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Synthesis of Ag nano/TiO_2 material by gamma Co-60 ray irradiation method for dye-sensitized solar cell application

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Abstract: Silver nano deposited on TiO_2 nano (Ag nano/TiO_2) materials with different initial Ag^+ content (0.1-0.75%, w/w) were synthesized by Co-60 gamma irradiation and used as photoanode of dye-sensitized solar cells. The characteristics of Ag nano/TiO_2 were determined by X-ray diffraction (XRD), transmission electron microscope (TEM) and UV-visible spectroscopy (UV-Vis). Bandgap energy values of Ag nano/TiO_2 materials were also determined. Ag nano/TiO_2 has improved efficiency of solar-to-electrical energy conversion of solar cells. The efficiency of solar cell assembled with Ag nano 0.75%/TiO_2 was of 4.71% which increased about 25.6% compared with that of the cell based on TiO_2 (3.75%). Preparation of Ag nano/TiO_2 material by gamma irradiation is promising method that may be applied on large scale for production of dye-sensitized solar cells and for other applications as well.

Keywords: *Silver nano, TiO_2, solar cell, gamma irradiation*

I. INTRODUCTION

Research and application of new energy resources are necessary and important to reduce dependence on fossil fuels. Development of use of solar energy is considered one of feasible solution to solve the world's energy crisis. Dye-sensitized solar cells that can replace conventional silicon-based solar cells have been intensively studied to convert solar energy into electricity due to their low cost, easy preparation and relatively high energy conversion efficiency [1-5]. Many methods have been studied to improve the conversion efficiency of dye-sensitized solar cells (DSC), including designing and producing the novel counter electrodes, electrolytes, dyes and semiconductor photoanode materials [1, 6, 7]. Among these, the photoanode plays a decisive part in determining the performance of cells [1, 6-8]. Many semiconductor materials have been studied for using as photoanode in DSC such as TiO_2, ZnO, SnO_2, Nb_2O_3, $SrTiO_3$. Especially, TiO_2 has been universally used due to its chemical stability, excellent charge transport capability, low cost and easy preparation [3, 9, 10]. In DSC, TiO_2 plays three main roles of providing a substrate for dye adsorption, accepting electrons from the dye's excited state and transporting the electrons from conduction band of TiO_2 to the conducting substrate then to the external circuit [9, 11]. TiO_2 possesses wide bandgap energy (anatase: 3.2 eV, rutile: 3.0 eV), then it can be excited by the ultraviolet (UV) light with wavelength shorter than 400

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nm only. Moreover, a high rate of recombination between electrons and holes in semiconductor reduces optical conversion efficiency and performance of cells [2, 6, 10, 12, 13]. To overcome this problem, TiO_2 has been modified on surface with metal in form of ions or as a solid metallic cover and nonmetal such as Fe^{3+}, Zn^{2+}, N_2, C, Au, Ag, Pt, etc. [2, 8, 10, 14, 15]. Surface modification of TiO_2 with Ag nanoparticles led to decrease in the bandgap energy of TiO_2 and increase in the solar energy conversion efficiency of DSC [9, 12, 13]. On the other hand, radiation treatment has been well known as an effective method to synthesize metal nanoparticles with controlled size and shape [13, 15, 16]. In the present study, Ag nano/TiO_2 material has been synthesized by Co-60 gamma irradiation and characterized for utilization as optical anode material to improve conversion efficiency of DSC.

II. EXPERIMENTAL

Materials

TiO_2 (Degussa P25, 20% rutile and 80 % anatase) was purchased from Sigma-Aldrich. $AgNO_3$ and ethanol of analytical grade were bought from Shanghai Chemical Regent Co., China. Fluorine-doped SnO_2 (FTO, 15Ω square) glass, surlyn, ruthenium complex dye (N719), electrolyte solution HPE are products of Dyesol Co., Australia.

Methods

Ag nano/TiO_2 materials were synthesized by gamma irradiation of Ag^+/TiO_2/ethanol/water mixture. First, 4g of TiO_2 was dispersed in 20ml of admixture solution of ethanol:water (1:1, v:v) by magnetic stirring for 30 min followed by ultrasonic vibrating for other 30 min. Second, $AgNO_3$ solution was added to the suspension to prepared the mixtures with desired silver content of 0.1%-0.75% w/w. The resulting mixtures were poured into glass bottles, capped and γ-irradiated with dose range of 6-30 kGy at the same dose rate of 1.3 kGy/h under the Co-60 irradiator at the Research and Development Center for Radiation Technology - VINAGAMMA. Finally, the obtained products were dried in oven at 60 ºC, then ground down to obtain Ag nano/TiO_2 powder.

After irradiation, the crystalline structures of Ag nano/TiO_2 materials were studied by X-ray diffraction (XRD, Advance 8, Bruker, Germany), using copper Kα radiation (λ = 0.154 nm). The size of Ag nanoparticles was evaluated by transmission electron microscopy (TEM) images on a TEM 1400, JEOL, Japan. UV-Vis spectra of Ag nano/TiO_2 were recorded on an UV-Vis spectrophotometer of Jasco-V630, Japan. From UV-Vis spectrum, the Kubelka-Munk plot that was used to calculate bandgap energy value of TiO_2 and Ag nano/TiO_2 was set up [17].

The DSC with an active area of 0.2 cm^2 were assembled as follows. TiO_2 and Ag nano/TiO_2 films were screen-printed on the FTO substrate to create anode electrode that was heated at 500 ºC for 30 min. A platin film was also printed on the FTO substrate and cathode electrode was heated at 400 ºC for 30 min. The anode and cathode electrodes were arranged into a sandwich type cells by using a ply of surlyn melted at 190 ºC. The dye solution and electrolyte were dropped into the cell via holes in back of the cathode electrode. The process was performed in a nitrogen gas chamber. Finally, the holes were sealed using a quick drying adhesives.

The photovoltaic characteristics (I-V) of DSC were recorded by using a Keithly 2400 Source Meter and 1.0 version of IV Keithly 2400 software. The light source was a AM 1.5 solar simulator from a 450 W halogen lamp with an infrared filter. The incident light intensity was 1000 W/m^2 calibrated with a standard Si solar cell.

Electrochemical impedance spectroscopy (EIS) of the TiO_2 and Ag nano/TiO_2 films were measured by an Autolab 302N (Eco chemie, Netherlands) in the frequency range of 0.1 Hz-100 kHz and under illuminations of 1000 W/m^2.

III. RESULTS AND DISCUSSION

TEM images of Ag nano/TiO_2 materials were showed in Fig 1. In which, Ag nanoparticles with dark color dispersed on the background of bright color TiO_2. The size of Ag nanoparticles was determined to be of 16.9, 18.4 and 19.8 nm corresponding to the initial Ag^+ content of 0.1 %, 0.5 % and 0.75 %. This result proved that the irradiation process created Ag nanoparticles dispered in the TiO_2 suspension. The obtained result was also in accordance with the result that reported by Zhang et al. [12]. Their study of the synthesis of Ag nano/TiO_2 using UV irradiation method showed Ag nano particles doped on TiO_2 surface with a wide distribution because of the rapid development in the particle size of Ag nano. In the present study, the size of Ag nanoparticles increased with increasing of the initial Ag^+ content. It may be explained by the agglomeration of Ag nano particles and the development of clusters when the ratio of initial Ag^+ increased.

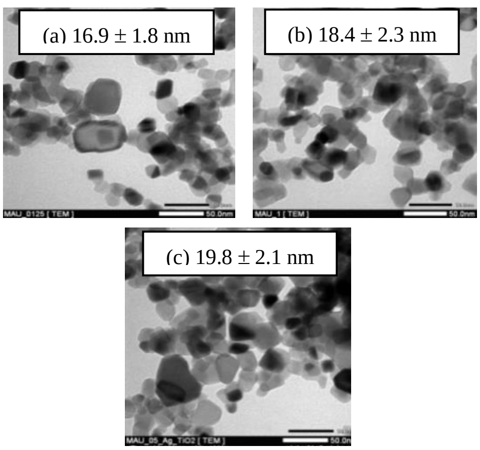

Fig. 1. TEM images of Ag nano/TiO_2 from (a) 0.1 %, (b) 0.5 %, (c) 0.75 % of Ag nano.

The optical property of TiO_2 and Ag nano/TiO_2 was investigated by UV-Vis absorption spectra in Fig. 2. The results suggested that configuration of the UV-Vis spectra of TiO_2 and Ag nano/TiO_2 was almost uniform. However, the optical density (OD) in the visible light region of Ag nano/TiO_2 samples was higher than that of TiO_2 and the OD increased with increasing content of Ag nano. This result may explain the color change from white of TiO_2 to reddish brown of Ag nano/TiO_2 and the higher the initial Ag^+ content the darker the color. In their recent studies, A. Laoui *et al.* also showed the change of optical properties of TiO_2 when it was modified with Pd nanoparticles by irradiation method [15]. On the other hand, the bandgap energy (Eg) of TiO_2 and Ag nano/TiO_2 was determined through Kubelka-Munk scheme from UV-Vis spectra presented in Table 1. The Eg value of Ag nano/TiO_2 decreased with increasing content of Ag nano. For instance, the Eg value decreased from 3.15 eV to 2.97 eV and 2.79 eV for the Ag nano/TiO_2 materials contained 0.25% and 0.75% of Ag nano, respectively. The Eg value reduced in the presence of Ag nano can expand the capacity of light absorption in the visible range of Ag nano/TiO_2 material.

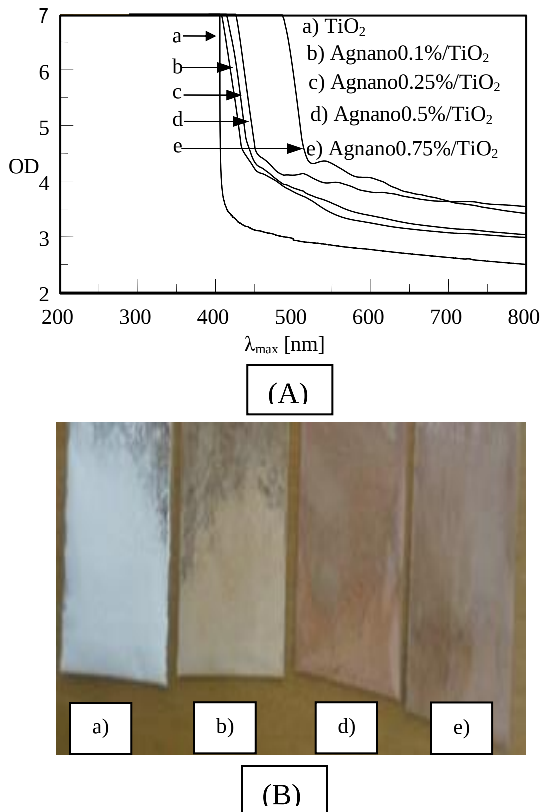

Fig. 2. UV-Vis absorption spectra (A) and photograph of Ag nano/TiO_2 materials (B): a) TiO_2, b) 0.25% Ag nano/TiO_2, d) 0.5% and e) 0.75% Ag nano on TiO_2.

Table I. Bandgap energy (Eg) of TiO_2 and Ag nano/TiO_2

Sample	Eg (eV)
TiO_2	3.15
Ag nano 0.1 %/TiO_2	3.09
Ag nano 0.25%/TiO_2	2.97
Ag nano 0.5%/TiO_2	2.81
Ag nano 0.75%/TiO_2	2.79

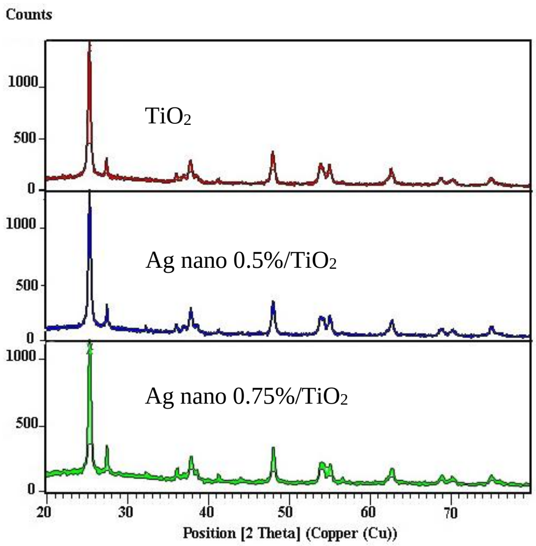

Fig. 3. XRD pattern of TiO_2 and Ag nano/TiO_2

XRD patterns of TiO_2 and Ag nano/TiO_2 was displayed in Fig. 3. There was no change in the diffraction peak position of anatase and rutile phase of Ag nano/TiO_2 compared with that of TiO_2. The recored results demonstrated that the irradiation process of synthesis of Ag nano did not change the structure of TiO_2. The diffraction peaks were observed at the 2θ = 25.35°, 37.76°, 47.93° and 75.03° conformed with anatase phase of TiO_2 that was represented the (101), (004), (200) ad (215) crystallographic planes, respectively. In addition to, the diffraction peaks at 2θ = 54.31° and 62.68° corresponded to rutile phase of TiO_2 and assigned with the crystallographic planes of (220) and (002), respectively [5]. The X-ray diffractogram results showed no characteristic peak of Ag nano in XRD patterns of Ag nano/TiO_2 materials and this may be due to the low content of Ag nano in Ag nano/TiO_2 materials [6, 12].

The performance of solar cells based on TiO_2 and Ag nano/TiO_2 with different Ag nano content was determined under the 1000 W/m^2 intensity light of the solar light model. The photovoltage results were indicated in Table II. The optical conversion efficiency of cell assembled with Ag nano/TiO_2 was higher than that of cell based on TiO_2 and the cell with Ag nano 0.75%/TiO_2 showed the best performance that was expressed through the parameters as short-circuit current (Isc), open-circuit potential (Voc), fill factor and efficiency (η) of 9.19 mA×cm^{-2}, 0.76 mV, 0.68 and 4.71%, respectively. The efficiency of cell with TiO_2 is of 3.75%. Thus, the conversion efficiency of cell with Ag nano 0.75%/TiO_2 film has been increased by 25.6% compared with that of cell based on TiO_2.

Table II. Performance parameters of DSC assembled with TiO_2 and Ag nano/TiO_2

Sample	V_{OC} (mV)	I_{SC} (mA×cm^{-2})	FF	η (%)
TiO_2	0.78	6.98	0.68	3.75
Ag nano 0.1%/TiO_2	0.75	9.18	0.65	4.44
Ag nano 0.25%/TiO_2	0.75	9.18	0.65	4.65
Ag nano 0.5%/TiO_2	0.77	9.18	0.67	4.67
Ag nano 0.75%/TiO_2	0.76	9.19	0.68	4.71

The electron transport properties of DSC with TiO_2 and Ag nano/TiO_2 films were studied by electrochemical impedance spectroscopy (EIS). The EIS results were shown in Fig. 4 and Table III. The charge transfer resistance (Rct) of Ag nano/TiO_2 films was smaller than that of TiO_2 film. Concretely, the Rct value of TiO_2 and Ag nano 0.75 %/TiO_2 film were 42.8 Ω and 34.9 Ω, respectively. According to the research of Wang *et al.*, the reducing resistance reflects the fast trasfer of electrons in the photo-anode after the addition of the silver nanowire in P25 films. The electrons can transferred and collected more easily and electron recombinations are decreased [18]. The result was suitable with the increase in the above conversion efficiency of cells with Ag nano/TiO_2 compared with that of the cell based on TiO_2.

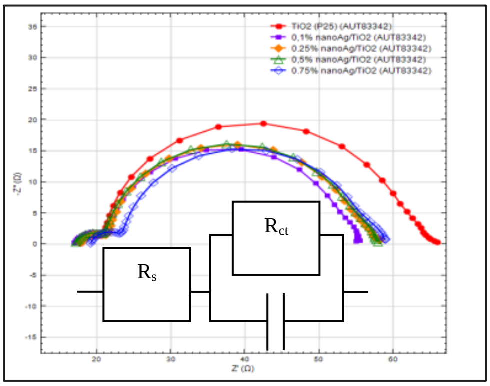

Fig. 4. Nyquist plot of TiO_2 and Ag nano/TiO_2 based DSC

Table III. Rct value of the DSC with TiO_2 and Ag nano/TiO_2 by EIS measurement

Type TiO_2	Rct (Ohm)
TiO_2 (P25)	42.8
0.1% Ag	34.1
0.25% Ag	35.5
0.5% Ag	36.1
0.75% Ag	34.9

IV. CONCLUSION

The Ag nano/TiO_2 materials with different Ag nano concents have been synthesized by gamma irradiation. The Ag nanoparticle size was estimated to be of 16-20 nm for the sample with initial Ag^+ content of 0.1-0.75%. There was no structural change of TiO_2 while the Ag nano can formed and deposited on TiO_2 by gamma irradiation. The Eg value of Ag nano/TiO_2 decreased from 3.15 eV (TiO_2) to 2.79 eV (Ag nano 0.75%/TiO_2) and the efficiency of cell assembled with Ag nano/TiO_2 increased from 3.75% (TiO_2) to 4.71%. Gamma irradiation is recognised as an effective method to prepare Ag nano/TiO_2 materials for solar cells and other applications as well.

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