

## SIZE EFFECT OF GOLD NANOPARTICLES ON OPTICAL AND ELECTRICAL PROPERTIES OF Au@TiO<sub>2</sub> NANOCOMPOSITE THIN FILMS

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**Abstract.** *This work studied on the influence of gold nanoparticle sizes on optical and electrical properties of Au@TiO<sub>2</sub> nanocomposite films. Here, the gold nanoparticles (AuNPs) with different sizes of 5 nm, 10 nm, 20 nm, 40 nm and 60 nm were dispersed onto nanoporous TiO<sub>2</sub> thin films to form Au@TiO<sub>2</sub> nanocomposite films. The field emission scanning electron microscope (FE-SEM) images showed that AuNPs were well dispersed on the TiO<sub>2</sub> films. The ultraviolet–visible (UV-vis) absorption spectra exhibited that all Au@TiO<sub>2</sub> nanocomposite films had a good surface plasmon resonance (SPR) effect of AuNPs with the resonance absorption peaks in the visible light region. The effect of AuNPs sizes on the film's photoluminescence property was investigated using excited laser light of 325 nm wavelength at room temperature. The electrical properties of Au@TiO<sub>2</sub> nanocomposite films were studied by recording the photocurrent under illumination of solar simulator and ultraviolet (UV) light source. Our results showed that the presence of gold nanoparticles significantly improved the photocurrent of Au@TiO<sub>2</sub> nanocomposite films and especially when AuNPs size was smaller than 20 nm. In addition, we also found that the photocurrent magnitude of the films with small AuNPs sizes (5 nm and 10 nm) under solar simulator light was*

*4 times larger than the one under UV light. These results indicated that AuNPs size had a great influence on the improvement of photocurrent in nanocomposite films.*

Keywords: gold nanoparticles; Au@TiO<sub>2</sub> nanocomposite; nanostructure; plasmonic; surface plasmon resonance.

Classification numbers: 81.07.-b; 78.20.-e; 73.63.-b.

## I. INTRODUCTION

In recent years, nanocomposite materials based on nanoparticles of gold embedded to TiO<sub>2</sub> nanostructure materials have attracted more and more attention of researchers in the world. As we all know that TiO<sub>2</sub> material has been widely used in many fields such as water splitting [1, 2], photocatalysts [3-5]; solar cells [6-8] as well as optoelectronic devices [8, 9], etc., because TiO<sub>2</sub> has many advantages: strong photocatalytic activity, chemical stability, environmental sustainability and ease to be fabricated in the form of nanostructures by variety of simple and inexpensive technologies. However, TiO<sub>2</sub> has a large band gap (3.2 eV), so it only absorbs the light in ultraviolet range (about 5% of sunlight energy), that greatly limits its applicability. Metallic nanoparticles, typically Au, Ag, are known to have a surface plasmonic resonance effect (SPR) that is created by the collective oscillation of conductive electrons induced by the electric field of incident light. The combination of metallic nanoparticles with semiconductor oxides is considered to enhance the SPR effect of the nanoparticles, leading to improvements in the electrical and optical properties of the combined materials that in turn can improve their photocatalytic properties.

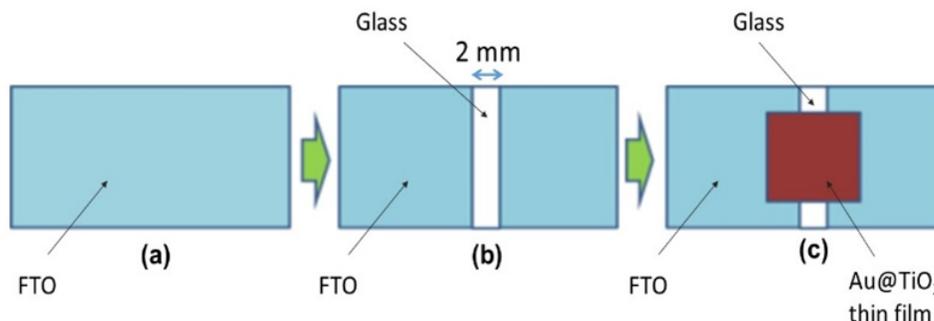
Many studies have demonstrated that the presence of AuNPs increased the photocatalytic activity of composite materials and thereby improved the decomposition efficiency of organic compounds [1,3,10], enhanced the efficiency of hydrogen production from water [1,11] or boosted the performance of plasmonic solar cells [6]. This is explained by the following: (i) the SPR effect of the AuNPs leads to extending the absorption of the Au@TiO<sub>2</sub> nanocomposite material to the visible light range, thereby increasing the light harvesting; (ii) AuNPs in contact with TiO<sub>2</sub> have formed a Schottky barrier, where electrons from n-TiO<sub>2</sub> to metal nanoparticles increased the ability to separate charge carriers, leading to increase photocatalytic as well as photochemical processes of the nanocomposite material [12,13]; (iii) the presence of metal nanoparticles increases light scattering, thus increasing light absorption. However, the role of AuNPs sizes on optical and electrical properties of nanocomposite thin films has not been adequately clarified.

Herein, we reported an approach of dispersing AuNPs with different sizes on the nanoporous TiO<sub>2</sub> films and then annealing to create Au@TiO<sub>2</sub> nanocomposite films. This work mainly focused on investigating the size effect of AuNPs on the optical and electrical properties of Au@TiO<sub>2</sub> nanocomposite films.

## II. EXPERIMENT

Au@TiO<sub>2</sub> nanocomposite films were synthesized on FTO glass (TEC 7, Sigma-Aldrich) and glass substrates. First, the FTO substrate was patterned as shown in Fig. 1. In order to make a non-conductive gap of 2 mm width, the FTO conductive layer was chemically etched with a 10 wt% HCl solution and zinc powder (Fig. 1b). Glass and patterned FTO substrates were cleaned by sequential ultrasonic vibration in deionized water, ethanol, acetone and deionized water as seen elsewhere [14]. Then, nanoporous TiO<sub>2</sub> films of 1 × 1 cm<sup>2</sup> area were screen-printed on the

substrates using titania nanoparticle paste containing 20 nm  $\text{TiO}_2$  nanoparticles, purchased from Solaronix (Fig. 1c). The films were dried and annealed at  $450^\circ\text{C}$  for 1 hour to get nanoporous  $\text{TiO}_2$  films. To prepare  $\text{Au@TiO}_2$  nanocomposite films, we used aqueous solutions containing AuNPs (0.1 mg/ml) with different sizes of 5 nm, 10 nm, 20 nm, 40 nm, and 60 nm, purchased from Alfa Aesar. A certain amount of AuNPs solution was slowly dripped on the nanoporous  $\text{TiO}_2$  films, followed by drying at  $100^\circ\text{C}$  for 5 minutes and annealing at  $450^\circ\text{C}$  for 1 hour in the air.

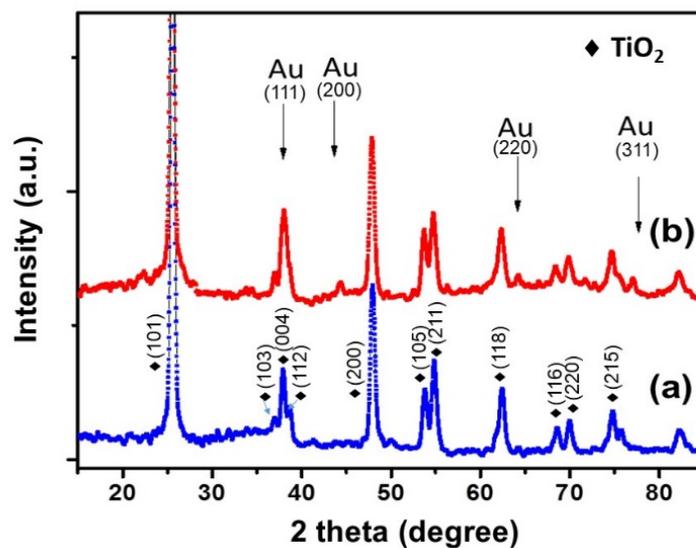


**Fig. 1.** The procedure for preparing the  $\text{Au@TiO}_2$ /patterned FTO electrodes: (a) FTO/glass electrode; (b) Etching process for patterning FTO electrode and (c) Preparing the  $\text{Au@TiO}_2$  nanocomposite film on patterned FTO electrode.

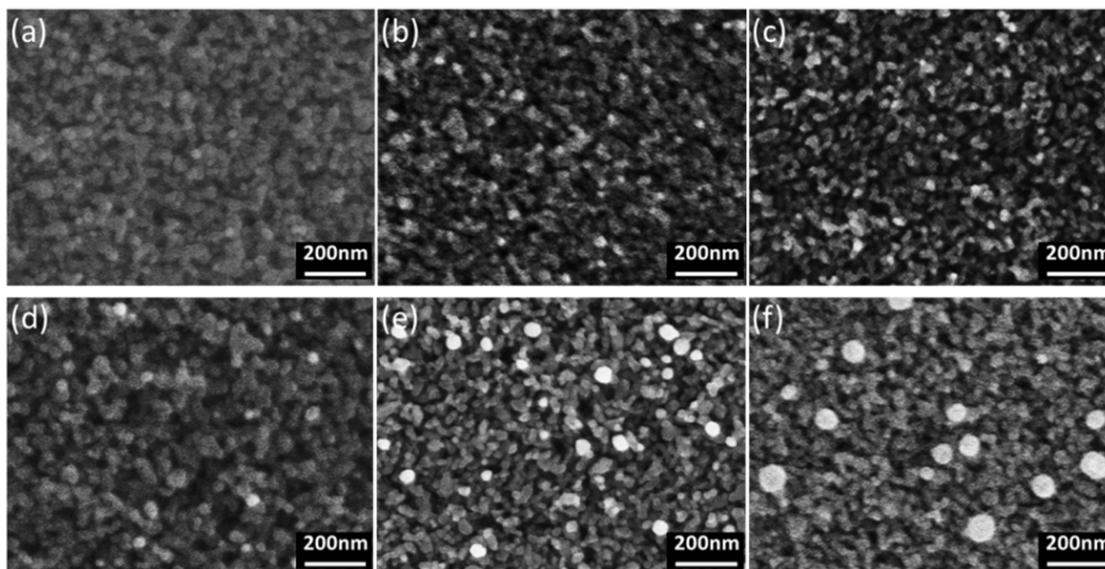
The obtained  $\text{Au@TiO}_2$  nanocomposite films were studied on morphology and structure by using a Hitachi field emission scanning electron microscope (FE-SEM) and X-ray Diffractometer EQUINOX 5000. The UV-vis spectra as well as the photoluminescence spectra have been carried out for studying optical properties of the materials. The UV-vis absorption spectra of the films were recorded using a Shimadzu UV-1800 spectrometer. The photoluminescence spectra of the films were measured by HORIBA iHR550 system at room temperature with laser excitation wavelength of 325 nm. Electrical properties of the materials were investigated by measuring the photocurrent of the films under light-on and light-off conditions using two light sources from solar simulator and 365 nm UV LED. The photocurrent was recorded by using the Keithley 2400 system at a potential of 1V, with and without illumination of the solar simulator system (Newport - Oriel 1A) and the UV LED source at the wavelength of 365 nm. The energy density of the UV-light beam was adjusted at  $5 \text{ mW/cm}^2$  (equivalent to 5% of the value of solar light).

### III. RESULTS AND DISCUSSION

Figure 2 showed the XRD patterns of  $\text{TiO}_2$  film and  $\text{Au@TiO}_2$  nanocomposite film after annealed at  $450^\circ\text{C}$  for 1 hour in air. In the case of  $\text{TiO}_2$  film without gold nanoparticles, the XRD pattern exhibited only the peaks corresponding to  $\text{TiO}_2$  anatase phase (JCPDS card No. 21-1272), as seen in Fig. 2(a). For the  $\text{Au@TiO}_2$  nanocomposite film (Fig. 2(b)), in addition to the peaks of  $\text{TiO}_2$  anatase phase, the other peaks appeared at 2 theta of  $38.2^\circ$ ;  $44.5^\circ$ ;  $64.3^\circ$  and  $77.2^\circ$  which can be indexed to the face-centered cubic (fcc) metallic Au (JCPDS card No. 04-0784). The results indicated that the presence of AuNPs in the nanocomposite films did not change the structure of  $\text{TiO}_2$  films.



**Fig. 2.** XRD patterns of the TiO<sub>2</sub> film (a) and Au@TiO<sub>2</sub> nanocomposite film (b).

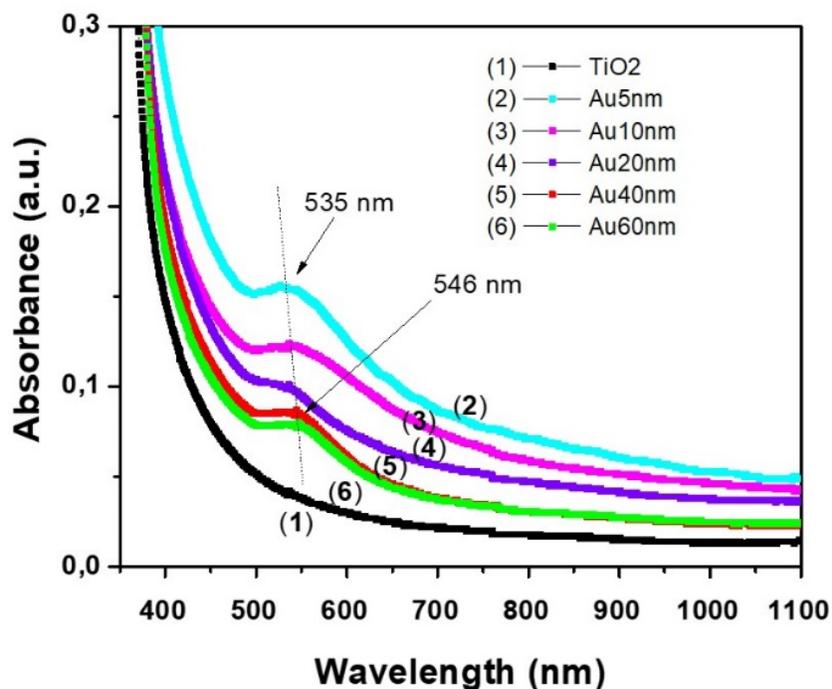


**Fig. 3.** FE-SEM images of Au@TiO<sub>2</sub> nanocomposite films with different AuNPs size. (a) TiO<sub>2</sub> films; (b); (c); (d); (e) and (f) are films with AuNPs size of 5 nm; 10 nm; 20 nm; 40 nm; 60 nm, respectively.

The FE-SEM images of the Au@TiO<sub>2</sub> nanocomposite films with the different gold nanoparticle size were given in Fig. 3. From the FE-SEM images, it can be seen that there was no change

in the morphology of the nanoporous TiO<sub>2</sub> films. Besides that, the AuNPs were dispersed fairly uniformly on the nanocomposite films and the size of gold nanoparticles kept unchanged after the process of preparing the Au@TiO<sub>2</sub> nanocomposite films.

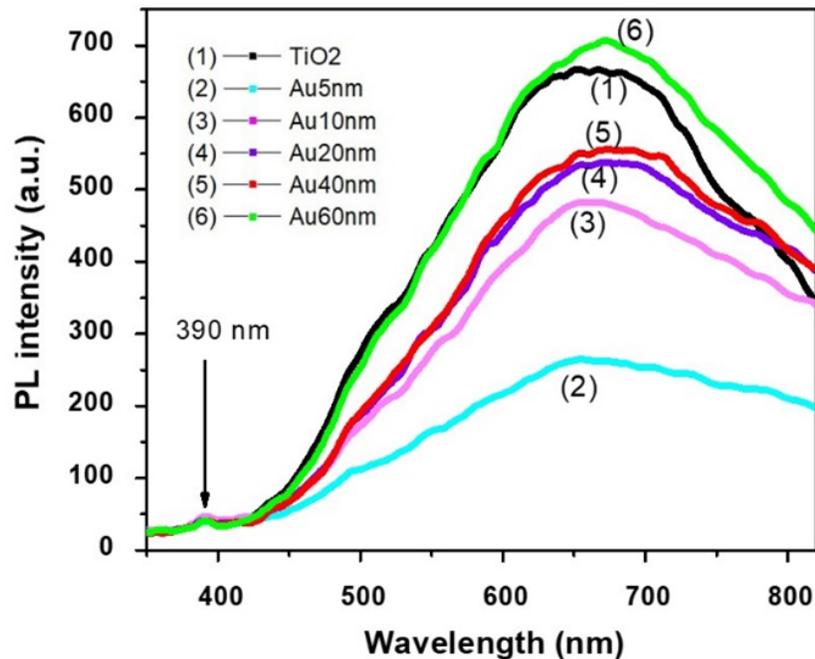
In order to study the optical properties, the UV-vis absorption spectra of the Au@TiO<sub>2</sub> films were recorded and the results were shown in Fig. 4. As we well know that the surface plasmon resonance effect of metal nanoparticles embedded to the semiconductor oxide materials was the main reason causing the phenomenon of plasmonic resonance absorption and then increasing absorbance of nanocomposite materials. Here, we also observed the appearance of plasmonic resonance absorption peaks of the AuNPs in all nanocomposite films. These peaks appeared in the visible light region and explained the increase in absorbance of all Au@TiO<sub>2</sub> films in comparison with the pure TiO<sub>2</sub> nanoporous film. When the size of the AuNPs increased from 5 nm to 60 nm, the intensity of these peaks significantly decreased and the peak position slightly red-shifted from 535 nm to 558 nm. This result agreed with the previous studies [13,15], where the authors indicated that the plasmonic resonance peak position shifted toward a longer wavelength with the increase in Au nanoparticles size.



**Fig. 4.** UV-vis absorption spectra of Au@TiO<sub>2</sub> nanocomposite films with different AuNPs sizes.

Figure 5 presented the photoluminescence (PL) spectra of the Au@TiO<sub>2</sub> nanocomposite films with different AuNP sizes. The spectra were measured in condition of room temperature and excitation laser light of 325 nm wavelength. As seen in Fig. 5, the PL spectra of TiO<sub>2</sub> and

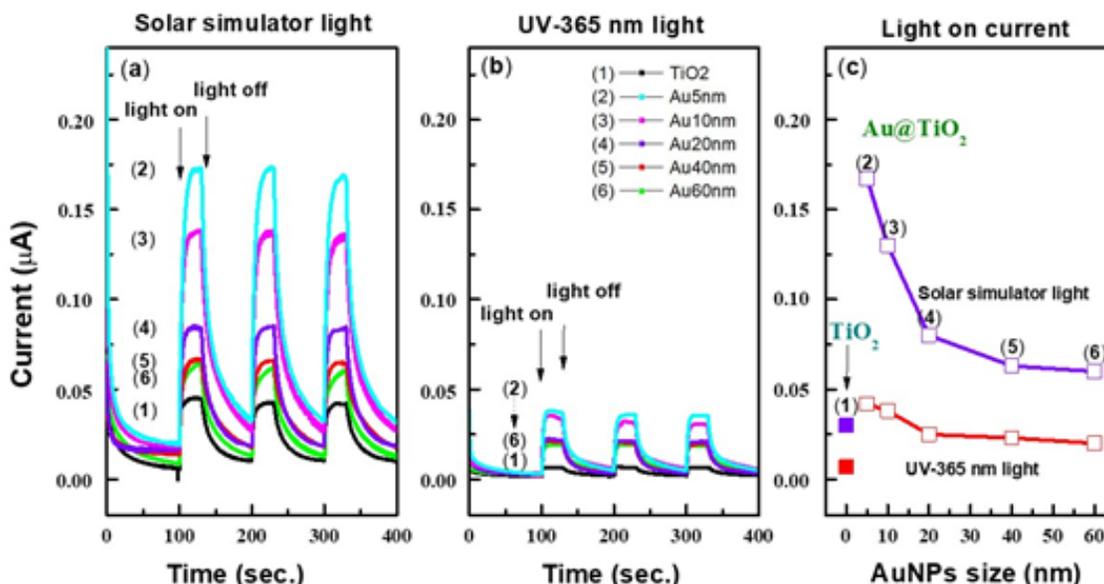
Au@TiO<sub>2</sub> nanocomposite films had the same shape. There was a very small peak located at the short wavelength of 390 nm corresponding to the emission from band to band in bulk TiO<sub>2</sub> materials while another strong and broad peak appeared in visible region. According to the authors of Refs. [16, 17], the broad band in the visible region were assigned to the emission from the surface states of TiO<sub>2</sub> nanoparticles. Due to the large amount of surface states of nanostructured materials, the PL intensity in the visible region was much higher than that of the bulk TiO<sub>2</sub>. Here, we also found that the presence of AuNPs caused a significant reduction in the fluorescence in the visible region of the Au@TiO<sub>2</sub> nanocomposite films. The largest reduction was observed on the film of 5nm AuNPs and it decreased with the increase in the size of AuNPs. In the case of 60 nm AuNPs, the photoluminescence spectrum of the composite film seems to be no change compared to that of the pure TiO<sub>2</sub> film. The photoluminescence reduction can be explained by the fact that Au nanoparticles in contact with TiO<sub>2</sub> created Schottky junctions, then reducing the surface states on TiO<sub>2</sub> nanoparticles as well as increasing electron transfer from TiO<sub>2</sub> to AuNPs [18].



**Fig. 5.** Photoluminescence spectra of Au@TiO<sub>2</sub> nanocomposite films with difference AuNPs sizes, recorded at room temperature under 325 nm laser excitation.

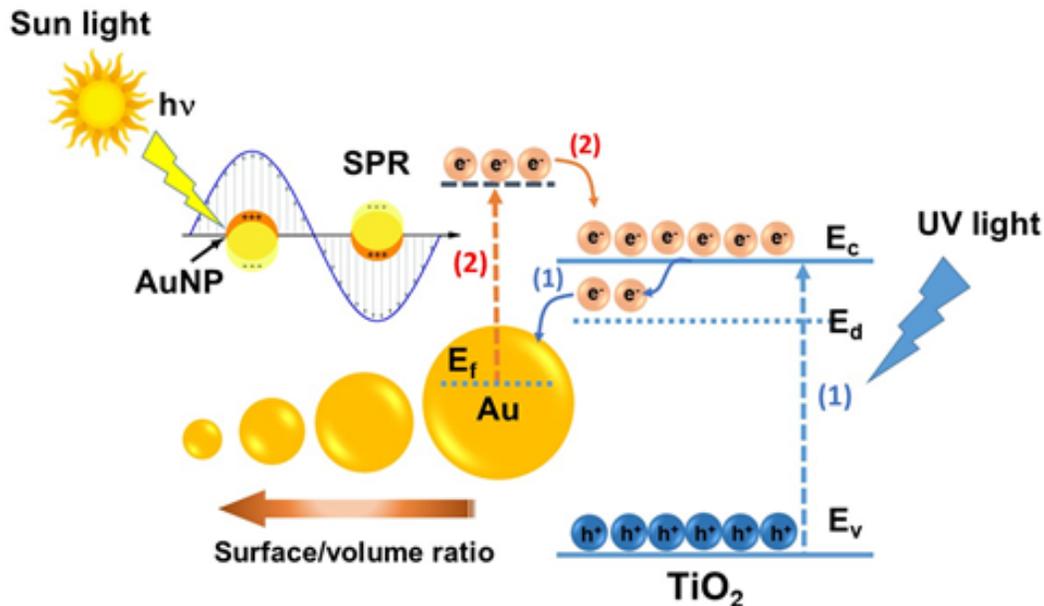
The electrical properties were investigated by recording the photocurrent of Au@TiO<sub>2</sub> films in the case with and without illumination using solar simulator light and the UV LED of wavelength at 365 nm, as shown in Fig. 6. The energy density of the UV-light beam was adjusted at 5 mW/cm<sup>2</sup> equivalent to 5% of the value of solar simulator light. Using the solar simulator or UV LED, the photocurrents of all the Au@TiO<sub>2</sub> nanocomposite samples were higher than that of the pure TiO<sub>2</sub> nanoporous film. Fig 6.c demonstrated that the magnitude of the photocurrents

increased with the decrease in AuNPs size and especially with AuNPs size below 20 nm. It should be noted that the photocurrents of samples illuminated under solar simulator were significantly higher than those under UV light, and this change achieved as high as 4.2 times in case of the 5 nm AuNPs@TiO<sub>2</sub> film. Our results showed that AuNPs sizes had a strong influence on the optical and electrical properties of the Au@TiO<sub>2</sub> nanocomposite films.



**Fig. 6.** Photocurrent of TiO<sub>2</sub> (1) and Au@TiO<sub>2</sub> nanocomposite films with the difference AuNPs sizes: (2)–5 nm; (3) – 10 nm; (4) - 20 nm; (5) – 40 nm; and (6) – 60 nm illuminated by solar simulator light (a) and UV-365nm light (b); and the comparison of the size effect of AuNPs on the electrical properties of Au@TiO<sub>2</sub> nanocomposite films (c).

This phenomenon can be explained by the possible mechanism of charge transfer processes in Fig. 7 as the following: When the samples were irradiated with a UV source of a wavelength of 365 nm (route 1), which is too far from the plasmonic resonance wavelength of AuNPs (535 nm), so only TiO<sub>2</sub> nanoparticles absorbed this light and generated carrier that contributed to the photocurrent. In this case, the higher photocurrents of the Au@TiO<sub>2</sub> nanocomposite films were attributed to the enhanced light trapping effect and improved electrical properties due to more efficient charge transfer & collection from TiO<sub>2</sub> to AuNPs compared to the pure TiO<sub>2</sub> film [18-20]. Moreover, the PL spectra of the Au@TiO<sub>2</sub> nanocomposite films in Fig. 5 also confirmed that the smaller AuNPs sizes had the stronger quenching phenomenon corresponding to the better charge transfer processes. When the AuNPs became smaller, their surface-to-volume ratio enlarged. As a result, the number and mobility of the surface electrons increased with the smaller AuNPs sizes. We believe that the increased surface conductance of the smaller metallic nanoparticle, especially AuNPs with a size below 10 nm, may account for the enhanced photocurrent observation. Our findings are in good agreement with previous studies reporting the greater shifting the Fermi level of TiO<sub>2</sub> incorporated with smaller AuNPs [21].



**Fig. 7.** Schematic illustration of the possible mechanism of charge transfer processes from photoexcitation under UV light (1) and visible light irradiation (2).

In the case of illuminating by solar simulator light (route 2), the plasmonic resonance effect of Au particles under visible light irradiation mainly contributed to the photocurrent of the Au@TiO<sub>2</sub> nanocomposite films. Here, "hot" electrons from AuNPs generated by photoexcitation and injected into the conducting region of TiO<sub>2</sub> to make the photocurrent much higher [22, 23]. However, "hot" electrons required enough energy to overcome the Schottky barrier between Au and TiO<sub>2</sub> [24]. This is the reason for explaining the dependence of the photocurrent on the size of AuNPs. As we know that the "hot" electron energy comes from the plasmonic resonance absorption of AuNPs and is proportional to the energy of the excitation light. When the size of AuNPs decreased, the resonance absorption peak was blue-shifted or moved toward higher energy, so the smaller the AuNPs size is, the higher "hot" electron energy is and the more easily the hot electrons injected into the TiO<sub>2</sub> conduction band. That is why the photocurrent of nanocomposite films strongly increased when size of AuNPs below 20 nm. In addition, the result that the photocurrents with the contribution of the SPR effect under solar simulator light were higher (as much as 4 times) than those with the effect of carrier separation under UV has affirmed that the plasmon resonance effect of AuNPs particles plays a decisive role in enhancing the photoelectric effect in Au@TiO<sub>2</sub> nanocomposite materials.

#### IV. CONCLUSIONS

The Au@TiO<sub>2</sub> nanocomposite films were successfully fabricated by embedding the AuNPs of different sizes on the nanoporous TiO<sub>2</sub> thin films, then annealing at 450°C in air for 1 hour. The effect of AuNPs sizes on electrical and optical properties has been studied using AuNP sizes of

5 nm, 10 nm, 20 nm, 40 nm and 60 nm. The room temperature photoluminescence properties of Au@TiO<sub>2</sub> nanocomposite films were investigated by using excitation laser light of 325 nm wavelength, the results have shown that the size of AuNPs has strong influence on the photoluminescence properties, especially for luminescence caused by surface states in the Au@TiO<sub>2</sub> nanocomposite films. Here, the smaller the AuNPs particle size was, the greater the ability to extinguish fluorescence was. The strongest PL quenching phenomenon was observed in the nanocomposite films of 5 nm AuNPs and the PL quenching decreased with increase in AuNPs size and did not observe for the film of AuNP size as large as 60 nm. The effect of the gold nanoparticle size on the photocurrent has been investigated, the result suggested that the AuNPs of the size less than 20 nm contributed more to the magnitude of photocurrent of the nanocomposite films. The finding that the value of photocurrent of the Au@TiO<sub>2</sub> nanocomposite films under solar simulator light was much higher than that under UV light was discussed. These results demonstrated that the gold particles plasmonic resonance effect has a great influence on the increase of photocurrent in nanocomposite films.

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