Hydrogen gas sensor based upon perylene-imide derivatives

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Abstract: Perylene-imide derivatives are industrially important pigments that exhibit a variety of shades from red *via* maroon to black. In the present investigation, we have synthesized novel perylene-imide derivatives with pyridyl rings in an attempt to apply them for H₂ gas sensors based upon proton acceptors. The two N atoms of the pyridyl rings which work as proton acceptors are found to remain unbonded in the solid state according to X-ray analysis and are thus available for protonation necessary for H₂ gas sensors. The H₂ gas sensors exhibit a significant change in electrical resistivity by about three orders of magnitude even under 0.01 % H₂.

Keywords: perylene-imide; hydrogen gas sensor; crystal structure.

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1 Introduction

Perylene-imide derivatives are industrially important organic pigments that exhibit a variety of shades from red *via* maroon to black (Herbst and Hunger, 1993). These materials have also attracted attention as photoconductors for electrophotographic photoreceptors (Loufty, 1989; Duff et al., 1990) as well as materials for optical disks (Mizuguchi, 1998). We report here a new application of perylene-imide pigments with two pyridyl rings (Fig. 1) for H₂ gas sensors.

We have recently developed a novel H₂ gas sensor utilizing a high proton affinity of 1,4-diketo-3,6-bis-(4'-pyridyl)-pyrrolo-[3,4-*c*]pyrrole (*p*-DPPP: Fig. 2(a)) (Takahashi and Mizuguchi, 2005). *p*-DPPP is a dipyridyl derivative of 1,4-diketo-3,6-diphenyl-pyrrolo-[3,4-*c*]pyrrole (DPP: Fig. 2(b)) used widely as a red pigment (Herbst and Hunger, 1993). *p*-DPPP exhibits a vivid red colour like DPP and is quite stable against heat and light irradiation. However, a drastic colour change occurs from red to violet when exposed to the vapour of nitric acid, accompanied by a reduction in electrical resistivity by five orders of magnitude (Mizuguchi et al., 1993). The present outstanding effect is found to occur due to protonation at the N atom of the pyridyl ring and indicates that *p*-DPPP can be used as a material for acid sensors. However, in view of the advent of fuel cells in the near future, we tried to transform it into a H₂ gas sensor with the following idea. We believed that H₂ can dissociate into atomic hydrogens even in the solid state in the presence of Pd or Pt (which works as a hydrogen trap) assisted by a high electric field. Then, the atomic hydrogen (H) protonates *p*-DPPP at the N atom of the pyridyl ring to release an electron that contributes to the electrical current: H + pyridyl ring → protonated pyridyl ring (N⁺H) + e⁻. We have realized these functions in interdigital electrodes as shown in Fig. 3(a) where a trace of Pd or Pt is directly sputtered onto ITO (indium-tin-oxide) electrodes in the form of islands (*ca.* 3 Å) (Fig. 3(b)). Then, *p*-DPPP layer is applied by vacuum evaporation (*ca.* 300 Å). H₂ is first adsorbed on the surface of *p*-DPPP and diffuses into the bulk where H₂ encounters sputtered Pd. Then, H₂ dissociates into hydrogen atoms under a high electric field: H₂ → H + H. At this moment, the N atom of the pyridyl ring of *p*-DPPP (strong proton acceptor) captures the proton by releasing an electron. The sensor exhibits a remarkable reduction of resistivity by two

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orders of magnitude even under 0.05 % H_2 . It is also interesting to note that only *para*-DPPP is effective for H_2 gas sensors while *ortho* and *meta*-isomers give poor sensitivity. This is because the N atom of the pyridyl ring is totally blocked due to the formation of $\text{NH}\cdots\text{N}$ intermolecular hydrogen bonds between the NH group of one molecule and the N atom of the pyridyl ring of the neighbouring one (Imoda et al., 2005; Hirota et al., 2006).

In the present investigation, we extend our idea to a larger chromophore such as a perylene-imide skeleton. We have synthesized novel perylene-imide derivatives with pyridyl rings in an attempt to apply them for H_2 gas sensors. There are *ortho*, *meta* and *para*-pyridyl derivatives abbreviated to OPP, MPP and PPP, respectively (Fig. 1). These compounds are found to exhibit a better sensitivity by one order of magnitude as compared with that of *p*-DPPP. Since the free state (*i.e.* unbonded state) of the N atom of the pyridyl ring is prerequisite for H_2 gas sensors, special attention has been paid to the crystal structure of the perylene-imide derivatives.

Figure 1 Molecular conformation: (a) OPP, (b) MPP and (c) PPP

Figure 2 Molecular conformation: (a) *p*-DPPP and (b) DPP

2 Experiment

2.1 Synthesis and crystal growth

OPP was synthesized by heating perylene-3,4,9,10-tetracarboxylic dianhydride and 2-aminopyridine at 490 K in dimethylnaphthalene for 3 hours. Likewise, MPP and PPP were synthesized with 3-aminopyridine and 4-aminopyridine, respectively. The products were then purified three times by sublimation at 760 K, using a two-zone furnace (Mizuguchi, 1981). Single crystals of OPP and MPP were grown from the vapour phase. On the other hand, single crystals of PPP were grown by recrystallization from solution in 1-chloronaphthalene using an autoclave.

2.2 Fabrication of H_2 sensors based upon OPP, MPP and PPP

The interdigital electrodes made of ITO (Fig. 3(a)) were prepared by lithographic techniques. Then Pd was sputtered directly onto the electrodes by a sputter equipment (E-1030 Ion Sputter from Hitachi Corporation) in such a way as to form islands of Pd so as to avoid their contacts (Fig. 3(b)) (thickness: *ca.* 3 Å). After that, a thin layer of perylene-imide was applied by vacuum evaporation (Tokyo Vacuum Co., Ltd.: model EG240) to the thickness of about 300 Å.

Figure 3 (a) Interdigital electrodes and (b) magnified Pd-sputtered electrodes

2.3 Experimental setup for measurements of the Seebeck effect

In general, carrier determination in highly resistive materials is not an easy task because the number of charge carriers is quite small. Figure 4 shows the experimental setup for measurements of the Seebeck effect for the determination of the charge carrier concentration (Ziman, 1972; Seeger, 1985). This method measures thermoelectric power which appears between hot and cold ends of a material. The hot end is made by a soldering iron with a small spring on top maintained at 100 °C while the cold end is the ITO electrode at room temperature. If the potential of the hot end is positive, then the carriers are electrons. Similarly, if the potential is negative, the charge carriers are holes.

Since the measurement of the Seebeck effect requires a temperature gradient along the direction of the film thickness, the perylene-imide layer in the H₂ gas sensor was prepared thicker (about 1200 Å) than the standard one (about 300 Å). Because of this, the present sensor was much less sensitive by about two to three orders of magnitude than the standard one. This trade-off is required for meaningful measurements of the Seebeck effect.

Figure 4 Experimental setup for measurements of Seebeck coefficient

3 Results and discussion

3.1 Crystal structure of OPP, MPP and PPP

Table 1 details the crystallographic parameters for OPP (Mizuguchi et al., 2005), MPP (Mizuguchi et al., 2005) and PPP (Hino et al., 2005).

In the unit cell of OPP, there are two independent molecules, A and B. The ORTEP plot of these molecules are shown in Fig. 5(a). Both molecules A and B are characterized by C_i symmetry. Two pyridyl rings are twisted in the same direction with respect to the perylene-imide skeleton by 77.7° in molecule A and 72.8° in molecule B. Molecules A and B are stacked alternately along the b axis as shown Fig. 5(b). It is apparent that the N atoms of the pyridyl ring remain unbonded (*i.e.* free) without being utilized for the formation of, for example, intermolecular hydrogen bonds. Therefore, the N atoms are in a position to accept protons. This is a prerequisite condition for H₂ gas sensors.

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Likewise, the N atoms of the pyridyl ring in MPP and PPP are found to be free according to the structure analysis. These results are given in Appendix.

Table 1 Crystallographic parameters

	OPP (<i>ortho</i>)	MPP (<i>meta</i>)	PPP (<i>para</i>)
Formula	C ₃₄ H ₁₆ N ₄ O ₄	C ₃₄ H ₁₆ N ₄ O ₄	C ₃₄ H ₁₆ N ₄ O ₄
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pccn</i>
Molecular symmetry	<i>C</i> _i	<i>C</i> _i	<i>C</i> ₂
<i>Z</i>	4	2	4
<i>a</i> , Å	17.599(1)	15.422(2)	21.232(2)
<i>b</i> , Å	7.1705(5)	3.8275(6)	15.890(2)
<i>c</i> , Å	20.679(2)	19.282(3)	6.9311(8)
α , °	-	-	-
β , °	111.004(5)	103.29(1)	-
γ , °	-	-	-
Density (g cm ⁻³)	1.49	1.63	1.55
<i>R</i> ₁	0.062	0.039	0.074

Figure 5 (a) Molecular conformation and (b) molecular arrangement of OPP

3.2 Performance of the H₂ gas sensor

Figure 6(a) shows the change in resistivity of the MPP sensor as a function of bias voltage when the sensor is exposed to 100 % H₂. It is remarkable to note that the resistivity decreases drastically by four orders of magnitude at room temperature. Likewise, the OPP and PPP sensors show similar sensitivity as shown in Figs. 6(b) and 6(c), respectively. All three sensors exhibit a high sensitivity, but their sensitivity is slightly different, depending on the site of the N atom.

The concentration dependence of the H₂ sensor is shown in Fig. 7 for MPP where the H₂ concentrations are 0.01, 0.05, 0.1, 1 and 100 %. Since the initial resistivity is $1.1 \times 10^8 \Omega \text{cm}$, a reduction of the electrical resistivity by about three orders of magnitude is observed even for the concentration of 0.01 %. Furthermore, the resistivity is found to

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decrease linearly with an increase of the H_2 concentration. A similar concentration dependence is also observed in the H_2 gas sensor based upon OPP and PPP.

Figure 8 shows the build-up of the MPP-based H_2 sensor in air when 100 % H_2 is on and off, respectively. The build-up time (80 % of the maximum time) is 1 s where the gain is *ca.* 3×10^4 . Gain is defined as the ratio of the initial resistivity to the final one. This indicates that response is quit fast in the gain range of several factors. The signal builds up and then remains nearly constant after a slightly decay. When H_2 is switched off, the signal decays and comes back to the initial state in 4 s.

Figure 6 Changes in resistivity of the sensors before and after H_2 (100 %) as a function of applied voltage (a) MPP, (b) OPP and (c) PPP

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Figure 7 Log-log plot of the resistivity of the MPP sensor and H_2 concentration: 0.01, 0.05, 0.1, 1 and 100 % H_2

Figure 8 Build-up and build-down of the MPP-based H_2 sensor in air when 100 % H_2 is on and off, respectively

3.3 Determination of the charge carrier

Figure 9 shows the thermoelectric power of the PPP sensor as a function of time. A positive potential appears, in the absence of H_2 , as soon as the contact is made between soldering iron and sample. Then upon introduction of 100 % H_2 , an additional increase in positive potential is recognized. This clearly indicates that the charge carrier is due to electrons. The present result directly bears out our proposed operation principle shown in Fig. 3(b). Likewise, the OPP and MPP sensors exhibit the same behaviour.

Figure 9 Thermoelectric power of the PPP sensor

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3.4 Influence of various gases on the gas sensor

We have studied the influence of various gases on the sensing characteristic: CH₄ (1 %), CO (2 %), CO₂ (24 %), NO (0.6 %), SO₂ (0.2 %), saturated vapour of CH₃OH, C₂H₅OH and H₂O moisture. The sensor was exposed to these gases with a flow rate of 2 l/min. No noticeable effect (*i.e.* less than 0.1 % in resistivity change) was recognized for these gases, indicating that the sensors are free from the influence of ambient gases. The present result is understandable as judged from the operation principle described in section 2.2.

4 Conclusions

High-performance H₂ gas sensors have been developed that utilize the proton affinity of perylene-imide derivatives with pyridyl rings. The two pyridyl rings are found to be unbonded as shown by X-ray analysis and are thus available for protonation necessary for H₂ gas sensors. The H₂ sensor exhibits a reduction of resistivity by about three orders of magnitude at room temperature even under 0.01 % H₂. Furthermore, the process is reversible, and the response is quite fast. The charge carrier is found to be electrons on the basis of the Seebeck effect. No noticeable effect of ambient gases (CH₄, CO, CO₂, NO, SO₂, CH₃OH, C₂H₅OH, and H₂O moisture) on the sensors is recognized.

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Appendix

The ORTEP plot of MPP is shown in Fig. 10(a). The molecule is characterized by C_i symmetry. Two pyridyl rings are twisted in the same directions by 54.9° . The molecules are stacked in a fashion 'hunter's fence' along the b axis, as shown in Fig. 10(b). The N atoms of the pyridyl ring are found to be unbonded.

Figure 11(a) shows the ORTEP plot of PPP. Contrary to OPP and MPP molecules, the PPP molecule has C_2 symmetry. Therefore, two pyridyl rings are twisted in opposite directions by 74.5° . The molecules are stacked along the c axis with a tilt angle of 31.5° between adjacent molecules as shown in Fig. 11(b). Here again, the N atoms of the pyridyl ring are free and thus in a position to accept protons.

Figure 10 (a) Molecular conformation and (b) molecular arrangement of MPP

Figure 11 (a) Molecular conformation and (b) molecular arrangement of PPP