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PHOTOCATALYTIC HYDROGEN PRODUCTION FROM WATER BY THE DECOMPOSITION OF POLY-VINYLCHLORIDE, PROTEIN, ALGAE, DEAD INSECTS, AND EXCREMENT

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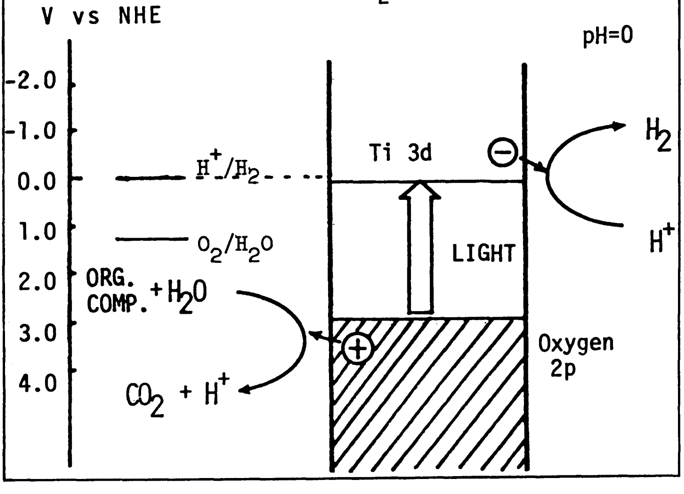
Xe-lamp irradiation of a platinized TiO_2 photocatalyst in the presence of water and chlorine or nitrogen containing organic molecules, synthetic or natural, leads to the production of hydrogen at room temperature without the release of halogen or nitrogen compounds in the gas phase.

The utilization of waste materials for the production of fuel is attractive. Many kinds of organic compounds contain heteroatoms, such as halogen, nitrogen or sulfur. For example, poly-vinylchloride, a synthetic polymer, is widely used in industry and its decomposition is still a very important problem. Trichloroethylene or chlorobenzene has also been used as solvents. Natural products from animals or plants, on the other hand, include proteins which contain nitrogen. The decomposition of these materials by heating procedure releases chlorine or nitrogen compounds into the air, which can be harmful to our health.

We have demonstrated hydrogen production from water and many kinds of organic compounds, i.e. solid carbon1), alcohols2), carbohydrates3) and so on4), taking advantage of the photocatalytic activity of semiconductor powders. Here we report that chlorine or nitrogen containing organic compounds could also be decomposed in water at room temperature to yield hydrogen by using a platinized TiO_2 photocatalyst, and furthermore, the chlorine or nitrogen stayed behind in the water phase as a water soluble species (HCl or NH_3). As a typical example of a chlorine containing polymer, we mainly used poly-vinylchloride. For nitrogen containing substances, the decomposition and H_2 production were examined using amino acids, protein, dead cockroaches, green algae(chlorella), and animal excrement.

The TiO_2 photocatalyst (300 mg), the organic substances (100-500 mg), and water (30 ml) were put in a Pyrex glass bulb (280 ml), and the bulb was deaerated and irradiated by a white light from a 500 W Xe-lamp. The evolved gases were trapped at -197 and -40°C, and analyzed by a mass-spectrometer and a pressure gauge.2,3) Pt metal was photoelectrochemically deposited on TiO_2 (Pt 5 wt %).5) TiO_2 powder was reduced by heating it in a hydrogen atmosphere (300 torr) at 650°C for 3 hours, before depositing Pt.

Fig.1 Energy diagram of a TiO_2 particle estimated from the data of TiO_2 single crystal.9)



(I) Poly-vinylchloride and other chlorine containing molecules ---- When the TiO_2/Pt photocatalyst(300 mg) and water was irradiated at room temperature in the presence of poly-vinylchloride powder(150 mg), gas bubbles were generated at an interval of several seconds. The mass analysis revealed the production of H_2 and CO_2 in the gas phase (Table 1(a)). The ratio of H_2 to CO_2 is 2.0 - 2.5. An interesting observation is that no Cl_2 could be detected in the gas phase, but the value of the pH decreased with time. For example, the pH of the solution decreased to 2.9 after two days of irradiation, and the formation of Cl^- ion was confirmed by using $AgNO_3$, that indicates the production of HCl in water. In a concentrated alkaline solution(5N NaOH), on the other hand, the irradiation leads to the production of pure hydrogen, the CO_2 being absorbed in the solution. Also in this case, Cl_2 was not detected in the gas phase, the Cl presumably forming NaCl. As is shown in Table 1(a), the amount of H_2 produced increased by about two times in basic solution. From these observations, the following scheme can be deduced as one of the main reaction paths in neutral aqueous conditions,

$$\leftarrow CH_2\text{-}CHCl \rightarrow + 4H_2O \longrightarrow 2CO_2 + 5H_2 + HCl \qquad (1)$$

which is essentially similar to the photoreaction we have studied for C + H_2O[1], CH_3OH + H_2O[2] and ($C_6H_{12}O_6$) + H_2O[3]. When electrons and holes are created by light in the TiO_2 photocatalyst particle, the $\leftarrow CH_2\text{-}CHCl \rightarrow$ would be oxidized and decomposed at the oxidizing site of the photocatalyst evetually forming CO_2 and HCl, and simultaneously H^+ in water (or H_2O under basic solution) would be reduced at the reducing site to form H_2. As is shown in Fig. 1, holes at the valence band locate deep enough to oxidize water and various kinds of organic compounds, and the position of the conduction band is nearly equal to the redox potential of H_2 production from water. The higher H_2 production in 5N NaOH solution may come from the oxidizing power of $\cdot OH$[6] formed easily from OH^- and come from the absorption of CO_2 by NaOH as Na_2CO_3 or $NaHCO_3$.

Trichlorobenzene and trichloroethylene can also be decomposed to produce hydrogen. (see table 1). However, we could not confirm the decomposition of Teflon which consists of strong C-F bonds. Polyvinyl alcohol and polyethylene made of only C, H, and O were decomposed to form only H_2 and CO_2.

(II) Amino acid and protein ----- The reactions were studied for glycine, the simplest amino acid, glutamic acid, the most common amino acid in living organism, and gelatine, a typical protein with molecular weight of 10,000 - 70,000. Irradiation of these amino acids or the protein in the presence of TiO_2/Pt catalyst leads to the production of H_2 and CO_2 in neutral water, and H_2 and NH_3 in basic solution(5N NaOH). Both NH_3 in neutral solution and CO_2 in basic solution were absorbed in the water and not released in the gas phase. The ratios of H_2 to CO_2 and NH_3 produced are about 1.2 - 1.4 and 3 - 4, respectively, for glycine. In table 1(b), the amount of hydrogen produced is summarized. The following reaction scheme is offered as one of the main paths for the decomposition of glycine based on the analysis of reaction products.

$$NH_2CH_2COOH + 2H_2O \longrightarrow 3H_2 + NH_3 + 2CO_2 \xrightarrow{H_2O(NH_3)} 3H_2 + 2CO_2 \quad \text{neutral condition}$$

$$\xrightarrow{NaOH(CO_2)} 3H_2 + NH_3 \quad \text{basic condition}$$

The lower reactivity of the glutamic acid may be caused by the difficulty of decomposing the longer methylene chain.

(III) <u>Chlorella, cockroach and excrement</u> ----- As an extention of the decomposition of amino acids and protein, we tried to produce hydrogen using a dead cockroach and green algae (Chlorella)7) which contain protein, fat, carbohydrates and other organic compounds. These components can be decomposed to produce H_2 as is shown in Table 1(b). We also tried to produce hydrogen from human urine and cow dung and other natural organic products. Table 1(c) summarizes the results of H_2 production from these materials. H_2 and NH_3 are produced successfully, especially in basic solutions.

In this manner, we could demonstrate that hydrogen can be produced photocatalytically from organic materials using TiO_2/Pt photocatalyst. The rate of hydrogen production increased by 10^2 times over that by TiO_2 alone,and did not remarkably decrease even after a week's irradiation. Not only organic compounds containing C, O and H, but also N or Cl containing compounds could be decomposed to produce H_2 by the photocatalytic process. In these cases, the reactivity for H_2 production is much increased compared with that of the direct decomposition of water into H_2 and O_2,8) presumably due to the irreversibility of the stable oxidized product (CO_2) and due to the smaller $\Delta G°$ for the reaction than for the direct decomposition into H_2 and O_2. The addition of RuO_2 (10 wt %) to TiO_2/Pt increased the reactivity by 2 - 3 times for the decomposition of solid polymer, i.e. poly-vinylchloride, in neutral solution. Compared with the thermal decomposition of these organic compounds, this method has the following features; (1) the reaction proceeds at room temperature in liquid water, (2) hydrogen gas is simultaneously produced with the decomposition of substrate, (3) Cl_2 or NH_3 is not released in the gas phase in the proper solution.

We have many kinds of waste organic chemicals, especially synthetic polymers, made from oil. Furthermore, a large amount of animal excrement is produced constantly. On the other hand, chlorella utilizes sun light 10 times more efficiently than the usual plants. As we have pointed out in the previous paper,3) H_2 production from photosynthetic products results in the two step decomposition of water into O_2 and H_2 combining the photosynthesis of green plant with photocatalysis of the TiO_2/Pt catalyst. Accordingly, the hydrogen production utilizing these organic materials is really attractive. At this stage, the wavelength of the light used for the photoreaction is limited by TiO_2 to 410 nm. However, this work shows the potential of this technique for the production of hydrogen fuel from many organic resources and waste materials.

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7. The composition of the chlorella used in this experiment; protein(60 %), carbohydrate(14 %), fat(11 %), other organic molecule(10 %), ash(5 %) and water(4 %).
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   The energy structure with flat band (Fig. 1) is valid for the particle whose size (≈300 Å) is smaller than the length of the depletion layer.

Table 1 The rate of H_2 production from water and various organic compounds using a TiO_2/Pt photocatalyst. (H_2: μmol/10 hours)

(a) Synthetic polymer
(b) Carbohydrate, protein, and fat
(c) Green algae, plant, insect and animal excrement

a)

REACTANT	FORMULA	H_2(μmol) neutral	H_2(μmol) 5N NaOH
I. <u>C,H,O COMPOUND</u>			
polyethylene	$\{CH_2CH_2\}$	17	93
polyvinyl alcohol	$\{CH_2CHOH\}$	45	86
II. <u>HALOGEN COMPOUND</u>			
poly-vinylchloride	$\{CH_2CHCl\}$	20	45
Teflon	$\{CF_2CF_2\}$	0.4	3.5
trichlorobenzene	$(C_6H_3Cl_3)$	35	48
trichloroethylene	$(CHCCl_3)$	16	55

b)

REACTANT	FORMULA	H_2(μmol/10hr) neutral H_2O
I. <u>CARBOHYDRATE</u>		
glucose	$C_6H_{12}O_6$	1130
sugar	$C_{12}H_{22}O_{11}$	920
starch	$(C_6H_{10}O_5)_n \doteqdot 100$	240
cellulose (filter paper)	$(C_6H_{10}O_5)_n \doteqdot 1000$	40
II. <u>PROTEIN(AMINO ACID)</u>		
glycine	NH_2CH_2COOH	220
glutamic acid	$HOOC(CH_2)_2CHNH_2COOH$	126
proline	$C_5H_9NO_2$	130
gelatin	glycine, proline, glutamic acid	71
III. <u>FAT</u>		
stearic acid	$CH_3(CH_2)_{16}COOH$	88
olive oil		32

c)

REACTANT	H_2(μmol) neutral	H_2(μmol) 5N NaOH
I. <u>GREEN ALGAE</u>		
chlorella	73	270
laver	0	332
II. <u>GREEN PLANT</u>		
rice plant	23	175
turf	20	98
III. <u>ANIMAL</u>		
cockroach	11	86
IV. <u>EXCREMENTS</u>		
human(urine, feces)	18	176
cow dung	12	198

(Experimental conditions)

1. 500 W Xe lamp (Ushio), 10 hours irradiation
2. TiO_2 (Katayama or Degussa)/Pt =300 mg
3. deionized water = 30 ml
4. H_2 production with the rate of 13 μmol/10 hours corresponds to the quantum yield of 0.1 % at λ = 380 nm.
5. poly-vinylchloride and other organic substances were purchased and used without further purification. A chlorella (Chlorella King) was purchased from Chlorella Industry Co. Ltd.[7] A cockroach, dried cow dung intended for feritilizer, olive oil for food, and rice plant were available locally.
6. The amount of organic substances used for the reactions are 1) 150 mg of polymer, 2) 500 mg of carbohydrates, protein, and fat, 3) 100 mg of algae or excrement and 4) one dead cockroach.
7. The experiment with D_2O instead of H_2O exhibited D_2 production (>90%), indicating that hydrogen comes not from the dehydrogenation of the substrate but from the reduction of water.

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