

Multiple Gas Sensing Device Based On Nano-Porous Structure Of Zeolite Coated With Nile Red Dye

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Abstract

Gas detection is vital in different fields including environmental applications, clinical analysis, and homeland security. To perform these tasks, the sensors need to be stable, sensitive and selective, operate at room temperature, rapidly respond, and easy to regenerate. On the other hand, most chemical sensors often suffer from a lack of selectivity, i.e., reacting more or less similarly to a collection of substances. As a result, this has led to false alert. Moreover, in a worse scenario, the molecules to be detected have been masked by some interfering compounds. In this research, a gas sensing device has been designed for manufacturing using CMOS technology. The device integrates a nanoporous zeolite/nile red dye unit with optoelectronic detector. The device will detect and measure more than one target gas at the same time. Since we are dealing with nanoporous structures of zeolites, the device is more accurate, more sensitive, can better differentiate and detect any one chemical component in a mixture of different gases. This is achieved by incorporating fluorescent dyes into the zeolites' cavities, measuring gas absorption, desorption and photo-chromic interaction of dye and gases, interfacing the zeolite/dye sensor arrays with light source and electronic detectors. The electronic part of the device is fully customized VLSI chip. The final device will be packaged into a portable unit.

Key words: gas sensor, zeolite, nile red dye

1. Introduction

Polluted air may contain gases which are harmful to human being, animals, or ecosystems. One of the common and significantly toxic gases is carbon monoxide (CO), which results from incomplete combustion of carbon-base fuels and substances. CO gas is colorless, odorless, tasteless and non-irritating; thus, it is difficult for human being to detect this gas. More than 50% of fatal poisonings in many industrial countries may result from CO poisoning [1]. Another toxic and extremely hazardous gas is hydrogen sulfide (H₂S), which is colorless, flammable, and smells like rotten egg. It is commonly found in places like sewers, manure stockpiles, mines, hot springs and holds of fishing ships. Concentrations above 100 parts per million (ppm) cause rapid temporary paralysis of the olfactory nerves in the nose, leading to a loss of the sense of smell. Besides, exposure to

lower concentrations of H₂S over period of time also causes similar effects of olfactory fatigue [2]. Methane (CH₄) is another common gas, which is also colorless, and odorless. Even though little information is available on its toxicity, methane is flammable, and forms explosive mixtures with air, thus may be harmful [3].

The above mentioned are just a few in the long list of gases that need to be early detected in order to protect humans, animals and ecosystems. As a result, there has been major focus on developing fast and sensitive methods to detect and quantify these gases. Spectrometric analysis certainly provides the most information about the species under test; however, it is also the most complicated and the actual devices are cumbersome and expensive [4]. Therefore, it is very helpful to have portable, accurate, sensitive, and selective devices with rapid

response so that they can be used outside laboratories.

2. Zeolites and Nile Red Dye

Zeolite and Nile Red dye (NR) are the two important chemicals to be used in the portable gas detection device for their own unique characteristics. Thanks to the porous structure and its adsorption property, the former has been used in different researches as a system to host other chemicals, to remove moisture, to filter and separate gases, etc. The latter has been utilized for its absorption and emission shift when adsorbing different chemicals. In this research, NR will be incorporated into the porous structure of Zeolite-Y forming the analog sensing front end of the portable device. The combination will convert the presence of particular gases into light of different wavelengths that will be converted into electrical signal to be processed by the electronic unit.

2.1 Zeolite Structure and Characteristics [15]

The novelty of zeolites comes from their microporosity and the topology of their framework. Firstly, thanks to the porous structure, zeolites have large adsorption surface. Their internal surface is highly accessible, and can compose more than 98% the total surface areas which are typically of the order of 300-700 m²/g. Secondly, the framework composition of zeolites depends on the synthesis condition, and the amount of aluminum within the framework can change over a wide range, with Si/Al ratio from 1 to infinity. As the Si/Al ratio increases, the hydrothermal stability as well as the hydrophobicity increases. Thirdly, in as-synthesized zeolites, the sorbed phase and organic non-framework cations can be removed, making the intracrystalline space available. Besides, the fact that zeolites retain their structure integrity after water having been removed makes zeolites different from other porous hydrates such as calcium sulfate (CaSO₄). Fourthly, the extra-framework cations are ion exchangeable, thus it gives rise to the rich ion-exchange property of zeolites. Finally, the crystalline nature of the framework guarantees that the pore openings are uniform throughout the crystal. Figure 1 shows the composite building blocks (CBU) and framework of zeolite X, Y, or faujasite (FAU)

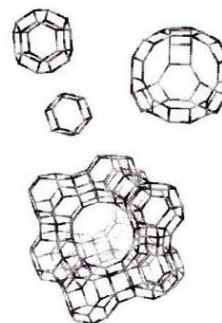


Figure 1: CBUs (top) and framework (bottom) of zeolite X, Y, or FAU [6].

2.2 Light Absorption and Aluoescence emission of nile red dye

NR is able to sense different polarities of the solvents and express them through fluorescence emission. The higher the polarity of the solution, which refers to the charge of its molecules, the bluer the fluorescent emission, the lower the polarity of the solvent is, the redder the fluorescent emission [7]. However, NR is an uncharged heterocyclic molecule and, therefore, it is quite soluble in organic solvents and lipids, but relatively insoluble in water. Moreover, NR fluoresces intensely, in varying color, in organic solvents, and hydrophobic lipids. On the other hand, NR acts as a hydrophobic probe, that is, its fluorescence maxima change depending on the relative hydrophobicity of the surrounding environments [8]. The absorption and fluorescence emission spectrum of NR (from PhotochemCAD database) is shown in Figure 2.

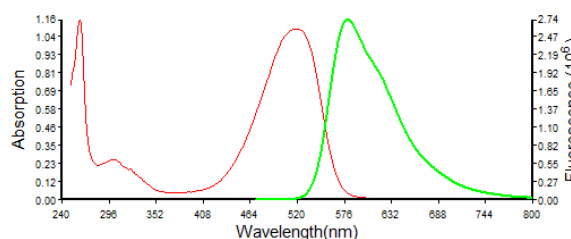


Figure 2: Absorption and fluorescence emission of NR.

3. Design of the multiple gas detection device

3.1 Overall design

The block diagram of the overall device is shown in Figure 3.

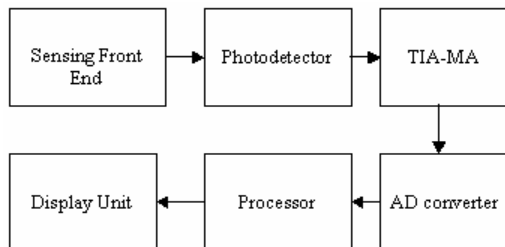


Figure 3: Block diagram of the sensing device.

Figure 4 shows the more detailed schematic of the device which can be fabricated on ceramic test bench.

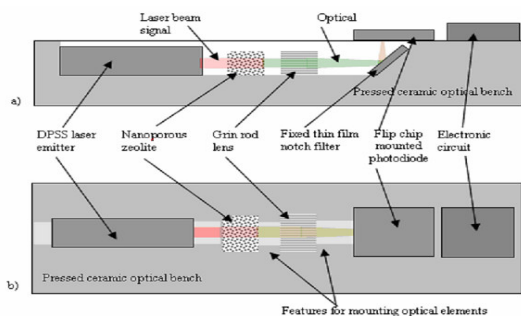


Figure 4: Detailed schematic of the device.

a) Side view and b) Top view.

3.2 Analog sensing front end

The schematic of the analog sensing front end is shown in Figure 5. It basically has a sensing arrays made of NR included in different types of zeolites housed by a glass chamber, a heating circuit, two valves to let the analytes in and out of the chamber, another two valves to allow the flushing gas (nitrogen) going in and out of the chamber to help remove the analytes.

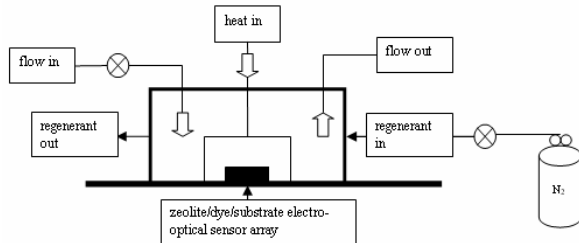


Figure 5: Analog sensing front end.

3.3 Optical filtering system

Two types of optical filters are needed in processing the optical signals: excitation filter and

emission filter. The former is placed between the light source and the zeolite/Nile Red sensor to allow light of desired wavelengths (from 500 to 600 nm) to excite the sensor. The latter filters out the excitation source, and allows only the fluorescence from the sensor to reach the photodetector. Since the bandwidth of a filter decreases with its thickness; therefore, by varying the thickness, the spectral responsivity of a sensor can be selectively modified to match a particular function.

3.4 Photodetector

Different types of photodetectors have been used to detect fluorescence including fluorescence microscope, photodiode, and photomultiplier tubes (PMTs). There is no doubt that fluorescence microscope is very helpful and give the richest information. However, for the development of a portable device which is supposed to have limited size and weight, either photomultiplier tubes or photodiodes should be considered. By comparison with PMTs based on different categories, photodiodes have more advantages [9,10]. Thus, a photodiode is considered in this research. A photodiode is a semiconductor device capable of proportionally converting light into either current or voltage, depending on the mode of operation. It can be used to detect fluorescence and can be accurately calibrated for measurements of low intensity from below 1 mW/cm² to 100 mW/cm² [11].

3.5 Electronic circuit design of the device

The block diagram of the electronic unit to process the electrical signal produced by the photodetector, is shown in Figure 6.

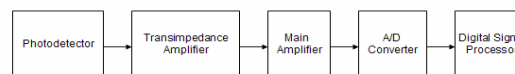


Figure 6: Block diagram of the electronic unit.

The unit basically consists of two parts: the signal conditioning and the digital signal processor.

Signal conditioning

The unit consists of two parts: an optical preamplifier and a main amplifier. The optical preamplifier plays a crucial role for interfacing the photodiode with the rest of the circuit. Optical preamplifier converts the current output of the photodiode in to a voltage output. Preamplifier determines the overall performance of the system

including sensitivity and dynamic range. The optical amplifiers used in this research is a transimpedance amplifier, which is a simple current to voltage converter.

The output voltage of the transimpedance amplifier is proportional to the photodiode current with 180° phase shift. The output has to be further amplified so that the voltage output can be used to signal processing. Furthermore, the maximum voltage output of the main amplifier should be between 0 to 5 V to be compatible with input specification for the A/D converter. Besides, the main amplifier output should be positive.

Figure 7 shows schematic of a modeled photodiode, a transimpedance amplifier and a main amplifier.

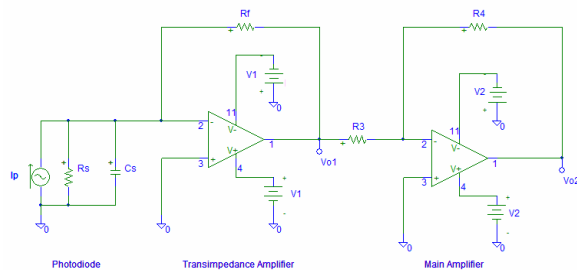


Figure 7: Schematic of the signal conditioning circuit.

Figure 8 shows the output waveform of the circuit in Figure 7.

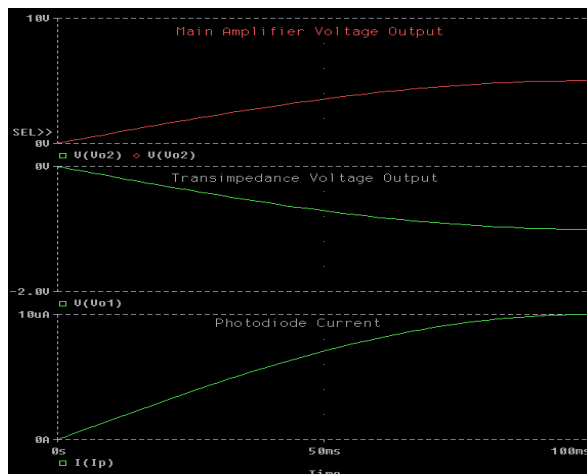


Figure 8: Simulation outputs of the photodiode, transimpedance amplifier, and main amplifier.

Digital processing unit

The block diagram of the digital processing unit is shown in Figure 9. It takes inputs from the

main amplifier and the controller, processes data and sends the results to the display unit.

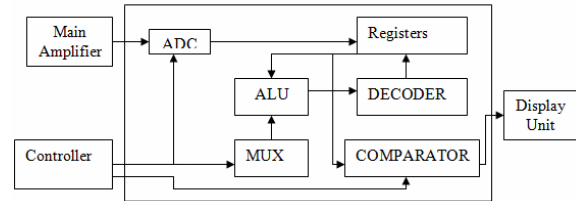


Figure 9: Digital processing unit.

The processing unit basically consists of:

- Analog-to-digital converter (ADC): to digitize the analog signal from the main amplifier,
- Set of registers: to store data,
- Arithmetic logic unit (ALU): to perform arithmetic and logical operations,
- Multiplexer: to fetch proper instructions to the ALU,
- Decoder: to access a particular register
- Comparator: for comparison purpose

3.6 Display unit

The display unit will display the gases detected by the device as well as their concentration.

4. Conclusion

The portable gas detector was designed. Experimental results so far include packaging of the analog sensing front end, VLSI design of front end electronic circuits, absorption and fluorescence emission of the zeolite-nile red combination. The complete system is designed for fabrication on ceramic test bench. The packaged system will be portable and could be used in different environments.

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