on to the pre-cleaned Al substrate at elevated temperature (~160°C) at a spray speed of 1 ml/min. Finally, TiO_2 coated Al substrate 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. It was noted that even though the use of I_2 is not essential, but the presence of I_2 in the spraying solution enhances the formation of reduced titanium species (blue TiO_2) due to the reaction of Al and I_2 during spray pyrolysis forming I- which may help reduction of TiO_2.

Characterization of the samples: The crystal structure of the various phases were studied by using powder X-ray diffractometer (Seifert diffractometer), using a Co source (λ = 0.178897 nm) operated at 40 kV and 30 mA.

SEM was carried out on a Zeiss AURIGA Modular Cross Beam workstation or on a Zeiss Gemini, both equipped with an in lens detector. All measurements were done at 4 kV on cross-sections of the samples. STEM, EDS and EELS was performed on an aberration-corrected FEI Titan Themis instrument with a corrector for the probe to get information on the size of the morphology, elemental distribution and oxidation state of the individual elements.

XPS analysis was carried out for confirming the oxidation states in reduced states of the TiO_2 semiconductor. XPS measurements were performed (Quantera II, Physical Electronics, Chanhassen, MN, USA) applying a monochromatic Al Kα X-ray source (1486.6 eV) and operating at 15 kV and 25 W. The binding energy scale was referenced to the C 1s signal at 285.0 eV. For investigation of the change of chemical composition with depth, sputtering with Ar plasma has been carried out. The sputtering spot size was 2 mm × 2 mm. Casa XPS software was used to analyze the experimentally obtained spectra. The fitting of spectra was performed after subtraction of a Shirley background. In all fits, the peak separation and the peak area ratios between the Ti 3p3/2 and the Ti 3p1/2 components were constrained to 5.7 eV and 2:1, respectively.

For light absorption measurement of the catalyst, the ultra-violet and visible light diffuse reflection (UV-Vis-DRS)spectra were recorded in the range of 190–800 nm using a double beam diffuse reflectance UV-Visible spectroscopy (SHIMADZU UV-2450). Here reflectance was measured at different stages of the catalyst with reference to $BaSO_4$ standard and the measured intensity was expressed as the value of the Kubelka–Munk function F(R).

Calculation of solar-to-hydrogen conversion efficiency (STH) and the quantum efficiency (QE)

STH calculation: The solar-to-hydrogen conversion efficiency was calculated by the following equation 1 in which the product of H_2 evolution rate and the Gibbs free energy for generating one mole of H2 from water was divided by the total power of incident simulative sunlight (AM1.5G) multiplied by the area irradiated by the incident light.

$$STH = \left[\frac{(mmol\, H_2/s) \times \left(\frac{273kJ}{mole}\right)}{P_{total}\left(\frac{mW}{cm^2}\right) \times Area(cm^2)} \right] \times 100\% AM1.5G \qquad (1)$$

For Xe lamp:

For 25 cm^2 area, 30 min, total H_2 produced = 3809 μL

STH=[(H2 mmol/s) * 273 kJ]/[intensity (mW/cm^2)* area cm^2] X 100

H_2 amount (for 25 cm^2) = 9.44 X 10^{-5} mmol s^{-1}

Then STH = [(9.44X 10^{-5} mmol s^{-1}) X 237 kJ/(100 (mW/cm^{2}x 25 cm^2)]*100

= 0.89 (%), for 100 mw/cm^2

QE calculation: The apparent quantum efficiency was calculated by the following equation 2. In the process, two electrons are required for the production of each hydrogen molecule, and hence it requires two photons in which N_{H2} and N_{hv} are number of hydrogen molecules produce per second and the photon flux respectively.

$$QE = \frac{2N_{H_2}}{N_{hv}} \times 100 \qquad (2)$$

The photon flux $N_{hv}$was calculated as follows;

N_{hv}= [P/E] where P is the power of the light (50 mW or 50 x 10^{-3} j/s) and E is the energy of photon (used 5mW 10 red LEDs 655nm, 25cm^2 area)

$$E = h\frac{c}{l}$$

$$E(photon) = \frac{h.c}{\lambda} = \frac{6.62607 \times 10^{-34}[j.sec] \times 2.99792 \times 10^{8}[m/sec]}{655.10^{-9}[m]}$$
$$= 3.03274 \times 10^{-19}[\frac{j}{Photon}] \qquad (3)$$

Hence

$$N_{hv}(for\ 30mW) = \frac{50 \times 10^{-3}\left(\frac{j}{s}\right)}{3.03274 \times 10^{-19}\left(\frac{j}{photons}\right)} = 1.648674 \times 10^{17}(photons/s)$$

N_{H2}= hydrogen production rate (molecules for second)

i.e.in this investigation, the observed hydrogen yield= 80X 10^{-6} l/min
then

$$N_{H_2} = \left[\frac{80 \times 10^{-6}\left(\frac{L}{min}\right)}{22.4\left(\frac{L}{mol}\right)}\right] \times \frac{6.0234 \times 10^{23}}{60}[H_2/sec]$$

Hence

$$QE = \frac{2 \times 3.5853 \times 10^{16}[H2/sec]}{1.648674 \times 10^{17}(photons/s)} \times 100 = 43.49\%$$

Catalytic nature and theoretical hydrogen amount calculations

Al foil weight = 5.400g

Area = 0.1m^2

film thickness = 2mg/cm^2

Hydrogen generation, (for 10 hrs) = 60ml/hr × 10 hr= 600ml

After 10 hours of reaction, hydrogen production rate decreases slowly but not completely ceased even after 48 hours. (Deactivation could be due to blocking of active sites of TiO_2 by AlOOH)

The catalyst was reactivated by sintering at 400°C. (Al^{3+} cannot be reduced to Al by sintering at 400°C)

More than 40 times regenerated (reactivated by heating at 400°C)

Total hydrogen volume generated approximately =(600 ml *40)

= 24.0 L

If H_2 if formed via the the following reaction,

$$2Al + 6\,H_2O \longrightarrow 2Al(OH)_3 + 3H_2$$

$$2 : 6 : 2 : 3$$

Theoretical value = $5.400g/27gmol^{-1}$ = 0.2mol

Theoretical value $= \frac{0.2\,mol}{2} \times 3$

= 0.3 mol =22400ml/mol × 0.3 mol

= 6.7 L

However pure Aluminum does not produce hydrogen in neutral distilled water without other initiators or in highly acidic/basic medium and it is not catalytic.