

Anomalous phenomenon in pyridyl-imidazoperylene H₂ gas sensor

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Abstract

Organic pigments were once extensively investigated as a photoconductor for the electrophotographic photoreceptor. Nowadays, they play an important role as colorants for color copies as well as materials for optical discs, electroluminescence, FET etc. Here, we report another novel application of organic pigments for H₂ gas sensors. We are involved in the research and development on H₂ gas sensors utilizing high proton affinity of the pyridyl rings integrated in the title compound (PIP). An anomalous phenomenon in PIP-based H₂ sensors has been observed that the sensor current increases even after H₂ interruption. Two N-sites in PIP are found to be involved in the protonation: N¹ at the pyridyl ring and N² at the five-membered ring. Among these, N¹ is especially sensitive to water moisture as well as H₂; whereas N² behaves as an ordinary proton acceptor as found in other pyridylring-integrated pigments. The anomalous effect is found to be due to the former N¹ behavior.

1. Introduction

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. 1(a)) [1]. *p*-DPPP is a dipyrindyl derivative of 1,4-diketo-3,6-diphenyl-pyrrolo-[3,4-c]pyrrole (DPP: Fig. 1(b)) used widely as a red pigment [2].

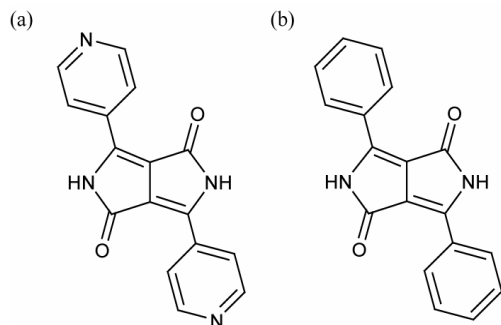


Figure 1. Molecular conformations: (a) *p*-DPPP and (b) DPP

p-DPPP exhibits a vivid red color like DPP and is quite stable against heat and light irradiation. However, a drastic color change occurs from red to violet when exposed to the vapor of nitric acid, accompanied by a reduction in electrical resistivity by five orders of magnitude [3]. 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 (about 3 Å) (Fig. 3(b)). Then, *p*-DPPP layer is applied by vacuum evaporation (about 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 orders of magnitude even under 0.05 % H₂.

In the present investigation, we aim at extending our idea to a larger chromophore such as perylene-imides. In this connection, we have synthesized the title compound (pyridyl-imidazoperylene (PIP): Fig. 2) in the expectation that PIP exhibits an even better performance than that of *p*-DPPP. Contrary to our expectation, the present sensor shows an abnormal effect that the sensor current increased even after H₂ interruption. The present phenomenon is also observed in pyridylimidazonaphthalene (*i.e.* naphthalene skeleton in place of the perylene one in Fig.1). This indicates that the anomalous effect is specific of the pyridylimidazo group [4]. With this point in mind, we intend to clarify the mechanism of the anomalous effect on the basis of the crystal structure as well as molecular orbital calculations.

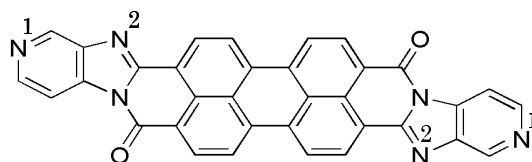


Figure 2. Molecular conformation: PIP

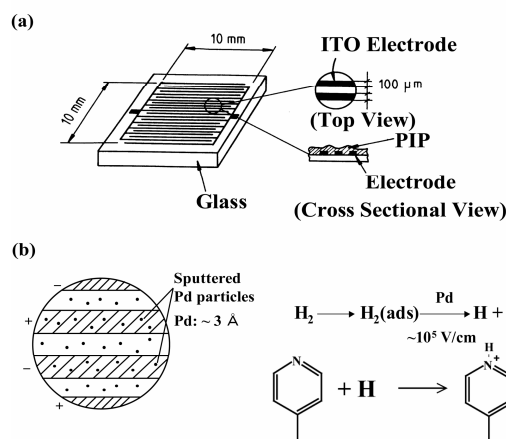


Figure 3. (a) Interdigital electrodes
(b) Magnified Pd-sputtered electrodes

2. Experiments

2.1 Synthesis and crystal growth

PIP was synthesized by heating perylene-3,4,9,10-tetracarboxylic dianhydride and diaminopyridine at 490 K in phenol for 5 h. The product was then purified by sublimation at 490 K, using a two-zone furnace [5]. Single crystals of PIP were grown from the vapor phase.

2.2 Fabrication of H_2 sensors based upon PIP

The interdigital electrode made of ITO (Fig. 3(a)) was prepared by photolithographic technique. Then, Pd was sputtered directly onto the electrode by a sputtering apparatus (E-1030 Ion Sputter from Hitachi Corporation) in such a way as to form islands of Pd so as to avoid Pd-Pd contacts (Fig. 3(b)) (thickness: about 3 Å). After that, a thin layer of PIP was applied by vacuum evaporation (Tokyo Vacuum Co., Ltd.: model EG240) to the thickness of about 300 Å.

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. Fig. 4 shows the experimental setup for measurements of the Seebeck effect for the determination of the charge carrier [6]. This method measures thermoelectric power that 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 PIP layer in the H_2 gas sensor was prepared thicker (about 1700 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.

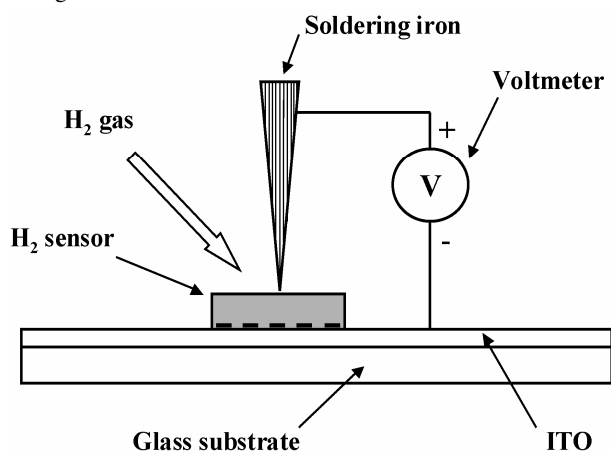


Figure 4. Experimental setup for measurements of Seebeck coefficient.

3. Results and discussion

3.1 Crystal structure of PIP

Table 1 details the crystallographic parameters for PIP. Fig. 5(a) shows the molecular conformation, showing that the present PIP is of the *trans* form. The molecules are stacked in parallel as shown in 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 prerequisite for H_2 gas sensors.

Table 1. Crystallographic parameters

PIP	
Formula	$C_{34}H_{14}N_6O_2$
Crystal system	triclinic
Space group	$P-1$
Molecular symmetry	C_i
Z	1
a (Å)	6.578(3)
b (Å)	9.123(5)
c (Å)	9.555(5)
α (°)	103.05(3)
β (°)	93.73(3)
γ (°)	90.84(3)
V (Å ³)	557.2(5)
Density (g/cm ³)	1.605

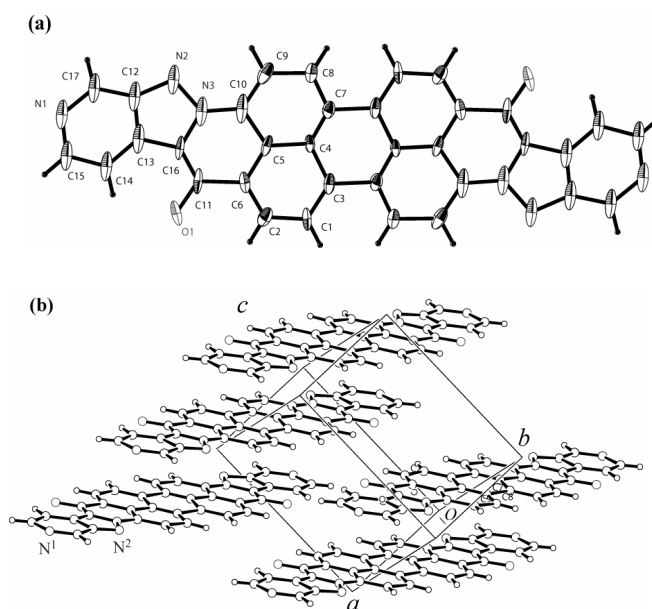


Figure 5. (a) Molecular conformation and (b) molecular arrangement of PIP

3.2 Anomalous effect of PIP-based H₂ gas sensors

Fig. 6(a) shows the standard build-up and build-down of the DPPP-based H₂ sensor in air before and after 100 % H₂. When H₂ is switched off, the signal decays and comes back to the initial state in 15 s. On the other hand, the PIP-based H₂ sensor shows faster build-up characteristic, but an anomalous effect is observed that the sensor current increases even after H₂ interruption. After about 150 seconds the current starts decaying shown in Fig. 6(b).

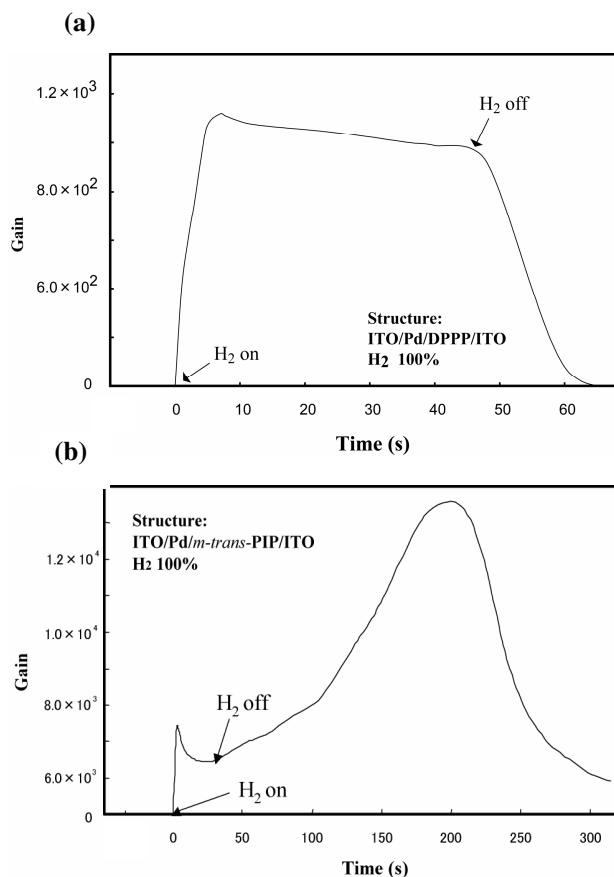
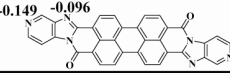


Figure 6. Response curve of the H₂ gas sensor based upon (a) DPPP, (b) PIP.

3.3 MO calculations of *trans*-PIP

Since the molecular structure is determined to be the *trans* form, MO calculations have been carried out in order to study the electron density on each atom as well as optical absorption bands of *trans*-PIP (Table 2). As revealed from this table, the following two N-sites are found to be involved in the protonation: N¹ at the piridyl ring (outer N) and N² at the five-membered ring (inner N). Furthermore, N¹ is more sensitive to proton than N² as judged from the amount of the negative charge. Therefore, the first protonation is expected to occur at the N¹ sites, followed by the protonation at the N² sites. We designate the former N¹-protonated state as the first protonated state while the latter N¹- and N²-protonated state is called the second protonated state.

Table 2. Electron densities of the N atoms and absorption bands of PIP according to the MO calculations.

	Charge of each site	Heat of formation (kcal/mol)	Wavelength (nm)	Osc. strength (f)
Initial	-0.149 -0.096 	213.6	483.6	1.88
First protonated (protonated N ¹)	-0.092 	531.5	474.6	1.93
Second protonated (protonated N ¹ , N ²)		1073.2	527.6	1.88

3.4 Absorption spectra of evaporated PIP

Fig. 7 shows absorption spectra of evaporated PIP as evaporated, as well as, before and after exposure to H₂. As evaporated, PIP exhibits blue, but the color changes soon to violet when the sample was kept in air ("before" state). Then, the color changes from violet to sky-blue upon exposure to H₂ ("after" state). As soon as H₂ off, the color returns to violet again of the "before" state. The color change from blue to violet in the initial state is also found to quickly occur when exposed to water vapor, indicating that water moisture in air is involved in the color change in the initial state.

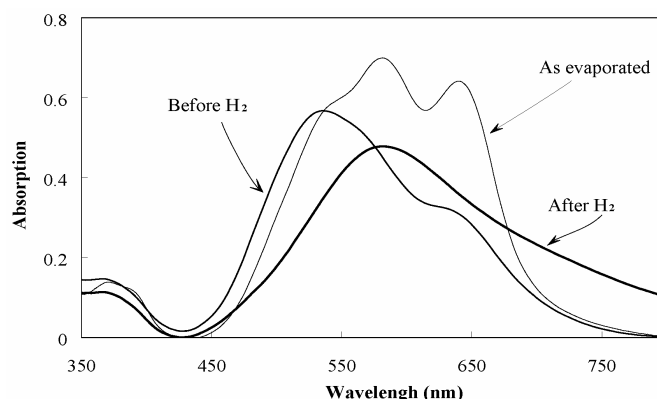


Figure 7. Absorption spectra of evaporated PIP: as evaporated, before and after introduction of H₂.

The above spectral changes can be interpreted in terms of the protonation at the N¹ and N² sites on the basis of the MO calculations (Table 2). That is, the first protonation occurs at the N¹ site by means of water moisture, followed by the second protonation at the N² site by protons dissociated from H₂ in the presence of Pd.

3.5 Measurement of the IR spectra

In parallel with the above experiment, IR spectra were also measured and their results are shown in Fig. 8(a). Figs. 8(b) and 8(c) show the standard IR spectra for water with hydrogen bonds and water vapour without hydrogen bonds, respectively. State 1 corresponds to the state as evaporated. States 2 and 3 are the colors of violet and sky-blue before and after exposure to H₂. State 4 corresponds to the violet color again after shut-off of H₂. The

broad band around 3400 cm^{-1} in states 2 and 4 is indicative of the OH stretching of the water molecule or NH (see Fig. 8(b)) caused by water moisture in air. The noisy bands in the region between $3400\text{--}3900\text{ cm}^{-1}$ in state 3 are assigned to the bands of water moisture in the absence of hydrogen bonds. Similarly, the broad band around $3400\text{--}3500\text{ cm}^{-1}$ in state 3 can be attributed to either OH or NH stretching.

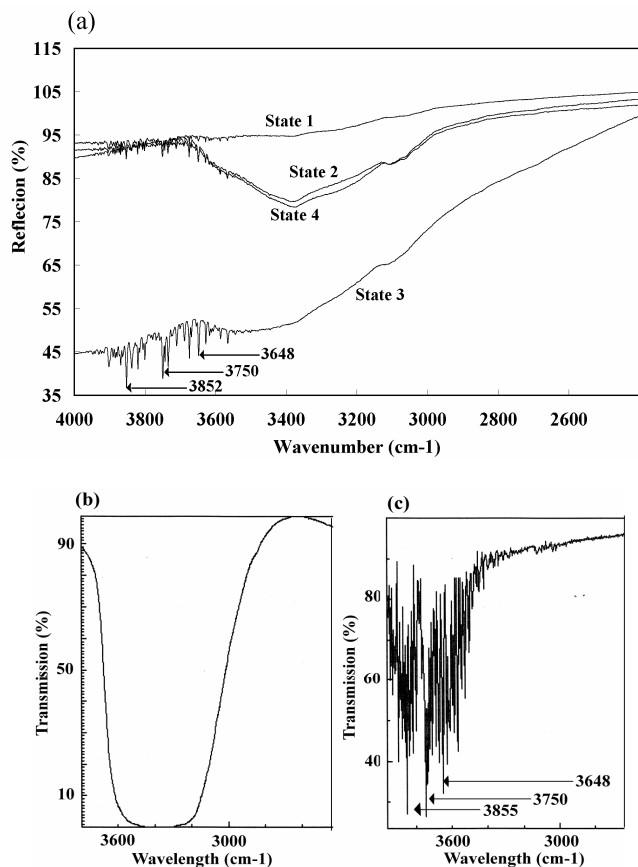


Figure 8. IR-spectra:

- PIP for various states: State 1 (as prepared), State 2 (exposure to air), State 3 (H_2 ON), and State 4 (after H_2 OFF)
- Water (with hydrogen bonds) [7]
- Isolated water (without hydrogen bonds) [7].

3.6 Carrier determination (Seebeck effect)

It is important to determine the charge carrier in order to clarify the anomalous phenomenon. We employed the thermoelectric power method (Seebeck effect) which measures the sign of the potential which appears between hot and cold ends in a material. If the potential at the hot end appears positive, then the charge carriers are electrons. On the contrary, if the potential is negative, the carrier is due to holes or cations.

Fig. 9 shows the result of the Seebeck effect of PIP when H_2 is on and off. Since the positive sign appears upon introduction of H_2 , the charge carriers are determined to be electrons. As soon as the shut-off of H_2 , the positive potential decays, indicating that the number of electrons is reduced. However, at this moment, the

sensor current starts increasing as shown in Fig. 6(b). This clearly indicates that the holes or cations are produced after shut-off of H_2 .

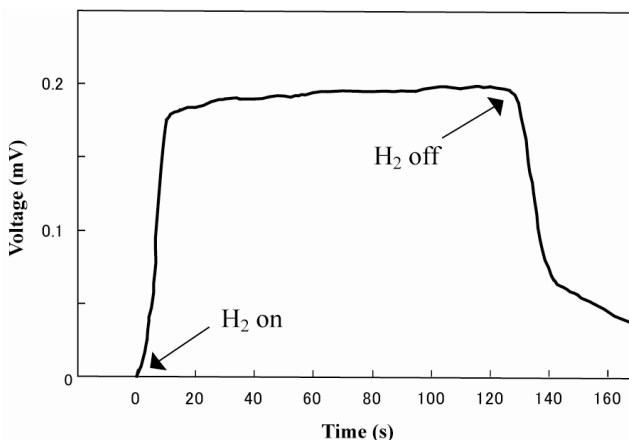


Figure 9. Thermoelectric power of the PIP

4. Discussion of the anomalous effect

We discuss the anomalous effect on the basis of the experimental results together with MO calculations in the following way. The results are summarized in Fig. 10.

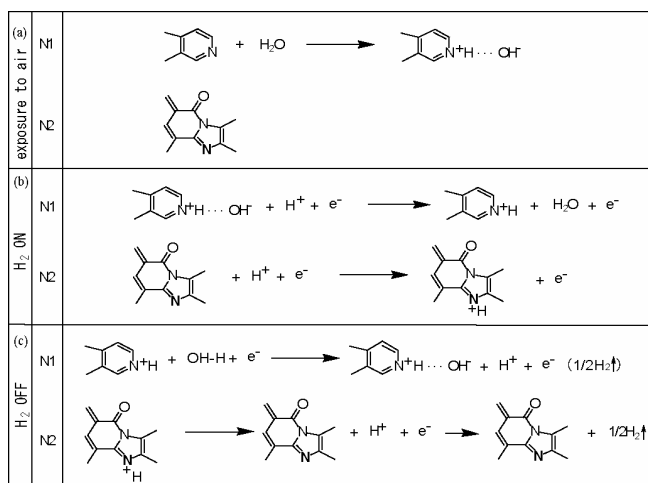


Figure 10. Protonation process upon ON/OFF of H_2 in H_2 gas sensors based upon PIP: (a) exposure to air, (b) H_2 ON and (c) H_2 OFF.

4.1 PIP sensor as prepared: Fig. 10(a)

The color of the H_2 sensor changes from blue to violet when it is allowed to stand in air (Fig. 7). We believe that the moisture included in air protonates only at the N^1 site (while the N^2 remains intact): N^1 (pyridyl rings) + $\text{H}_2\text{O} \rightarrow \text{N}^1\text{H}^+\cdots\text{OH}^-$ where the OH^- is hydrogen-bonded to NH^+ as a counter ion. This gives the OH^- stretching band around 3400 cm^{-1} (Fig. 8(b)). The color change caused by the protonation at the N^1 site in good agreement with the result of MO calculations (Table 2).

4.2 State after H₂ introduction: Fig. 10(b)

Upon introduction of H₂, both N¹ and N² sites are involved in the reaction. At first, H₂ is dissociated into protons (H⁺) on Pd assisted by a high electric field (see Fig. 3(b)). The proton reacts with OH⁻ at the N¹ site to yield (isolated) water plus one electron that contributes to the current. The isolated water without hydrogen bonds give noisy bands around 3400-3900 cm⁻¹ (Fig. 8(c)). In parallel, protonation occurs at the N² site to release one electron. This also contributes to the current. The NH⁺ stretching is observed around 3400 cm⁻¹ in Fig. 8(c). During the protonation process at both N¹ and N² sites, the color of the sensor changes from violet to sky-blue. This is in good accord with the result of MO calculations.

4.3 State after H₂ interruption: Fig. 10(c)

As soon as the shut-off of H₂, the (isolated) water molecule reacts with NH⁺ at the N¹ site to give NH⁺...OH⁻, accompanied by release of H⁺. Both the H⁺ and e⁻ contribute to the current for a while as shown by Fig. 6(b) and also suggested by the Seebeck experiment (Fig. 9). Eventually, the H⁺ recombines with e⁻ to give 1/2 H₂. This results in the decrease of sensor current. On the other hand, at the N² site, desorption of H⁺ takes place to recombine with e⁻, ending up with the formation of 1/2 H₂. This leads to the reduction of the sensor current which is the normal decay process observed in DPPP-based H₂ sensors. The shut-off of H₂ recovers the violet state (state 4 in Fig. 8(a)).

As revealed from the preceding discussion, the anomalous effect is found to arise from the formation of protons (Fig. 10(c)) at the N¹ site. The anomalous effect lasts as long as the protons remains unreccombined. The interval of the anomalous effect depends obviously on the quantity of the (isolated) water molecule. In turn, it depends on the exposure time of H₂. In fact, it is experimentally confirmed that the interval of the anomalous effect becomes shorter as the exposure time is shorter.

5. Conclusions

An anomalous phenomenon in PIP-based H₂ sensors has been observed that the sensor current increases even after H₂ interruption. The conclusions drawn from the present investigation can be summarized as follows:

1. Two N-sites in PIP are involved in the protonation: N¹ at the pyridyl ring and N² at the five-membered ring.
2. N¹ is especially sensitive to water moisture as well as H₂; whereas N² behaves as an ordinary proton acceptor as found in other pyridylring-integrated pigments.
3. The charge carriers are determined to be electrons.
4. The anomalous effect is caused by the formation of H⁺ at the N¹ site, which increases the sensor current even after the shut-off of H₂.
5. The interval of the anomalous effect depends on the exposure time of H₂. The interval of the anomalous effect becomes shorter as the exposure time is shorter.

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Author Biography

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