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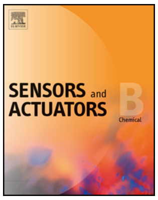

Comparative study of ultraviolet light and visible light on the photo-assisted conductivity and gas sensing property of TiO_2

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ABSTRACT

The photoconductivity and the gas sensing property of TiO_2 at room temperature under ultraviolet (UV) irradiation were compared with those under visible light irradiation (≥420 nm), respectively. It was found that UV light could cause the photoconductivity of TiO_2 and its sensing response to both ethylene and oxygen, while the visible light at 420 nm could cause the photoconductivity of TiO_2 and its sensing response to oxygen but not to ethylene. This indicates that the photo-assisted gas sensing performance of TiO_2 was dependent on its light-excited behavior: The intrinsic excitation of TiO_2 induced by UV light could produce both the holes and electrons, which exhibited a respective response to ethylene and oxygen, while the extrinsic excitation of TiO_2 induced by visible light maybe only produced the free electrons but not free holes, resulting in only a response to oxygen. Furthermore, it was found that the visible-light enhanced conductivity maybe depend on the Ti–bonded hydroxyls (Ti–OH) at TiO_2 surface. With the removal of Ti–OH by increasing temperature, the visible light could not produce the photoconductivity of TiO_2. It was proposed that Ti–OH groups act as the shallow trapped level to cause the extrinsic excitation of TiO_2.

1. Introduction

It is well known that the intrinsic light absorption of metal oxide semiconductors allow for the possibility of utilizing gas sensing at room temperature over semiconductors and then the implementation of the corresponding sensors as the portable devices with low power consumption [1–3]. During the process of a n-type semiconductor sensor adsorbing gases under light irradiation, the intrinsic excitation of n-type semiconductor induced by light can generate the free electron-hole pairs, and change the intergrain potential barrier to decrease the depletion layer between the semiconductor and the adsorbed gas, resulting in the change of photo-current of sensor (i.e. detecting gases) [1]. Many semi-conductor materials, such as ZnO [4], SnO_2 [5,6], WO_3 [7], and In_2O_3 [8] can be improved their gas sensitivities by introducing UV light. As a typical n-type semiconductor, TiO_2 also exhibited a good photo-assisted sensing property for many gases, such as formaldehyde [9–11], ethanol [12], and so on. Our previous work also showed that TiO_2 film sensor could make a good response to C_2H_4, CO, H_2, and O_2 under UV irradiation at room temperature [13,14].

At present, the photo-assisted gas sensing study for TiO_2 was mainly paid attention to the promotion effect of intrinsic-excitation of TiO_2 induced by UV light on its response to gases. Here, the energy of light is higher than the band gap energy (Eg) of TiO_2, the electrons in valence band (VB) would be excited into the conductive band (CB), resulting in the increase in the conductivity of TiO_2, and also the change of its gas sensitivity. In general, this intrinsic-excitation of TiO_2 cannot occur if the energy of light is lower than the Eg of TiO_2 [1]. However, some defects might be formed in the lattice structure of TiO_2 during the preparation process. These lattice defects can cause the change in the periodic field produced by the periodic array atoms, resulting in a new energy level (defect levels) appeared in the band gap region of TiO_2 [15]. In this case, a light with an energy lower than the Eg of TiO_2 can also cause the electron excitation (i.e., the extrinsic excitation) due to the presence of defect level, which resulted in the increase of charges and then the photo-conductivity of TiO_2 [16,17]. Panayotov et al. [18] have reported that the presence of the shallow trapped level (the Ti–OH sites induced by the defect level) in TiO_2 could cause the electron transfer from the shallow trapped level to the CB of TiO_2 under visible light irradiation. In addition, it was also reported that

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the oxygen vacancies (OVs) of TiO_2, located near to the CB of TiO_2, could also cause the extrinsic excitation of TiO_2 with the introduction of visible light [19,20]. Although this extrinsic excitation of TiO_2 is less than its intrinsic excitation (cannot exhibit an obvious visible-light absorption), this former behavior maybe also exert an effect on the gas sensing performance of TiO_2 like that of the latter.

To study the effect of the extrinsic excitation of TiO_2 on its gas sensing property, in this work a commercial anatase TiO_2 film sensor was prepared and then investigated into its photo sensing property and its response to ethylene under visible light. After comparing the result with that of the intrinsic excitation induced by UV irradiation, it was found that the gas sensing property of TiO_2 induced by extrinsic excitation is different from that induced by intrinsic excitation.

2. Experimental

2.1. Preparation of TiO_2 sensor sample

The TiO_2 film sensor device sample was prepared according to our previous work [13,14]: A commercial alumina sheet (1.5 cm × 1 cm × 0.8 mm) with a comb-like gold electrodes (used as the substrate for TiO_2 sensor) was first washed in acetone, ethanol, and deionized water in sequence and then dried in air. Meanwhile, a 30 mg commercial TiO_2 powder with an average size of 60 nm (>99.8 wt% purity, Aladdin) was dispersed into a 1.0 mL terpineol solvent under ultrasonic treatment for 40 min. This obtained TiO_2 suspension (50 μL) was dropped onto the surface of the pretreated comb-like gold electrode sheet. Then, the substrate coated with TiO_2 suspension was dried at 100 °C for 1 h and calcined in air 600 °C for 2 h in a tube furnace with a heating rate of 2 °C min^{-1}. After cooling down to the room temperature, a TiO_2 sensor device sample was obtained. Note that the terpineol solvent in sample has been volatilized or decomposed during the treating process.

In addition, a certain amount of above TiO_2 powder was calcined in air 600 °C for 2 h with a heating rate of 2 °C min^{-1}. After cooling down to the room temperature, the obtained powder was used to test the characteristics.

2.2. Characteristics of TiO_2 sample

X-ray diffraction (XRD) pattern of sample was recorded on a Bruker D8 Advance powder X-ray diffractometer using Cu Ka radiation (λ = 0.15418 nm) operated at 40 kV and 40 mA. The Ultraviolet-visible diffuse reflection spectra (UV–vis DRS) of sample was measured with a Varian Cary 5000 UV–vis-NIR spectrophotometer.

2.3. Photoelectrochemical performances

The electrochemical properties of the samples were performed by an electrochemical analyzer using a three-electrode configuration. A 500 W Xe lamp with an IR (>760 nm) reflection plate and another UV (<420 nm) cut-off plate was used as the light source with the radiation distance of 15 cm onto the sample surface. A fluorine-doped tin oxide (FTO) conductive glass coated with the material film was used as a working electrode, Pt wire as a counter-electrode, and Ag/AgCl (in saturated KCl (aq)) as a reference electrode. An aqueous solution of Na_2SO_4 (0.02 M) was used as an electrolyte. The working electrodes were prepared by drop-coating, where the FTO conductive glass electrodes were first washed in an ultrasonic bath with ethanol, deionized water, and then dried at 80 °C for 2 h. A 5 mg TiO_2 powder sample was added to 800 μL absolute ethanol to make a slurry and then the suspension was dispersed by ultrasonic for 3 h. Then, a 20 μL slurry was injected onto the conductive surface of a 2.5 cm × 1.0 cm FTO glass electrode with the cell size of 5 mm × 5 mm. The coated FTO glass electrode was then dried at room temperature for about 12 h. The transient photocurrent response for TiO_2 stacks in the air was recorded on an electrochemical analyzer (Epsilon, BAS, USA) at the operation voltage of 0.5 V under light irradiation.

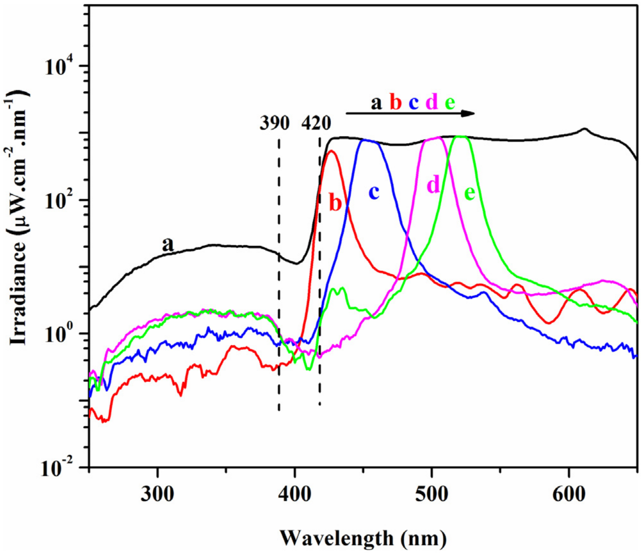

Fig. 1. The irradiance distribution at the surface of sensor sample with different light sources: (a) Xe, (b) Xe + 420, (c) Xe + 450, (d) Xe + 500and (e) Xe + 520.

2.4. Photo response and gas sensing performances

Photo response and gas sensing experiments were performed in a JF02E gas sensing test system (Kunming GuiYanJinFeng Tech. Corp. LTD) as reported in our previous work [13,14]. In this work, a 50 W Xe lamp with an IR (>760 nm) reflection plate and another UV (<420 nm) cut-off plate was used as visible light source (420–760 nm, labeled as Xe). During the testing process, different bandpass filters (420, 450, 500 and 520 nm) were introduced into the lamp to obtain the corresponding visible light resources, which marked as Xe + 420, Xe + 450, Xe + 500 and Xe + 520, respectively. The irradiance intensity of the different light resources to the surface of gas sensor sample has been measured by the SpectriLight ILT 950 adjustment spectrometer system. As seen in Fig. 1, the Xe light also owned the irradiance intensity in the UV region (321–390 nm). After adding the bandpass filter, the irradiance intensities in both UV region and visible light (380–780 nm) had been obviously weakened, which the light intensity values are shown in Table 1. Note that the Xe + 420 light sources showed a lower intensity than other visible light sources (Xe + 450, Xe + 500 or Xe + 520) in the UV light region of 321–390 nm and the visible light region of 380–780 nm, respectively, but it owned the stronger intensity of light at 420 nm than others.

The gas sensing properties of the film samples were investigated in a chamber made of stainless steel having a total volume of 100 mL. During the testing process, the voltage was controlled at 8.5 V. The high purity N_2 was used as the reference gas. Ethylene and oxygen gas (balance with high purity N_2) were used as the probe gas. After pretreated at 100 °C for 1 h at N_2 atmosphere, the sample was cooled down to room temperature and the probe gas with a flow rate of 250 mL min^{-1} was introduced. Note that all the above experiments were carried out at room temperature.