

Detection and identification of gaseous organics using a TiO₂ sensor

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Abstract

It is well established that volatile organic compounds (VOCs) can be mineralized to innocuous organic compounds when illuminated by ultraviolet (UV) light [J. Photochem. Photobiol. A 108 (1997) 1]. The focus of this research is the development of a TiO₂-based microsensor that uses these photocatalytic reactions to identify specific gaseous organic compounds and allow operation at ambient temperatures. TiO₂ microsensors are produced using thick-film lithographic methods and cermet materials. TiO₂ and platinum films were deposited on an alumina substrate. Tests were conducted in a closed quartz glass cell at ambient temperatures and pressures. As the sensor was exposed to a variety of gaseous organic constituents in the presence of UV light, electrical characteristics of the sensor were measured. Individual gases including methylene chloride, ethanol, benzene, acetone, xylene and isopropanol produced unique signatures as they were oxidized on the sensor surface. Sensors were renewable and reusable. © 2002 Elsevier Science B.V. All rights reserved.

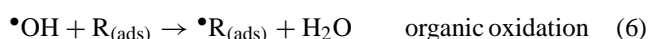
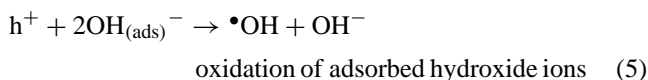
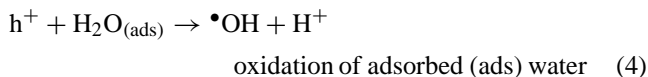
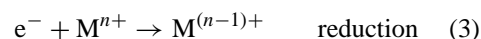
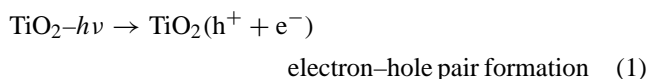
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1. Introduction

In both process industries and environmental cleanup efforts, it is oftentimes critical to rapidly and accurately assess the type and concentration of organics present in an atmosphere. Current devices capable of achieving this include Dräger tubes, electronic sensors and rapid gas chromatographs. Although these devices are effective, they can be expensive, limited to analyzing one compound, have high detection limits, detect just the presence or absence of a compound, detect only one family of compounds (with a functional group common to all compounds in that family), are not as portable as desired, and/or are not reusable. There is a need for a miniature system capable of rapidly and accurately identifying different families of gaseous organic constituents in an ambient atmosphere. This work investigates how titanium dioxide (TiO₂) can be used to produce such a sensing device.

Numerous studies over the past 10 years have examined and detailed how TiO₂ interacts with and oxidizes organic compounds in the presence of light [1–5]. TiO₂ is a semiconductor with bandgap energy of 3.2 eV. When excited by light of energy equal to or exceeding its bandgap energy, electrons are promoted from the valence band to the conduction band leaving positive holes in the valence band (Eq. (1)). These electrons and holes are capable of, respectively, reducing

and oxidizing compounds at the TiO₂ surface. If the electrons and holes do not recombine to produce heat (Eq. (2)), they can follow the reductive and oxidative pathways indicated by reactions (3)–(7) [1–4]. In addition, holes often react with water or hydroxyl ions sorbed to TiO₂, producing hydroxide radicals which, in turn, oxidize sorbed organics:



where $h\nu$ is the light energy, h^+ the hole, e^- the electron, M^{n+} the oxidized compound and $\text{R}_{(\text{ads})}$ the adsorbed organic species.

A variety of gaseous compounds have been oxidized with TiO₂, including formaldehyde, trichloroethylene, propionaldehyde, pyridine, naphthalene, tetrachloroethylene, benzene, toluene, ethylene, etc. Results from these studies

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have shown effective (up to 100%) removal and conversion (mineralization) of these organics into less toxic compounds [5]. Degradation kinetics, pathways and byproducts of these reactions have been studied and are known [6–15].

Several studies have taken known sorption reactions on TiO_2 further and examined TiO_2 for use as a sensing medium based on these sorption reactions. TiO_2 is an effective oxygen sensor, since oxygen diffuses into TiO_2 oxygen vacancies increasing the TiO_2 resistivity. This is especially noticeable at elevated temperatures [16–18]. Thin films of TiO_2 have been used at elevated temperatures (100–500 °C) to detect different types of alcohol including ethanol, methanol and propanol [19]. Chemisorption of gases on the TiO_2 particle surface changes surface states and charge distribution of the TiO_2 producing a concomitant change in resistivity [20]. The changes that occur have been used to derive current, phase lag and surface potential interactions that produce one-point relationships unique to individual compounds sorbing onto TiO_2 [21]. Chemisorption of compounds on the TiO_2 surface has also been used to capture distinct responses from applied sinusoidal voltages on rutile TiO_2 films in the presence of various organic gases. These responses were enhanced in the presence of 700 nm light [22]. However, none of these studies use the photocatalytic properties of TiO_2 .

Sensors developed in this study are thick-film anatase TiO_2 cermet sensors that operate at room temperature and photocatalytically respond to a variety of organic gaseous constituents in the presence of ultraviolet light (253.7 nm). Gases sorbed and oxidized at the TiO_2 particle surface change the surface states and charge distribution of TiO_2 . These changes can be measured by using a systematic approach that analyzes resistance signatures from the anatase TiO_2 sensors, allowing individual gaseous constituents to be distinguished and profiled. Special purpose software allows complex information to be extracted from the sensor that normally is not taken advantage of with chemical sensors. Electrical perturbations including actual peak applied potential, average applied potential, applied potential rate change and applied potential waveform shape (stair-step,

square wave, differential pulse) are controlled using programmable microcontroller devices.

2. Experimental

2.1. Preparation of TiO_2 sensors

The TiO_2 gas microsensors were fabricated by first screening platinum (Heraeus Conductor Paste, Product LP11-4493) electrodes onto aluminum oxide (Coors Corporation) substrates with a hydropneumatic industrial thick-film screen printer (Presco Model 873 with Ikegami optics). The substrates were air-dried and then fired (Lindberg type 51524 furnace) according to the profile listed in Fig. 1 to remove the organic vehicle carrying the platinum.

The electrodes were inspected and tested for conductivity. Degussa TiO_2 was combined with an organic vehicle (Heraeus vehicle RV-025) using 1.0 g of TiO_2 to 6.5 g of vehicle. The TiO_2 paste was screened onto the platinum electrodes, air-dried and fired at 350 °C for 2 h to remove the vehicle. Sensors were stored in Petri dishes (to keep them dust-free) in an ambient atmosphere until needed.

2.2. Hardware and software configuration of sensors

The hardware configuration for all tests is as follows. Sensors were connected to an integrated circuit (IC) test clip. The test clip was connected to a National Instruments CLB-50 screw-down terminal board via twisted pair ribbon cables. The terminal board was linked to a data acquisition system (DAQ Card-1200). A Compaq Presario 1200 PII computer was used to control the system using software developed at Argonne National Laboratory (Argonne's Data Acquisition and Analysis (DA²) version 1.11ssd (stair-step development)). Leads from the sensor were encased by an aluminum-covered stopper with two injection ports built into it. The injection ports allowed for liquids to be injected into the jar and for air to purge the jar. Tests were conducted by

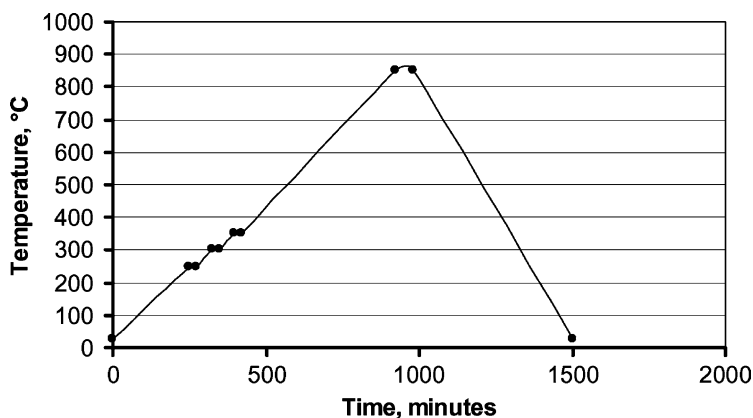


Fig. 1. Furnace firing profile for platinum electrodes.

inserting the sensor into a 410 ml quartz bell jar and sealing the jar with the stopper. The quartz jar was then positioned inside of a photochemical chamber reactor (Rayonet Photochemical Reactor Chamber RMR Model 600) containing eight ultraviolet lights (253.7 nm) producing 0.1 Einstein/min.

2.3. Testing procedures

During the first phase of sensor testing, a sensor was clipped to an IC test clip and inserted into the quartz bell jar in darkness. The jar was flushed with compressed air (through the inlet and outlet ports in the stopper) for at least 10 min at the rate of 11/min. The compressed air flow was turned off and a cyclic potential sweep from 0 to +5.0 V, +5.0 to 0 V, 0 to -5.0 V, and -5.0 to 0 V was applied to the sensor via the software controls. The resulting voltage–current measurements were captured as a resistance curve with the data acquisition system. The resistance curves contain some redundant information but represent a suitable method for initial characterization of electrical property changes in the TiO₂ films. Triplicate resistance curves were acquired for every new condition imposed on the sensor system. In the second phase of sensor testing, all UV lights were turned on and three resistance curves were recorded. During the third phase, the UV lights were turned off and a compound was injected into the jar and equilibrated for 2 min in darkness and so its vapor would saturate the atmosphere inside of the jar. Three resistance curves were taken and recorded with the sensor remaining in the dark. Following this phase, the UV lights were turned on, a stopwatch was begun, and three resistance curves were immediately recorded (phase 4). After 5 min of illumination, three final resistance curves were recorded (phase 5). The UV light was turned off and three final resistance curves were taken (phase 6). The stopper was removed from the bell jar, and

the sensor and bell jar were flushed with compressed air for 10 min and allowed to equilibrate with the atmosphere for approximately 4 h before another test commenced.

All initial and duplicate tests used new sensors. Sensors were used multiple times in some situations to test the integrity of the sensor and the reproducibility of its signal and possible contamination of the sensor. Multiple use of sensors is described in Section 3. Reused sensors were allowed to equilibrate with the ambient atmosphere for at least 4 h before reuse occurred.

Collected resistance curves were evaluated for qualitative changes (slopes, plateaus, drop-offs, inflection points and spikes) and the locations of these features in relation to one another.

3. Results and discussion

The resistance curves shown in Figs. 2–4 depict responses of the sensors and illustrate their capacity for detecting and distinguishing specific contaminants. The compounds used to assess sensor response include methylene chloride, ethanol, benzene, acetone, xylene and isopropanol. The (saturated) concentrations of these compounds used in the experiments are shown in Table 1.

Table 1
Concentrations of contaminants present in the experiments

Contaminant	Concentration (ppmv)
Methylene chloride	464000
Ethanol	59000
Benzene	126000
Acetone	285000
Xylene	13000
Isopropanol	43000

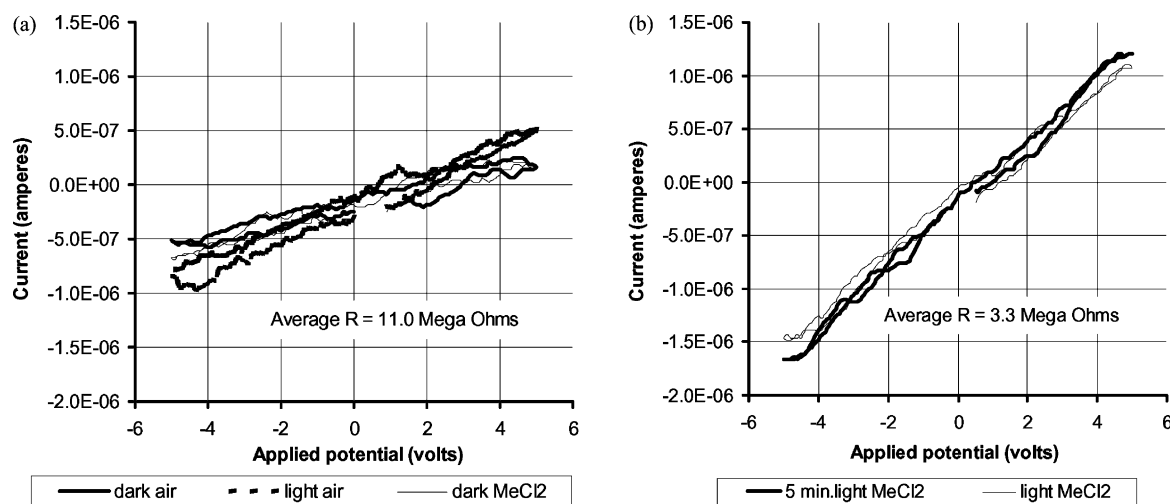


Fig. 2. (a) The responses of the TiO₂ sensor during phases 1–3, and (b) phases 4 and 5. The contaminant used was methylene chloride (MeCl₂). Resistances (*R*) are averaged and shown.

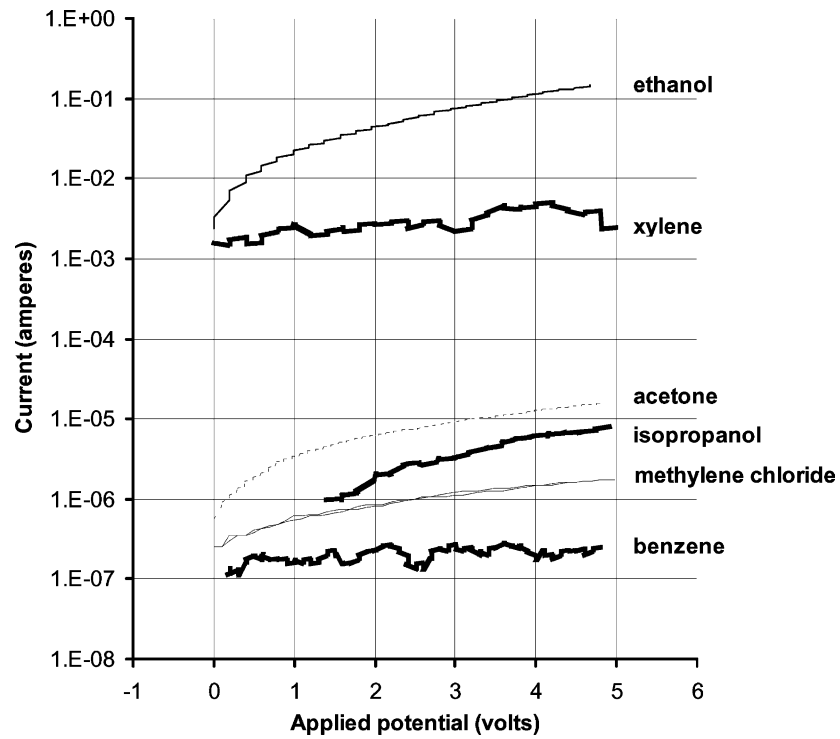


Fig. 3. Linear sweep response of the TiO_2 sensor to saturated concentrations of various compounds in an air atmosphere. Voltage and current are both direct.

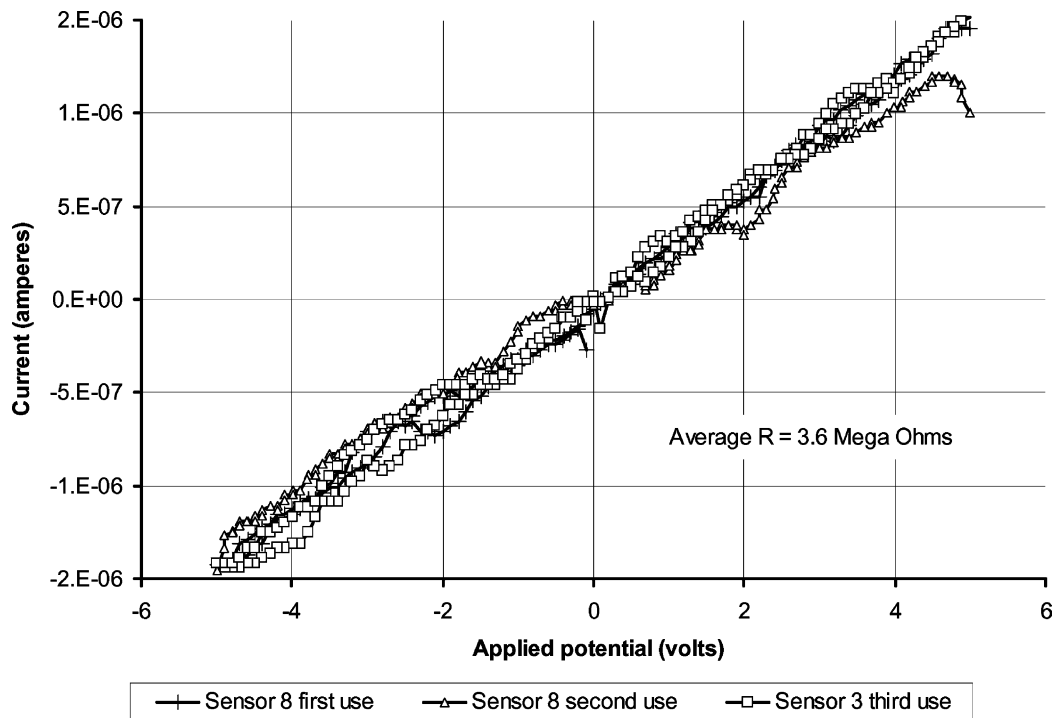


Fig. 4. The response of two sensors to methylene chloride in the presence of UV light. Sensor 8 was used twice within 1 week. Sensor 3 had been used twice before this experiment to detect isopropanol. The responses followed the same curve, producing an average resistance of $3.6\text{M}\Omega$.

Figs. 2–4 show the responses of the TiO₂ sensors to various conditions and demonstrate: (1) dependence of the sensor response to a given compound on the presence of light, (2) the unique response to individual compounds in the presence of light, (3) the signal reproducibility between sensors in response to one specific compound, and (4) the impact of time on sensor storage and signal generation.

Fig. 2a shows three responses of the sensor. The first is to air in the absence of light (phase 1), the second is to air in the presence of UV light (phase 2), and the third is to methylene chloride in the dark (phase 3). Fig. 2b shows the response of the same sensor to methylene chloride upon illumination (phase 4) and with an extended illumination period (phase 5).

The response curves in Fig. 2a reveal that very little change, if any, in sensor resistance occurs in the dark with and without methylene chloride present and in air when illuminated. This response is expected, since there is no significant oxidation of contaminant on the TiO₂ surface. When the sensor is illuminated in the presence of methylene chloride, however, the resistance of the sensor changes dramatically from the signatures gathered in Fig. 2a, producing a unique signal that is unaffected by the illumination period (from seconds to minutes) as demonstrated in Fig. 2b. The signatures in Fig. 2b have very different slopes than those gathered in Fig. 2a. Similar results have been obtained for all other compounds tested in this study.

Fig. 3 demonstrates the unique sensor responses obtained from sensor exposure to different compounds in the presence of UV light (phase 4 tests).

As shown in Fig. 3, distinct responses are obtained from the TiO₂ sensor as it is exposed to saturated concentrations of various constituents in air. These results can be explained by the photocatalytic properties of TiO₂, and the known photoreactions of TiO₂ as described in Eqs. (1)–(7) [23–25]. Certain organic compounds exhibit a specific affinity for TiO₂, allowing varying amounts of charge transfer to occur between the TiO₂ and the sorbed constituent. Functional groups dictate the orientation of the sorbed compound to the TiO₂. This orientation affects both how the compound is bound to the TiO₂ surface, and the pathway where charge transfer will occur from the TiO₂ to the compound [23–25]. As Fig. 3 shows, compound properties influence TiO₂ conductivity. This phenomenon can be used as the basis for developing sensor selectivity.

Both the recovery of a sensor and ability to renew the sensor are demonstrated in Fig. 4. The curves in Fig. 4 show three respective responses: (1) the response of a newly fabricated sensor (sensor 8) to methylene chloride, (2) the response of sensor 8 to methylene chloride a week after the initial test was performed, and (3) the response of a different sensor, sensor 3, to methylene chloride. Sensor 3 previously had been used twice to detect isopropanol.

Fig. 4 shows the response of sensor 8 to methylene chloride in the presence of light is consistent from one run to another. Sensor 8 had been used, then regenerated by exposing it to ambient air for 24 h prior to using it for the second test.

Sensor 3 had been used twice in the previous year to detect isopropanol. The data from both sensors 3 and 8 shown in Fig. 4 demonstrate that the sensors can be renewed and regenerated, and perform consistently without any gross variance occurring in signal response. These data also indicate that the TiO₂ is not fouled, but is “renewable”, producing consistent, predictable results when reused. Sensors 3 and 8 were not screened onto the same substrate during fabrication; sensor 8 was manufactured 1 year after sensor 3 had been fabricated. The data in Fig. 4 indicate that the manufacturing process is capable of producing consistent sensors from batch to batch, and the pastes used in manufacturing processes can be stored for at least a year without alteration in their chemical properties.

4. Conclusions

Results from this study show that the TiO₂ sensor is capable of detecting and distinguishing a variety of compounds in ambient air. Resistance curves produced in this study clearly show a marked difference in output signal for each contaminant. Saturated concentrations of xylene, ethanol, acetone, isopropanol, methylene chloride and benzene in air all produced unique, distinguishable voltammograms upon sensor illumination with UV light. Resistance curve slopes and shapes are unique for each compound, providing the necessary information for future analyses that would use pattern recognition tools to resolve the generated signals.

The resistance curves do not change when the sensors are illuminated over several minutes (provided the concentration of contaminant is sufficient to propagate the signal). This is beneficial since no correction factor needs to be introduced to compensate for shifts in signal response. Sensor fabrication is simple, and the signal response from sensors obtained from different batch productions is consistent and reproducible. Sensors are renewed simply by exposing the sensor to ambient air for a short period of time. This is beneficial because it eliminates the need for chemical or thermal regeneration sometimes associated with chemical sensors. Sensors can be reused several times, even to detect compounds other than those detected initially. Signal response was not impaired after sensor reuse.

Acknowledgements

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