Article

The Response of UV/Blue Light and Ozone Sensing Using Ag-TiO\textsubscript{2} Planar Nanocomposite Thin Film

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Abstract: We successfully fabricated a planar nanocomposite film that uses a composite of silver nanoparticles and titanium dioxide film (Ag-TiO\textsubscript{2}) for ultraviolet (UV) and blue light detection and application in ozone gas sensor. Ultraviolet-visible spectra revealed that silver nanoparticles have a strong surface plasmon resonance (SPR) effect. A strong redshift of the plasmonic peak when the silver nanoparticles covered the TiO\textsubscript{2} thin film was observed. The value of conductivity change for the Ag-TiO\textsubscript{2} composite is 4–8 times greater than that of TiO\textsubscript{2} film under UV and blue light irradiation. The Ag-TiO\textsubscript{2} nanocomposite film successfully sensed 100 ppb ozone. The gas response of the composite film increased by roughly six and four times under UV and blue light irradiation, respectively. We demonstrated that a Ag-TiO\textsubscript{2} composite gas sensor can be used with visible light (blue). The planar composite significantly enhances photo catalysis. The composite films have practical application potential for wearable devices.

Keywords: light sensor; SPR; composite; ppb-level ozone

1. Introduction

Due to growing environmental awareness, photocatalysts have been identified as green materials for reducing air pollution [1]. Titanium dioxide (TiO\textsubscript{2}) is a popular photocatalytic material with considerable development potential [2,3]. With a bandgap of about 3.2 eV at an absorption wavelength of around 360 nm, TiO\textsubscript{2} is a widely-studied n-type metal-oxide semiconductor (MOS) that is commonly used in photocatalysts and gas sensors [4–6]. Enhancing light response is an important application of the light-harvesting and gas sensing capabilities of TiO\textsubscript{2}. According to researchers, doping noble-metal particles can enhance the photocatalytic and degradation efficiency of TiO\textsubscript{2} for chemical or biological matter. Absorption spectra also show good response in visible light when TiO\textsubscript{2} nanocomposites (metal-doped TiO\textsubscript{2}) are used [7–12]. Several methods, such as metal particle doping, polymer nanocomposites, and core-shell nanoparticles [13–16], have been developed to enhance photocatalysis. The primary reason for this enhancement is that the surface plasmon resonance (SPR) produced by these metal nanoparticles can significantly change the visible light response and electrical properties of semiconductors. Via the SPR effect, the metal-nanoparticle composite provides additional electrons to the semiconductor. Different metal nanoparticles (Ag, Au) doped on MOSs are widely used in many fields to generate SPR and enhance photocatalysis; they are also used in gas sensors, environmental protection technologies, solar cells, energy storage devices, and photovoltaic materials [17–19]. For example, researchers have applied SPR with magnetic microspheres for prion protein detection [20–22], a magnetic biochip (Au/Fe\textsubscript{3}O\textsubscript{3}/Au) for antigen detection [23], core-shell γ-Fe2O3@Au nanoparticles for low-field nuclear magnetic resonance [24], a gold film-coated side-polished fiber for temperature sensor
fabrication \[25\], and Au@SiO$_2$ core-shell NPs into TiO$_2$ scaffold layer to increase the power conversion efficiency of solar cells \[26\].

With their excellent characteristics, MOSs doped with metal nanoparticles are highly desirable composite materials. In this study, we discuss the Ag-TiO$_2$ planar composite film \[17\]. The methods used in the complexation of metal nanoparticles in TiO$_2$ are primarily chemical-based. However, it is difficult to ensure the uniform doping of silver nanoparticles in TiO$_2$ for large-scale and mass production \[18,19,27–29\]. We coated silver nanoparticles with TiO$_2$ by electron-beam (e-beam) evaporation during the semiconductor fabrication process to ensure that the silver nanoparticles were in complete contact with the TiO$_2$, without the use of high-temperature annealing, while still successfully sensing 100 ppb ozone \[17\]. This approach can significantly improve the practical application of silver particles in areas such as the manufacturing of gas sensors and wearable devices. We discuss the electrical properties, light response, conductivity change, and gas sensing of the Ag-TiO$_2$ composite film for the detection of light and gas molecules.

2. Materials and Methods

We prepared the silver nanoparticles on a non-conductive glass and performed radio-frequency (RF)-magnetron sputtering at room temperature to deposit a silver film 10 nm thick. This film was then annealed at 250 °C for 1 h to produce nanoparticles. TiO$_2$ film was overlaid with silver nanoparticles. Using a Ti$_3$O$_5$ tablet as a starting material, we then performed e-beam evaporation at a working pressure of approximately 0.1 Torr to produce TiO$_2$ films with thicknesses of 10 nm, 20 nm, 30 nm, and 40 nm. The reaction equation is as follows \[30,31\]:

$$2\text{Ti}_3\text{O}_5 + \text{O}_2 \rightarrow 6\text{TiO}_2$$

(1)

We labeled the Ag-TiO$_2$ films with thicknesses of 10 nm and 20 nm as AT10 and AT20, respectively. We labeled the TiO$_2$ films with thicknesses of 10 nm and 20 nm as T10 and T20, respectively. Using RF-magnetron sputtering, we deposited a gold film with a thickness of 100 nm on the sample as a measuring electrode. We used a multimeter (Keithley 2400) to measure the electrical properties. We determined the particle sizes, morphologies, and lattice structures of the silver nanoparticles by scanning electron microscopy (SEM) and X-ray spectroscopy, and measured the absorption spectra with a UV-Vis spectrometer.

In the experiments conducted to determine the light response and ozone detection, we used ultraviolet (UV) light and blue light-emitting diode as light sources. These measurements are described in detail elsewhere \[32–34\].

3. Results

3.1. Characteristics of Ag-TiO$_2$

Figure 1 shows SEM images of the Ag nanoparticles and Ag-TiO$_2$ film \[35\]. In Figure 1a, we can see that the Ag nanoparticles are almost spherical in shape. The silver nanoparticles have a uniform distribution with ring-like aggregates. There are four main nanoparticle groups with diameters of 5 nm, 15 nm, 25 nm, and 35 nm, respectively, and a maximum size of about 70 nm, as shown in the inset of Figure 1a. The average size is about 28 ± 13.26 nm. There are few particles whose sizes are over 80 nm. Figure 1b shows the Ag nanoparticles covering the TiO$_2$ film; grains can be clearly observed on this Ag-TiO$_2$ composition film, with average sizes ranging from 50 nm to 80 nm. This indicates that the particle sizes increased after the deposition of the 20 nm thick TiO$_2$ film on the Ag nanoparticles. The image of the Ag-TiO$_2$ composite film also shows an uneven surface.

Figure 2 shows the X-ray diffraction pattern of the Ag-TiO$_2$ composite, in which we can see no distinct peak for the TiO$_2$ film. The small peak at $2\theta = 38.08$ can be indexed as (111) for the silver nanoparticles. TiO$_2$ films, without having undergone an annealing process by e-beam evaporation, are amorphous \[3\].
At wavelengths of 428 nm to 500 nm with TiO$_2$ films of 10–30 nm, the absorbance for a TiO$_2$ film thickness of 10–30 nm is less than 20%, indicating a significant absorbance at ~500 nm. The resonance peak of the silver nanoparticles is significantly affected by the TiO$_2$ film covering. The plasmon resonance of the silver nanoparticles was redshifted from a wavelength of 330 nm to 500 nm due to the SPR of isolated silver nanoparticles. We found the resonance peak of the silver nanoparticles to be significantly affected by the TiO$_2$ film or the distribution of the silver nanoparticles.

The optical energy gap (E$_g$) can be calculated using the Tauc equation:

$$\alpha(h\nu) = \frac{A(h\nu - E_{LO})^{1/2}}{h\nu}$$

where $E_{LO}$ is the frequency of the LSPR, $W_p$ is the plasma frequency of the large metal, and $\alpha$ is the absorption coefficient. This formula is briefly explained by the Drude model:

$$E_{LO} = \frac{hW_p}{2(\pi\alpha)^{1/2}}$$

This difference may be due to the size, shape, and distribution of the silver nanoparticles.

Figure 3a shows the transmittance and absorption spectra of the samples (Ag, T10, AT10, AT20, AT30, and AT40), as measured by a UV-Vis spectrometer. The absorption spectrum of the silver nanoparticles alone (without TiO$_2$ film) exhibits a clear and sharp peak at 429 nm, indicating silver spherical nanoparticles with average sizes ranging from 30 to 50 nm [36,37]. This absorption spectrum indicates a localized SPR (LSPR) [38]. We can also see an unapparent peak at 360 nm in the absorbance curve. The two resonance peaks in the UV-Vis spectra of the silver nanoparticles are due to the influence of the added silver nanoparticles. The spectra of AT10, AT20, AT30, and AT40, respectively, show that all of the TiO$_2$ films were highly transparent, i.e., more than 80%, in the visible region. Both the pure TiO$_2$ and AT10 nanocomposites exhibit transmission edges at about 350 nm. The transmission spectra of AT10 and AT20 reveal a redshift to 428 nm to 500 nm, which is less than 20%, indicating that the composite films have a significant absorbance at ~500 nm.

The UV-Vis transmission spectra of the Ag-TiO$_2$ composites also show the transmittance to be more than 80% in the visible region. Both the pure TiO$_2$ and AT10 nanocomposites exhibit transmission edges at about 350 nm. The transmission spectra of AT10 and AT20 reveal a redshift to 428 nm to 500 nm, which is less than 20%, indicating that the composite films have a significant absorbance at ~500 nm.
The optical transmission spectra of T10 show that all of the TiO$_2$ films were highly transparent, i.e., more than 80%, in the visible region. Both the pure T10 and AT10 nanocomposites exhibit transmission edges at about 350 nm. The transmission spectra of AT10 and AT20 reveal a redshift due to the influence of the added silver nanoparticles. The spectra of AT10, AT20, AT30, and AT40 exhibit transmission edges at ~330 nm and a broad wave around 500 nm [17,19,20,29,30]. The transmission spectra of the semiconductor and metal nanoparticles overlap, which indicates that the TiO$_2$ and Ag metal nanoparticles were simultaneously excited by the light. There was also an edge at around 330 nm of the TiO$_2$ film and a peak at 500 nm due to the SPR of isolated silver nanoparticles in the samples. We found the resonance peak of the silver nanoparticles to be significantly affected by the TiO$_2$ film covering. The plasmon resonance of the silver nanoparticles was redshifted from a wavelength of 428 nm to 500 nm with TiO$_2$ films of 10–30 nm. As the thickness of the TiO$_2$ film increased to 40 nm, the redshift to 540 nm became more evident. The shift in the plasmon on this nanocomposite may be primarily attributable to the change in the permittivity of the medium. After coating, the oxide film has a much higher permittivity ($\varepsilon_m$). This variety of plasmonic peak can be briefly explained by the Drude model [43]:

$$W_{LSPR} \approx \frac{W_p}{\sqrt{1 + 2\varepsilon_m}}$$

where $W_{LSPR}$ is the frequency of the LSPR, $W_p$ is the plasma frequency of the bulky metal, and $\varepsilon_m$ is the dielectric constant of the medium. However, the shift values of the experimental data and those calculated by the Drude model are slightly different. This difference may be due to the size, shape, and distribution of the silver nanoparticles.

The UV-Vis transmission spectra of the Ag-TiO$_2$ composites also reveal the transmittance to be less than 20%, which indicates that the composite films have a significant absorbance at the ~500-nm wavelength (blue light). The transmittance at wavelengths ranging from 300 to 600 nm is also less than 80%. This can be attributed to the fact that silver nanoparticles scatter the unabsorbed photons under light irradiation, resulting in an increase in the average photon path length, which increases the absorption [44].

Both the absorption peak of TiO$_2$ and the Ag resonance showed a redshift, which indicates a reduction in the optical bandgap energy. The optical energy gap ($E_g$) can be calculated using the Tauc equation:

$$(\alpha h\nu)^{1/p} = A(h\nu - E_g)$$

where $A$, $E_g$, $h$, and $\nu$ are constant, energy gap, plank constant, and frequency, respectively; $p$ is the characteristic value of the optical absorption process, which is equal to 2 because TiO$_2$ is an indirect energy gap material; and $\alpha$ is a coefficient. When the thickness of TiO$_2$ was increased from 10 nm to 40 nm, the bandgaps of T10, AT10, AT20, AT30, and AT40 were 3.84 3.88, 3.75, 3.66, and 3.66 eV, respectively. The band gaps shown in Figure 3b are smaller than that of the 10 nm TiO$_2$ film with increases in the thickness of the TiO$_2$. The bandgap reduced no further when the TiO$_2$ thickness was greater than the size of the Ag nanoparticles [45].

3.2. UV and Blue Light Response

Figure 4a,b show the resistance–time relationship (bias: 1 V) of the Ag-TiO$_2$ nanocomposite film (10 and 20 nm) and the TiO$_2$ film (10 and 20 nm) under UV irradiation. Electrons and holes are generated when the films are irradiated by UV light, and the increased number of free electrons reduces the resistance. The light response of the composite was more significant than that of the TiO$_2$ film, which means that the composite produced more electrons after UV irradiation [46].
The value of $S$, faster than those of the TiO$_2$ and recombination rates of electrons and holes in the Ag-TiO$_2$ composite film, is attributed to the change in carrier density ($\Delta n$) and carrier mobility ($\Delta \mu$). The resistance curves of AT10 and AT20 are more stable and significant than those of T10 and T20. The change is small for TiO$_2$ under the same UV intensity. The differential curve fluctuated widely and was smoothed and averaged by several points. This variation is due to the SPR of the silver nanoparticles, whereby the silver nanoparticles provide TiO$_2$ with hot electrons and reduce its optical band gap, thus generating more electrons in the conduction band of TiO$_2$ with UV light irradiation.

The insets of Figure 4a,b show the relationship between the rate of photocurrent change and the detection time. The current density is given by $J = \frac{\Delta \sigma}{\Delta d}$, where $\Delta \sigma$ is the conductivity change, respectively. According to the above equation, the percentages of photocurrent change rates of AT10 and AT20 are 0.7–0.8 and 0.1–0.2, respectively. The value of $\Delta \sigma$ for Ag-TiO$_2$ is 4–8 times greater than that of TiO$_2$, which means that the conductivity of the semiconductors was obviously improved by doping them with metal nanoparticles. The conductivity increase indicates that either the carrier density or carrier mobility increased.

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Table 1. The response ((I$_L$ – I$_d$)/I$_d$) of light for 50 s light irradiation.

|       | T10 | AT10 | T20 | AT20 |
|-------|-----|------|-----|------|
| UV    | 0.2%| 1.7% | 0.1%| 1.2% |
| Blue  | X   | 0.45%| X   | 0.46%|
When the Ag-TiO$_2$ composite film is irradiated by blue light, the silver nanoparticles absorb the blue light to produce hot electrons for TiO$_2$ and reduce the resistance value (Figure 5). This means that the composite film can absorb blue light. However, the 10 nm and 20 nm-thick TiO$_2$ films showed no response to blue light.

![Figure 5. Ag-TiO$_2$ composite film is irradiated by blue light.](image)

3.3. Gas Sensing

Ozone is known to be an oxidizing gas. Figure 6 shows the resistance–time relationship of films at an ozone concentration of 100 ppb, which is the index value indicating damage to human health. TiO$_2$ is an n-type semiconductor, and we generated more electrons and holes by light irradiation [47,48]. The ozone concentration of the test box is simultaneously measured by a commercial ozone monitor (2B Tech 106-L) [32,33]. When strongly oxidizing O$_3$ was introduced (25 °C and relative humidity ~45 ± 3%), adsorption and desorption reactions occurred simultaneously. Since an oxidizing gas was adsorbed on the TiO$_2$, the free electrons were trapped, causing a decrease in the number of free electrons and an increase in resistance. In our experiment, UV and blue light were used to excite electrons, and thereby, facilitate gas absorption by the films. In Figure 6a, we can see a noticeable change in the resistance upon the introduction of ozone to the test chamber. There was little difference in the resistance changes of films under different types of light irradiation. Figure 6b shows the dR/dt versus time relationship of films under different types of light. The resistance changes of T20 (UV), AT20 (UV), and AT20 (blue) were 0.005, 0.03, and 0.02, respectively, at 100 ppb of ozone. Thus, the composite film AT20 exhibited a better response than the TiO$_2$ film. The sensitivities of ozone for 300 s exposure are shown in Table 2. The sensitivity, i.e., AT20 (UV) > AT20 (Blue) > T20 (UV) >> AT20, revealed the good performance of the composite film with respect to ozone. The response of the composite film increased by roughly six and four times under UV and blue light irradiation, respectively. The silver nanoparticles enhanced the effectiveness of the transfer of free electrons from the conduction band of TiO$_2$ to ozone. Thus, we demonstrated that the Ag-TiO$_2$ composite gas sensor can be used with visible light. In Table 3, we summarize the sensitivities for ozone using different materials, as obtained by various research groups.

Table 1. The response ((IL - Id)/Id ) of light for 50 s light irradiation.

Table 3. Sensitivities for ozone using different materials.
In this study, we successfully used a composite of silver nanoparticles and titanium dioxide film (Ag-TiO$_2$). Ultraviolet-visible spectra revealed that silver nanoparticles have a strong SPR effect. In addition, we observed a strong redshift of the plasmonic peak when the silver nanoparticles covered the TiO$_2$ thin film.

When measuring the light and gas responses, we found the light response of the composite film to be more versatile and responsive due to the SPR effect with UV irradiation. Under UV and blue light irradiation, the silver-nanoparticle electrons become excited and supplement those of the TiO$_2$. We determined that the SPR effect provides additional electrons to the TiO$_2$, thereby improving the light response and sensitivity of the gas sensor. We also found the conductivity of TiO$_2$ to increase with Ag doping. In our experiments, the Ag-TiO$_2$ nanocomposite film successfully sensed 100 ppb ozone. The gas sensor can also be operated with blue light; the results showed that the composite film could absorb blue light, and thus, can be used for application in different sensors such as gas sensors, light sensors, biosensors, and smart windows [53].

**4. Conclusions**

In this study, we successfully used a composite of silver nanoparticles and titanium dioxide film (Ag-TiO$_2$). Ultraviolet-visible spectra revealed that silver nanoparticles have a strong SPR effect. In addition, we observed a strong redshift of the plasmonic peak when the silver nanoparticles covered the TiO$_2$ thin film.

When measuring the light and gas responses, we found the light response of the composite film to be more versatile and responsive due to the SPR effect with UV irradiation. Under UV and blue light irradiation, the silver-nanoparticle electrons become excited and supplement those of the TiO$_2$ film. The value of conductivity change for Ag-TiO$_2$ is 4–8 times greater than that of TiO$_2$ under light irradiation. We determined that the SPR effect provides additional electrons to the TiO$_2$, thereby improving the light response and sensitivity of the gas sensor. We also found the conductivity of TiO$_2$ to increase with Ag doping. In our experiments, the Ag-TiO$_2$ nanocomposite film successfully sensed 100 ppb ozone. The gas sensor can also be operated with blue light; the results showed that the composite film could absorb blue light, and thus, can be used for application in different sensors such as gas sensors, light sensors, biosensors, and smart windows [53].

**Author Contributions:** C.-H.W. conceived and designed the experiments, and wrote the manuscript; T.-H.L. and P.-Y.S. performed the experiments.

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