

Solar Energy Materials & Solar Cells 60 (2000) 361-365

Solar Energy Materials & Solar Cells

www.elsevier.com/locate/solmat

Multiphoton semiconductor photocatalysis

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Abstract

A composite catalyst consisting of Nb_2O_5 and platinized TiO_2 particles is found to initiate up-hill chemical reactions via a low-energy multiphoton process involving step-wise transition of electrons across the traps in Nb_2O_5 to the conduction band of Nb_2O_5 and then to the conduction band of TiO_2 . \bigcirc 2000 Elsevier Science B.V. All rights reserved.

Keywords: Semiconductor particle; H2 generation; Photocatalysis

It is well known that photogenerated carriers in semiconductor particles initiate up-hill chemical reactions such as hydrogen production from water in the presence of a hole scavenger [1,2]. The process is single-photon mediated (i.e. each electron transfer to a chemical species, utilizes only one photon) and only high band gap (BG) semiconductors could be used, because the low BG materials are susceptible to photocorrosion. A multiphoton catalytic process based on stable high BG semiconductors and capable of creating high chemical potential is most desirable for photochemical utilization of solar energy. In this note we describe for the first time a model semiconductor particulate system possessing the ability to drive uphill chemical reaction via a multiphoton process consuming low-energy (even IR) photons. Niobium pentoxide particles in contact with platinized titanium dioxide particles are found to photoproduce hydrogen from water in the presence of a hole scavenger (e.g. ethanol) when irradiated with visible, red and IR light. The mechanism involved is explained as a transfer of electrons from the valence band (VB) of Nb_2O_5 to an interband trap site in Nb_2O_5 and then (directly or via an another trap site) to the conduction band (CB) of Nb₂O₅. The transfer of electrons from the CB of Nb₂O₅ to the low-lying CB of a TiO₂ particle separates the charges, suppressing the capture of electrons by the traps or the holes in VB.

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Fig. 1. The H_2 yield when $Nb_2O_5/TiO_2/(Pt)$ catalyst in 5% ethanol is irradiated with lamp (a)-(c).

The composite $Nb_2O_5/TiO_2(Pt)$ catalyst was prepared by grinding Nb_2O_5 (0.5 g, crystallite size ca. 330 nm, Fluka) and platinized TiO₂ (0.5g, crystallite size ca. 30 nm, Degussa P25) in an agate mortar. 0.1 g of the mixture was suspended in 20 ml of water containing 5% ethanol (Fluka, 99.9%) in a Pyrex flask and deaerated by purging pure argon. The flask was irradiated with (a) 60 W tungsten filament lamp (Philips), (b) 60 W tungsten filament lamp with a red glass bulb which transmits light $\lambda \ge ca$. 600 nm, (c) 60 W tungsten filament lamp coated with a thick layer of lamp soot to cut-off all visible light emanating from the filament. The estimated intensities of illumination near the reaction vessel from the sources a, b, c are ca. 200, 85, 2.5 W m⁻² respectively. Hydrogen accumulation in the flask as monitored by gas chromatography is indicated in Fig. 1. Although all precautions were taken to exclude BG radiation (Nb₂ O_5 or TiO₂), a continuously increasing hydrogen signal was noticeable in all the cases. Hydrogen signal was again detected when the flask was irradiated with pure monochromatic sodium or He-Ne laser light. The following blank experiments were also conducted (1) Nb₂O₅ in 5% ethanol, (2) TiO₂ (Pt) in 5% ethanol, (3) 5% ethanol irradiated with the above sources of light, (4) Nb_2O_5/TiO_2 (Pt) in 5% ethanol in the dark at room temperature and elevated temperatures $(25-75^{\circ}C)$. A hydrogen signal was not observed in any of the above blank experiments except in (2), where minute quantities of hydrogen [less than the level in (a), (b) or (c)] were detectable on prolonged illumination with the tungsten filament lamp (other light sources did not yield hydrogen signals in this case). The above experiments unequivocally demonstrate that sub-BG radiation including IR photons of energy less than ca. 1.1 eV (the bulb coated with lamp black transmit mostly radiation of wavelength < ca. 1100 nm)



Fig. 2. The absorption spectrum of a suspension of electron-trapped Nb₂O₅. Inset: Schematic energy-level (scale, eV/normal hydrogen electrode) diagram illustrating the multiphoton charge-transfer process in Nb₂O₅/TiO₂(Pt).

are able to photoreduce water with the concomitant oxidation of ethanol. We give the following explanation.

A photon with sub-BG energy elevates an electron from the VB of Nb₂O₅ to a trap site in the interband region of Nb₂O₅ and subsequently the absorption of further photons, transfer the electron to the CB of Nb₂O₅ transiting across other trap sites. The electron on reaching the CB of Nb₂O₅ falls into the low-lying CB of a TiO₂ particle in contact with the Nb₂O₅ particle (inset Fig. 2), i.e.,

$$hv_1 + Nb_2O_5 \rightarrow e^-(T_1 - Nb_2O_5) + h^+(VB - Nb_2O_5),$$
 (1)

$$hv_2 + e^-(T_1 - Nb_2O_5) \rightarrow e^-(T_2 - Nb_2O_5),$$
 (2)

$$hv_3 + e^-(T_2 - Nb_2O_5) \rightarrow e^-(CB - Nb_2O_5),$$
 (3)

$$e^{-}(CB - Nb_2O_5) \rightarrow e^{-}(CB - TiO_2), \tag{4}$$

where T_1 , T_2 , are the trap sites in Nb₂O₅ and transition of the electron to the CB of Nb₂O₅ could occur via absorption of several low-energy photons. As the lifetime of an electron in a trapped state is quite high, the probability of the above transitions are significant even at low intensities of illumination. Localization of the electron in TiO₂

and the hole in Nb_2O_5 suppresses recombinations or capture of electrons by a trap in Nb_2O_5 . Electrons transferred to TiO_2 that accumulate on Pt islets on TiO_2 reduce water, i.e.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-.$$
⁽⁵⁾

Holes in Nb_2O_5 are accepted by hydroxyl ions to yield hydroxyl free radicals via the reactions

$$OH^- + h^+ \to OH^{\bullet}, \tag{6}$$

$$C_2H_5OH + OH \rightarrow oxidation \text{ products.}$$
 (7)

Acetaldehyde, acetic acid and carbon dioxide are detected as oxidation products of ethanol ($\Delta G > 0$ for reduction of water with formation of these compounds).

During irradiation with light sources (a)-(c), Nb_2O_5 in the composite catalyst gradually turned blue. The absorption spectrum of the blue product is presented in Fig. 2. Nb₂O₅ films deposited on conducting glass reduced electrochemically or Nb_2O_5 powder reduced with a powerful electron donor (e.g. Sn^{2+}) produce the same coloration and absorption spectra. It is known that trapped electrons in transition metal oxides give rise to a blue coloration with a strong absorption peak in red extending into the infrared region [3-5]. Formation of blue colour in the catalyst indicates the filling of the traps during the transition of electrons to the conduction band in step-wise excitations. With white, red and IR light, the blue coloration is produced only in the presence of TiO_2 (platinized TiO_2 is more effective). However, when a suspension of Nb₂O₅ in aqueous alcoholic solution is illuminated with a mercury lamp, Nb₂O₅ develops a blue colour and H₂ evolution is noticed. Spectroscopic examination revealed that the UV ($\lambda \leq 400$ nm) component of the tungsten filament lamp is beyond the limit of detectability and could not account for the observed H₂ signal. Furthermore, the hydrogen signal was observed when light of the tungsten filament lamp was filtered through a potassium dichromate solution which cuts-off light of $\lambda \leq 460$ nm. Here the most likely predominant process is the elevation of the VB electrons to the CB of which some are transferred to water and the others fall back into the trap sites. Although there is no direct evidence to prove that step-wise excitations raise electrons to CB of Nb_2O_5 , we are unable to suggest any other mechanism which can explain the observed H₂ evolution and the development of blue coloration in Nb₂O₅. As stated earlier, some hydrogen evolution was noticed with the catalyst TiO₂(Pt) under visible light (tungsten filament lamp) irradiation. Possibly, doping by Pt extends the spectral response of TiO₂ slightly towards the visible region [6]. Transition metal oxides such as WO₃, Nb₂O₅ have defects, which readily trap electrons. However, in the former oxide, CB position is not favourable for reduction of water. The attractive feature of devising semiconductor photocatalysts that depend on sub-BG electron trapping, is the ability to achieve wide charge separation to high potentials utilizing several low-energy photons for one singleelectron transfer. We have found that the above system photogenerates hydrogen from water in the presence of several other sacrificial hole scavengers.

Acknowledgements

This work is partly supported by the grant RG/95/P/04 from the National Science Foundation of Sri Lanka.

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