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Photocatalytic Hydrogen-Generation from Sucrose Using Polyoxotungstate Nano-Clusters

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Abstract

The photocatalytic reaction of polyoxotungstate $[BW_{12}O_{40}]^{5-}$, $[SiW_{12}O_{40}]^{4-}$, $[PW_{12}O_{40}]^{3-}$ and $[AsW_9O_{33}]^{9-}$ led to the generation of hydrogen gas from aqueous sucrose solution under irradiation of UV light. These photoreactions for each polyoxotungstate were investigated for dependence of pH level and it was displayed that hydrogen gas was obtained at low pH (around pH 2-3) without heterogeneous cocatalyst such as platinum or RuO_2. The colorless solutions changed to blue-colored solution called heteropoly blue. It indicated that one- or two-electron reduced species were produced with accompanying dehydrogenation of sucrose. Especially, the reaction of $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$ resulted in the generation of hydrogen gas with a higher yield than others. UV spectra of $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$ aqueous solution in the presence of sucrose exhibited two absorption peaks around 490 and 730, and 495 and 695 nm, respectively. The intensity increased with elapsing time of UV light irradiation. Moreover, prolonged photolysis of $[BW_{12}O_{40}]^{5-}$ with sucrose gave rise to a decrease of these absorption peaks for the UV spectra of solutions at each pH level, and blue-colored solution changed to brown after irradiation for 10 days. In addition, the photolysis of 1.9 mM solutions of $[BW_{12}O_{40}]^{5-}$ and $[SiW_{12}O_{40}]^{4-}$ were carried out in the presence of sugarcane juice at pH 2 level, and 0.15 ml and 0.51 ml of hydrogen gas were obtained from 60 ml of sugarcane juice, respectively.

Keywords: photoreaction, polyoxotungstate, hydrogen, sucrose, sugarcane juice

1. Introduction

Recently, hydrogen gas is attractive as a viable and clean fuel without CO_2 emissions. Photochemical generation of hydrogen can be regarded as indirect preservation of solar energy, and will provide an effective method for convenient use of solar energy [1]. Polyoxometalates have been investigated for photocatalytic reaction to decompose organic compounds such as alcohol, amine, ethers, alkenes, olefins and thiophenes [1-10]. The reaction was often mentioned as the dehydrogenated reaction with accompanying H_2-formation by using cocatalyst such as platinum or RuO_2, because it is known that the photolysis in the presence of heterogeneous catalyst leads to an increase in the rate of hydrogen formation.

Polyoxometalates are well-defined early transition metal-oxide nano-clusters with unique structural characteristics and multiple functions, which have significantly impacted the development of materials with catalytic, photochemical, electrochemical and magnetic properties [2, 11-14]. The photoreaction of polyoxometalates, which is initiated by the photoexcitation of the oxygen-to-metal charge transfer (O→M LMCT) bands of polyoxometalate, has been studied for the photoluminescence, photo-chromism and photocatalyst [13]. The photocatalytic reaction of polyoxometalate results in the dehydrogenative oxidation of organic substrates

Polyoxometalate, which consists of the fragments of semiconductor, exhibits photocatalytic reaction in a solution under the homogeneous system. It can also be characterized that this photocatalytic dehydrogenated reaction does not emit CO_2 gas from organic compounds.

For $[BW_{12}O_{40}]^{5-}$/MeOH aqueous system, Yamase *et al*. reported that two-electron species $[H_2BW_{12}O_{40}]^{5-}$ formed by photo-disproportionation of one-electron species $[HBW_{12}O_{40}]^{5-}$ worked as a photo-catalyst for MeOH→ H_2 + HCHO [6]. They suggested photocatalytic H_2-formation of polyoxotungstate $[BW_{12}O_{40}]^{5-}$ for the dehydrogenative oxidation of methanol at 2<pH<6 as follows;[2,6]

$$[BW_{12}O_{40}]^{5-} + CH_3O \xrightarrow{h\nu} [BW_{12}O_{40}]^{6-} + \dot{C}H_2OH + H^+$$

$$[BW_{12}O_{40}]^{6-} + CH_3OH \xrightarrow{h\nu} [BW_{12}O_{40}]^{7-} + \dot{C}H_2OH + H^+$$

$$2[BW_{12}O_{40}]^{6-} \longrightarrow [BW_{12}O_{40}]^{5-} + [BW_{12}O_{40}]^{7-}$$

$$[BW_{12}O_{40}]^{5-} + \dot{C}H_2OH \longrightarrow [BW_{12}O_{40}]^{6-} + HCHO + H^+$$

$$[BW_{12}O_{40}]^{7-} + 2H^+ \longrightarrow [BW_{12}O_{40}]^{5-} + H_2\uparrow$$

By utilizing such as waste water/biomass instead of chemical reagents (alcohol, amine, ester, etc.) for photo-catalytic generation of hydrogen, it would provide a sophisticated method to yield hydrogen gas.

Sugarcane has been considered as a candidate of biomass. The juice including mainly 12-20 wt% of sucrose is a rich organic source and expected to be an effectual electron donor. We focused on the photocatalytic H_2-generation reaction of polyoxotungstates by means of sugarcane juice, which is one of the biomass, and investigated the H_2-generation reaction of polyoxotungstate under irradiation of UV light without any cocatalyst. As a preliminary experiment, 15 wt% sucrose solutions instead of sugarcane juice were used for the photoreaction of each polyoxotungstate and the amounts of evolved hydrogen gas at the different pHs were compared for each polyoxometalate. In this work, four kinds of poly-oxotungstate; $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, $[BW_{12}O_{40}]^{5-}$ and $[AsW_9O_{33}]^{9-}$, were investi-gated in the photolysis. In addition, the prolonged photolysises of $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$ were carried out in the presence of sugarcane juice. It was suggested that the photolysis of polyoxotungstate has potential to yield hydrogen gas from biomass.

2. Experimental

2.1 Material

All chemicals were obtained from KANTO CHEMICAL Co., Inc., and $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$ were also purchased as $Na_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$. All of the solutions were adjusted at different pH values by diluted HCl and NaOH solution. Sucrose solution was prepared by 15 g of sucrose (PDH PROLAB.) added into 100 ml distill water. Fresh sugarcane juice, (BRIX=18.2 or 21.2) heated at 90˚C for 5 hours in a water bath, was used for the photolysis. $Na_9[AsW_9O_{33}]\cdot 19.5H_2O$ and $K_5[BW_{12}O_{40}]\cdot 15H_2O$ were synthesized by literature procedures and the resultant crystals were characterized by infrared spectra, respectively.[15, 16]

2.2 Photolysis of polyoxotungstates

The photoreaction was carried out by using 37 ml quartz tubes sealed by rubber cap containing the mixed solution of 20 ml of sucrose solution (15 wt%) and 10 ml of aqueous solution including 0.3 g of each polyoxotungstate. Resultant solutions were adjusted around pH$\simeq$ 2, 3, 4, 5, and 6 by hydrochloric acid or sodium hydroxide solution, respectively. After purging with nitrogen, the solutions were irradiated under 15W mercury lamp, and gas chromate-graphy (SHIMADZU, GC-14B) on an active charcoal packed column was em-ployed for analysis of hydrogen gas. FT-IR and UV spectra were recorded on Perkin Elmer System 2000 FT-IR and LAMBDA 650 UV-vis spectrometer. The photolysis of sugarcane juice was investigated by an SEN UVL20PL-6 20W low pressure mercury lamp suspended in a quartz jacket of 110 ml of photoreaction cell. The quartz jacket was surrounded by the sample solution.

3. Results and discussions

3.1 Preparation of polyoxometalates

$[AsW_9O_{33}]^{9-}$ and $[BW_{12}O_{40}]^{5-}$ were synthesized by literature procedures [15, 16] and colorless crystals were obtained as sodium and potassium salts, $Na_9[AsW_9O_{33}]$ and $K_5[BW_{12}O_{40}]$, respectively. These resul-tant crystals were characterized by infrared spectra. Fig. 1 exhibits IR spectra of these polyoxotungstates. The characteristic of metal-oxygen stretch peaks from 1000 to 400 cm^{-1} agreed with the literature data [15, 16].

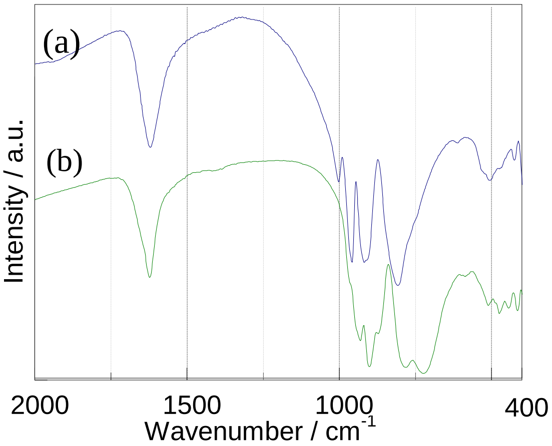

Fig.1 IR spectra of polyoxotungstate, $[BW_{12}O_{40}]^{5-}$ (a) and $[AsW_9O_{33}]^{9-}$ (b)

3.2 Hydrogen generation from sucrose solution

The photolysis of aqueous solution including 15 wt% sucrose solution (20 ml) and aqueous solution (10 ml) including 0.3 g of polyoxotungstates was carried out in the quartz tubes without cocatalyst. The dependence of pH was investigated for each photoreaction of sucrose solution (at $2<pH<6$). Each result was shown as the volume of hydrogen gas analyzed by gas chromatography. As shown in Fig. 2, the photolysis of each polyoxotungstate solution in the presence of sucrose produced most hydrogen gas at low pH level. Especially, $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$ exhibited to generate 1.15 and 0.90 (L/mol catalyst) of hydrogen gas at pH$\simeq$2 solution, respectively.

For the photolyte of $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$, hydrogen gas was produced at a range of pH values between 2 and 5. The natural pH, at which the solution includes sucrose and $[SiW_{12}O_{40}]^{4-}$, and $[BW_{12}O_{40}]^{5-}$ without adjusting pH, was 2.07 and 5.93, respectively. It was in agreement with the result of the photolysis of $[BW_{12}O_{40}]^{5-}$ in coexistence with methanol [6]. It is suggested that $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$ will be able to be applied in solutions at a wide range of pH levels for the photocatalytic H_2-generated reaction.

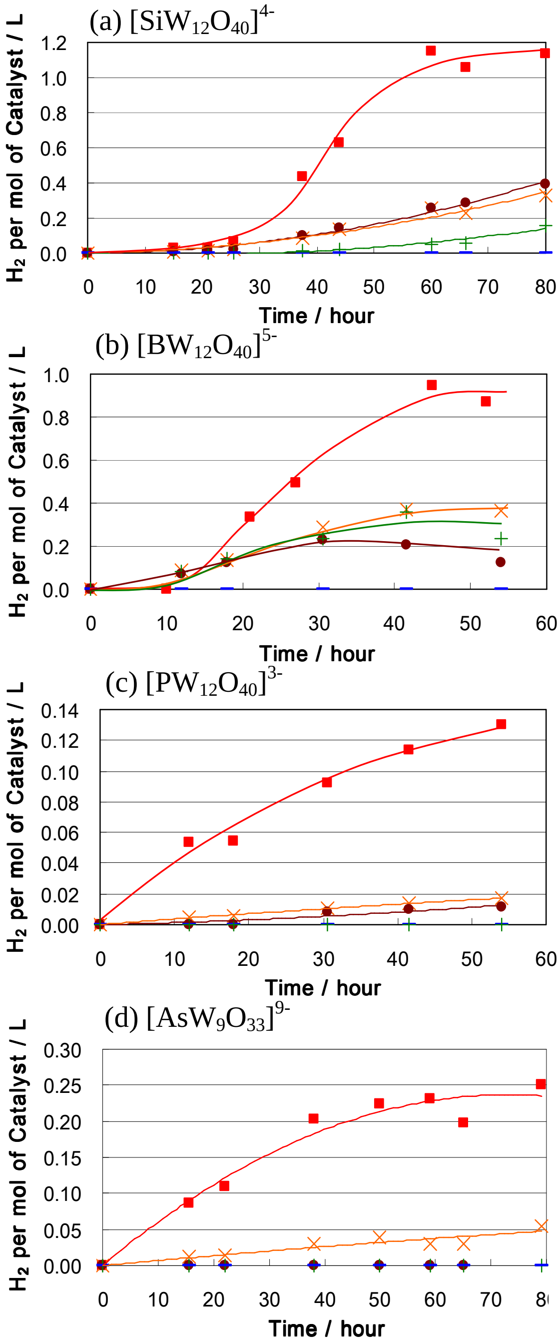

Fig. 2 Total volume of the generated hydrogen gas per 1 mol of catalyst by photoreaction of each polyoxotungstate at pH≃ 2 (-■-), 3 (-×-), 4 (-●-), 5 (-+-), and 6 (—)

The steady-state photoredox reaction of $[SiW_{12}O_{40}]^{4-}$ in the presence of sucrose at pH 1.96(natural pH), 3.04, and 5.66 led to the appearance of new absorbance bands around 490 and 730, as shown in Fig. 3. The typical absorption bands developed during the photoreaction at each pH, due to the *d-d*, and *d-d* or intervalence transitions, respectively [6].

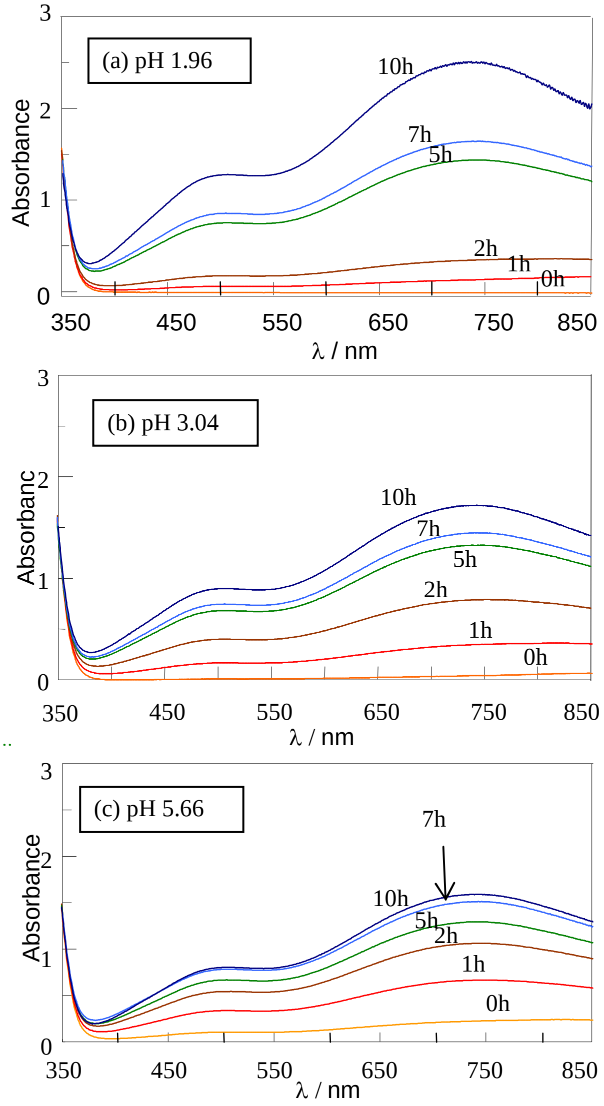

Fig. 3 Electric absorption of spectral change of $[SiW_{12}O_{40}]^{4-}$ with sucrose solution at pH levels of 1.96, 3.04 and 5.66

The solutions at natural pH exhibited a deep blue color after irradiation for more than 5 hours (Fig. 3). Similarly, prolonged photolysis of $[BW_{12}O_{40}]^{5-}$ at pH level (2.48, 3.35, and 5.93(natural pH)) exhibited absorbance bands around 495 and 695 nm, as shown in Fig. 4. The absorption bands around λ= 495 and 695 nm also developed during the photolysis and the solution at low pH exhibited high intensity of absorption band as well as the spectra of $[SiW_{12}O_{40}]^{4-}$. After 10 days, the prolonged photolysis of $[BW_{12}O_{40}]^{5-}$ produced brown-colored solution at each pH, and the absorption at 695 nm rapidly decreased.

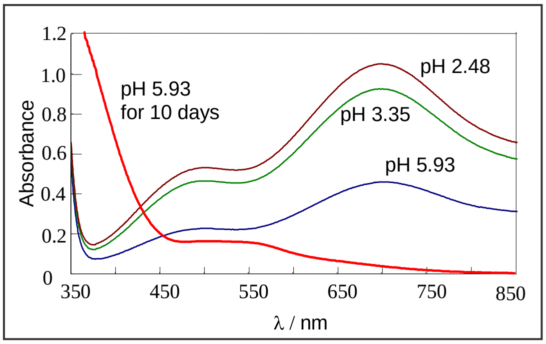

Fig. 4 Electronic absorption spectra of $[BW_{12}O_{40}]^{5-}$ solution in presence of sucrose at pH levels of 2.48, 3.35 and 5.93 after irradiation of UV light for 28 hours and 10 days

It is known that the photolysis of aqueous solutions containing $[BW_{12}O_{40}]^{5-}$ and MeOH at pH<2 lead to the formation of the brown species $[BW_{12}O_{37}(H_2O)_3]^{5-}$ [6, 17]. The successive disproportionations between protonated two-electron-reduced species $[H_2BW_{12}O_{40}]^{5-}$ results in the six-electron-reduced species $[BW_{12}O_{37}(H_2O)_3]^{5-}$ in strong acidic media [2, 6, 17]. Therefore, it was expected that the brown-colored species was the six-electron-reduced species. In fact, IR spectrum of the precipitation obtained by adding CsCl to the brown-colored photolyte showed the same characteristic pattern with $K_5[BW_{12}O_{37}(H_2O)_3]$ solid.

3.3 Hydrogen generation from Sugar-cane juice

Fresh sugarcane juice was heated in order to avoid producing a lot of CO_2 by its fermentation. 20 ml of aqueous solution including 0.15 mmol of $[BW_{12}O_{40}]^{5-}$ and $[SiW_{12}O_{40}]^{4-}$ added to 60 ml of the sugarcane juice were exposed to UV-light at pH 2.55 and 2.10, respectively. Each anaerobic solution was rapidly photo-reduced in the presence of sugarcane juice to give a blue species as well as the sucrose solution, and the photolysis led to the generation of hydrogen gas from the blue solution. The volumes of generated hydrogen are shown in Fig. 5. The respective amounts of hydrogen gas approximated to 150 and 510 μl.

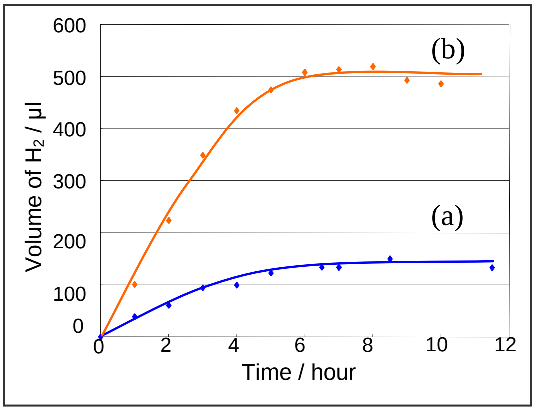

Fig. 5 Plots of the volume of hydrogen gas against the irradiation time for sugarcane juice containing $[BW_{12}O_{40}]^{5-}$ at pH 2.55 (a) and $[SiW_{12}O_{40}]^{4-}$ at pH 2.10 (b)

4. Summary

The photolysis of four polyoxotungstates, $[BW_{12}O_{40}]^{5-}$, $[SiW_{12}O_{40}]^{4-}$, $[PW_{12}O_{40}]^{3-}$ and $[AsW_9O_{33}]^{9-}$, evolved hydrogen gas from aqueous sucrose solution at low pH level. Especially, the photoreaction of $[SiW_{12}O_{40}]^{4-}$ provided 1.15 L/mol catalyst of hydrogen gas at pH$\simeq$2. The photolysis of $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$ generated hydrogen gas in a range of pH level between 2 and 5. It is suggested that $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$ solutions will be able to be used at a wide range of pH levels for the photocatalytic H_2-generated reaction.

In addition, the photoreaction of polyoxotungstate $[BW_{12}O_{40}]^{5-}$ and $[SiW_{12}O_{40}]^{4-}$ in presence of sugarcane juice also evolved hydrogen gas. These results display that the photoreaction of polyoxometalates in presence of biomass would provide an effective strategy to yield hydrogen gas.

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