

Physics of Functional Materials and Devices
Prof. Amreesh Chandra
Department of Physics
Indian Institute of Technology Kharagpur

Lecture 37, Week 9

Sensors

Till now we had been discussing about the properties of solids, liquids and melts. We have talked about the synthesis protocols by which you can make these materials. As you move from bulk to nano size materials you expect properties to change. Properties like magnetism will also change. Now, it is time to shift our focus on the applications of these functional materials and how you can tune the functionalities of these materials by various routes. The first example which I will start with is sensors.

So, let us Today start with our discussion on the use of functional materials in sensors. Before we start talking about the use of functional materials in sensors, we must understand what is a sensor, what type of sensor are we talking about. So, there would be a brief introduction to the field of sensor and their type. What happens in sensors? What is the basic principle of sensors? I will give you an idea about the basic principle by using gas sensor as a typical example.

Now, once we have the idea how the sensor works, we will then understand the properties of the material which needs to be tuned. So, that it can become useful for sensors using tin oxide which is a very commonly used sensing material I will explain the use of electrode materials in gas sensing. What is a sensor? If you look into books, if you go to some internet sources, you go to some library you will find that sensor is defined as a device. that responds to a physical stimulus. That stimulus can be heat, light, sound, pressure, magnetism, stress, strain, gas or humidity or any other stimuli.

After responding to the change in the physical stimulus, it transmits a resulting impulse to the control unit which then measures this change and based on the magnitude of change you back calculate or estimate the magnitude of the physical stimuli. Now, the sensors can be classified under two categories, one this could be principle of operation on which the sensor can be classified with or using the principle of conversions you can classify the types of sensors. If you talk in terms of principle of operation, you can have two types of sensors. You can have active sensor or a passive sensor. What is an active sensor? It is a sensor that converts one form of energy directly into another without the need of external source of energy or excitation.

For example, thermometer it is an active sensor. If you have a passive sensor then here the conversion from one form of energy into another is controlled in a way by the excitation from an another source. So, you need another source to actually detect the change just like seismic sensors. If you want to classify sensors based on the principle of conversion, you can have physical sensors or you can have chemical sensors. In physical sensors, you will find that it is going to measure a physical quantity and convert it into a signal which can be read by a detector or an instrument.

For example, it can be a gas sensor or an electrochemical sensor in comparison you have chemical sensors as the name suggest it would transform chemical information ranging from concentration of a specific sample component to total composition analysis into a analytically useful signal and these are like pressure sensors. Let us understand what is a gas sensor? These are quite talked about in India. What is it going to look like? It will have two components. First it will have an active material which will interact with the environment and generate a response. So, it is an active material.

Now, if the response has been generated what will you do with that response? You need to have a device which will capture this response from the active material which is interacting with the environment or the surroundings. and then convert this response into a reading or a data which can be quantified or interpreted. by the end user. So, this is what a gas sensor looks like. So, you have been seeing that there has been evolution of gas sensors you had from Davies lamb to canary bird sensor to modern day sensors.

This is a typical way you have the sensor operation. So, you have a gas which is interacting with the element that element is transferring the response to a device and then device is giving you a data which can be interpreted. If I look into gas sensors only, there can be various types of gas sensor. You can have catalytic bead gas sensors, you can have infrared gas sensor or you can have semiconductor metal oxide gas sensors. So, you in catalytic bead gas sensors you have two beads which are there.

one is active bead the other is the passive bead, one accepts the gas then change its signal and as the response changes then with the reference bead signal you can take the difference of the two and because the passive bead is not changing the signal you will know that whatever change is coming because of the adsorption of the gas it is coming in from the adsorbed gas. These are generally extremely reliable and they are less sensitive to temperature or humidity variations. But combustible gases that have oxygen concentration below 10 percent are not easy to detect using the bead gas sensors. Then you can have infrared gas sensors. So, you can detect the inflow and outflow of a gas and then you can monitor the hydrocarbon vapors or carbon dioxide or nitric oxides using these sensors and they can even detect gases in inert atmosphere.

They can be made very specific to a particular target gas, but for example, gases like acetylene cannot be detected using infrared sensors. So, you need to have molecules which are infrared active. Then came the semiconductor metal oxide gas sensors which are very simple to understand what you have is typically two electrodes and they are connected by a metal. If a gas gets adsorbed on the metal surface, then what will happen? It will change its resistance and because of that if there is a current which is flowing between the two electrodes which is connected by a metal, then because of the adsorbed gas molecules the resistance will change and the magnitude of current which is reaching from one electrode to the other will change and hence that would give you a signal that tells that there is some species which has got adsorbed on the metal surface. So, if you look into the working principle of a gas sensor, you will find that the basic principle of sensing is the change in conductivity.

Why? Because of the interaction of chemically active material with the analyte gas. Now, if there is adsorption, the surface of the metal oxide will come in contact with the analyte gas and you will see modulation in their conductivity and that means, the resistance would change. If the resistance changes the flow of current would get modulated and you will have the readings which will show reduction in gas. If there are oxidizing gases you will see reduction in conductivity, if you have reducing gases then you will see increase in conductivity.

For example, if you take oxygen gas what will happen? Oxygen will get adsorbed on the surface. Now, this oxygen will have what? It would take an electron and would have the form of ion O_2^- . Now, along with this it would then have another electron and go into $2O^-$. Now, O^- plus electron will give you O^{2-} . So, you basically go to the ionized state.

Now if you go to an ionized state, you have changed the concentration of electron in the metal and hence the resistance is changing because now the gas is actually adsorbed, it is not absorbed that is fine, but there is adsorption and it has reached certain level of penetration within the surface of the metal which was connecting the two electrodes. Let us take SnO_2 as an active material. SnO_2 you can use it as electrochemical material for energy devices, you can use it for catalysis, you can also use it for gas sensing. What we had talked about that a material should have two or more than two applications and then only it will be called as functional material. Hence, SnO_2 is a typical functional material.

You can synthesize various forms of materials. So, let us talk about two forms of materials which are routinely used. One is solid structures and other are hollow structures. What do we mean? Solid structure means that the particles would be solid whereas, hollow structures means that these particles would have a cavity in the middle. So, what will

happen? If you have hollow structures the specific surface area would be much larger because the outer surface as well as the inner surface will be available to interact with the incoming analyte gas.

So, is there any advantage or not, but when you make a material what you should do? You should first ensure that they stabilized in the desired crystallographic arrangement. So, you can clearly see that it is easily possible to use auto combustion routes to the SnO₂ structure which can be compared with the JCPDS card number 41-1445 that is the standard data and JCPDS means it is basically the joint committee on powder diffraction standards. So, it has the standard data from which you can compare the diffraction pattern which you are getting and if it is similar to what it is mentioned in the standard graph, you can then believe that the material which you are synthesizing has been formed. These are the typical scanning electron microscopes of the SnO₂ nanospheres, nanoflakes, and hollow nanoparticles. One can clearly see from the scales that if you see the scale, you will find that the hollow spheres have the dimensions of 100 to 200 nanometers.

So, these are the typical features which we are talking about you can clearly see this is solid and this is hollow. These are the BET surface area isotherms from where you can calculate the surface area of these materials. the technique will be discussed in the last two weeks of this lecture course, but it is the BET surface area which is used to calculate the specific surface area of these particles. So, for this hollow structures you will see that there are two surfaces which will contribute in the surface area. Therefore, the solid structure has 8-meter square per gram surface area whereas, the specific surface area for the hollow structures are of the value of nearly 45 meter square per gram because both inner and outer surfaces are becoming available for adsorption of the gas and as expected the planar morphologies have an intermediate surface area value.

Now, you have formed a material, you have characterized it, you know that one of them is having extremely high surface area. Then can it be used in an experiment which is going to be used to determine its gas sensing ability. This is a typical gas sensing setup. What are there? You have a gas regulator. So, you control the rate at which the gas is going to enter the chamber and interact with the active material.

That is done using the mass flow meter. Then you have the sample holder on which you will place your sample and a heating unit. So, you can heat the sensor and also see how it will react to the incoming gas. Then you have the supply which will control the heater current and you have the sensor or the receiver which is going to measure the change in response signal. In this case it can be voltage or current and then you can use a data controller to obtain the data and then analyze the data.

This is a typical electrode. which is used. So, what is there? You have reference connection which is connected to the reference electrode, then you have the working electrode which

is in the middle and then you have the counter electrode which is connected to the counter connection. So, this is what you have as a starting electron. What you do? On this you deposit your active material. What is the active material? In this case SnO_2 .

So, now you have deposited the active material on top of this electron. Before you start detecting the gas concentration, you must clean the chamber in which you are going to push in the gas which you want to cells. So, you just purge the gas with chamber with dry air for 3 hours. Now the response of a sensor is given by change in resistance of the sensor after the introduction of the analyte molecule minus the resistance of the sensor in presence of dry air divided by the resistance in presence of dry air and because you are talking in terms of percentage the whole thing is multiplied by 100. That is the formula which is used to find out the resistance or change in the response characteristics.

As you had seen the hollow structures had much higher surface area. So, they would be absorbing much more incoming analyte gas molecules and therefore, you expect much larger change in them. So, if you look into the properties, you can clearly see that the response characteristics of nano flakes, nano spheres are quite low compared to that what you get in hollow nanoparticles. You can just look at the scale. So, this is up to 20 percent, this is up to 30 percent.

So, if it is nearly 20 percent change in the response, here it is nearly 30 percent change in the response percentage if you use hollow particles as the active material. So, what have you understood? Not only you can change the type of gas sensor by changing the material itself. Suppose you do not want to use SnO_2 , you can use TiO_2 . You say I want to use copper oxide or I want to use cerium oxide. You can have different materials and you make different types of sensors.

In addition by changing the morphology that is shape and size of the particles, you can also change the response characteristics of these gas sensors. In addition, you will find that the response characteristics can also be changed by changing the temperature. Why? Because if you give energy to the system, you have given the system more energy to absorb higher number of molecules which are coming in. And therefore, you will find that the response characteristics can also be tuned by changing the temperature. So, gas sensors can be used at different temperatures and if you have defined that there is a particular temperature at which the gas sensor has to perform the best, then you must also characterize the performance of the gas sensor at that given temperature.

Now, what is the limit of detection? How much you can detect? So, lower is the concentration up to which you can detect the presence of a particular gas, higher is the sensitivity of the sensor. If there is let us say not parts per million ppm, but you are able to detect ppb parts per billion. then obviously, you are developing a sensor which is very sensitive. Even slightest of concentrations of gas which you want to detect can be detected

using those kinds of sensors. Limit of detection is defined as $3\sigma/S$, where σ is the standard deviation, of response versus concentration curve and S is the slope of the curve.

Typically for ethanol using SnO_2 as the active sensing element the LOD which you could obtain is approximately 400ppb. So, even 400 parts per billion if such low concentrations of ethanol is present in the gas or the environment in which the sensor is being used you will be able to detect its present. So, you can have very sensitive sensors using the right choice of materials. Now, the next factor is will you use a sensor only once or will you use it many times? Obviously, you want to use it many times not only as a function of months, but also as a function of days and within a day you want to use it many times. So, you must calculate two more factors those are response and recovery time as a function of cycling. For determining the response in recovery time using SnO_2 , you will find that the way I have told you to fabricate the sensor using the hollow structures, you can get the response and recovery time of approximately 7 and 30 seconds respectively.

So, you can get the response from the sensors within 7 seconds. get the value, let the sensor rest for 30 second and then reuse it you will be able to recover the response characteristics quite nicely. And then you will find that these sensors can be stable for couple of months. As you standardize you can increase the duration from months to years to many years. Typically, if you have the volatile organic compound-based sensors, you must understand that what is the mechanism which is occurring so that there is a sensing property coming in.

What is happening? When a gas is actually exposed to a sensing element. what is happening? The higher number of gas molecules will diffuse on the surface of the hollow structure as well as within the hollow structure. So, here as well as inside in comparison to solid structures when the diffusion or adsorption will take place only on the upper surface and therefore, the change would be higher in hollow or solid structures. obviously, functional materials which you have made such as hollow structures you will have much higher changes being observed. Why I am telling you that is because you can make n numbers of hierarchical structures.

You can change their shapes and morphology. You will find that their responses would be very different and therefore, you can make large number of sensors. Hopefully, in today's lecture it is clear that functional materials are also very useful for sensor technologies. The materials which we have discussed in this course are useful for sensor technology and there are very simple ways to tune the response characteristics as well as the sensitivity of these sensors and as you can do that the range of applications of these sensors is very very large. To develop more understanding about this topic you can read into these books and in the next lecture which we will start in week 10, we will move to next round of applications such as electrochemical sensors, batteries, supercapacitors.

I thank you for attending lecture number 4. of week 9. Thank you very much.