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An Article on Nano Structure-Based Metal Oxide Gas Sensor

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Abstract

In the present scenario the air quality is deteriorating day by day. The air we breathe contains various amounts of gases that may be harmful to human health. It is critical to detect their presence because the inhabited environment we live in is populated not only by humans but also plants and animals so the safety of their lives is paramount.

Keywords: Chemisorption, Gas Sensors, Physisorption

Introduction

Gas detection devices or gas sensor in the first instance, are safety-related equipment that are primarily used to safeguard personnel and assure plant safety. Gas detection systems are designed to detect toxic gas concentrations, trigger alarms, and – to the practicable extent – activate countermeasures before a hazardous scenario for people, assets, or the environment arises.

1.0 Need of Gas Sensors

Portable (or semi-portable) gas measurement equipment and fixed installation gas detection system both exist. The safety of a zone that could be affected by toxic gases and vapors is highly dependent on the gas detection tools reliability, particularly the quality of the sensors utilized. In contrast to portable device sensors, fixed installation sensors including their electronics are continually operational 24 hours a day throughout the year merely in case of a random gas release. It works even in life-threatening environmental conditions, such as -50°C to 65°C, high relative humidity, in outdoor applications with rainy, storm and snowfall or hot desert conditions and EM disturbances or strong vibration. There is a continuous crossover between gas detection technology on the one hand and method of instrumentation on the other. Despite their origins as safety technology, several gas detection transmitters have such superior measuring performance that they are increasingly being used as an analyzing instrument in the field of process instrumentation.

1.1 Gas Sensors

"The gas sensor is one of the classifications of chemical sensors. The gas sensor is a device that measures the concentration of the gas that comes in contact with it [1]". Characteristic of the gas that is detected by the gas sensors is their breakdown voltage that is specific for a particular gas. In this way gas sensor identifies the gas by measuring their breakdown voltage. While current discharge in the device gives the concentration of the gas [2]. Transducers detect gas molecules and provide an electrical signal proportional to their concentration.

The industrial revolution has played a great deal to upgrade the living standard of a new generation. Industrialization demands specific gas recognition and observation for the benefit of society. Pollution of the environment by these gases poses a threat to public health. As a result, it is necessary to monitor the level of pollution in the atmosphere to take suitable measures to reduce pollution. There is a massive demand for checking of useful as well as flammable/harmful gases. To monitor different types of gases, varieties of gas sensors device have been developed and many of them are existing commercially. Gas sensors are of great help in various fields whether it is industry, medical, scientific or environment, gas could be both harmful and useful. In both the cases it's detection is necessary and beneficial for the humans and other living beings [2].

"A sensor is made up of sensitive semiconductor material (n-type or p-type) that is either in bulk or placed on a suitable support (nanoscale) and is used to perform molecular recognition. The analyte recognition process happens on the sensing element's surface or in the bulk of the material, resulting in a concentration-dependent change property that can be converted into an electrical signal (changing in resistance) by the suitable transducer. This simple transduction mechanism allowed for the creation of devices in a variety of shapes and sizes [1]".

"Classical Taguchi sensors have sensitive material in the form of the sintered porous ceramic body (Figure 1). Other examples of sensors bearing different forms and dimensions are shown in Figure 2.

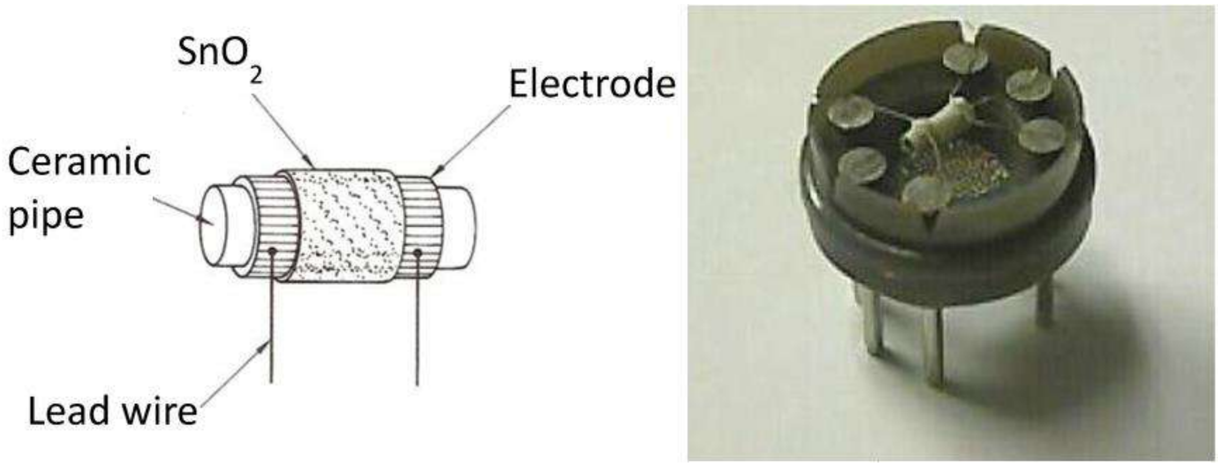


Figure: 1 Schematization and picture of Taguchi gas sensor [2].

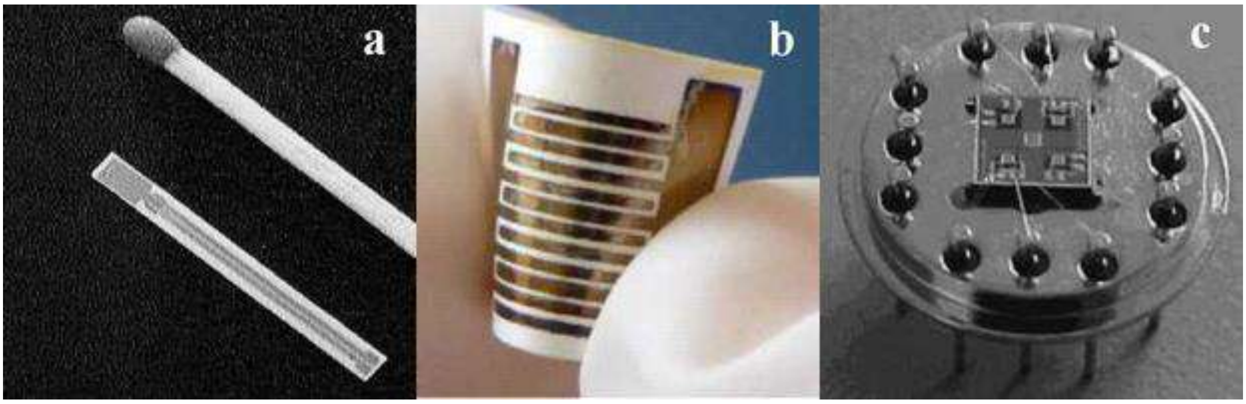


Figure: 2 Gas sensors with different configurations [2].

Planar-type gas sensors are constituted of a sensing thick/thin layer deposited by chemical or physical methods onto a ceramic substrate with interdigital electrodes (Figure 2 a). The sensing layer can be deposited also on plastic support, thereby allowing the fabrication of flexible gas sensors (Figure 2 b).

Even though these sensors are modest but several applications require further miniaturization. Compatibility with the integrated circuit (IC) technology, in particular, is increasingly widely pursued. Top-down techniques have been used to fabricate fully integrated devices, however, the top-down approach often has higher throughput and is more suited to large-scale integration. Micro machined sensors can be manufactured on a chip substrate using these processes, allowing for easy interface with traditional silicon microelectronics. (Figure 2 c)" [2].

Sensors, on the other hand, are becoming increasingly common in our daily lives. Our environment is rapidly varying, and sensors are a vital part of that change. Sensors are commonly agreed upon to have the following characteristics:

- Direct contact with the examined subject
- Convert chemical reaction (non-electric) information into electric signals
- React quickly
- Work continuously, at least in iterative cycles.

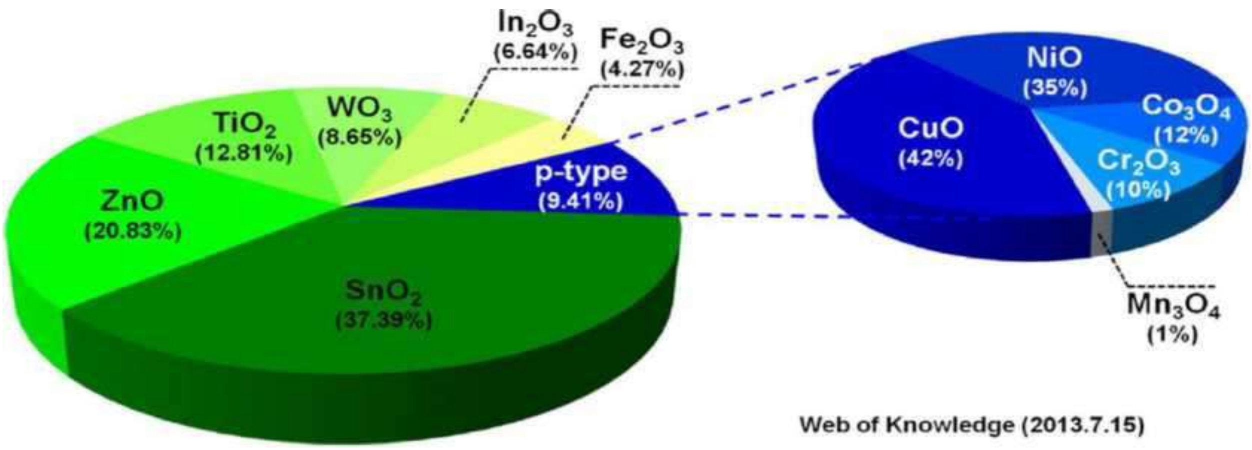
The essential characteristics parameters of a sensor are:

- Sensitivity
- Stability
- Repeatability

In most cases, a sensor is used if all the three components are precisely determined for a specific range of measured values and operation time. If the output of a highly sensitive device deviates significantly during the measurement time, the data acquired may not be accurate, and the measurement may not be repeatable. Other sensor qualities, such as selectivity and linearity, can often be adjusted by adding more sensors or employing signal conditioning circuits. Sensor classification techniques might be either simple or extremely complicated.

1.2 Sensing Materials

"Since the primary tin dioxide sensor innovated within the 1970s for home gas alarms, there has been a rise in the demand for high-performance solid-state gas sensors. Results of a search study on semiconductor metal oxides used as sensing materials for gas sensors, including both the n-type and p-type oxides [2]", are briefly explained in the graph shown in Figure 3.



"**Figure: 3** Studies on n- and p-type oxide semiconductor gas sensors (internet search of Web of Knowledge) [3]".

"Because of their comprehensive structural, physical, and chemical properties and functions, metal oxides are found as one of the most common, inclusive, and, most likely, largest classes of materials. Metal oxides such as SnO_2, ZnO, TiO_2, and others are commonly used as sensing layers in devices, but ternary and more complex oxides are also used in practical gas sensors. [4]".

"Many metal oxides are suitable for detecting combustible, reducing, or oxidizing gases by conductive measurements. The following oxides show a gas response in their electrical conductivity: Cr_2O_3(chromium oxide**)**, Mn_2O_3 (Manganese oxide), Co_3O_4, NiO, CuO, In_2O_3, WO_3, TiO_2(tin dioxide), V_2O_3, Fe_2O_3, GeO_2, Nb_2O_5, MoO_3, Ta_2O_5, La_2O_3, CeO_2, Nd_2O_3[**5**]". "Metal oxides chosen for gas sensors are often determined from their electronic structure. The range-scale of electronic structures of oxides is so broad, that metal oxides were classified into two following categories [6]":

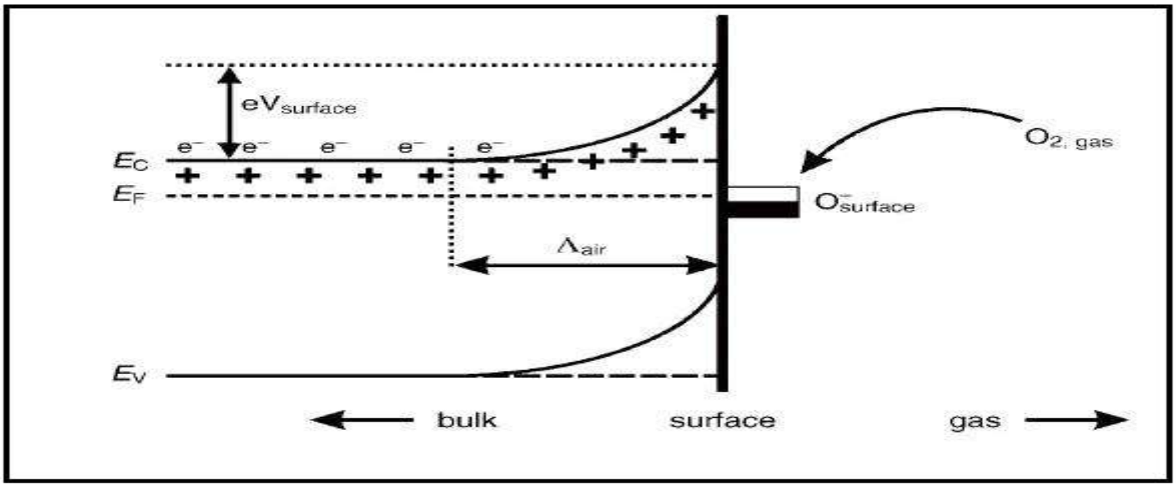
(1) "Transition-metal oxides (Fe_2O_3, NiO, Cr_2O_3etc.)

(2) Non-transition-metal oxides which include (a) pre-transition-metal oxides (Al_2O_3 etc.) and (b) post-transition-metal oxides (ZnO, SnO_2, In_2O_3 etc.)

Therefore, only transition-metal oxides with d^0 and d^{10} electronic configurations show their real gas sensing application. The d^0 configuration is observed in binary transition metal oxides such as TiO_2, V_2O_5, etc., while the d^{10} configuration is observed in post-transition metal oxides, such as ZnO and SnO_2 [**7**]".

1.3 Basic Mechanism of Gas Sensor

"The gas sensing mechanism of those sensors participates in the adsorption of atmospheric oxygen on the surface of oxides which extracts electrons from the semiconductor resulting in a change in carrier density and conductivity [8]"."Schematic of band bending is shown in figure 4 [9] showing on interaction with oxidizing or reducing gases, adsorbed oxygen concentration, and thereby conductivity changes. The change in conductivity is that the measure of gas concentration [10]"."In comparison to pre-transition-metal oxides (MgO, *etc.*), transition-metal oxides behave differently because the energy difference between a cation d^nconfiguration and either a d^{n+1} or d^{n-1} configurations is often relatively small [11]". "They can change forms in several different kinds of oxides. So, they are more sensitive than pre-transition-metal oxides to environment. Only transition-metal oxides with d^0 (TiO_2, V_2O_5, WO_3), binary transition-metal oxides and d^{10} (ZnO, SnO_2), post-transition-metal oxide electronic configurations find their real gas sensor application [7]".



"**Figure: 4** Schematic of band bending after chemisorptions of charged species on the surface of n-type semiconductors [9]".

1.4 Characteristic of Gas Sensor

1.4.1 Sensitivity:

This is a sensor device feature that indicates how the chemical and physical properties of the gas sensing material change when exposed to gas. It is measured by the change in resistance or any other parameter that responds to a little variation in concentration to a particular gas. The sensitivity highly depends on the film thickness, the porosity of the material, operating temperature, pressure and the presence of other interfering gases, etc. It also depends on the choice of the material. So, for better sensitivity, we have to select the best gas at its optimum detecting temperature. Since the reaction mechanism takes place in the external layer surface, so we have to design our device in such a way that maximum interaction surface is obtained. Mathematically,

$$\text{Sensitivity} = \frac{\text{Change in resistance}}{\text{Change in concentration of the gas}}$$

The sensitivity should be as high as possible.

1.4.2 Selectivity:

A gas sensor can select a specific gas from a combination of gases. Selectivity plays an important role in the identification of gases. For example, in industry, various gases are released as waste products and we need to measure the concentration level of a particular gas. Here our sensor must be selective to that specific gas to discriminate it from other gases.

1.4.3 Stability:

This characteristic indicates the reproducibility of measurement overtime under the same condition It means the device should produce the same result for a given excitation if the measurement is done repeatedly even after a long time. The stability of the device is of great concern for the fidelity and faithfulness of a system.

1.4.4 Response time:

This characteristic indicates the operating speed of the device. It is the time interval over which the characteristic parameter (higher resistance) achieves a fixed percentage (usually 90%) of the final value for a particular concentration of gas exposure. Response time depends upon the shape and size of the sensor, sensor material, sensing gas, position and geometry of the electrode and operating temperature, etc. A small value of response time is always desirable for a good sensor [12].

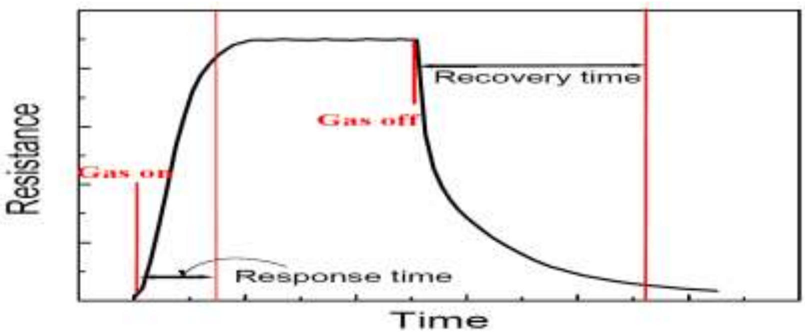


Figure: 5 Response and recovery analysis through resistance *vs* time

1.4.5 Recovery time:

When the sensor is removed from the gas exposure, recovery time is the time that takes for the sensor resistance to reach 70% of its saturated value from its final value. A good sensor should have a short duration of this time, to reuse it multiple times [12].

1.5 Fundamentals of metal oxide gas sensors

The essential studies of interaction mechanisms of metal oxides with a gas molecules is an important aspect for device formation and material selection for sensing any particular gas shown in **figure 6**, There are three conceivable interactions between a solid surface and gas molecules in general [11].

- Physical adsorption (physisorption):-The force of attraction that is existing between the adsorbate and adsorbent are Vander Waal's force, the adsorption is also known as physisorption or Vander Waal's adsorption relies [13].
- Chemical adsorption (chemisorption):-The force of attraction that is existing between the adsorbate particles and adsorbents are almost of the same strength as a chemical bond, the adsorption is called chemical adsorption or chemisorptions [13].
- Non-reversible reactions with the solid surface that typically leads to the formation of new compounds. During gas sensor operation this type of interaction is usually not desired and avoided as far as possible.

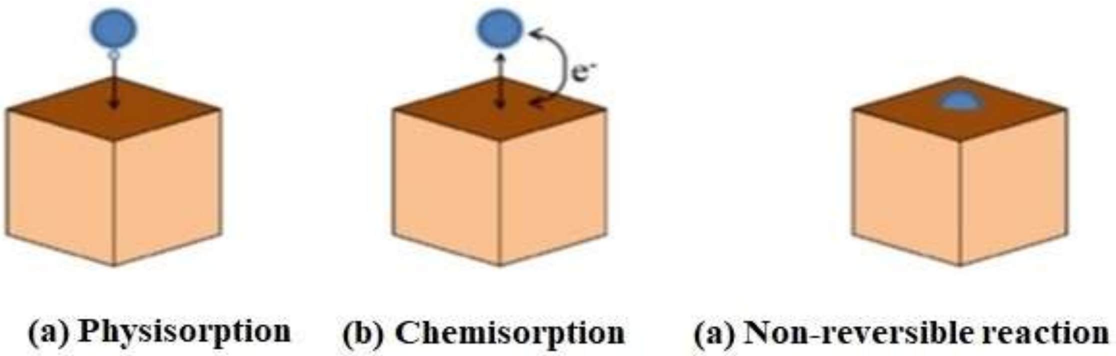


Figure: 6 Interaction mechanisms between a solid surface and gas molecules.

1.6 Nanosensors

Continuous physical properties are possessed by bulk material. Micron-sized material shows the same nature, but when particles attain Nano-scale dimension, conventional principles of physics are not capable of describing their behavior. To understand material behavior at this low dimension quantum mechanics has to be applied. The same material at the nanoscale can have different properties as of the bulk. Types of nanomaterials are classified based on dimension. It was discovered that the quantum confinement effect at the nanoscale level greatly improves the electrical or optical properties of the material, which can be used in a variety of applications. The sensor is one of the devices where this phenomenon is used to enhance the performance of the device. Nanosensor is an extremely small device capable the detecting and responding to stimuli with dimensions on the order of one billionth of a meter. Different nanomaterial types are mentioned in Table 1 given below:

Table: 1 Different Nanomaterials dimension and nanomaterial type structure

Nanomaterial Dimension	**Nanomaterial Type**
All three dimensions <100nm	Nanoparticles, quantum, dots, nanoshells, nanorings, microcapsules
Two-dimension < 100nm	Nanotubes, nanofibers, nanowires
One dimension < 100nm	Thin films, layers, coatings

There are number of methods for making nanosensors now proposed, including top-down lithography, bottom-up assembly, and molecular self-assembly, among others. When we talk about nano gas sensors, surface phenomenon plays a vigorous role, and reducing the size of the sensor at the nano level improves surface phenomenon as the S/V ratio increases. To miniaturize the devices, it is always required to reduce the size of the sensing part. Better conduction properties at the nanoscale level help in increasing the sensitivity of the gas sensor, it is feasible to evaluate very small amounts of samples, to detect directly without needing labels, and to delete some reagents.

1.7 Factors Affecting the Sensor Characteristics

The specifications for each gas sensor are determined by the application. Materials with high sensitivity and low detection limits are required. Scientists and engineers have always been interested in these materials. The primary ways for improving the gas sensitivity of metal-oxide sensor materials are listed in this section.

1.7.1 Size and Shape Effects

Metal oxide sensors are distinguished by the three main characteristics: receptor, transducer, and usefulness, with the transducer being the most essential. The microstructure of the components, specifically the grain size (D) and the depth of the surface space-charge layer, are intimately linked to the transducer function (L) [14]. When grain size is D ≤ 2 L, the sensor's responsiveness is dramatically improved. It has been established that decreasing grain size causes an exponential rise in sensor response due to an increase in the surface-to-volume ratio.

1.7.2 Gas Concentration

The gas concentration is another important affecting factor gas sensor characteristics. All the sensors are generally supplied with the information of a range of the concentration wherein the sensor exhibits a dependent behavior towards gas. Above the range, the sensor is termed to be in saturation wherein all the available adsorption sites are being occupied by the target gas. Up to saturation limits, the change in response increased linearly with an increase in gas concentration.

1.7.3 Doping

Doping metal oxide sensing films is a conventional gas sensor method. The basic approach of doping is to improve catalytic activity while adjusting the intrinsic metal oxide's electrical resistance [15], [16], [17]. Because the dopant is usually very active, it reacts with adsorbed molecules first. The dopant is widely disseminated on the metal oxide matrix, as illustrated in Figure 7, and is present near all intergranular contacts.

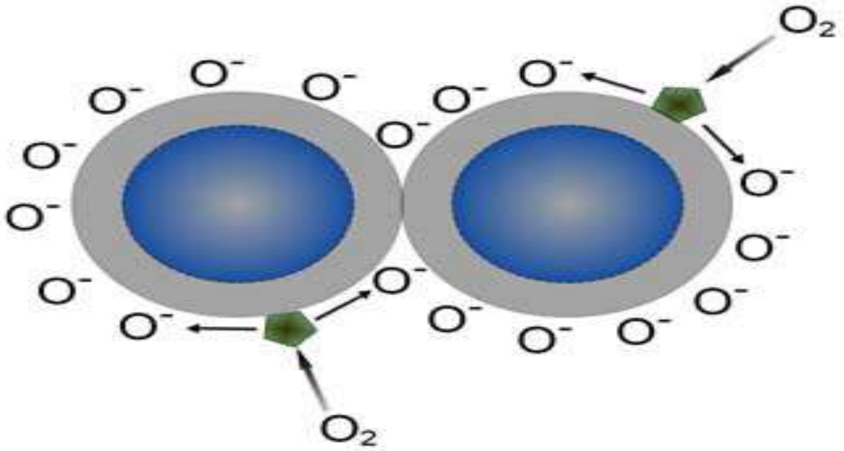


Figure: 7 Oxygen spillover process in the surface of doped metal oxides [19]

The oxygen molecules preferentially react with the dopant in air, creating oxygen anions, which subsequently spill over into the metal oxide matrix. When the target gases are adsorbed on the dopant surface and then travel to the oxide surface to react with surface oxygen species, the surface conductivity is increased [18].

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