Hardware Design for Multiple Gas Detection System Using Zeolite Coated with Nile Red

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Abstract

The research goal is to develop a multiple gas sensing device which integrates a zeolite-Y/nile-red sensing front end with optoelectronic detector. The highly fluorescent nile red dye, included in the nanoporous structures of zeolite Y, responses to different gases by emitting fluorescence of different wavelengths. In addition, the size of the pores of zeolite Y's can be utilized to allow gases whose molecule is smaller than the pores to enter and react with the included dye. Since nanoporous structures of zeolites are manipulated, the device is expected to be more accurate, and more sensitive. Also it is able to better differentiate and detect one target in a mixture of different gases. This is achieved by incorporating fluorescent dyes into the supercages of zeolite Y's, measuring gas absorption, desorption and photo-chromic interaction of dye and gases, interfacing the zeolite/dye sensor arrays with light source and electronic detectors.

Key words: gas sensor, zeolite Y, nile red dye

1. Introduction

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, selective, operating at room temperature, rapidly responding, 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, these sensors may lead to false alerts. Even worse, the molecules to be detected could be masked by some interfering compounds which may result in failure to detect the targets. Several investigators have been working towards multi-gas detection systems [1, 2].

It is of utmost importance for the practical application of emergent nanotechnologies which rely on conventional technologies for commercialization. Much of the current effort in nano-electronics is directed towards integration of nano-science into macroscopic products to enhance product performance, or enable the product to be reduced in overall size. With major strides in the area of light activated processes in nano-porous zeolite/dye, the optical properties of zeolite/dye can also be used in the development of optical chemical nano-sensor. This research attempts to incorporate nile red dye into different types of zeolite Y's, study the combinations' optical characteristics, and integrate the zeolite-Y/nile-red combinations and optoelectronics into a gas detector with more accurate, sensitive, and selective capability. Consequently, the detector is able to detect many gases simultaneously in a cost effective unit.

2. Zeolite and Nile Red Dye

2.1 Zeolite

According to the mineralogist community, a zeolite can be defined as crystalline aluminosilicates with a 4-connected tetrahedral framework structure enclosing cavities occupied by organic non-framework cations and water molecules, both of which have considerable freedom of movement,

allowing ion exchange and reversible dehydration [3]. The 4-connected tetrahedral frameworks are composed of TO_4 (where T stands for any tetrahedral species, and can be Si^{IV}, Al^{III}, P^{V}, Zn^{II}, etc), with oxygen atoms connecting neighboring tetrahedral. Different zeolites have different framework composition, different guest species, and different extraframework cation content. Besides, they can have different crystallographic symmetry, and different properties. Figure 1 shows the framework structure of zeolite-Y.

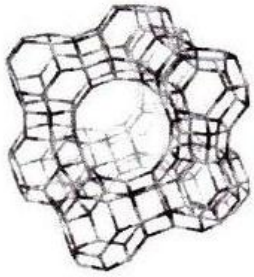


Figure 1: The framework structure of zeolite-Y [4].

Applications of zeolites have been found in different areas including adsorbent applications, catalysis applications, ion-exchange applications, etc. 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 m^2/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 ($CaSO_4$). 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 [5].

Zeolites are ideal inorganic hosts for a large variety of guest molecules. Zeolite-based host-guest systems are a type of advanced materials in which zeolites act as host for encapsulating and organizing species, crystalline nanophase, and supramolecular entities inside the zeolite pores. Space confinement and host-guest interaction give rise to composite materials with novel optical, electronic, and magnetic properties.

2.2 Nile Red Dye

Nile Red (NR) is a highly solvatochromic organic dye whose chemical structure is shown in Figure 2. It can be dissolved in a number of different solvents resulting in solutions of different colors. NR molecule behaves differently in various solvents, and its behavior is expressed via the emission of light in discrete parts of the visible light spectrum. For instance, if dissolved in water, NR solution takes on a strong blue color, whereas in toluene, the solution displays a yellow color [6]. NR has found applications in different fields thanks to its unique properties.

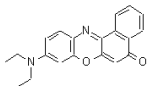


Figure 2: Chemical structure of Nile Red dye [7].

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 [6]. 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. Thanks to its unique properties, NR has been used as a biological imaging tool because it reveals information about the sample that it is exposed to. Fowler and Greenspan were successful in using NR as a fluorescent hydrophobic probe to detect neutral lipid deposits in tissue sections [8].

3. Incorporation of Nile Red into the Supercages of Zeolite Y's

Nile red can be included inside the supercage of zeolite-Y via chemical reaction. In this research, the synthesis of the zeolite-Y/nile-red inclusions was performed following the steps below [9]:

- Step 1: adding 0.36g 1-napthol (Wako Inc.) to 20ml acetic acid (Fisher Scientific, concentrated).
- Step 2: adding the resulting solution to 0.8g zeolite-Y powder (Wako Inc.).
- Step 3: reflux the resulting solution for 30 minutes.
- Step 4: dissolve 0.28g 5-nitroso 2-diethylaminophenol hydrochloride (Chemistry Lab, Temple University) into 12ml acetic acid and 1ml concentrated hydrochloric acid (Fisher Scientific, concentrated), and continue to reflux the resulting solution for 3 hours.
- Step 5: increase the pH of the resulting solution to 11 using ammonium hydroxide (Fisher Scientific, concentrated).
- Step 6: extract the precipitate from the resulting solution using centrifuge (the precipitate was placed in test tube and centrifuged for 1 minute so that all powder settled down on the bottom of the test tube and the top solution was removed).
- Step 7: clean the powder with ethanol

Three different zeolites-Y (ammonium Y, hydrogen Y and sodium Y) were used in this research.

During the chemical reaction, the color of the solution changed from brown to blue indicating nile red dye was formed. The equipment and change in the solution color are shown in Figure 3.

Figure 3: The reflux system used to synthesize zeolite/nile-red inclusion.

After the chemical reaction, the zeolite-Y/nile-red inclusion was cleaned with ethanol using ultrasound cleaner followed by centrifuging the mixture to extract the inclusion from ethanol. The process was repeated until the ethanol became transparent.

The images of the grain size and appearance of the pure zeolite sodium Y and the cleaned zeolilte-Y/nile-red combinations (Figure 4) were taken using Scanning Electron Microscope (SEM), Hitachi S4700. The energy dispersive spectra of the samples were taken using Energy Dispersive Spectroscopy (EDS), Phoenix EDAX, to detect the component elements of the zeolites and zeolite/nile-red combinations.

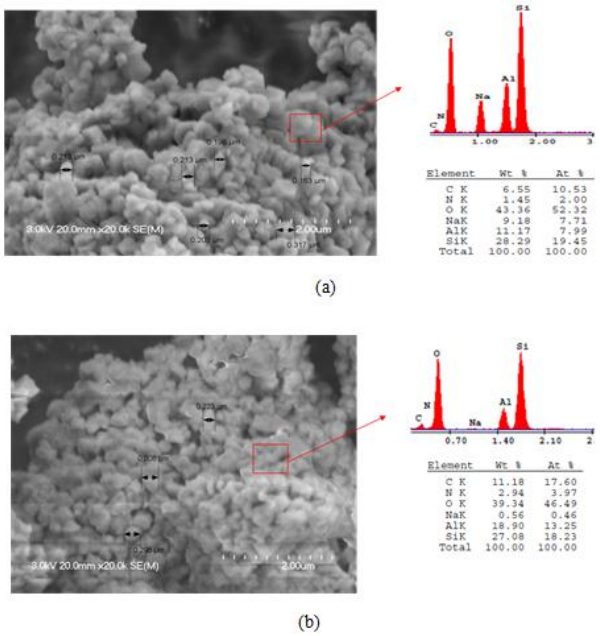
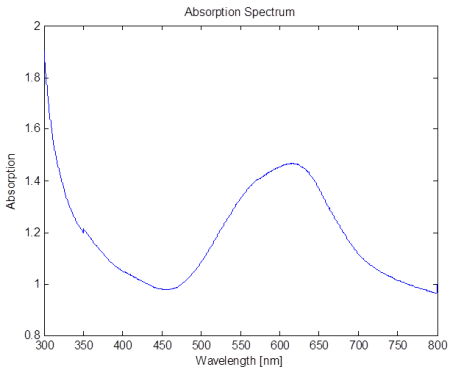


Figure 4: SEM and EDS of pure zeolite sodium Y and zeolite-sodium-Y/nile-red inclusion.
a) Pure zeolite sodium Y.
b) Zeolite-sodium-Y/nile-red inclusion.

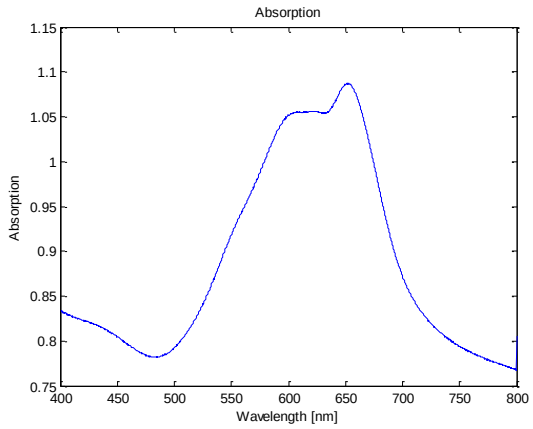
4. Optical Characteristics of Zeolite-Y/Nile-Red Inclusions

4.1 Light Absorption

After being synthesized, the zeolite-Y/nile-red combinations were cleaned using ultrasonic cleaner and centrifuge. The light absorption spectra of the unclean sample and the clean sample are shown in Figure 5.



(a)



(b)

Figure 5: The light absorption spectra of the zeolite ammonium-Y/nile-red combinations.
a) Uncleaned combination
b) Combination cleaned using ultrasonic cleaner and centrifuge

The absorption spectrum in Figure 5a does not reflect the individual peaks of free nile red dye, nile red adsorbing to the external surface of zeolite Y, and nile red inside zeolite Y; instead, the spectrum shows the sum of the above-mentioned peaks. However, the peaks in the spectrum (Figure 5b) are much more pronounced, which is easier to determine the value of the component peak.

4.2 Absorption Spectrum Decomposition

The absorption spectra of zeolite/nile-red combinations usually contain two or more peaks which are closed to one another. Therefore, spectral decomposition is needed to evaluate the location and the intensity of the component peak in the spectrum. Those peaks give indication where nile was adsorbed. The decomposition of the absorption spectra was performed using Origin8.5.1 (OriginLab).

Figure 6 shows the decomposition of the absorption spectrum of zeolite-ammonium-Y/nile-red inclusion.

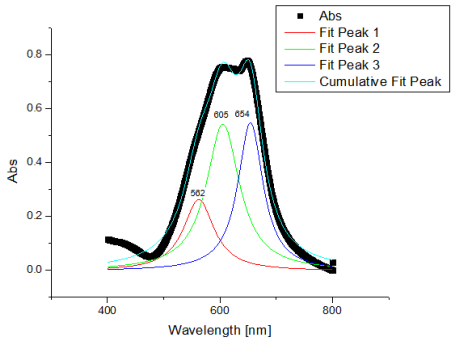


Figure 6: Decomposition of the absorption spectrum of zeolite-ammonium-Y/nile-red inclusion.

The black curve in Figure 6 represents the absorption spectrum of the nile red adsorbing inside the cages of zeolite ammonium Y. The blue, green, and red curves are the decomposed from the black by estimating three peaks on the black curve.Summing the blue, green, and red curves results in the turquoise curve. The cumulative curve and the original absorption curve match pretty well, which indicates that the estimation of the three peaks was very close.

4.3 Fluorescence Emission

When excited with light source of 543nm, the zeolite-Y/NR combinations emit fluorescence of different wavelengths. Moreover, the fluorescence spectra shift when exposed to different gases. This feature was employed in this research to detect different gases. After being cleaned and baked to removed moisture or gases trapped in the zeolite structures, the zeolite-Y/nile-red inclusions were exposed to acetone, ethanol, methanol, and deionized water (aqueous). The fluorescence emission was obtained using the confocal microscope Leica TCS SP1. Figure 7 shows the fluorescence emission of the zeolite-hydrogen-Y/nile-red inclusion exposed to different solvents.

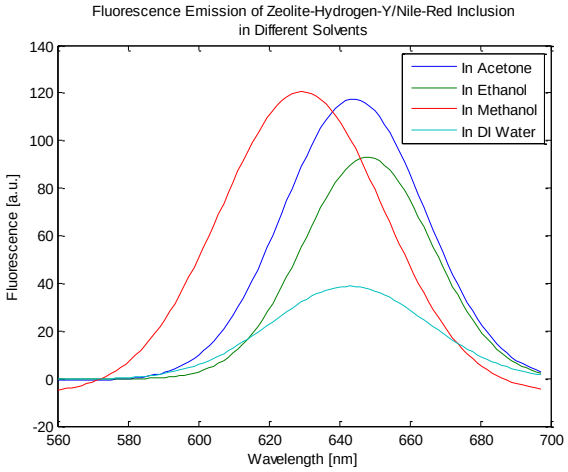


Figure 7: The fluorescence emission of zeolite-hydrogen-Y/nile-red inclusion in different solvents.

The experimental average wavelength at the peaks and the standard deviation in the fluorescence spectra of different zeolite-Y/nile-red inclusions exposed to different solvents are summarized in Table 1.

Table 1:Experimental data of the fluorescence emission of different zeolite-Y/nile-red inclusion in different solvents.

H2YNR inclusion baked at 100°C for 2.5 hr in different solvents	Average Peak [nm]	Standard Deviation
Acetone	644.45	1.50
Ethanol	647.03	1.58
Methanol	629.19	0.81
DI Water	641.49	3.83
NaYNR inclusion baked at 100°C for 2.5 hr in different solvents		
Acetone	660.90	1.28
Ethanol	659.19	1.40
Methanol	659.55	1.17
DI Water	659.33	0.98
NH_3YNR inclusion baked at 100°C for 2.5 hr in different solvents		
Acetone	637.17	0.34
Ethanol	632.95	0.74
Methanol	640.15	0.36

5. Design of the Gas Detection Device

5.1 Overall design

The block diagram of the overall device is shown in Figure 8.

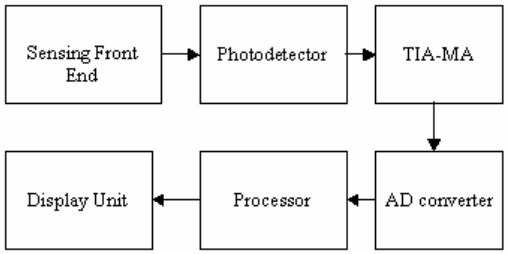


Figure 8: Block diagram of the sensing device.

5.2 Analog sensing front end

The analog sensing front end consists of a sensing array made of NR included in different types of zeolites-Y housed in a glass chamber, a heating circuit to remove trapped moisture and/or gases in the zeolite-Y/nile-red combinations, two valves to let the analytes in and out of the chamber, second two valves to allow the flushing gas (nitrogen) to go in and out of the chamber to help remove the analytes. The schematic design of the analog sensing front end is shown in Figure 9.

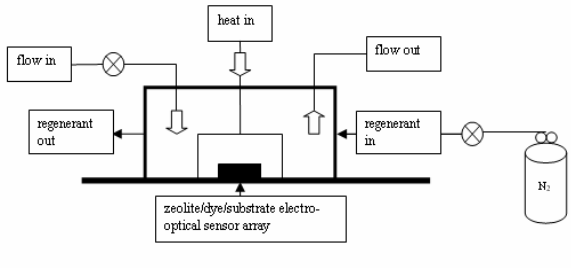


Figure 9: The schematic design of the analog sensing front end.

5.3 The Optical System to Excite the Sensor and to Collect the Output Fluorescece

The optical system consists of: 1) excitation source, 2) excitation filter, 3) dichroic filter, 4) the specimen holder, 5) fluorescence tunable bandpass filter, 6) collection lens, and 7) photodetector. The block diagram of the optical system is shown in Figure 10.

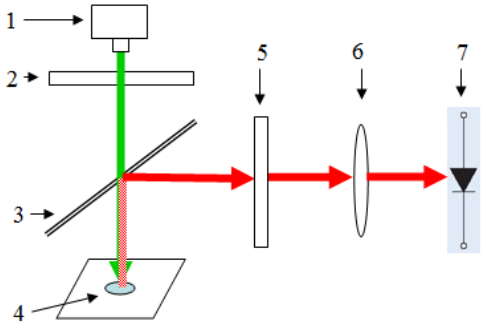


Figure 10: The diagram of the optical system.

The excitation source (Figure 10-1) is a green laser diode whose light is filtered out by the excitation filter (Figure 10-2) to produce light with wavelength of 543 nm. This is the excitation wavelength used to excite the zeolites-Y/nile-red combinations to study their fluorescence response when exposed to different test gases. The dichroic filter (Figure 10-3) allows the excitation light to pass through to excite the zeolites-Y/nile-red combinations on the specimen holder (Figure 10-4). At the same time, the dichroic filter reflects the emitted fluorescence from the zeolites-Y/nile-red combinations to the optical tunable bandpass filter (Figure 10-5). The tunable bandpass filter allows light of particular wavelength to pass through based on the angle of the light incidence.

5.3 The Flowchart of the Processing Steps

The flowchart for steps to be done by the processing unit is shown in Figure 11.

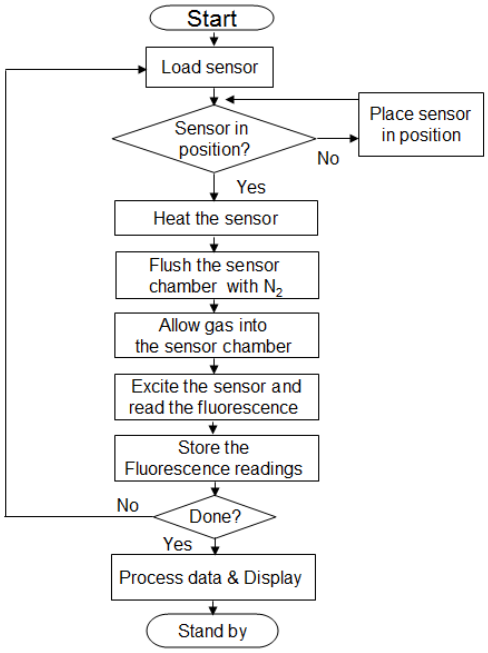


Figure 11: The flowchart for the steps to be done by the processing unit.

When the device is started, it loads the sensor into position (in case more than one sensing element is to be used to detect different gases). The sensing element is then heated to remove trapped gases or moisture in the zeolite structure. Then, sensor chamber is flushed with nitrogen gas to 1) cool down the sensing element, and 2) to remove gases in the sensing chamber. After tha t, gas will be filled in the chamber, and the sensing element will be excited by the laser source. The fluorescence output will be filtered out and converted into electrical signal which is then digitized and stored for further processing. After the data were analyzed, the display unit will show the detected gas(es) with concentration.

6 Conclusion

The development of zeolite sensor was accomplished. The whole system consists of zeolites-Y with the incorporation of nile red in their nano-structure, opto-electro transducer, optical excitation and fluorescence collection systems, electronic circuit, and display unit. The hardware for the processing unit was designed and simulated to show the performance of the functions and the interface among different modules in the system. The next step in this research includes studying the response of the zeolite-Y/nile-red combinations to toxic gases and integrating the whole system into a portable sensing device.

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