

Hydrogen gas sensor utilizing a high proton affinity of Copper-phthalocyanine derivative with pyridyl rings

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Abstract

We have previously developed a H₂ gas sensor that utilizes a high proton affinity of diketodipyridylpyrrolopyrrole (DPPP). We found that the N atom of the pyridyl ring of the DPPP can easily be protonated by protons dissociated from H₂ to induce a remarkable change in electrical resistivity by several orders of magnitude. In the present investigation, an attempt has been made to develop an even better H₂ gas sensor on the basis of a copper-phthalocyanine derivative with pyridyl rings (PPc). The sensor based on PPc exhibits a change in electrical resistivity by two orders of magnitude even under 0.05 % H₂. Additionally, the sensor is found to operate reversibly and is quite insensitive to ambient gases such as CH₄, CO, CO₂, NO, SO₂ and H₂O moisture.

Keywords: hydrogen gas sensor, copper-phthalocyanine, pyridyl ring

1 Introduction

Copper-phthalocyanine (CuPc; Fig. 1(a)) is an industrially important blue pigment used as colorant in painting industries as well as in imaging areas. CuPc is an entirely planar molecule whose chromophore is a macrocyclic ring system around the central Cu metal comprising 18 conjugated π -electrons [1].

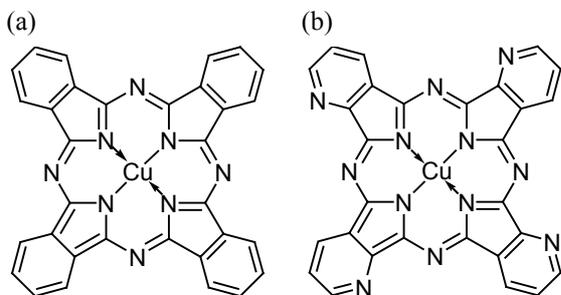


Fig. 1: Molecular conformation: (a) CuPc and (b) PPc.

We have carried out a series of investigations on H₂ gas sensors utilizing a high proton affinity of organic pigments that have pyridyl rings connected directly to the chromophore [2]. 1,4-Diketo-3,6-bis-(4'-pyridyl)-pyrrolo-[3,4-c]pyrrole (DPPP), for example, is a dipyrindyl derivative that possesses a high proton affinity because of the N atoms of the pyridyl rings. A drastic change in shade as well as electrical conductivities by several orders of magnitude was observed due to protonation at the N atom. Therefore,

DPPP had newly attracted attention as a material for H₂ gas sensor.

In the present investigation, pyridyl-copper-phthalocyanine (PPc; Fig. 1(b)) has been newly synthesized in an attempt to apply it for H₂ gas sensors. PPc molecule possesses four pyridyl rings in place of phenyl rings in CuPc and connected directly to the macrocyclic ring system. PPc is highly expected to gain an advantage in stability and costs over DPPP. This paper describes the performance of H₂ gas sensor based upon PPc.

2 Experiment

2.1 Operation principle and fabrication of the H₂ gas sensor

Fig. 2(a) shows the interdigital electrodes made of ITO (Indium-Tin-Oxide). The sensor based on the interdigital electrodes includes two important functions: one is to dissociate H₂ into protons and the other is to detect the change in electrical conductivity due to protonation. In order to dissociate H₂, we incorporate a thin layer of Pd since H₂ is known to be unstable on Pd. At the same time, we apply a rather high electric field between electrodes in order to assist the dissociation of H₂. The successful result is obtained by sputtering Pd directly on the interdigital electrodes in the form of islands as shown in Fig. 2(b), followed by application of PPc by vacuum evaporation. The sensor structure is ITO/Pd/PPc/ITO.

H₂ gas is first adsorbed on the surface of sensor material and encounters Pd to dissociate into protons as shown in Fig. 2(b). At this moment, protonation

takes place at the N atom of the pyridyl ring to release one electron. This contributes to the decrease in resistivity.

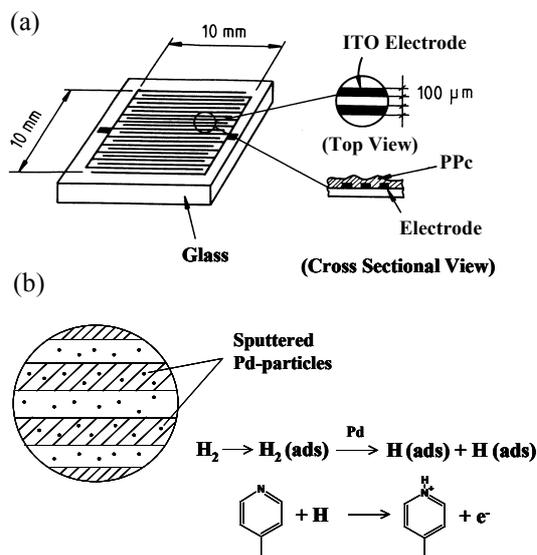
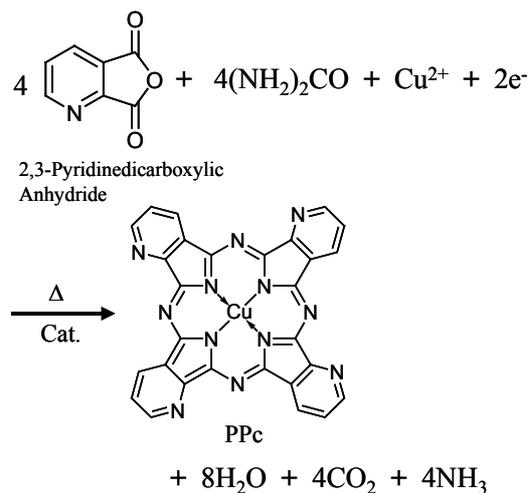


Fig. 2: (a) Interdigital electrodes and (b) magnified Pd-sputtered electrodes.

2.2 Synthesis of PPc

PPc was synthesized by the following solvent method. 2,3-Pyridinedicarboxylic anhydride and urea were heated at 200 °C in trichlorobenzene for 12 hours in the presence of copper (I) chloride and ammonium molybdate. The reaction scheme is shown below.



2.3 TGA/DSC measurements

Fig. 3 shows the TGA (thermogravimetric analysis)/DTA (differential thermal analysis) curves of PPc. PPc (subl. temp.: over 500 °C) is found to be thermally more stable than CuPc (subl. temp.: around

450 °C, not shown here). Therefore, purification by sublimation under vacuum could not be carried out with our sublimation equipment made of pyrex glass that softens above 530 °C. For this reason, PPc was used without further purification for the H₂ sensor.

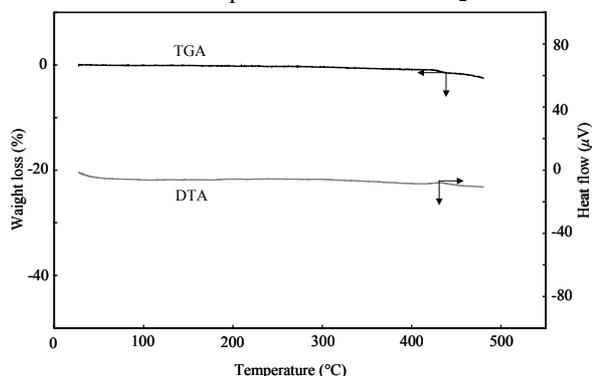


Fig. 3: TG/DTA curves measured on powdered PPc in vacuum.

2.4 Model experiment for protonation with vapors of HNO₃

Protonation experiment with vapors of HNO₃ was performed for PPc in order to confirm the protonation at the N atom of the pyridyl ring. Fig. 4 shows the absorption spectra of evaporated PPc before and after protonation. It is apparent that protonation brings about a significant change in optical absorption.

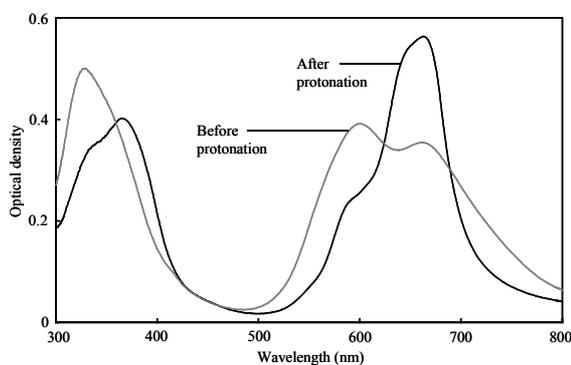


Fig. 4: Absorption spectra before and after protonation.

3 Results and Discussion

3.1 Performance of the H₂ gas sensor

Fig. 5 shows the change in resistivity of the H₂ gas sensor as a function of bias voltage upon exposure to 100 % H₂. The resistivity decreases drastically by four orders of magnitude at room temperature. Fig. 6 shows the correlation between the resistivity and the H₂ gas concentration: 0.05, 0.1, 1, 10 and 100 %. Since Fig.6 is a log-log plot, the resistivity decreases linearly with the increasing of the H₂ concentration. It

should be noted that the resistivity change in two orders of magnitude is achieved with 0.05 % H₂.

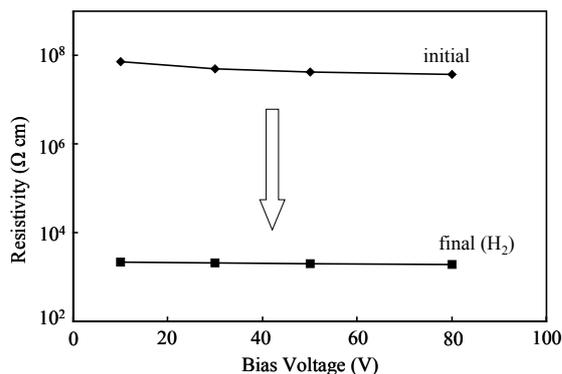


Fig. 5: Change in resistivity of the sensors initial and final (100 % H₂) as a function of applied voltage.

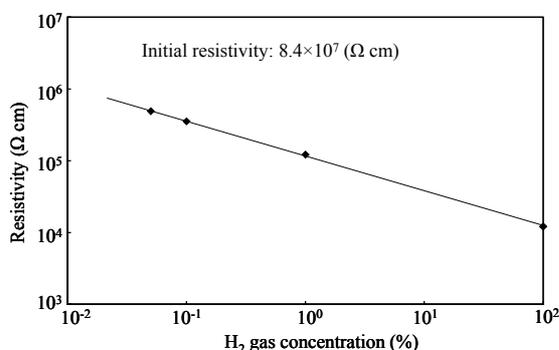


Fig. 6: Log-log plot of the resistivity of the PPc sensor and H₂ concentration: 0.05, 0.1, 1 and 100% H₂.

Fig. 7 shows the build-up and build-down of the sensor signals as a function of time. The maximum gain is about 22,500. The build-up and build-down time (80 % of maximum value) amount to about 8 sec. Since the sensor operates for a change of, for example, several factors, the response of the present sensor appears to be quite rapid. An additional appealing point is the reversibility of the sensor, showing that the signal comes back completely to the initial state when H₂ is switched off.

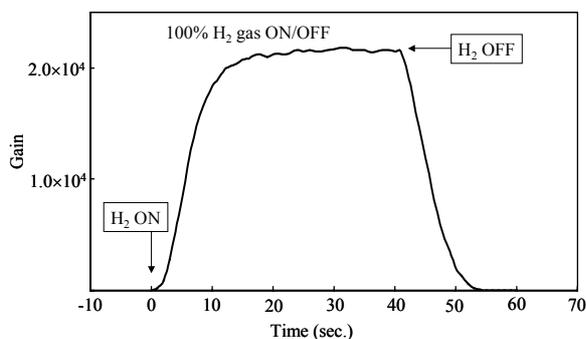


Fig. 7: Buildup of PPc sensor signal as a function of time.

3.2 Influence of various gases on the gas sensor

The influence of various gases (CH₄, CO, CO₂, NO and SO₂ gases together with H₂O moisture) on the sensing characteristics has been tested. No noticeable effect 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 2.1.

3.3 Trial for the charge-carrier determination

A trial was made to determine the charge-carrier on the basis of the Seebeck effect [3]. This information is crucial in order to support our proposed operation principle shown in Fig. 2. However, no meaningful result is not yet obtained at the present stage of investigation.

3.4 Reversibility of the sensor as viewed from MO calculations

As shown in Fig. 7, the signal decays completely as soon as H₂ is switched off. We discuss here why the return process is so rapid from the standpoint of the stability of protonated state. As a measure of the stability, we evaluated the heat of formation for variously protonated states in terms of MO (molecular orbital) calculations. We believed that if the heat of formation increases considerably upon protonation, then the protonated PPc can immediately be stabilized to the initial state by releasing protons.

Since PPc does not represent a completely saturated entity (closed shell), the present calculation has been made using pyridyl metal-free phthalocyanine in stead of PPc. Table 1 shows the heat of formation for variously protonated PPc, using the AM1 Hamiltonian in MOPAC program package. Protonation is assumed to occur at the N atom of the pyridyl ring located at the periphery of the PPc. As evident from the calculated results, the heat of formation increases drastically as the number of protonation site increases. This suggests that the protonated PPc has a tendency to release protons to return to the non-protonated, initial state. The present consideration provides a tentative explanation why the return process is so fast.

Table 1: Heat of formation of variously protonated PPc at the N atom of the pyridyl ring as obtained by MO calculations.

Protonated state	Heat of formation (kcal/mol)
non-protonated (initial)	389.18
mono-protonated	520.45
di-protonated (adjacent pair)	714.34
di-protonated (diagonal pair)	721.38
tri-protonated	960.92
tetra-protonated	1246.26

Nevertheless, it is interesting and instructive but not conclusive.

4 Conclusions

A high-performance H₂ gas sensor has been developed that utilize a proton affinity of copper-phthalocyanine derivatives with pyridyl rings. Reductions of resistivity by two orders of magnitude are achieved at room temperature for 0.05% H₂.

Furthermore, the process is reversible and the buildup and builddown times of the sensors are rapid. No noticeable effect of ambient gases (CH₄, CO, CO₂, NO and SO₂ gases together with H₂O moisture) is found in the present sensors.

References

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