Fundamentals and Mechanisms of Light-Activated Gas Sensors

Subjects: Physics, Applied

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The light-activated gas sensors show promising results, particularly using visible light as an external trigger that lowers the power consumption as well as improves the stability, sensitivity and safety of the sensors. It effectively eliminates the possible damage to sensing material caused by high operating temperature or high energy light.

Keywords: light-activated gas sensors ; gas sensors ; conductometric transducers ; resistors ; heterojunctions

1. Introduction

Gas sensors play a pivotal role in monitoring and detecting the presence of specific gases in various applications, ranging from environmental monitoring to industrial safety and healthcare. The need for more accurate, sensitive and selective gas sensors has led to ongoing research in this field. The ability to detect and quantify specific gases or volatile organic compounds is essential for ensuring safety, quality and compliance [1][2]. Traditionally, gas sensors have relied on well-established principles of chemical interactions, which are inherently affected by factors like temperature, humidity and the presence of interfering gases [3][4].

In recent years, an emerging and fascinating approach that has garnered considerable attention is the combination of light sources with gas sensors [5][6]. Light-assisted techniques have offered a transformative approach to address the limitations of traditional gas-sensing technologies and harness the power of illumination to influence and enhance their gas-sensing capabilities [7][8]. Researchers worldwide have been instrumental in advancing this technology by utilising various forms of electromagnetic radiation, such as ultra-violet (UV) [9][10][11][12], visible light [13][14], and infra-red (IR) radiations [15] to improve gas-sensing performances. These sensors have gained significance due to their ability to provide high sensitivity, short response times and low power consumption in gas detection, at least with visible light, while also expanding their applicability in various environments. However, the effect of visible light on the gas sensors has gained more attention than any other light because of its low cost and low power consumption [16]. Moreover, utilising visible light as an activation source offers the advantage of making various light sources commonly available in everyday life suitable for light-activated gas-sensing technologies. This practical approach broadens the range of applicable light sources to those accessible throughout a person's lifetime. Moreover, employing visible light sources serves to avoid potential harm to sensing materials that may occur with UV light, with the dual purpose of reducing the thermal effect and ozone generation in oxygen-rich environments [17].

2. Fundamentals and Mechanisms of Light-Activated Gas Sensors

Gas sensors are founded upon the fundamental principle that they operate by recognising the changes that occur when target gases interact with a sensing material. This specific interaction leads the gas molecules to adsorb or absorb onto the sensor's surface or within its material structure, respectively. Depending on the type of sensor and the gas involved, sorption behaviour can lead to changes in the sensor's electrical, optical or thermal properties based on the concentration of the target gas [18]. Understanding and controlling sorption behaviour is crucial for designing effective gas sensors with high sensitivity and selectivity [19][20].

Light irradiation upon the gas sensors effectively modifies the sorption behaviour and improves its kinetics due to the photoexcitation of charge carriers in semiconductors [9]. It is well known that when light energy is absorbed by gas molecules or sensing materials, it leads to electronic transitions [21][22][23]. In simpler terms, photons (hν), or packets of light energy, knock electrons from their stable positions, creating both negatively charged electrons (e^-) and positively charged holes (h^+) in conduction and valence energy bands, respectively, when inorganic semiconductors are considered (**Figure 1**).

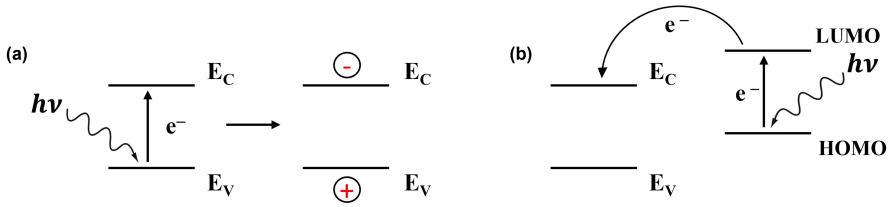

Figure 1. Schematic view of light-induced charge carrier generation in an inorganic semiconductor (E_V and E_C are the top of the valence band and the bottom of the conduction band, respectively) (**a**) and in a dye/inorganic semiconductor heterojunction device (HOMO and LUMO are the highest occupied and lowest unoccupied molecular orbitals, respectively) (**b**).

Semiconductors have a specific energy gap between their valence and conduction bands or highest occupied molecular orbital and lowest unoccupied molecular orbital in molecular semiconductors, known as the bandgap or molecular bandgap [24][25]. The excitation of electrons to higher energy levels alters the conductivity of the material via the change in free charge carrier density. But more interesting is the increase in the relative response (RR), which can even depend on the wavelength. Thus, with carbon nanotubes, it was shown that the RR was multiplied by a factor of 1.5 when changing from 365 nm (0.42–0.55 mW cm^{-2}) to 275 nm (8–10 mW cm^{-2}), while the response was barely visible in the dark [26].

In further depth, the interaction between light and gas sensors is rooted in the principles of photochemistry and semiconductor physics [27]. It involves a series of reactions initiated by the absorption of photons [28][29]. Most conductometric devices are sensitive to light [30][31]. In the case of dye-sensitized semiconductors, e.g., perylenediimide/SnO_2 heterojunction device, light absorption generates e^- that are injected in the conduction band of the semiconductor, increasing its conductivity; meanwhile, the generated holes can recombine with adsorbed O^{-2} ions, leading to O_2 formation, facilitating its desorption (Equation (1)). In this case, the choice of the dye allows the use of a lower energy light compared to what is needed to excite the semiconductor [30]. Another key effect of light is its impact on gas desorption [32], often of O_2 in atmospheric conditions, but not only oxygen.

$$h^+ + O^-_{2(ads)} \rightarrow O_{2(ads)} \quad (1)$$

In addition to photo-stimulated desorption, photo-stimulated adsorption was also mentioned in the case of MoS_2-based NO_2 sensors [33]. This could be due to the increase in free adsorption sites related to oxygen desorption under illumination. Meanwhile, the oxygen in the surroundings reacts with the photo-induced electrons, generating additional photo-induced oxygen ions (Equation (2)) [10].

$$O_{2(ads)} + e^- \overset{hv}{\rightarrow} O^-_{2(ads)} \quad (2)$$

So, in general, light absorption modifies the adsorption–desorption equilibrium and can explain why recovery time can be reduced [34].

Initially, the idea of light activation on gas sensing was ignited by D. A. Melnick. He explored the mechanism of oxygen adsorption and its impact on the conductivity of porous sintered zinc oxide samples, particularly when exposed to UV light [35]. This study involved examining the photoconductance of zinc oxide samples, wherein their electrical conductivity changed upon exposure to light. It is observed that the conductivity increases during illumination and decreases when the light source is turned off. In ZnO, which is an n-type semiconductor, chemisorbed oxygen acts as a trap. So, under illumination, oxygen desorption leads to a conductivity increase. Photo-stimulated adsorption and desorption of oxygen were also evidenced in the case of SnO_2 and TiO_2 [23].

In 1962, T. Seiyama introduced the first ever metal oxide-based gas sensors working at high temperatures, over 400 °C, detecting several gases, including toluene, benzene, CO_2, propane and ethyl ether [36]. This effect drew the attention of many researchers to use an external trigger to improve or enhance the sensing properties of gas sensors. Performance-wise, these gas sensors, which operate at high temperatures, certainly secured fast kinetics with superior sensing responses towards various gases. However, the increasing in demand for portable and multifunctional devices led the researchers to focus on reducing power consumption by lowering the operating temperature of the gas sensors. J.T. Cheung demonstrated and patented the light-assisted gas sensors in the 1990s [37], demonstrating the interest of light irradiation for stimulation of desorption of gas from the surface of the sensing material at room temperature. The approach of using light in gas sensors ignited the light-assisted gas sensing technology, resulting in numerous scientific publications

in the following years. In addition, the visible light can be used as an external trigger for inversion in the nature of majority charge carriers in devices, as soon as ambipolar materials are involved [38].

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