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Photocatalytic Hydrogen Production from Water Using Heterogeneous Two-dimensional Rhodium Coordination Polymer $[Rh_2(p\text{-}BDC)_2]_n$

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Heterogeneous dinuclear rhodium(II) coordination polymer, $[Rh_2(p\text{-}BDC)_2]_n$ (p-BDC = 1,4-benzenedicarboxylate), which formed self-assembly infinite two-dimentional slit sheets structure was performed as hydrogen production catalyst for photochemical reduction of water under visible light irradiation in the presence of a multicomponent system containing $Ru(bpy)_3^{2+}$, MV^{2+}, and EDTA–2Na.

As molecular hydrogen is considered to be an ideal future energy source, the photochemical reduction of water to hydrogen using a catalyst is under intense investigation with the aim of developing an efficient method for converting solar radiation into chemical energy. A large number of photocatalytic hydrogen production systems have been developed in the past decades. Such systems usually consist of a photosensitizer (PS), an electron relay (ER), several sacrificial donors (SD), and hydrogen production catalyst (HPC).[1,2] So far, while heterogeneous metal colloid or semiconductor HPC has been extensively studied, there are relatively few reports on complex HPC.[3–5] However, complex HPC has been shown to exhibit catalytic activity and can be obtained by simple, cost-effective and environmentally innocuous routes. Therefore, complex HPC is still in the development stage and several aspects of this relatively new technology are yet to be explored.

Microporous coordination polymers consisting of metal ion and organic ligands are an emerging class of porous material. At present, their applications are focused on not only gas adsorption properties but also on heterogeneous catalytic performance.[6] Previously, we have specifically studied the synthesis of microporous rhodium coordination polymer that was anticipatated to be catalytically useful.[7] Herein, we describe photochemical hydrogen production from water using microporous coordination polymer $[Rh_2(p\text{-}BDC)_2]_n$ (**Rh-1**) in the presence of a multicomponent system containing $Ru(bpy)_3^{2+}$, MV^{2+}, and EDTA–2Na under visible light irradiation. Moreover, gas adsorption measurements, interaction between MV^{2+} and **Rh-1** in aqueous media and stability of **Rh-1** in this catalytic reaction are studied and discussed.

All chemicals were purchased from commercial sources and used without further purification. $[Rh_2(p\text{-}BDC)_2]_n$ (solvothermal reaction at 160 °C for 8 h)[7] and $[Rh_2(C_6H_5COO)_4]$[8] (**Rh-2**) were prepared according to a previously reported method. **Rh-1** has a two-dimensional square grid sheet assembly structure as shown in Figure 1. Synthesized **Rh-1** was grinded with agate mortar. SEM imaging of **Rh-1** revealed almost sphere shape particles of around 2.0 µm in size. (Figure S1)[14]

To evaluate the adsorption properties and the apparent surface area of this material, high-resolution N_2 adsorption isotherms for dehydrated **Rh-1** were measured at 77.4 K. (Figure 1) The isotherm revealed a type I behavior having sharp micropore filling in the range of low relative pressure. Fitting the data with the Langmuir and BET equations gave apparent surface area of 727.2 and 474.7 $m^2\,g^{-1}$, respectively. In the pore size distribution (insert picture of Figure 1b), one sharp peak is obserbed at 4.6 Å, indicating that the obtained coordination polymer has uniform micropores without nanopores.

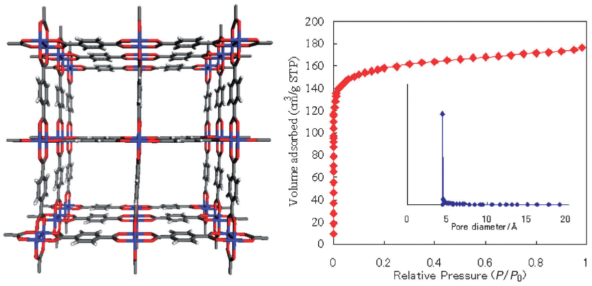

Figure 1. (a) Self-assembly coordination structure of $[Rh_2(p\text{-}BDC)_2]_n$ (**Rh-1**) (b) N_2 adsorption isotherm on **Rh-1** (insert picture: distribution of pore diameter of Rh-1).

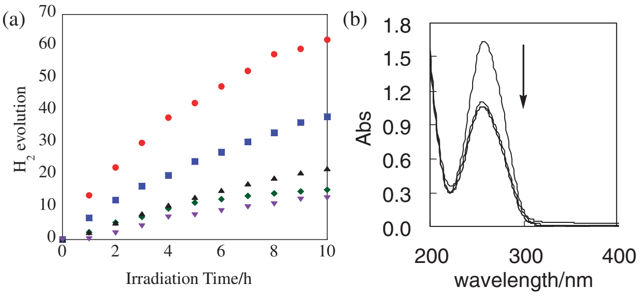

Figure 2. (a) Time course of H_2 evolution from water in the presence of multicomponent system (●: Rh-1, ■: Rh-1 and acetate buffer solution (pH 4.8), ▲: Rh-2, ◆: Rh-1 and 0.5 M NaCl, ▼: TiO_2). (b) Time-dependent UV–vis spectrum of MV^{2+} adsorption on Rh-1 (0, 15, 30, and 60 min).

Photochemical reduction of water using **Rh-1** was carried out in the presence of $Ru(bpy)_3^{2+}$, MV^{2+}, and EDTA–2Na. The time course of H_2 evolution is shown in Figure 2a. The method of measurement is given in ref 9. The initial slopes of H_2 evolution for **Rh-1** were measured to be 13.8 µmol h^{-1} with 5.50 h^{-1} TOF (turnover frequency). Prolonged irradiation led to increased H_2 production; total amount of hydrogen production reached 62.2 µmol with 24.9 TON based on **Rh-1** and 124.3 TON based on $Ru(bpy)_3^{2+}$ after 10-h irradiation. The apparent

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quantum yield of **Rh-1** is 5.96% at 450 nm. Under the same light-harvesting conditions, the activity of **Rh-1** was 4.8 times greater than that of anatase TiO_2 (BET surface area 40.0 $m^2\,g^{-1}$) after 10-h irradiation. **Rh-2**, which formed similar building block structure, was also used as homogeneous HPC under the same catalytic conditions. However, compared with Rh-1, the catalytic activity of **Rh-2** was evidently low (10-h irradiation: 22.1 µmol H_2 gas). These results indicated that coordination polymer involved Rh_2 activity site was obviously an advantage. And it was assumed that almost all of the catalytic reaction originated on the **Rh-1** surface and inner pore space near to the surface, because the pore size of **Rh-1** (4.6 Å) is narrow for MV^{2+} or MV^{+} (MV^{2+} width: 4.2 Å) to enter the pores.

Several control experiments were carried out to ascertain that photoinduced hydrogen evolution was promoted by the **Rh-1**. No H_2 evolution was detected with the omission of any of the components $(Ru(bpy)_3{}^{2+}$, MV^{2+}, EDTA–2Na, and **Rh-1** in the reaction system. And as expected, no H_2 evolution was also observed without light irradiation. Interestingly, the addition of acetate buffer (adjusted pH 4.8; 0.07 M CH_3COONa and 0.03 M CH_3COOH) led to greater decrease of H_2 evolution. This source may be related to the influence of pH, binding buffer anion to catalytic activity site and so on, as previously reported.[10] Actually, H_2 evolution decreased in the presence of an excess of NaCl. These results demonstrated that the hydrogen production activity site is an axial site of Rh_2 in **Rh-1**. The difference of amount of hydrogen production depend on particle size (0.5 µm in size) was also investigated. However, minor changing of particle size was not influenced in this catalytic reaction. To confirm whether the MV^{2+} interacted with **Rh-1** in aqueous media, time-dependent UV–vis spectra were measured.[11] As shown in Figure 2b, it shows decrease in the absorption band of MV^{2+}. Therefore, weak interaction existed that caused surface adsorption between MV^{2+} and the surface of **Rh-1**. These results clearly meant that efficient electron transfer occurred by MV^{2+} adsorption on the surface of **Rh-1**.

Finally, to prove the stability of the catalyst in this reaction, the catalyst before and after the reaction was analyzed by XPS and Fourier transform infrared (FT-IR) spectra.[12] Figure 3 shows the XPS and FT-IR spectra. In the XPS spectrum, it is evident that the binding energy of Rh ($3d_{5/2}$, $3d_{3/2}$) in **Rh-1** before and after the reaction are both around 308 or 313 eV without any obvious gap. No new binding energy was apparent. These results prove that photocolloidalization of **Rh-1** did not occur. In the FT-IR spectrum of **Rh-1**, the main peaks caused by vibrations of the organic linker before and after catalytic reactions were not different. These positive results demonstrated that **Rh-1** is stable in this catalytic reaction. In other words, photocatalytic activity is a characteristic property of **Rh-1**, the end of reaction is caused by other factor such as hydrogenation of MV^{2+}.[13]

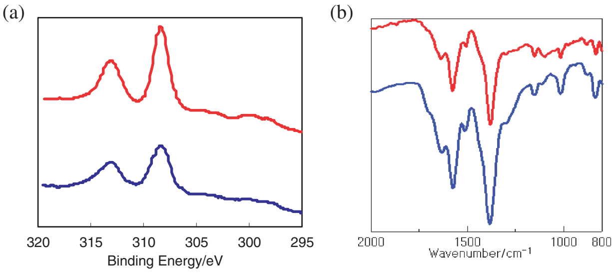

Figure 3. XPS (a) and FT-IR (b) spectra of Rh-1 before and after catalytic reaction (blue line: before reaction; red line: after reaction).

In summary, we have successfully developed a rhodium coordination polymer as heterogeneous catalyst for photochemical hydrogen production from water in a multicomponent system under visible light irradiation. Extend studies are now in progress in our group.

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9 Photocatalytic reactions were carried out in a closed gas circulation system with a pyrex reaction cell under oxygen-free conditions. The amount of H_2 evolution was determined by using online gas chromatography (Shimadzu; GC-8A, with a TCD detector, a molecular sieves 5A column, ultrapure Ar carrier gas). The reaction solution (10.0 mL, pH 4.30) containing EDTA–2Na (150 mM), $Ru(bpy)_3{}^{2+}$ (0.10 mM), MV^{2+} (5.0 mM), and $[Rh_2(p\text{-BDC})_2]_n$ (0.005 mmol) was degassed through repeated freeze–pump–thaw cycles. The reaction solution was stirred by magnetic stirrer and irradiated at 300 K using a 500 W Xe lamp (USHIO Co.) equipped with an optical cut-off filter (>400 nm).

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11 An adsorption solution containing 0.02 mmol complex and 1.0 mM MV^{2+} was stirred for 0, 15, 30, and 60 min.

12 XPS were recorded on JPS-9010 (JOEL) with Mg Kα X-ray source (10 kV, 10 mA). FT-IR spectra were recorded on a JASCO 4100 FT-IR spectrometer in KBr disk at room temperature.

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