Gasochromic WO3 Nanostructures

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Gasochromic WO3 nanostructure sensors work based on changes in their optical properties and color variation when exposed to hydrogen gas. They can work at low or room temperatures and, therefore, are good candidates for the detection of hydrogen leakage with low risk of explosion. Once their morphology and chemical composition are carefully designed, they can be used for the realization of sensitive, selective, low-cost, and flexible hydrogen sensors.

Keywords: gasochromic ; nanostructured WO3 ; gas sensor ; hydrogen gas ; sensing mechanism

1. Hydrogen Gas

Hydrogen is a gas with no color, odor, or taste and cannot be detected by human senses [1][2]. Due to its efficiency, renewability, and green nature, it can replace fossil fuels in the near future [3]. Nevertheless, because of its small size, high diffusion coefficient, and consequently easy permeation through most materials, it is difficult to store hydrogen. Furthermore, hydrogen is highly explosive with a broad flammability range (4–75 vol%) and possesses an extremely low ignition energy [4][5]. Therefore, it is important to develop low temperature, reliable and safe gas sensors for detecting hydrogen gas. So far, several gas sensors based on different mechanisms have been reported for sensing hydrogen, including fiber-optic [6], catalytic [7], electrochemical [8], acoustic [9], resistive [10], thermoelectric [11], and gasochromic sensors [12]. Each of these sensors has its own merits and shortages [13]. For example, resistive gas sensors are inexpensive, simple in design and operation, highly responsive, and exhibit good stability [14][15][16]. However, they can only work efficiently at high temperatures [17], which increases the risk of hydrogen explosion during detection. Gasochromic sensors have the advantage of working at low temperatures, which can significantly decrease the risk of hydrogen explosion. Furthermore, in some cases, they can be fabricated on flexible substrates, with eye-readable color changes, which remarkably facilitate the detection of hydrogen in different places. In addition, the removal of electrical power from ambient atmosphere, high resistance to electromagnetic noise, and compatibility with optical fibers make them advantageous in hydrogen gas detection [18].

2. WO_3 and Its Crystal Structures

Tungsten trioxide (WO_3) is a very promising metal oxide with diverse properties. It has an n-type (E_g = 2.60–3.25 eV) [19][20] semiconducting nature and unique electrical properties. Further, it is transparent to visible and infrared light. Therefore, it has been used in different applications including smart windows [21], photocatalysts [22], solar cells [23], humidity sensors [24], and gas sensors [25]. Moreover, due to its excellent coloration efficiency [26], WO_3 is the most used chromogenic material in photochromic, electrochromic, and gasochromic applications [27].

Tungsten oxide has a perovskite-type WO_6 octahedral crystal structure. In its structure, W^{6+} ions occupy the corners of the octahedra, and oxygen ions are located at mid-crystal edge. In the ideal form, the octahedra are connected at the corners. The central atom (C) is absent and this defective perovskite configuration is often referred to as the ReO_3 structure [28]. Similar to the behavior of most perovskites and ceramics, depending on the temperature, WO_3 crystals can structurally transform in the following order: Monoclinic (ε-WO_3, < −43 °C), triclinic (δ-WO_3, −43 to 17 °C), monoclinic (γ-WO_3, 17–330 °C), orthorhombic (β-WO_3, 330–740 °C), and tetragonal (α-WO_3 > 740 °C) [29][30]. The monoclinic crystal structure is the most stable at room temperature [30]. The large voids generated in WO_6 octahedral networks in the WO_3 structure induce some variations in the position of W and in the WO_6 octahedron orientation. Thus, displacement of tungsten from the center of the octahedron and tilting of the WO_6 octahedra are two kinds of distortions [26], which lead to 11 different structures of WO_3 [31]. The gasochromic coloration of crystalline WO_3 is associated with changes in its structure from monoclinic to tetragonal and cubic [32]. For example, Inouye et al. [33] reported crystal structure transition from monoclinic to tetragonal in RF-sputtered WO_3 films upon exposure to hydrogen gas. However, the structure of hydrated $WO_3 \cdot xH_2O$ sensors does not change during gasochromic detection of hydrogen gas [32].

3. Chromogenic: Definition, Materials and Basics

Chromogenics is a Greek word with the stem “chromo” for color. It refers to the study of materials whose optical properties (or color) change as a function of external ambient conditions [31]. Chromogenic materials generally have wide bandgaps and are transparent in the visible range, but they reversibly change from being transparent to a dark color in the presence of an electric field (electrochromic coloration), light (photochromic coloration), or when they are exposed to a gas (gasochromic coloration) [34]. Therefore, gasochromism refers to reversible changes in optical properties or color when a material is exposed to a gas [3][35]. Gasochromic materials exhibit a promising potential for use as gas sensors. WO_3, which is light yellow in color, is one of the most important chromogenic materials known thus far. It exhibits a deep blue color upon exposure to hydrogen gas [36]. In addition to WO_3, other materials reported for gasochromic applications include V_2O_5 [37][38][39][40], VO_x [41], MO_x [42], MoO_3 [43], $(MoO_3)_{1-x}$ $(V_2O_5)_x$ [44], mixed silver/nickel ammonium phosphomolybdate [45], $(Ti\text{-}V\text{-}Ta)O_x$ [35], $Ni(OH)_2$ [46], peroxopolytungstic acid [47][48], and metals like Y [49]. This effect has also been exploited for the detection of other gases such as volatile organic compounds [50], NO_2 [51], H_2S, SO_2 [52], NH_3 [53], XeF_2 [54], cyclohexane [55], CO, and Cl_2 [46]. Among the different gasochromic materials available, the most important ones are WO_3 and MoO_x. However, due to its weak color change properties and the existence of several phases whose formation depends on the growth method, molybdenum oxide has received less attention for gasochromic studies [56].

4. Gasochromic Properties of WO3 nanostructures

The ability of WO_3 to undergo reversible changes in its optical properties when exposed to an electric field was first reported by Deb in 1973 [57]. Nineteen years later, Ito [58] reported the potential of WO_3 for gasochromic studies. Thus far, the optical properties of WO_3 nanostructures have been modulated by applying an electric field (electrochromism), UV irradiation (photochromism), or a gas (gasochromism) [59]. Gasochromic coloration of WO_3 is mostly associated with hydrogen gas [35]. In contrast to the electrochromic response, the presence of catalytic noble metals on the surfaces of WO_3 nanostructures is necessary to induce an acceptable gasochromic effect. The most common catalysts used are Pd [60][61], Au [30], and Pt [62][63]. They promote chemical reactions by reducing the activation energy between WO_3 and hydrogen gas. Color changes occur in gasochromic WO_3 sensors when H^+ ions intercalate with the WO_3 layer after the dissociation of gas molecules (H_2) into atoms by the action of noble metals. The optical properties of WO_3 films can be reversibly changed with the insertion and extraction of H^+ ions and electrons into the WO_3 films, which is accompanied by redox changes leading to the formation of W^{5+} ions [64][65]. Gasochromic measurements are often carried out by monitoring optical properties, such as absorbance/transmittance/reflectance in convenient wavelength ranges (visible-NIR) [66]. Such measurements offer simple, low-cost, and highly selective analytical methods for detecting specific gases [30]. In addition, the stability of the gas sensor can be enhanced as measurements are most often conducted at low or room temperatures.

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