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Catalysis Today 27 (1996) 271–277

CATALYSIS TODAY

Hydrogen production from water and conversion of carbon dioxide to useful chemicals by room temperature photoelectrocatalysis

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Abstract

A thin film anatase titania photocatalyst having 60% quantum efficiency measured without applied bias potential can produce hydrogen from water at rates of 26 with bias by a mercury lamp as a light source and 0.075 to 0.42 without bias by the sunlight both in units of $l/h/m^2$-irradiation cross section on photocatalyst surface and a single unit photoelectrocatalysis system can be formed with the photocatalyst and an electrocatalyst consisting of zinc oxide and copper which when combined together can stably convert 82% of carbon dioxide to hydrocarbons in terms of current efficiency including 44% for methane and 24% for ethylene without deactivation of the reactions by operating the system under a pulsed bias between the photocatalyst and the electrocatalyst.

Keywords: Hydrogen production from water; Carbon dioxide conversion; Room temperature photoelectrocatalysis

1. Introduction

Utilization of natural resources combined with photoelectrocatalysis to produce ‘clean fuel’ such as hydrogen and to pursue ‘chemical recycling’ of carbon dioxide continue to attract attention due to emerging new and relatively immediate applications in addition to their more direct original purposes which require long range research.

Future environmental and energy problems need to be solved under the guideline of environmentally compliant technology which justly includes utilization of mild energy sources such as the sunlight or any other light sources containing ultraviolet rays and other wavelength range light that are left unused or not actively utilized. Light energy and water as a hydrogen resource enable processes free from creating additional pollutants unlike those dependent on fossil fuels.

Basic information from studies in photocatalysis and photoelectrocatalysis are recently being applied to reduction of untreated toxic materials in atmosphere or in solution and sterilization or deodorization in room air [1]. In future, a more ambitious but ultimately desirable control of chemical balance in closed space may become possible. In all cases the unique characteristic of photocatalytic system is utilized, viz. chemical conversion of low concentration materials under light at room temperature through decomposition, oxidation and reduction processes.

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SSDI 0920-5861(95)00198-0

We report here some new results on production of hydrogen and conversion of carbon dioxide, including information on the intrinsic property of titania photocatalyst by measuring its quantum efficiency under irradiation of constant photon density for the first time, and also a novel system operating method in running photoelectrocatalytic reactions, that makes possible stable formation of hydrocarbons from carbon dioxide without deactivation.

2. Experimental

Thin film titania is prepared by a sol-gel method starting from titanium tetraisopropoxide following a procedure suggested by Sakka et al. [2]. Repeated coating of a pre-conditioned sol onto a substrate under moisture-free atmosphere is followed by controlled oxidation each time. This process is typically repeated fifteen to twenty times to attain optimum thickness. The substrate can be a conductive glass [3] or a metal such as titanium as in this paper with dimension of 50 × 50 × 0.5 mm. Electrocatalysts are platinum, copper or copper modified on surface by zinc oxide with a typical size of 20 × 20 × 0.5 mm. The substrate and the electrocatalyst are perforated to pass protons in direction perpendicular to the surfaces. Material characterizations include X-ray diffraction (XRD), laser Raman spectroscopy (LRS), atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Quantum efficiency of the photocatalyst is measured by a system specially made for our purpose by Japan Spectroscopic Co. (JASCO).

Fig. 1 is a single unit photoelectrocatalysis system which consists of a perforated thin film titania and an electrocatalyst where a proton separator (Nafion, a DuPont brand) is placed between them to form one unit. In this way the photocatalyst and the electrocatalyst do not directly contact each other and therefore recombination of titania-produced protons and dioxygen which occurs on the electrocatalyst can be avoided. The protons are effectively separated and supplied to the electrocatalyst side with minimum travel distance for efficient production of hydrogen and hydrogenation of carbon dioxide. Key reactions are described in Fig. 1. We note that standard supported metal catalysts (platinum metal particles dispersed on titania for example) are much less efficient than the present thin film type for the reason inferred above and also the latter enables more variety of activity measurements and surface characterizations.

In some cases a bias potential between photocatalyst and electrocatalyst is applied to enhance mobility of electrons generated in photocatalyst. However, all of the features observed do occur without the bias although photocurrents detected

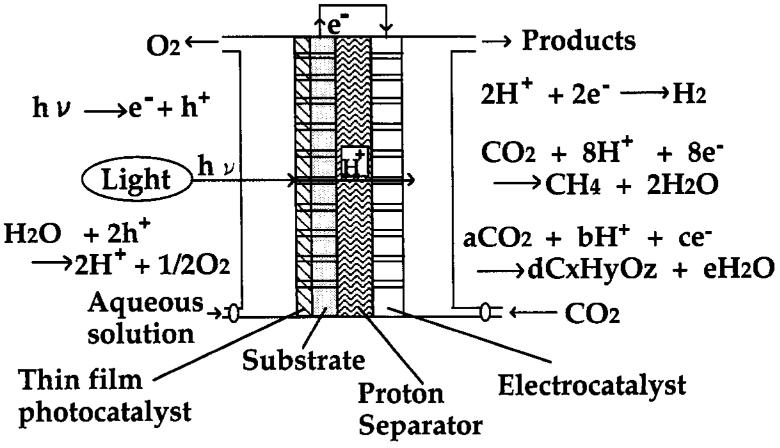

Fig. 1. Single unit photoelectrocatalysis system.

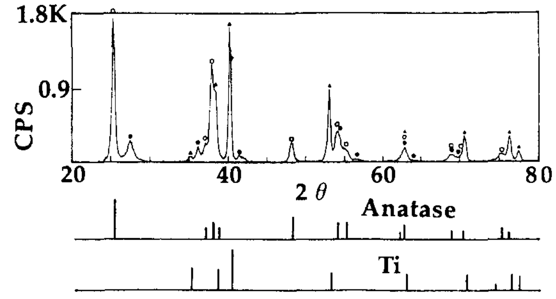

Fig. 2. Bulk crystal structure of an anatase thin film measured by XRD.

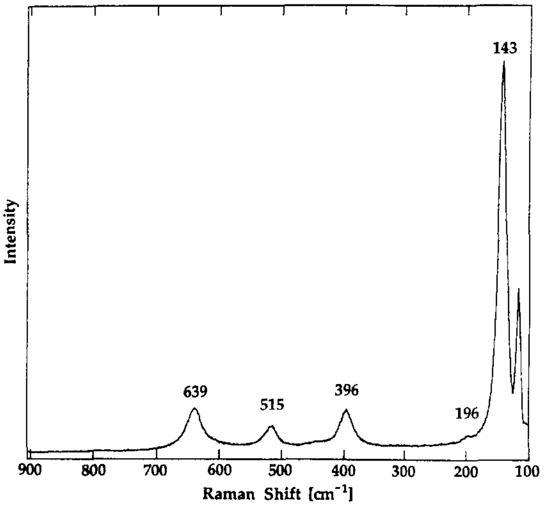

Fig. 3. Surface crystal structure of an anatase thin film measured by LRS.

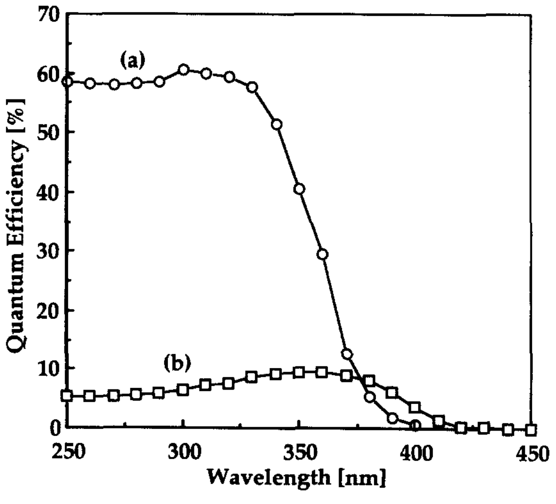

Fig. 4. Quantum efficiency of titania thin film measured by constant photon light irradiation without applied bias potential: (a) anatase and (b) rutile.

may be small in some cases. An electrolyte solution used is 0.1 mol/l $KHCO_3$. Light sources are either a 500 W mercury lamp or the sunlight.

3. Results and discussion

We have previously reported that titania thin films prepared by the sol-gel method on conductive glass as a substrate reach maximum activity in terms of biased photocurrent when we have essentially 100% anatase crystal structure, homogeneously spread crystallites, stoichiometry of O/Ti at strictly 2.00 and film thickness of 0.5 micron as observed by XRD, AFM and RBS [3]. We now find that these features apply also to titania formed on titanium substrate and as explained below we have more new data on the intrinsic characterization of titania.

For the maximum activity of photocatalytic water dissociation the structure of titania film is preferred to be in anatase form not only in the bulk as indicated by XRD in Fig. 2 but equally important at its surface as shown by LRS in Fig. 3. These Raman peaks correspond to those of anatase close to its single crystal which have appeared at 640, 515, 400, 197 and 144 cm^{-1} [4]. An AFM image indicates that the film is formed by a collection of uniformly sized crystallites of about 25 nm which is the optimum size and large enough to be uninfluenced by quantum size effect [5].

We have measured quantum efficiencies of thin film titania without bias potential under constant photon irradiation. Fixed number of photons at $2 \cdot 10^{14}$ photons/cm^2 s was constantly irradiated onto the TiO_2/Ti sample while the wavelength was varied systematically by 10 nm increments. The generated current from the photocatalyst was constantly monitored. The counter electrode in this case was platinum. Fig. 4 shows a comparison of the above anatase and a rutile film prepared by the same method but under different thermal treatments and their structures were confirmed by XRD. Very large difference between the two is apparent and also the threshold wavelengths indicate the difference in band gaps of these two photocatalysts. A systematic decrease in the quantum efficiency was observed as the percentage of rutile structure was increased [5].

The quantum efficiency for anatase remains almost constant as the wavelength decreases once it reaches about 60%. The efficiency therefore is no longer dependent on the photon energy once it reaches a level sufficiently above the band gap energy of about 3 eV. It should be noted that Fig. 4 gives the 'external' quantum efficiency which is defined as the sum of efficiency for photon absorption and the 'internal' quantum efficiency. Some photons are reflected without being absorbed. The internal quantum efficiency is for the process of having the electrons excited from valence band to conduction band resulting in the formation of electron-hole pairs while some portion of the electrons recombine with the holes so that the efficiency is for the generation and destruction of electron-hole pairs. The external quantum efficiency of 60% is quite high and the internal quantum efficiency is higher than this by definition. Minimization of photon reflection may become possible by patterned surface modification of the photocatalyst.

With the same experimental setup, the changes in photocurrent under biased potential have been measured and they are consistent with the trends observed in quantum efficiency data throughout the bias potential up to about 2 [V vs. SHE] [5]. That is, the photocurrent obtained under bias was higher for anatase compared to rutile. This means that the intrinsic physical property of titania on the photon excitation of electrons is directly reflected on the performance of the photocatalyst with the bias potential. This is an important information for the photoelectrocatalytic conversion of carbon dioxide as the reaction system is operated under bias.

In spite of the long years of research on titania, the discussion of whether anatase or rutile is better for the decomposition of water has not been concluded. Two opposing papers are referred to in that respect. Production of spin adducts due to water decomposition species on anatase as measured by electron spin resonance indicated that this crystal structure may be the more advantageous [6]. However recent photocurrent measurements indicate that rutile is the better [7]. Our demonstration based on quantum efficiency seems more convincing and show the intrinsic and inherent difference of the two. More details on the structural effects are reported elsewhere [5].

The system in Fig. 1 with the above TiO_2/Ti photocatalyst and platinum as an electrocatalyst produces hydrogen at a rate of 26 $l/h/m^2$ irradiation cross section on photocatalyst surface with the mercury lamp as a light source.

A hybrid system exactly like the one shown in Fig. 1 is modified for photocurrent measurement by the sunlight so that the face of photocatalyst becomes almost perpendicular to the sun. On a sunny day in Japan, our TiO_2/Ti system without bias potential produced hydrogen at the rate ranging from 0.075 to 0.42 $l/h/m^2$-irradiation cross section on photocatalyst surface, where the rate depends on the time of day. The maximum rate of hydrogen production on titania is believed to be the highest thus far.

Over the years, other photoactive materials and semiconductor oxides with a reasonably small bandgap and appropriate oxidation and reduction potentials for water splitting with or without dopants have been tried. Some successes have been reported in such endeavors, however they were often not reproduced. As far as pure titania is concerned, it seems that our optimized anatase thin film is reaching near its maximum attainable performance. At this point, further development of more active photocatalysts must wait for the unraveling of detailed reaction mechanism identifying the elementary steps and the rate determining step in parallel with detailed material characterizations. Surprisingly, few new experimental attempts have been made in this regard despite the length of time elapsed since the first scientific demonstration of water splitting on titania [8]. We are currently trying to apply a femtolaser technique to follow the water decomposition process on titania in real time.

We now turn to the subject of photoelectrocatalytic conversion of carbon dioxide. Basic research in this area is not only important from

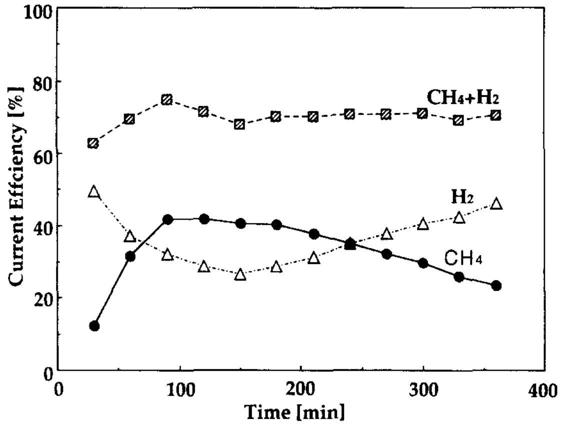

Fig. 5. Competitive reactions between the proton recombination and the methanation of carbon dioxide on a ZnO/Cu electrocatalyst.

the viewpoint of recycling the ‘green gas’, but, also, it enables us to understand the nature of how this chemically very stable molecule with a very negative Gibbs free energy can be activated and reacted [9], the knowledge of which can be applied to other stable chemicals. Electrochemical reduction of carbon dioxide has been studied intensely since, on towards the late 1980’s [10]. Among the metal elements which can be used safely as electrodes, the best activity for methanation in terms of current efficiency is attained by copper, however it is reported to be about 18% [11]. Interestingly, copper is at the apex of the ‘volcano’ curve following the well-known plot of current efficiency versus percentage d-character. However, like most electrochemical reactions involving formation of hydrocarbons, the reaction deactivates quickly.

In order to increase the selectivity towards methane, we added an optimum amount of zinc oxide in an island form on the surface of copper. The coverage of ZnO is optimized. As a result the current efficiency increased to 42% at the maximum as measured by a system with platinum as a counter electrode (Fig. 5). There appears to be a competition between the two major reactions, viz. proton recombination to form hydrogen and CO_2 methanation. As also shown in Fig. 5 the sum of the two current efficiencies remains almost constant while the two vary differently with time. The ability to stabilize the protons on ZnO surface [12] may be contributing to the increased efficiency for CO_2 methanation. Zinc oxide itself shows no activity to hydrogenate CO_2. Thus, carbon dioxide molecule is expected to be initially activated on copper and then it migrates onto ZnO to react with the protons. In this way, some of the protons may be prevented from easily recombining on copper. These features are shown by a schematic diagram in Fig. 6. The zinc oxide remains intact as confirmed by the Auger Zn peak ($L_2M_{45}M_{45}$) extracted from XPS analysis after the reaction, i.e., the peak for ZnO is maintained while that for Zn does not appear. Therefore ZnO does not reduce to Zn, at least not to the extent shown by XPS.

Analyses by XPS and AES after the electrochemical reaction indicate that an increasing amount of carbonaceous overlayer develops with time. This, however, is understandable considering the fact that the reaction is operated at room temperature so that the accumulating amounts of hydrocarbons would have difficulty desorbing at such low temperature. The gradual deactivation for methane production in Fig. 5 relates to this.

With the anatase titania photocatalyst and the zinc oxide/copper electrocatalyst, photoelectrocatalytic conversion of carbon dioxide was tested with the system described in Fig. 1 and the mercury lamp. Under a condition where a constant bias potential is applied between photocatalyst and electrocatalyst, the energy efficiency is 10.5%, which is by definition the total heat energy attained by combustible products formed (as fuels) divided by total photoelectrical energy supplied. As for the current efficiencies of the gaseous products, we obtained for methane 17%, ethylene

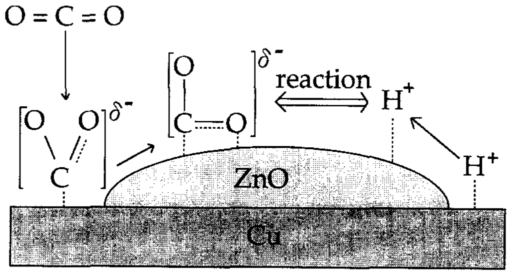

Fig. 6. Schematics of the activation and the migration of carbon dioxide and proton on a ZnO/Cu electrocatalyst.

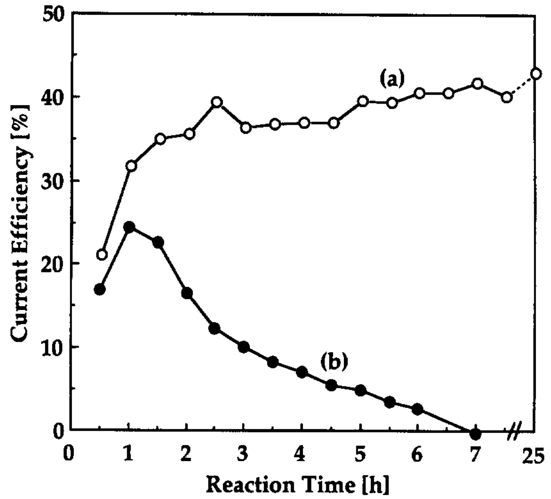

Fig. 7. Non-deactivating pulse bias operation for stable conversion of carbon dioxide to methane: (a) Pulse bias, (b) Constant bias. Photocatalyst: TiO2/Ti. Electrocatalyst: ZnO/Cu.

11% and hydrogen 42%, respectively. This means 58% of carbon dioxide is converted by hydrogenation. Other products dissolved in the solution are mainly formic acid and ethanol. Under the conditions studied, deactivation of the hydrogenation reactions are unavoidable. Thus far, our main interest has been to increase the selectivity towards gaseous hydrocarbons such as methane and ethylene which are automatically separated from the solution and to be able to achieve this without deactivation.

This problem, however, is now solved by a technique where the bias potential is applied in a pulse mode. The pulse technique was recently used in a regular electrochemical reduction of carbon dioxide with a pair of copper electrodes which prevented the deactivation of hydrocarbon production [13]. We have applied the same technique to the photoelectrocatalysis system. The results are remarkable increase in activity for methane and ethylene production and equally importantly these reactions do not deactivate. Fig. 7 shows an example case for CO_2 methanation by this technique. The same feature is observed for ethylene production in the 25 h run. These and more details on the CO_2 conversion are reported elsewhere [14].

The energy efficiency in this pulse bias case increased somewhat to 12% while there was a dramatic increase to 82% for the conversion of carbon dioxide. And the current efficiencies for hydrocarbons greatly increased to stable activity levels, viz. methane 44%, ethylene 24%, on the average and hydrogen was effectively suppressed to only 18%.

Analysis by AES indicates no formation of carbonaceous overlayer after the pulse bias compared to the constant bias operation and changes in oxidation state of copper as observed by XPS also seems to play an important role [14]. Reaction mechanism may be controlled differently under the pulse condition. We know from studies in C_1 chemistry such as CO and CO_2 hydrogenation reactions on supported metal catalysts that the initially active carbidic carbon formed during these reactions can form a network of carbon resulting in graphitic carbon, which is much less reactive. A similar phenomenon could be occurring by the usual constant bias technique. The pulse bias may effectively reverse the reaction periodically or trigger different reaction routes that can avoid causes for deactivation. There are an optimum on-off period and a bias potential range in pulsing for the best performance of the system [14].

4. Conclusions

Anatase titania thin film is intrinsically advantageous over rutile for water decomposition as can be observed by high quantum efficiency under unbiased condition as well as by photocurrent with bias potential between photocatalyst and electrocatalyst. The thin film photocatalyst produces attractive amount of hydrogen. However, more extensive atomic level analysis on the detailed reaction mechanism is needed in order to design better photocatalyst. A single unit photoelectrocatalysis system operated under pulse bias technique greatly increases the activity and selectivity toward formation of gaseous hydrocarbons such as methane and ethylene without deactivation of the reactions.

Acknowledgements

This project is conducted as a part of the industrial technology development promotion program of the Research Institute of Innovative Technology for the Earth supported by the Ministry of International Trade and Industry.

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