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Hydrogen Production from Water Using Novel Three-dimensional Interpenetrated Zn–Pd Coordination Polymer

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A novel three-dimensional interpenetrated coordination polymer, $[Zn\{Pd(INA)_4\}]_n$ (INA = isonicotinate), was synthesized and structurally characterized. This material was performed as a hydrogen production catalyst for photochemical reduction of water in the presence of $[Ru(bpy)_3]^{2+}$, methyl viologen, and EDTA–2Na.

Issues related to energy and environmental problems are important topics to be dealt with in the 21st century on a global level. A promising solution is the development of catalytic systems that can harness the energy in sunlight and use that energy to decompose water into hydrogen and oxygen. The reductive side of this reaction has been studied for the past several decades with multicomponent systems containing $[Ru(bpy)_3]^{2+}$ as a photosensitizer, methyl viologen (MV^{2+}) as an electron relay, a sacrificial agent, and a hydrogen production catalyst (HPC).[1] Up to now, while metal colloid or heterogeneous semiconductor HPC has been studied extensively, there are relatively few reports on complex HPC.[2] However, complex HPC has been shown to exhibit catalytic activity and can be obtained by cost-effective and environmentally harmless routes. Therefore, complex HPC is still in the developmental stage, and several aspects of this relatively new technology have yet to be explored.

During the past several years, microporous coordination polymers, known as metal–organic frameworks (MOFs), which are constructed from metal ions as building block and organic linkers as building units, have received much attention as new types of gas adsorbent material.[3] At present, their applications are focused not only on gas storage but also on heterogeneous catalysts.[4] As one example, we have demonstrated that several Ru and Rh coordination polymers serve as an efficient HPC for the photochemical production of hydrogen from water in the presence of multicomponent systems. The catalytic activities of these HPCs are far superior to that of their building blocks (homogeneous Ru or Rh catalyst).[5] We ascertained that the reason for the high catalytic performance lies in effective electron transfer caused by the electron relay (MV^{2+}) physical adsorption occurring on the surface of the coordination polymers, the same phenomenon that has been reported for semiconductor particles, platinum catalysts, polystyrene latex, and Pyrex glass.[6] As the next step, in order to develop a heterogeneous complex HPC, we proposed construction of a novel coordination polymer that involved a building unit as a promising site for catalytic activity.

In this letter, we describe the synthesis, structure, identification, and photocatalytic reaction of a novel three-dimensional interpenetrated Zn–Pd coordination polymer that is likely to become a promising material for HPC. Additionally, interaction between MV^{2+} and the coordination polymer in aqueous media, transition of UV–vis spectrum of this catalytic reaction system, and theoretical calculation are studied and discussed.

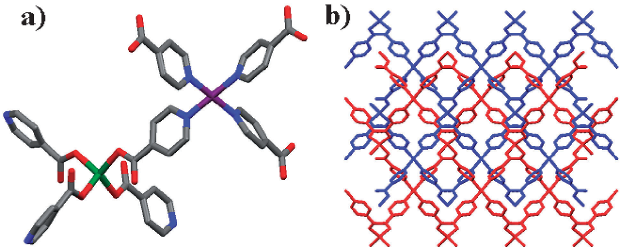

Figure 1. X-ray structure of **Zn–Pd-1**: a) structure of Pd(II) and Zn(II) metal center (●, Pd; ●, Zn; ●, C; ●, N; ●, O), b) packing view of twofold three-dimensional interpenetrated structure. Hydrogen atom and guest H_2O molecules are omitted for clarification.

The coordination polymer $[Zn\{Pd(INA)_4\}]_n$ (**Zn–Pd-1**) was prepared by the reaction of $Zn(NO_3)_2$ (0.20 mmol), $K_2[PdCl_4]$(0.050 mmol), and H-INA (0.20 mmol) in water (2.0 mL) at room temperature for 2 weeks. Elemental analysis of **Zn–Pd-1** is as follows: Calcd for $[Zn\{Pd(INA)_4\}(H_2O)_8]$: C, 35.73; H, 4.39; N, 6.82%. Found: C, 35.84; H, 4.01; N, 6.97%. The FT-IR spectrum shows carboxylate peaks at 1619 and 1549 cm^{-1} and carboxylic acid peaks are not found.

The crystal structure of **Zn–Pd-1** was determined by X-ray single-crystal diffraction.[7] As shown in Figure 1a, Pd(II) metal is coordinated by N atoms of four INA ligands and forms a $[Pd(INA)_4]$ unit. The carboxylate of the unit is bridged to mononuclear Zn(II) metal. Zn(II) metal is also bridged by four carboxylate O atoms of INA (Figure 1a). A packing view of **Zn–Pd-1** shows that the structure is a twofold interpenetrated three-dimensional framework (Figure 1b). Therefore, there is a closed pore and not enough coordination space for the storage of gas. The Langmuir surface area and pore volume of **Zn–Pd-1** calculated by an N_2 adsorption isotherm at 77 K and 760 mmHg are 14.1 $m^2\,g^{-1}$ and 0.0047 $cm^3\,g^{-1}$, respectively. From these results, we anticipated that a catalytic reaction using **Zn–Pd-1** would occur almost on the surface because the pore size of **Zn–Pd-1** is too small for MV^{2+} to enter.

As before the treatment of **Zn–Pd-1** in the catalytic reaction, synthesized **Zn–Pd-1** was ground with agate mortar. Scanning electron microscope (SEM) imaging of the **Zn–Pd-1** particles revealed polyhedral shapes smaller than 10 μm (Figure 2). Photochemical hydrogen production using **Zn–Pd-1** was performed in the presence of a light-harvesting system (LHS) solution containing $[Ru(bpy)_3]Cl_2$, MV^{2+}, and EDTA–2Na.[8]

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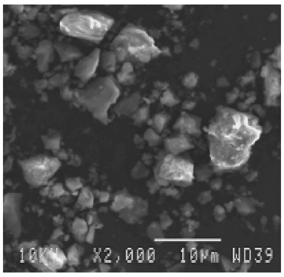

Figure 2. SEM image of ground **Zn–Pd-1**.

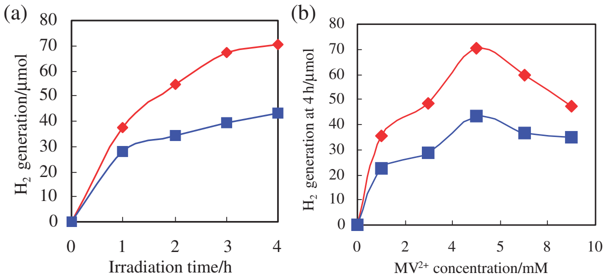

Figure 3. (a) Time course of H_2 generation from water using HPC in the presence of a multicomponent system containing 0.1 mM $[Ru(bpy)_3]^{2+}$, 5.0 mM MV^{2+}, and 150.0 mM EDTA–2Na under >420 nm irradiation; (b) MV^{2+} concentration (1.0, 3.0, 5.0, 7.0, and 9.0 mM) vs. H_2 generation (µmol) in the presence of 0.1 mM $[Ru(bpy)_3]^{2+}$, 150.0 mM EDTA–2Na, and 0.005 mmol HPC under >420 nm irradiation (HPC materials: ◆, **Zn–Pd-1**; ■, $[Pd(H\text{-}INA)_2(INA)_2]$).

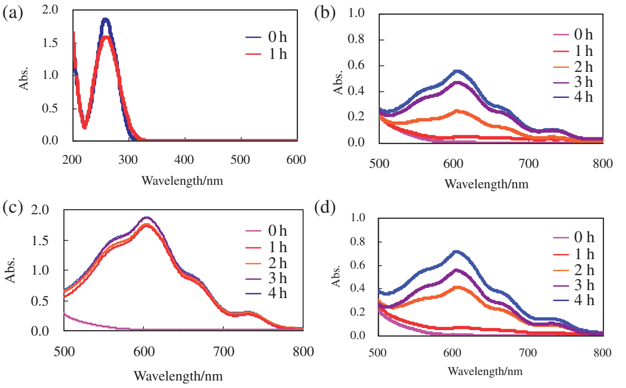

Figure 4. Time dependence UV–vis spectrum. a) MV^{2+} adsorption to **Zn–Pd-1**; b) $[Ru(bpy)_3]^{2+}$, MV^{2+}, EDTA–2Na, and **Zn–Pd-1**, 450 nm irradiation; c) $[Ru(bpy)_3]^{2+}$, MV^{2+}, and EDTA–2Na, 450 nm irradiation; d) $[Ru(bpy)_3]^{2+}$, MV^{2+}, EDTA–2Na, and $[Pd(H\text{-}INA)_2(INA)_2]$, 450 nm irradiation.

The method of measurement is given in ref 9. As a reference sample, $[Pd^{II}(H\text{-}INA)_2(INA)_2]$ was also prepared by a procedure similar to that reported in the literature.[10] The time course of H_2 evolution using these HPCs are shown in Figure 3a.

The initial slope of the H_2 evolution for **Zn–Pd-1** was determined to be 37.3 µmol h^{-1} with 14.9 TOFs (TON based on **Zn–Pd-1**/h). The amount of generated H_2 increased with time. After 4 h irradiation, 70.6 µmol H_2 gas was observed. The TON (turnover number) at 4 h was 28.2 based on **Zn–Pd-1** and 141.2 based on $[Ru(bpy)_3]Cl_2$. $[Pd^{II}(H\text{-}INA)_2(INA)_2]$, which formed a similar building unit, was also used as homogeneous HPC in the presence of LHS solution. However, compared with that of **Zn–Pd-1**, the catalytic activity of $[Pd^{II}(H\text{-}INA)_2(INA)_2]$ was evidently low (4 h irradiation: 43.2 µmol H_2 gas). The reaction stage, in which the electron transfer from MV^+ to HPC occurs, affects the catalytic reaction activity in this reaction. Therefore, we also investigated the dependence of the catalytic activity on the MV^{2+} concentration. Figure 3b plots the concentration of MV^{2+} vs. H_2 generation at 4 h irradiation in the presence of 0.1 mM $[Ru(bpy)_3]^{2+}$, 150 mM EDTA–2Na, and 0.005 mmol HPCs (**Zn–Pd-1** or $[Pd^{II}(H\text{-}INA)_2(INA)_2]$). As verified, the optimal concentration of MV^{2+} for this system was found to be 5.0 mM. Moreover, in an all-MV^{2+} concentration, the amount of H_2 evolution of **Zn–Pd-1** was greater than that of $[Pd^{II}(H\text{-}INA)_2(INA)_2]$. In comparison studies, we also investigated the catalytic activities of Pt catalysts, anatase–TiO_2, and previously reported coordination polymer HPCs in the presence of the same molarity LHS solution. As reference Pt catalysts, we used the well-studied molecular catalysts, $[Pt(bpy)Cl_2]$ (homogeneous)[11] and Pt–PVP (heterogeneous, PVP = poly(vinylpyrrolidone), Tanaka Kikinzoku Kogyo, 4.0 wt % Pt loaded, 2.0 nm in size, 13.3 mg). As expected, the catalytic activity of the Pt–PVP catalyst (604 µmol at 4 h irradiation) was far superior to that of **Zn–Pd-1**. However, the catalytic activity of **Zn–Pd-1** was about 2.1 times greater than that of the $[Pt(bpy)Cl_2]$ catalyst (34.2 µmol at 4 h irradiation). Moreover, the activity of **Zn–Pd-1** was also superior to that of anatase TiO_2 (BET surface area: 40.0 $m^2\,g^{-1}$, 2.83 µmol H_2 at 4 h), previously reported coordination polymer HPCs $[Ru_2(p\text{-}BDC)_2]_n$ (40.8 µmol H_2 at 4 h), and $[Rh_2(p\text{-}BDC)_2]_n$ (37.9 µmol H_2 at 4 h). Therefore, while **Zn–Pd-1** was not equal to the heterogeneous Pt–PVP catalyst, it was adequate for the complex HPCs.

As a control reaction, we confirmed that no H_2 evolution was detected with the omission of any of the components ($[Ru(bpy)_3]^{2+}$, MV^{2+}, EDTA–2Na, and **Zn–Pd-1**) in the reaction system. Additionally, no H_2 evolution was observed using $[Zn(CH_3COO)_2]$, which formed a similar building block structure. This indicated that Pd(II) is a catalytically active site for this reaction. These results also showed that a coordination polymer incorporating $Pd(INA)_4$ was obviously an advantageous HPC material.

To confirm whether the MV^{2+} was absorbed on the surface of **Zn–Pd-1** in aqueous media, time-dependent UV–vis spectra were measured.[12] Figure 4a shows a decrease in the absorption band of MV^{2+} by 14.3%.

As mentioned above, **Zn–Pd-1** does not have large pores for guest adsorption. Therefore, we ascertained a decrease in the number of MV^{2+} molecules assigned to physical adsorption on the surface of **Zn–Pd-1**. In fact, a similar phenomenon has also been reported for semiconductor, platinum, and coordination polymer catalysts.[5,6] This suggests that efficient electron transfer occurred by MV^{2+} adsorption on the surface of **Zn–Pd-1**.

Next, we confirmed the time dependence of MV^+ concentration in a reaction solution using **Zn–Pd-1** under 450 nm irradiation. In comparing **Zn–Pd-1** (Figure 4b) with $[Pd^{II}\text{-}(H\text{-}INA)_2(INA)_2]$ (Figure 4d) or a noncatalyst condition (Figure 4c), the concentration of MV^+ using **Zn–Pd-1** was obviously low. This indicates that **Zn–Pd-1** effectively quenched the MV^+ radical more than did $[Pd^{II}(H\text{-}INA)_2(INA)_2]$.

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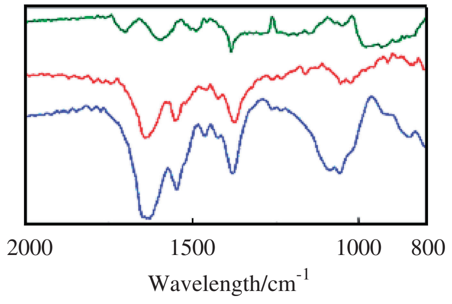

Figure 5. FT-IR spectra of **Zn–Pd-1** (–, 0 h irradiation; –, 1 h irradiation; –, 4 h irradiation). The HPCs were separated from the reaction solutions with membrane filters, and then the residues (**Zn–Pd-1**) were dried in a vacuum oven.

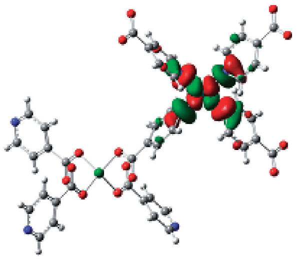

Figure 6. Calculated LUMO of model structure of **Zn–Pd-1**.

To prove the stability of the HPC in this reaction, the HPC before and after the reaction was analyzed by Fourier transform infrared (FT-IR) spectra. As shown in Figure 5, the main peaks caused by the vibrations of the organic linker before and after 1 h irradiation were not different. However, to compare with 4 h irradiation, weak peak shifts were observed. Therefore, long-time irradiation caused partial decomposition of **Zn–Pd-1**.

As previously mentioned, **Zn–Pd-1** was synthesized in water. In other words, **Zn–Pd-1** was unusually stable in water. Finally, in order to investigate the reason for the decomposition sequence of **Zn–Pd-1**, we applied the hybrid density functional theory (HDFT) calculation to **Zn–Pd-1**.[13] Figure 6 shows the LUMO (lowest unoccupied molecular orbital) of **Zn–Pd-1**. As confirmed, the LUMO of **Zn–Pd-1** was localized at σ-antibonding orbital between the $d_{x^2-y^2}$ of Pd and the surrounding (Pd–)INA ligands, but not at the Zn(II) ion site. This result indicated that the one electron reduced from MV$^+$ was received at the Pd(II) site of **Zn–Pd-1**. These results also indicated that it is possible to decompose **Zn–Pd-1** through leading to labile Pd–INA bonds by one-electron reduction. The results agreed with the previous report of theoretical calculation of the [Pt(en)Cl$_2$] molecular catalyst by Batista et al.[14] Therefore, we considered that one of the possible sources of reaching the ceiling of H_2 evolution by the long-time irradiation was a partial decomposition of the Pd–INA bond by one-electron reduction from the MV$^+$ molecule.

In conclusion, we have successfully synthesized a novel Zn–Pd coordination polymer as an effective heterogeneous catalyst for the photochemical production of hydrogen from water. The catalytic activity of **Zn–Pd-1** is the highest of any previously reported coordination polymer-HPCs. Extensive studies are now in progress in our laboratory.

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7 Crystal data are as follows: $C_{24}H_{16}N_4O_{10}PdZn$, orthorhombic, space group *Ccce* (No. 68), $a = 16.958(9)$ Å, $b = 18.523(9)$ Å, $c = 25.085(12)$ Å, $V = 7934(9)$ Å^3, $Z = 8$, $R_1 = 0.090$ (all data), $wR_2 = 0.173$ (all data), GOF = 1.001. CCDC: 770549.
8 The reaction solutions (10.0 mL, pH 4.30) containing EDTA–2Na (150.0 mM), [Ru(bpy)$_3$]$^{2+}$ (0.1 mM), MV^{2+} (5.0 mM) were degassed through repeated freeze–pump–thaw cycles. Then, the reaction solution (10 mL) and ground HPC (0.005 mmol) were shifted to a reaction vessel under an Ar atmosphere with a glove box.
9 Photocatalytic reactions were performed in a closed gas circulation system with a Pyrex reaction cell under non-oxygen conditions. The amount of H_2 generated was determined by gas chromatography (Shimadzu, GC-14B, using a TCD detector, molecular sieve 5A column, and ultrapure Ar carrier gas). The reaction solution was stirred by a magnetic stirrer and irradiated with a 500 W Xe lamp (USHIO Co.) equipped with an optical cut-off filter (>400 nm).
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12 An adsorption solution (10 mL) containing 0.02 mmol complex and 1.0 mM MV^{2+} was stirred for 1 h.
13 DFT calculation was performed by the use of LANL2DZ basis set for Pd atom, 6-31G* for Zn atom, and 4-31G for INA ligands. The hybrid DFT method (B3LYP) was applied for calculation on Gausssian 09. The model approximates an infinite coordination structure as a cluster model. The whole geometry was taken from data of X-ray crystal structure analysis.
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