

Effect of Silver Nanoparticles Size Prepared by Photoreduction Method on Optical Absorption Spectra of TiO₂/Ag/N719 Dye Composite Films

C. Photiphitak, P. Rakkwamsuk, P. Muthitamongkol, C. Sae-Kung, C. Thanachayanont

Abstract—TiO₂/Ag composite films were prepared by incorporating Ag in the pores of mesoporous TiO₂ films using a photoreduction method. The Ag nanoparticle sizes were in a range of 3.66-38.56 nm. The TiO₂/Ag composite films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The TiO₂ films and TiO₂/Ag composite films were immersed in a 0.3 mM N719 dye solution and characterized by UV-Vis spectrophotometer. The TiO₂/Ag/N719 composite film showed that an optimal size of Ag nanoparticles was 19.12 nm and, hence, gave the maximum optical absorption spectra. The improved absorption was due to surface plasmon resonance induced by the Ag nanoparticles to enhance the absorption coefficient of the dye.

Keywords—Silver nanoparticle, TiO₂/Ag composite films, Optical properties, surface plasmon resonance

I. INTRODUCTION

SURFACE plasmon resonance induced by silver nanoparticles leads to an increase of the absorption coefficient value of dye in dye-sensitized solar cells [1]-[5]. These effects have been theoretically described as an increase in local electromagnetic field nearby metal surfaces which is found when the wavelength of the irradiation sources are correlated with the optical absorption of the surface plasmon resonance [6]-[10]. Therefore, modification of surfaces for the enhancement of optical absorption is a promising procedure in an optoelectronic application approach [11]. Several methods for fabrication of the silver nanoparticles were studied such as magnetron sputtering of titania (TiO₂)/silver (Ag) films [12], electrochemical deposition of the Ag nanoparticles by double pulse method on Indium Tin Oxide (ITO) [13], loading of Ag

and AgCl onto anatase TiO₂ nanotube that were grown by a hydrothermal treatment [14] and loading of the Ag nanoparticles onto self-organized TiO₂ nanotube layers using photocatalytic reduction [15], [16].

Recently, C. Wen *et al.* generated the Ag island films by depositing 3.3 - 6 nm thick Ag nanoparticle layer on TiO₂ film electrode using thermal evaporation [1]. The results from this work show the possibility of using plasmon resonance effect to enhance the absorption of the Ru-dye and extend photoresponse.

In this study, we prepared 3.66 - 38.56 nm in size of the Ag nanoparticles using photoreduction method. The Ag nanoparticles were deposited on to mesoporous anatase TiO₂ films electrode with wormlike pores. The Ag nanoparticles were incorporated thoroughly into the pore of the mesoporous TiO₂ film electrode. The effects of Ag nanoparticle size on the optical absorption of TiO₂/Ag/N719 dye composite films were investigated.

II. EXPERIMENTAL DETAILS

TiO₂ paste (Dyesol) was screen printed 3 layers on a fluorine-doped-tin-oxide (FTO) glass substrate (2×3 cm.). A screen with a 200 mesh was used to obtain a TiO₂ layer with a thickness of approximately 10 μm. In order to avoid contamination on the fresh film, screen-printing was performed in a clean-room environment. After drying at 55 °C for 30 min, the electrodes were sintered at 450 °C for 30 min, and then cooled down at room-temperature. The electrodes were immersed in a 3×10⁻⁴ M of N719 dye solution, namely, *cis*-diisothiocyanato-bis (2,2'-bipyridyl-4,4' dicarboxylato) ruthenium (II) bis (tetrabutyl -ammonium) in absolute ethanol for 24 h. The excess dye was removed from the electrode by rinsing in ethanol.

In order to deposit the Ag nanoparticles on the TiO₂ film, a 2×3 cm² FTO glass with 0.5×1.2 cm² TiO₂ films was immersed in the 0.1 M AgNO₃ solution for five seconds, then rinsed with DI water and dried in a N₂ stream. The films were then exposed to UV irradiation at λ = 254 nm using a Spectroline CM-10 Fluorescence Analysis Cabinet to an intensity of ~ 0.31 mW/cm², as shown in the scheme in Fig. 1. We designed the experiment to vary exposure times for 5, 10, 15, 20, 30, 60, 90, 120, 150, 180 and 240 minutes for the photocatalytic reduction of Ag⁺ to metallic Ag nanoparticles.

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Finally, the TiO_2/Ag composite films were immersed in dye solution for 24 h.

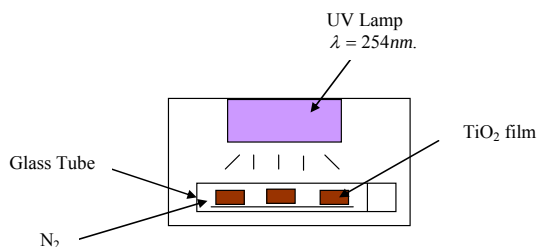


Fig. 1 Schematic diagram of UV exposed Instrument.

Optical absorption spectra of the composite film samples were measured using a UV-Visible Spectrophotometer (Jasco model: V-530). In order to observe the microstructure and elemental analysis of the obtained Ag nanoparticles, the Ag nanoparticles were prepared on a carbon coated copper grids for the observation by transmission electron microscopy (JEOL model: JSM-2010). The X-ray diffraction (JEOL- 300) pattern was obtained by measuring directly the Ag/TiO_2 film on the glass substrate. Scanning electron microscope (JEOL model: JSM-6301F) was employed to record cross-sectional view of the Ag/TiO_2 films.

III. RESULTS AND DISCUSSION

A. Morphology of the TiO_2/Ag Deposit Films

The TiO_2 films were loaded with Ag nanoparticles using the AgNO_3 soaking/ UV illumination treatment described in the experimental section. After the films were irradiated by the UV light they turned brownish grey in a few minutes due to photocatalytic reduction of Ag^+ to Ag [17]. The Ag nanoparticles on the TiO_2 particles were not readily observed by SEM as shown in Fig.2. However, The TiO_2/Ag composite films were characterized with EDX technique attached to the Transition electron microscope. We found that the peak of the Ag nanoparticles were represent, so the TiO_2/Ag composite films consist of the Ag nanoparticles on surface of TiO_2 films as shown in Fig. 3.

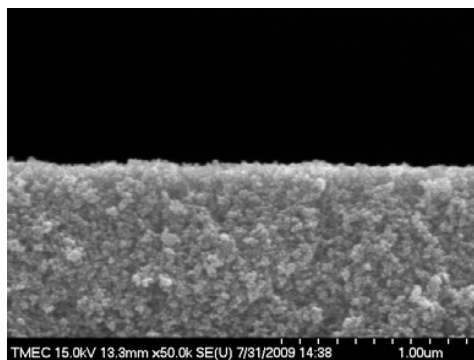


Fig. 2 SEM image of cross-section TiO_2/Ag composite films with UV exposed 120 min.

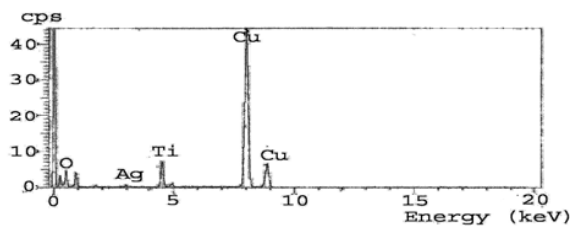


Fig. 3 EDX image of the Ag nanoparticles with UV exposed 120 min on TiO_2 films.

Fig. 4 shows a TEM image of the TiO_2/Ag composite films. We found that the TiO_2 particles were nanorods and the length were approximately 25 nm and the spherical Ag nanoparticles adsorbed on surfaces of the TiO_2 nanorods. The XRD result shows that the Ag particles in the TiO_2/Ag composite films have Face Centered Cubic structure as shown in Fig. 5.

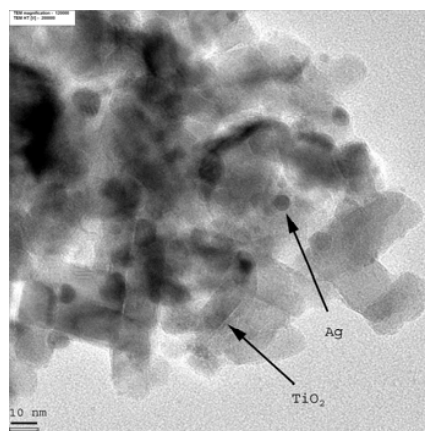


Fig. 4 TEM images of TiO_2 films after immerse in 0.1 M of AgNO_3 solution and then exposed UV for 120 minute.

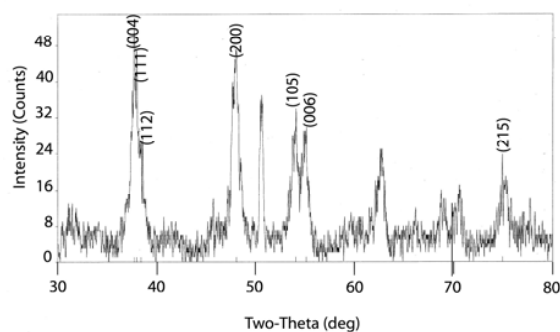


Fig. 5 XRD of the Ag nanoparticles on TiO_2 film having a Face Centered Cubic structure.

The Ag nanoparticles were prepared on the carbon coated copper grid and exposed to UV exposure times of vary time to UV exposed at 0, 5, 10, 15, 20, 30, 60, 90, 120, 150, 180 and 240 minutes, respectively. We found that the spherical Ag nanoparticles were distributed on the carbon coated copper grid as shown in Fig. 6. It was found that the sizes of the Ag nanoparticles depended strongly on the UV exposed time as

shown in Fig.7. At the 240 min. exposure time, we found that the Ag nanoparticles had a biggest size of approximately 38.56 nm.

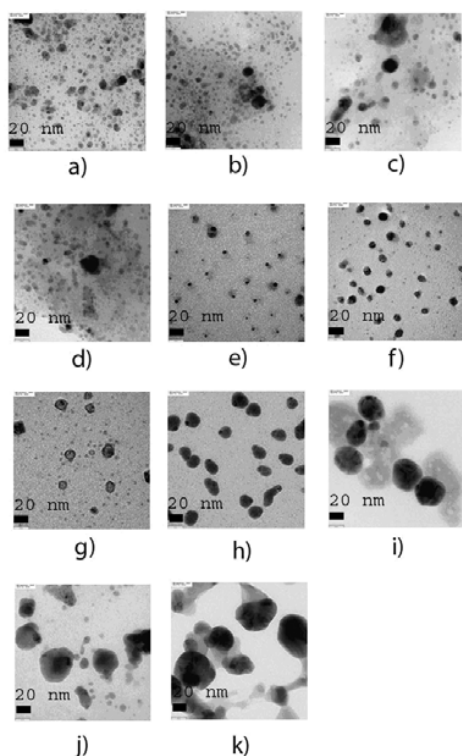


Fig. 6 TEM images of the Ag nanoparticles on carbon coated copper grid at UV Exposure times of (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 30 min, (f) 60 min, (g) 90 min, (h) 120 min, (i) 150 min, (j) 180 min and (k) 240 min.

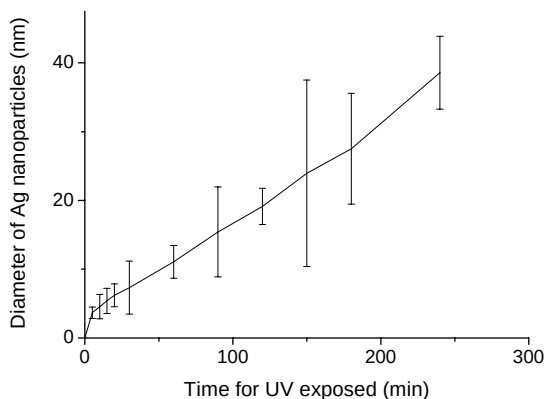


Fig. 7 Relation between the UV exposed time versus size of Ag Nanoparticles.

B. The effect of size of Ag nanoparticles on optical absorption spectra

TiO₂/Ag composite films were prepared in various sizes between 3.66 – 38.56 nm and measured by UV-spectrophotometer, then compared to the bare TiO₂ film. Fig.8 shows optical absorption spectra of the TiO₂ films before and

after immersion of AgNO₃/UV exposure without immersed N719 dye. We found that the optical absorption of the TiO₂ after immersed AgNO₃/UV exposed were increased (red shifted) when the diameters of the Ag nanoparticles increased because of the surface plasmon resonance as described by Mafune *et al.* [18].

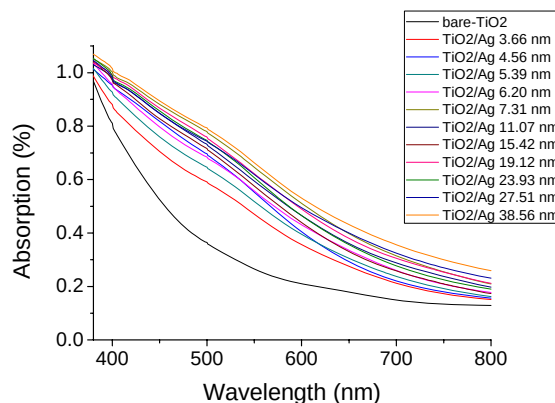


Fig. 8 Optical absorption spectra of the TiO₂/Ag films without N719 dye with various particles size

Fig.9 shows optical absorption spectra of the TiO₂/Ag films with N719 dye. The result shows that with the Ag nanoparticles, the peaks in the absorption spectra of N719 dye are all red-shifted. However, comparing to the TiO₂ film without the Ag nanoparticles, we found that the TiO₂/Ag films consisting of the Ag nanoparticles size of ~19.12 nm had a maximum red-shift at 600 – 800 nm. Therefore, in our experiment, the Ag nanoparticles size of 19.12 nm was an optimized size to increase the absorption coefficient of the dye. In addition to using the surface plasmon resonances contributing to the absorption coefficient of the dye, the absorption of the Ru-dye can be generated by the metal-ligand charge-transfer transition. Ru-dye exhibits two $\pi \rightarrow \pi^*$ intraligand transition in the UV and $t_2 \rightarrow \pi^*$ MLCT transitions in the absorption maximum at 396 and 534 nm [19].

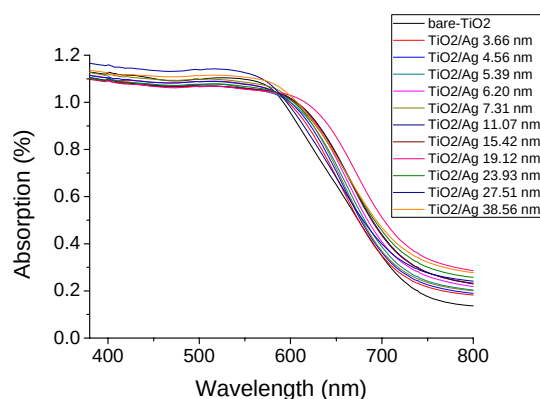


Fig. 9 Optical absorption spectra of TiO₂/Ag films with N719 dye with various particles sizes.

IV. CONCLUSION

The mesoporous TiO₂ films were improved by intercalating of the Ag nanoparticles into TiO₂ films by photoreduction method and immerge in N719 dye solution for 24 hr to enhance the optical absorption spectra of the TiO₂/Ag/N719 dye composite film. The Ag nanoparticles were face centered cubic structure and the size was in range of 3.66 – 38.65 nm. The TiO₂/Ag composite films were characterized by XRD, SEM, TEM and UV Spectrophotometer. the optimum size of 19.12 nm Ag nanoparticles was found to improved the optical absorption spectra of the TiO₂/Ag/N719 dye composite film in a range of 600 – 800 nm because of the maximum absorption coefficient of the N719 dye resulted from the surface plasmon resonance. So the Ag nanoparticles size of 19.16 nm was selected for the most promising efficiency of the dye-sensitized solar cell.

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