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Some Properties of TiO_2/Au Nanocomposite Thin Films Produced by Spincoating Method for Application in Plasmonic Solar Cells

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Abstract: The TiO_2/Au nanocomposite thin films play a very important role in the plasmonic solar cell. In such as composite systems, the localized surface plasmon resonance (LSPR) of embedded metal nanoparticles determines the light absorption enhancement of the semiconductive part (TiO_2); hence, enhances the efficiency of the plasmatic solar cell. The characterizations of the TiO_2/Au nanocomposite thin films – such as light absorption, scattering and LSPR capacities - depend on many parameters: sizes, weight ratio of metal nanoparticles, thickness of the thin film layers and the arrangements of TiO_2/Au composite in integrated-matrix system. In this work, we outline the preparation method of the TiO_2/Au nanocomposite thin films, then we investigate the effect of technological conditions – such as TiO_2/Au mixture solution concentration, TiO_2/Au weight ratio and number of spin-coating layers – to the surface morphology of the nanocomposite to find out the optimum fabrication conditions. Some experimental results of thin film such as structural property (X ray diffraction, thin film morforlogy…) and optical property (absorption coefficience concerning LSPR…) will also be shown and discussed.

Keywords: TiO_2/Au thin film, LSPR, plasmonic solar cell.

1. Introduction

Recently, fossil energy sources are depleted due to the increasing exploitation of the countries. Beside, the extraction and over usage have caused many consequences such as environmental pollution, the greenhouse effect and climate change. Therefore, one of serious challenges to mankind is to ensure the energy security or energy sustainability. This challenge has to be answered with a

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solution to produce the renewable energy sources, One of them is the solution transforms of solar energy into electrical energy based on photovoltaic cells [1-4]. Up to now there are three solar cell generations have been developed, among them the plasmonic solar cells, belonging to the third generation, are promissing and that is promise new type and they are getting the most attention of scientists [3-8, 9-10]. In the plasmonic solar cells, the most important structure is the structure of the integrated noble metal nanoparticle (TiO_2/Au (Ag….) system. This, so called plasmonic nanostructures where the plasmonic resonance induces a dipole on the metal nanoparticle, enhance electric field around the metal nanoparticle, could support the formation of the surface plasmon resonance in response to a photon flux, localizing electromagnetic energy close to their surfaces. The enhanced photovoltaic properties from the incorporation of metal nanoparticles/ semiconductor have been studied for various systems [5 -8,11,12]. So far, the plasmonic solar cells are developed at the beginning stage that many research issues, including both theoretical and practical problems must be overcome [5-8, 11-13].

In previous reports, we have also designed and produced some samples of the plasmonic solar cells, investigated the structural, electrical and optical properties, however, the obtained results of electrical and optical properties were still limited [14]. In this work we focused on the spincoating method for fabricating TiO_2/Au thin film through two steps: preparation of TiO_2/Au sol solution and using this sol solution for spincoating to create TiO_2/Au thin films, after that we have investigated the effect of technological conditions such as TiO_2/Au solution concentration, Au/TiO_2 weight ratio and number of spin-coating layers on structural and optical properties of the TiO_2/Au thin films.

2. Experiment

All the precursors with high purity were purchased from commercialized distributors: Chloroauric acid 99.98 % ($HAuCl_4$), Sodium borohydrid 99.8% ($NaBH_4$) from MERCK, German; pure Titanium dioxide nanoparticles (TiO_2) from Sigma, America and polyvinyl pyrrolidone 98% (PVP – MW 30000 Dal) from Korea. The TiO_2/Au composite thin films were prepared by sol-thermal calcinations on 1cm× 2cm ITO substrates (from France) and sheet resistance of 200-250 Ω/square.

Firstly, to create 5% of Au/TiO_2 weight ratio composite (labeled as TiO_2/Au 5%): 25 mg of TiO_2 was dispersed into 25 ml of $HAuCl_4$ 1mM, which contained 250 mg PVP. The mixture was gently mixed by magnetic stirring to obtain a homogenous aqueous solution. After that, we added a small amount of ice-cold 0.01M $NaBH_4$ to Au^{3+} from chloroauric acid to Au^0. The solution color changed to a typical dark red. We have used centrifugation to get higher concentration solution, then the solution was dispensed in ethanol – later called xerogel, which contained the mixture of TiO_2 and Au nanoparticles. Secondly, we created TiO_2/Au thin film xerogel on ITO substrate by spin-coating method. In particular, 50 μL of xerogel solution was deposited on ITO plate spinning at 3000 rpm for 30s. In the next step- calcinations step, the remained organic precursors and unnecessary reaction products were evaporated substrate by heating process at 450^{o}C for 1hour. Finally we received TiO_2/Au nanocomposite thin films. Thin films 10% of Au/TiO_2 weight ratio composite thin film

(labeled as TiO_2/Au 10%) was prepared by the same method, where the used amount of $HAuCl_4$ 1mM solution was 50mL.

In this paper We selected the TiO2/Au 5% composite for next investigations. First, different concentrations TiO2/Au 5% composite were prepared by increasing the amount of added TiO2 nanoparticles, while the weight ratio of Au/TiO2 was kept constant. Typically, the mixture of TiO2/Au in PVP in ethanol was diluted to different concentrations (Table 1). The concentrations of the samples were defined by the precursor TiO2 colloids in xerogel solution.

Table 1. The precursor amounts used in different the composite thin films on ITO substrates (samples) for investigating the effect of the TiO_2/Au precursor concentration on the filling efficiency

Sample	Amount of precursor TiO_2 nanoparticles in xerogel solution	Amount of initial TiO_2/Au mixture before centrifugation	Amount of added ethanol in xerogel
M1	10mg/ml	25ml	2500 µl
M2	40mg/ml	25ml	625 µl
M3	50mg/ml	25ml	500 µl

The crystal structure of the synthesized products was analyzed by X-ray diffraction (XRD) using X-ray diffractometer Siemens D5005 , Bruker, Germany, with Cu-$K_{\alpha 1}$ radiation (λ = 0.154056 nm). The surface morphology of the samples was investigated by using a Nova NANOSEM 450 scanning electron microscope and Dektak 150 Profiler, Vecco, USA. The UV-vis absorption spectra were measured by Shimadzu UV 2450 PC spectrometer, Japan.

3. Results and discussions

3.1. Crystal structure and morphology

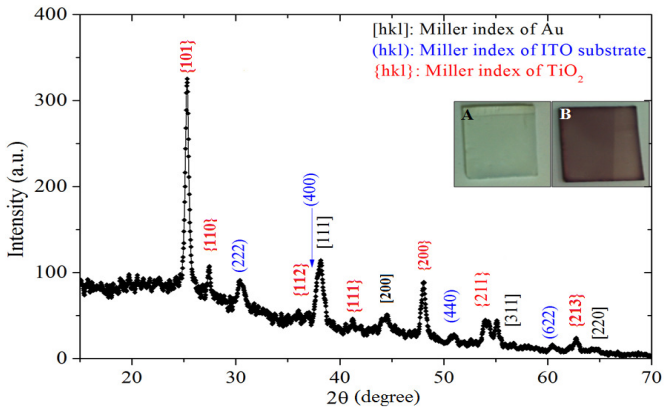

Fig. 1. X-ray diffraction parttern of TiO_2/Au nanocomposite thin film prepared by calcinated spin-coating method. The weight ratio of Au:TiO_2 was 5%. Inset: ITO substrate without (A) and with TiO_2/Au composite (B)

Fig. 1 shows XRD pattern of TiO_2/Au 5% nanocomposite thin film spincoated on ITO substrates, where the inset shows the picture of the TiO_2 thin film (A) and TiO_2/Au composite thin film (B) on ITO substrate. TiO_2/Au nanocomposite thin film exhibits characteristic dark red of gold nanoparticles. The typical peaks of ITO substrate arise at 30.5°, 37.1°, 51.0° and 60.4°, corresponding to (222), (400), (440) and (622) planes, respectively. Existence of TiO_2 in nanocomposite shows in the peaks at 25.3°, 27.5 °, 36.0°, 41.3°, 48.1°, 54.1° and 62.8°, coinciding with previous published results, which relate to {101}, {110}, {112}, {111}, {200}, {211} and (213) of anatase structure of TiO_2 [15]; while the presence of Au nano-colloids is demonstrated via typical peaks face-centered cubic structure of Au at 38.2°, 44.4° and 64.6° corresponding to [111], [200] and [220], respectively .(CAS: 7440-57-5) [16]

3.2. The effect of the TiO_2/Au mixture solution concentration

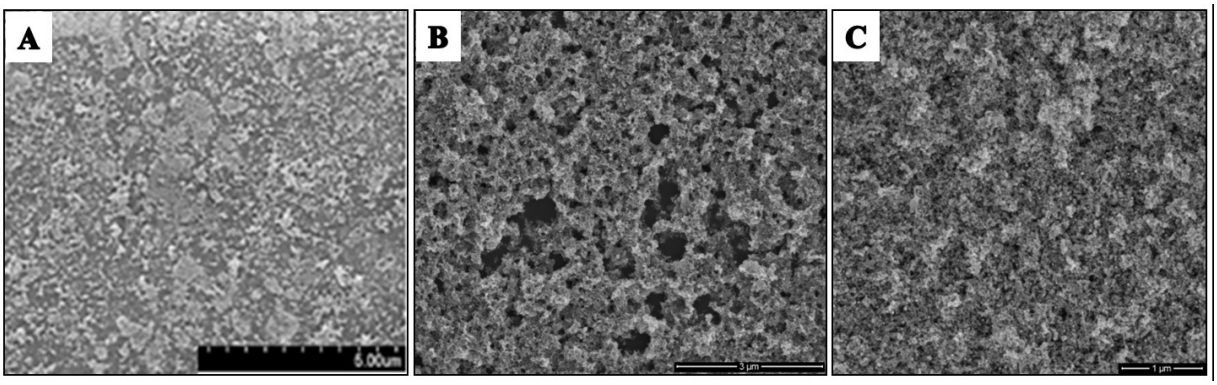

Fig. 2. SEM images of TiO_2 /Au nanocomposite thin films spincoated on ITO substrates with different concentrations of TiO_2/Au sol solution: a) 10mg/ml, b) 40mg/ml and c) 50mg/ml.

Scanning electron microscopic (SEM) images of TiO_2/Au nanocomposite thin films with different concentrations of TiO_2/Au sol solution on ITO substrate are presented in the Figure 2. In M1 sample, when the solution concentration of TiO_2/Au is 10mg/ml, there are a lot of voids on ITO surface (A). Total filled-up area has decreased significantly when the TiO_2/Au sol solution concentrations are increased (Fig 2b). Especially, the unfilled areas disappear when TiO_2/Au solution concentration are 50mg/ml (Fig 2c). In further investigations, we use this concentration of TiO_2/Au precursors to synthesize TiO_2/Au nanocomposite thin films.

3.3. Thickness control

The thickness of TiO_2/Au nanocompsite thin film depends on various parameters, such as viscosity and concentration xerogel solution, rotation speed while spin-coating... In this works, we fixed all of these parameters and control thickness of films via controlling times of repeating spincoating TiO_2/Au solution onto substrate.

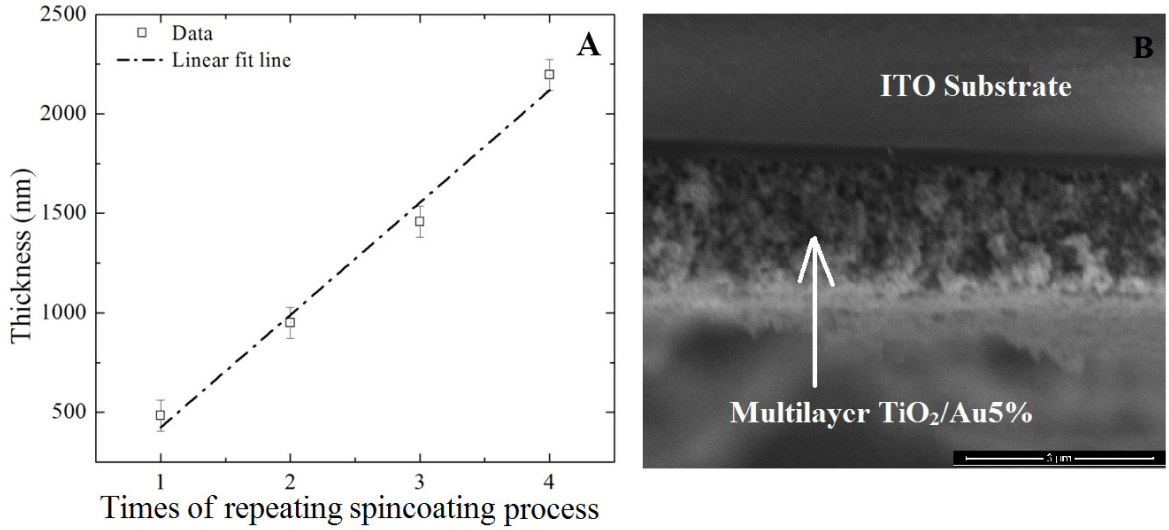

Fig. 3. The Plot dependence of the TiO_2/Au nanocomposite thin film thickness on times of repeating spincoating (a); and SEM image of four layers TiO_2/ Au nanocomposite thin film (b).

As we increased the thickness of the TiO_2/Au by repeating the spin coating – calcinations process multiple times, the composite thin film could be considered as a multilayer of films and thickness of each layer was about 480 nm ± 77.5 nm (Fig. 3A). Table 2 shows TiO_2/Au nanocomposite thin films thickness measured by Dektak 150 equipment system when the coating time was 1, 2, 3 and 4, respectively

Table 2. Thickness of TiO_2/Au nanocomposite tin film when spin- on 1, 2, 3 and 4 layer

Multilayer	1-time coating	2-time coating	3- time coating	4-time coating
Thickness (nm)	483.0	950.0	1460.0	2190.0
Standard error (nm)	77.5	77.5	77.5	77.5

Cross-section SEM image of the 4-time spin-coated TiO_2/Au 5% composite on ITO substrate is shown in Figure 3B. No layer boundary could be observed disjunction occurs. Continuous one layer thin film was formed this result implied that the obtained films were homogenous

3.4. Optical properties

As we know that light scattering by metal nanoparticles is of special research interest because of many applications in the energy field where nanocomposite particles are used to increase the efficiency of solar cells, the way these nanoparticles scatter light is of vital importance to the research.

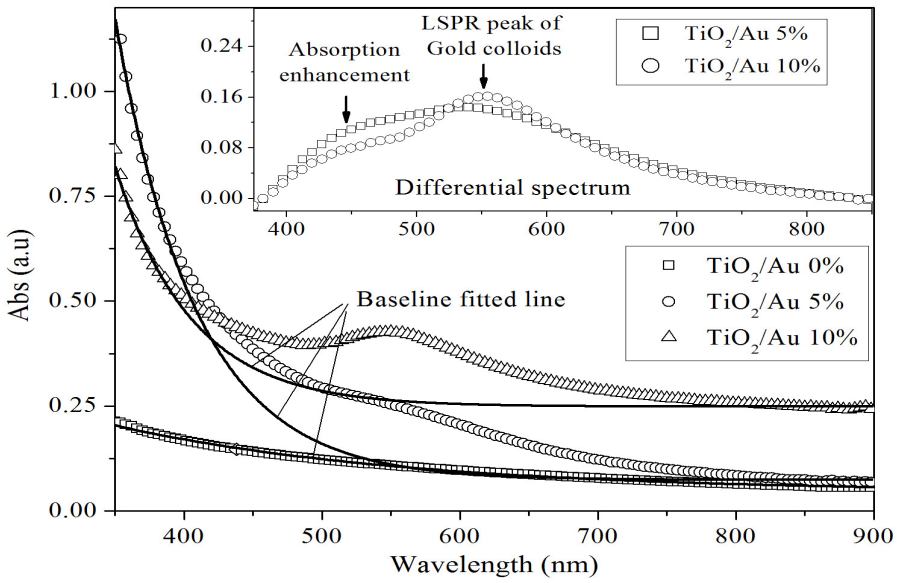

Fig. 4. The absorption spectra concerning the Localized Surface Plasmon Resonance (LSPR) of TiO_2/Au 0%, TiO_2/Au 5%, TiO_2/Au 10% nanocomposite thin films.

Light scattering is, in general, the attenuation of a beam of light by metal nanoparticles, either by absorption or scattering. The sum of these two parts is known as the extinction. For particles with diameters well below the wavelength of light, a point dipole model describes well the absorption and scattering of light. The scattering and absorption cross-sections, C_{scat} and C_{abs}, respectively are given by the followings [17-19]:

$$c_{scat} = \frac{1}{6\pi}\left(\frac{2\pi}{\lambda}\right)^4 |\alpha|^2,\ c_{abs} = \frac{2\pi}{\lambda}\mathrm{Im}|\alpha|^2, \text{where } \alpha = 3V\left[\frac{\varepsilon_p/\varepsilon_m - 1}{\varepsilon_p/\varepsilon_m + 2}\right] \qquad (4.1\ \text{a,b,c})$$

Here V is the particle volume, ε_p is the dielectric function of the particle and ε_m is the dielectric function of the embedding medium. We can see that when $\varepsilon_p = -2\varepsilon_m$, the particle polarizability will become very large. This is known as the surface plasmon resonance. This sometime is called the dipole plasmon resonance of the particle. At surface plasmon resonance condition the scattering cross-section can well exceed the geometrical cross section of the particle.

Concerning our obtained results, in general, the LSPR absorption properties of the TiO_2/Au 0%, TiO_2/Au 5% and TiO_2/Au 10% are illustrated in Figure 4. The results show that the absorption spectra enhanced in the range of 500 nm - 600 nm and absorption intensity increases when Au concentration being in the sample increases. We used absorption of TiO_2 thin film without Au nanoparticle (TiO_2/Au 0%) as the base level. In absorption range from 350 nm to 900nm an experimental exponential (function not shown) occurs. TiO_2 particles usually have good light absorption at near UV band (data not shown), then decay as the wave-length shifts to red region, where we can consider as an exponential decay. We use that decay as baseline level for data manipulation of two other spectra of

TiO_2/Au 5% and of TiO_2/Au 10%. An exponential decay was employed as baseline (see Fig. 4 – baseline fitted line) for the region of [350nm-400nm] and [750nm-900nm], where the typical surface Plasmon resonance of gold nanoparticles does not occur [16, 20]. Then the baselines are distracted from the original spectra to get the different spectra (Fig. 4 – inset) of TiO_2/Au 5% composite and of TiO_2/Au 10% composite thin films,respectively. We can see that there are enhancements arising at characteristic SPR peak of Gold nanoparticles around 540 nm. We also see there are abnormal peaks arising at near-UV region from 430 nm to 450 nm. The origin of these peaks is still unrevealed. They might relate to the phenomenon of the presence of a thin Au coat around the TiO_2 particles during synthesis process. $AuCl^{4-}$ ions from $HAuCl_4$ adsorbed on surface of the semiconductor nanoparticles during mixing and these ions were reduced to Au atom then attached on the surface of the TiO_2 particles meanwhile the free ions were reduced to Au nanoparicles. The presence of this enhancement also occurred at the absorption spectra of xerogel solutions (data not shown). However, more investigation are needed to clarify the origin of this enhancement.

4. Conclusions

In conclusion, we have synthesized TiO_2/Au nanocomposite thin film from TiO_2/Au solution with different Au/TiO_2 weight ratio on the ITO substrates by spin coating method. Our results show that the whole ITO substrate is filled with relatively homogenous TiO_2/Au composite at 50 mg/ml concentration of precursor TiO_2 nanopartciles in xerogel solution. Thickness of the thin film can be increased by multiple-time coating, while the homogeneity of the composite layer does not change. In our spinning conditions, each coating time would create reproducibly 480 nm ± 77 nm thick layer, which shows that we have to coat the ITO substrate at least 4 times to reach usual thickness of plasmonic solar cells.

Based on the produced TiO_2/Au thin film we have investigated the absorption coefficiency concerning the LSPR of the thin film. The result show that 5% of Au/TiO_2 weight ratio is the critical ratio to allow LSPR of the Au particles in the composite thin film. Higher amount of Au in the complex results in higher LSPR intensity. Besides, there is unrevealed absorption enhancement arisen at the region from 400 nm to 450 nm, which increases the light absorption ability of the thin film.

Acknowledgments

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