Hydrogen Gas Sensor Based Upon Proton Acceptors Integrated in Copper-Tetra-2,3-Pyridinoporphyradine

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Abstract—We have previously developed a novel H_2 gas sensor based upon a high proton affinity of diketodipyrrolopyrrole. Protonation is found to bring about a remarkable reduction of the electrical resistivity and this effect has been applied to H_2 gas sensors. In the present investigation, an attempt was made to integrate proton acceptors (i.e., pyridyl rings) into copperphthalocyanine in order to improve the sensor characteristics. The present sensor exhibits a remarkable change in electrical resistivity by three orders of magnitude even under 0.01% H_2 . Furthermore, the sensor is found to operate reversibly at room temperature and is scarcely influenced by ambient gases such as CH_4 , CO , CO_2 , NO , SO_2 , CH_3OH , C_2H_5OH , and H_2O moisture.

Index Terms—Copperphthalocyanine (CuPc), hydrogen sensor, proton affinity, pyridyl ring.

I. INTRODUCTION

FUEL CELLS based upon H_2 have recently attracted attention as a clean energy source for the future [1]. However, hydrogen is the smallest atom and, thus, the H_2 gas can leak easily. In addition, it can catch fire, for example, from a spark. For this reason, reliable, inexpensive H_2 gas sensors are in great demand. The sensors based on a catalytic combustion [2], [3] as well as on an oxide semiconductor such as SnO_2 [2], [4] are two major products used widely in various industrial environments. The former utilizes a combustion heat of H_2 with O_2 in air; whereas the latter relies on the change in electrical resistivity due to H_2 in combination with a molecular sieve for H_2 . These sensors operate, however, in a limited range of H_2 between several 10 ppm and 4% H_2 (i.e., the LEL: lower explosion limit). In addition, the sensor requires external heating of about 200 °C–350 °C for the proper operation. Another type of the sensor is based upon field effect transistor (FET) [5] which utilizes a Pd or its alloy as the gate electrode. However, the output signal becomes rapidly saturated as the H_2 concentration exceeds 1%. On the other hand, a novel surface acoustic wave (SAW) type sensor prepared on a piezoelectric material functions in a wide range between 10 ppm and 100% H_2 [6]. Again, the present sensor requires external heating of about 130 °C in order to achieve a quick response of about 4 s.

In the course of our investigation on electronic structure of diketodiphenylpyrrolopyrroles known as red pigments [7], we encountered a high proton affinity of 3,6-bis(4'-pyridyl)-pyrrolo[3,4-c]pyrrole-1,4-dione [*p*-DPPP:

Fig. 1(a)] due to the N atoms of the pyridyl rings [8]. Interesting to say, protonation at the N atom brings about a drastic color change from red to violet, accompanied by a reduction in electrical resistivity by five orders of magnitude, as well as the appearance of photoconduction [8]. Among these outstanding effects, we focused especially on the resistivity change for potential applications to acid sensors. Later, however, we found it more fruitful to transform the acid sensor into a H_2 gas sensor in view of the advent of the fuel cell in the near future. We believed that H_2 can be dissociated into atomic hydrogens even in the solid state in the presence of a small amount of Pd or Pt (used as a hydrogen trap) in combination with an application of a high electric field of about 10^5 V/cm. Then, the atomic hydrogen (H) protonates *p*-DPPP at the N atom of the pyridyl ring to simultaneously release an electron that contributes to the electrical current: $H + \text{pyridyl ring} \rightarrow \text{protonated pyridyl ring (N}^+H) + e^-$. We have realized these ideas in interdigital electrodes, as shown in Fig. 2(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. 2(b)] [9], [10]. Then, *p*-DPPP layer is applied by vacuum evaporation (ca. 300 Å). H_2 is first adsorbed on the surface of *p*-DPPP and diffuses into the bulk, where H_2 encounters sputtered Pd. Then, H_2 becomes unstable on Pd and dissociates into hydrogen atoms assisted by a high electric field: $H_2 \rightarrow H + H$. At this moment, the N atom of the pyridyl ring captures the proton, ending up with a release of one electron. The sensor exhibits a remarkable reduction in resistivity by two orders of magnitude even under 0.05% H_2 [9].

Next, an attempt was made to extend our idea to a larger chromophore such as perylene-imide derivatives with two pyridyl rings [11] [Fig. 1(b)]. The present sensor exhibits even a higher sensitivity than that of *p*-DPPP by one order of magnitude.

A further trial was made in the present investigation to integrate pyridyl rings, in place of phenyl rings, at the periphery of the copperphthalocyanine (CuPc), as shown in Fig. 1(c). Four pyridyl rings are directly connected to the macrocyclic ring system composed of 18π -electrons. The present paper describes the synthesis of Cu-PPc and the performance of the H_2 sensor.

II. EXPERIMENT

A. Preparation of Cu-PPc and Its Purification

Cu-PPc was synthesized according to the reaction scheme shown in Fig. 3. 2,3-Pyridinedicarboxyrate (8.46 g, 56.7 mmol), urea (10.0 g, 166.7 mmol), and copper (I) chloride (1.55 g, 15.6 mmol) were heated at 200° in trichlorobenzene (200 ml) in the presence of hexa-ammonium heptamolybdate tetrahydrate (0.032 g, 0.026 mmol) as the catalyst. The product was filtered

Manuscript received May 9, 2006; revised August 3, 2006; accepted August 11, 2006. The associate editor coordinating the review of this paper and approving it for publication was Dr. Subhas Mukhopadhyay.

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Digital Object Identifier 10.1109/JSEN.2007.894155

Fig. 1. Molecular conformation: (a) Diketodipyridylpyrrolopyrrole, (b) perylene-imide derivatives with pyridyl rings, and (c) copper-tetra-2,3-pyridinoporphyra-dine (Cu-PPc).

Fig. 2. (a) Interdigital electrodes. (b) Magnified Pd-sputtered electrodes.

Fig. 3. Reaction scheme for the synthesis of Cu-PPc.

and washed with toluene and methanol, and then boiled with 1N HCl and 1N NaOH solutions to eliminate impurities such as unreacted cuprous salts. Finally, 4.5 g of the crude product was obtained in 54.6% yield based upon 2,3-pyridinedicarboxyrate.

Fig. 4. Experimental setup for measurements of the sensor characteristics.

The product was then purified by sublimation under vacuum, using a two-zone furnace [12].

B. Equipment

UV-VIS absorption spectra were recorded on a UV-2400PC spectrophotometer from Shimadzu. Thermogravimetric analysis and differential thermal analysis (TGA/DTA) measurements were made on powdered samples under vacuum by means of a Rigaku Thermo Plus 2 TG-8120 at a heating rate of 10 °C/min.

C. Fabrication of Sensors

The interdigital electrodes as shown in Fig. 2(a) were prepared by photolithographic technique. The electrodes were made of indium-tin-oxide (ITO). An extremely small amount of Pd was then sputtered directly onto the electrodes (E-1030 Ion Sputter from Hitachi Corporation) in such a way as to form islands of Pd so as to avoid their contacts. The optimum thickness of Pd layer is about 3 Å. Then, a thin layer of Cu-PPc was applied by vacuum evaporation to the thickness of about 100 Å (Tokyo Vacuum Company, Ltd.: model EG240).

D. Measurements of the Sensor Performance

Fig. 4 shows the experimental setup for measurements of the electrical resistivity. The current induced upon exposure to H₂ was passed through a resistance of 10 kΩ connected in series with a bias voltage supply, and the voltage generated was then amplified by about 10³ times. Fig. 5 illustrates the sample chamber used for the study of the influence of various gases on the sensor characteristics. Measurements were made with a flow rate of 2 l/min.

Fig. 5. Sample chamber for measurements of the effect of ambient gases on the sensor characteristics.

Fig. 6. Experimental setup for measurements of the Seebeck effect.

E. Experimental Setup for Measurements of the Seebeck Effect

Fig. 6 shows the experimental setup for measurements of the Seebeck effect [13], [14]. This method serves as a good means to determine the charge carrier in high-resistive materials and evaluates 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; whereas the cold end is the ITO electrode at room temperature. If the potential of the hot end is positive, then the carrier is electrons. Similarly, if the potential is negative, the charge carrier is due to holes.

Since the measurement of the Seebeck effect requires a temperature gradient along the direction of the film thickness (Fig. 6), the Cu-PPc layer of the H₂ gas sensor was prepared thicker (about 1200 Å) than the standard one (about 100 Å). Because of this, the present sensor was much less sensitive by about two to three orders of magnitude than the standard one. This tradeoff is required for meaningful measurements of the Seebeck effect.

F. Molecular Orbital (MO) Calculations

MO calculations provide information about the heat of formation (i.e., stability) of a molecule. The response time of the sensor after H₂ is off is considered to be closely correlated to the stability of protonated Cu-PPc. If the heat of formation of protonated species is much higher than that of the initial state, the decay process seems to proceed rapidly by immediately giving up protons. For this reason, the heat of formation of the initial and protonated species can be a good measure for the study of the decay process.

Fig. 7. Spectrum (a) is the solution spectrum of Cu-PPc in dimethylsulfoxide, and spectra (b) and (c) are the absorption spectra of evaporated Cu-PPc before and after protonation, respectively.

As a matter of fact, calculations should be made on Cu-PPc. However, no appropriate parameters for the Cu atom are available in the WinMOPAC program package [15]. In addition, Cu-PPc does not represent a completely saturated entity (closed shell) like metal-free-PPc. Therefore, metal-free PPc was used as the substitute for Cu-PPc. MO calculations were carried out by optimizing geometry for the initial as well as variously protonated states of metal-free PPC by means of the AM1 Hamiltonian in the WinMOPAC program package [15].

III. RESULTS AND DISCUSSION

A. Characterization of Cu-PPc in Solution and in the Solid State

Fig. 7(a) shows the solution spectrum in dimethylsulfoxide. The solution spectrum exhibits one single absorption band around 640 nm, which is typical of metal phthalocyanine compounds as characterized by *D*_{4h} symmetry [7]. On the

Fig. 8. TGA/DTA curves measured on powdered Cu-PPc under vacuum.

Fig. 9. Change in electrical resistivity of the sensor as a function of applied voltage before and after introduction of H₂. Fig. 10. Log-log plot between the resistivity of the sensor and the H₂ concentration.

Fig. 11. Buildup and build-down of the Cu-PPc sensor as a function of time.

other hand, Fig. 7(b) and (c) shows the solid-state spectra of evaporated Cu-PPc before and after protonation with the vapors of nitric acid. This is a model experiment of the H₂ gas sensor and how the optical absorption changes when the sensor captures protons. The absorption spectrum before protonation is basically quite similar to that of CuPc [7]. Then, protonation brings about a spectral change in such a way that the intensity of the two visible bands was reversed.

Fig. 8 shows the TGA/DTA curves of Cu-PPc under vacuum. Cu-PPc is surprisingly stable up to about 500 °C, which exceeds even the thermal stability of CuPc (around 450 °C) known as the most stable phthalocyanine [7].

B. Performance of the H₂ Gas Sensor

Fig. 9 shows the change in electrical resistivity of the sensor as a function of bias voltage when the sensor is exposed to 100% H₂. The resistivity decreases drastically by four orders of magnitude at room temperature. The present sensitivity is nearly equivalent to that of perylene-imide derivatives [11] and is better than that of *p*-DPPP by one order of magnitude [9]. Furthermore, bias-voltage dependence is scarcely observed, indicating the ohmic contact between Cu-PPc and ITO-electrodes.

Fig. 10 shows the sensitivity of the sensor as a function of H₂ concentration (0.01%, 0.05%, 0.1%, 1%, and 100%), where the resistivity and the H₂ concentration are displayed in a log-log plot. The resistivity change of three orders of magnitude is observed under 0.01% H₂. Furthermore, the resistivity is found to decrease linearly with increasing H₂ concentration.

The response time of the sensor is shown in Fig. 11. The maximum gain is about 22 500, where the gain is defined as the ratio of the initial resistivity to the final one. The build-up and build-down time (80% of maximum value) amount to about 8 s. However, the gain change in several factors is sufficient for the detection of H₂, and thus the sensor response is quite rapid. An additional appearing point is the reversibility of the sensor as characterized by the fast decay of the signal when H₂ is switched off.

The decay is likely to proceed as a result of H₂ desorption: $H^+ (ads) + e^- \rightarrow 1/2 H_2$. Whether desorption occurs with ease or with difficulty can be closely correlated to the stability of protonated species. Table I shows the heat of formation of variously protonated metal-free PPc at the N atom as deduced from MO calculations, where the heat of formation serves as a measure of the stability. It is apparent that the heat of formation increases significantly as the extent of protonation proceeds from *mono* to *tetra* protonation. In other words, protonated species have a tendency to give up protons as quick as possible and come back to the initial state. This could explain why the decay process is quite rapid in Cu-PPc. However, the present interpretation is not yet conclusive and requires further investigation.

C. Influence of Various Gases on the Sensor

As judged from the operation principle of our sensor described in Section I, the sensor is expected to be quite inert

TABLE I
HEAT OF FORMATION OF VARIOUSLY PROTONATED META-FREE PPC

Protonated state	Heat of formation (kJ/mol)
non-protonated (initial)	1629.1
mono-protonated	2178.6
di-protonated (adjacent pair)	2990.2
di-protonated (diagonal pair)	3019.7
tri-protonated	4022.4
tetra-protonated	5216.8

Fig. 12. Thermoelectric power of the Cu-PPc sensor upon introduction of H₂.

against ambient gases. The effect of various gases was tested on the sensing characteristics with a flow rate of 2 l/min: CH₄ (1%), CO (2%), CO₂ (24%), NO (0.6%), SO₂ (0.2%), saturated vapor of CH₃ OH, C₂ H₅ OH, and H₂O moisture. No noticeable change in electrical resistivity (less than 0.1%) was recognized for these gases. In addition, 100% H₂ was also introduced, while the above gases flowed through the chamber. Only normal change in resistivity reduction was observed due to H₂, quite independent of the ambient gases. This indicates that the sensor is free from the influence of ambient gases.

However, it is important to note that the present sensor is also quite sensitive to protons (i.e., acids), since our sensor has been transformed from an acid sensor to the H₂ sensor as stated in Section I. In order to discriminate H₂ from protons, we use a composite device with two sensors with or without Pd (or Pt). The sensor without Pd is sensitive to protons but insensitive to H₂. On the other hand, the sensor with Pd is only sensitive to H₂. Then, H₂ can be detected when the sensor with Pd responds; whereas an acid is detected when both sensors operate.

D. Determination of the Charge Carrier and the Operation Principle of the Sensor

As presented in Section I, the sensor operates in two steps: carrier formation and carrier transport. The former process assumes the electron conduction as illustrated in Fig. 2(b): H₂ → H + H, and H + pyridyl ring → protonated pyridyl ring (N⁺ H) + e⁻. In order to support the present mechanism, it is necessary to verify the electron conduction.

Fig. 12 shows the change in thermoelectric power of the Cu-PPc sensor upon introduction of H₂ as a function of time. A positive potential appears at the hot end (see Fig. 6) as soon as the contact is made between the soldering iron and the surface of sample. Then, upon introduction of 100% H₂, an additional increase in positive potential is recognized. These results indicate evidently that the charge carrier is due to electrons. The

present result directly supports the operation principle of the H₂ gas sensor.

Finally, it is important to note that CuPc is widely known as the hole conductor [16], [17]; whereas Cu-PPc is found to be an electron conductor. The difference in molecular structure between CuPc and Cu-PPc consists only in the ring at the corner: phenyl or pyridyl ring. In the case of CuPc, the charge transfer level (O₂/O₂⁻) is located near the valence band. Therefore, the adsorption of O₂ on CuPc gives rise to a hole in the valence band even at room temperature [17]: O₂ (ads) + e⁻ (valence band) → O₂⁻ (ads) + |e|⁻ (valence band). Replacement of the phenyl ring by pyridyl rings might presumably shift the charge transfer level (O₂/O₂⁻) upward so that the charge transfer cannot take place with thermal energy at room temperature. This ends up with electron conduction of Cu-PPc.

E. Some Aspects of Intelligent Sensors

Our sensor can easily be fabricated on a glass substrate with ITO as well as on a polyethylene terephthalate (PET) with ITO. In this sense, a flexible H₂ sensor is possible. Furthermore, our sensor is also sensitive to acid, as described in Section III-C. The composite device with two small sensors with or without Pd (or Pt) (see Section III-C) can serve as a sensor for both H₂ and acids.

IV. CONCLUSION

High-performance H₂ gas sensor has been developed that utilizes the proton affinity of copperphthalocyanine derivative with pyridyl rings (Cu-PPc). Remarkable reduction in electrical resistivity by three orders of magnitude even under 0.01% H₂ is achieved at room temperature. 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, CH₃ OH, C₂ H₅ OH, and H₂ O moisture) on the sensor is recognized.

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