Au-Loaded Titanium Dioxide Nanoparticles Synthesized by Modified Sol-Gel/Impregnation Methods and Their Application to Dye-Sensitized Solar Cells

Hathaithip Ninsonti, 1,2 Weerasak Chomkitichai, 2,3 Akira Baba, 2 Natda Wetchakun, 4 Wiyong Kangwansupamonkon, 5 Sukon Phanichphant, 6 Kazunari Shinbo, 2 Keizo Kato, 2 and Futao Kaneko 2

1 Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
2 Center for Transdisciplinary Research, Niigata University, Niigata 910-2181, Japan
3 Department of Science, Faculty of Science and Technology, Uttaradit Rajabhat University, Uttaradit 53000, Thailand
4 Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
5 National Nanotechnology Center, National Science and Technology Development Agency, Pathumthani 12120, Thailand
6 Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Correspondence should be addressed to Sukon Phanichphant; sphanichphant@yahoo.com

Received 3 December 2013; Accepted 10 March 2014; Published 7 April 2014

Academic Editor: K. R. Justin Thomas

Copyright © 2014 Hathaithip Ninsonti et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Au-loaded TiO₂ nanoparticles were synthesized by the modified sol-gel method together with the impregnation method. Anatase phase of TiO₂ was obtained in all samples with an average particle size of 20 nm. For the enhancement of DSSCs, the dye-sensitized solar cells composed of the ITO/Au-loaded TiO₂/N-719/electrolyte/Pt were fabricated. Au-loaded TiO₂ films were deposited by using squeegee method. Finally, the fabricated cells were studied upon an irradiation of solar light to study the performance. The fabricated cell with up to 1.0 mol% Au-loaded TiO₂ could enhance the performance by localized surface plasmon effect and scattering property.

1. Introduction

Recently, an increase in energy demand has led to significant progress in environmental remediation and renewable energy technologies such as photocatalytic oxidation, adsorption/separation processing, solar cells, fuel cells, and biofuels. One of the various renewable energy options, solar cell, stands out as the most ultimately sustainable choice in terms of its availability and huge potential. The solar cell for renewable energy options is applied through catalyst materials. Titanium dioxide (TiO₂) is one of the most efficient materials for dye-sensitized solar cells (DSSCs) due to its chemical stability, nontoxicity, good electrical properties, and inexpensiveness [1–4]. The phase structure of TiO₂ exists in three polymorphs: anatase, rutile, and brookite. The anatase TiO₂ is used as dye-sensitized solar cells material because it has band gap energy of 3.2 eV of which the absorption thresholds correspond to 380 nm, suggesting that it is easy for photon-electron transfer under solar light irradiation [3]. At the present time many studies on dye-sensitized solar cells (DSSCs) have been reported due to their high efficiency property and low cost of materials [1–4].

In the active layer of DSSCs, a monolayer of organic dye molecules covered with covalent bond on anatase TiO₂ film is generally used [5]. When the metal nanoparticles are incorporated in TiO₂ film of DSSCs, localized surface plasmon or light scattering can enhance the electric field on the active dye layer which can increase the light absorption [6–8]. Moreover, metal nanoparticles can perform as an electron acceptor from the photo-excited semiconductors.
Therefore, the electron transfer rate could be improved and the increase of photocurrent was obtained [6, 9]. Au has several advantages such as high conductivity and chemical and thermal stability [10]. For these reasons, Au nanoparticles were chosen to induce light scattering and localized surface plasmon excitation for the improvement of DSSCs performance.

There are many ways to synthesize TiO$_2$, such as precipitation method [11–13], solvothermal method [14–17], sol-gel method [18–22], spray pyrolysis [23–26], and microwave method [27–29]. Sol-gel process consists of 2 main reactions, hydrolysis and condensation [18–22, 30–33]. In our previous work, we reported the preparation of TiO$_2$ by the modified sol-gel method using cellophane membrane to decrease the diffusion rates of reactants in hydrolysis and condensation steps. This synthesis method had many advantages such as good reproducibility, good ability to obtain TiO$_2$ in nanosized scale, and good production for high purity products [30, 31].

In this research, TiO$_2$ and Au-loaded TiO$_2$ nanoparticles were synthesized by the modified sol-gel method and coupling the modified sol-gel with impregnation methods, respectively. The as-prepared samples were characterized by X-ray diffractometry, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectrophotometry, and Brunauer-Emmett-Teller techniques. The obtained particles were used to enhance DSSCs performance.

2. Experimental

2.1. Preparation of TiO$_2$ Nanoparticles. Titanium dioxide (TiO$_2$) nanoparticles were synthesized by the modified sol-gel method [30, 31]. Titanium tetraisopropoxide (Ti[OCH(CH$_3$)$_2$])$_4$ (TTIP), Aldrich, England), absolute ethanol (C$_2$H$_5$OH, Merck, Germany), and ammonia (NH$_3$, Merck, Germany) were used as the starting materials for synthesizing TiO$_2$ nanoparticles. Titanium tetraisopropoxide (20 mL) was dissolved in 250 mL absolute ethanol and mixed until a homogeneous solution was obtained. The mixture of TTIP and absolute ethanol was loaded into a cellophane membrane and suspended for 1 h in a clear solution containing a 1:1 ratio of ethanol (95%) and deionized water and 7 mL of ammonia solution (25%) as shown in Figure 1. After the completion of the dialysis process, the suspension was centrifuged at 7500 rpm for 10 min, washed with deionized water, and then dried in an oven at 60°C for 24 h. The white powders were then calcined in a furnace at a temperature of 400°C for 3 h.

2.2. Preparation of Au-Loaded TiO$_2$ Nanoparticles. The nominal 0.50–3.0 mol% Au-loaded TiO$_2$ powders were prepared by the impregnation method. The appropriate amounts of gold (III) chloride hydrate ([H(AuCl$_3$)$_2$]$_2$H$_2$O, Electron Microscopy Science) solution were added in TiO$_2$ nanoparticles as described previously in Section 2.1. Then, the as-prepared samples were mixed until being homogeneous. Finally, the obtained powders were dried at 60°C for 24 h and calcined at 400°C for 3 h.

2.3. Characterization of TiO$_2$ and Au-Loaded TiO$_2$ Nanoparticles. The crystal structure and crystallinity of TiO$_2$ and Au-loaded TiO$_2$ nanoparticles were examined by X-ray diffractometry (IDX-3530, JEOL, Japan) using the Ni-filtered monochromatic with CuK$_\alpha$ radiation. The detection range was 15–75° with the step size of 0.10° (2θ)/s. Morphologies and particle sizes of TiO$_2$ and Au-loaded TiO$_2$ nanoparticles were investigated by scanning electron microscopy (SEM, JSM5410-LV, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). The chemical composition of TiO$_2$ and Au-loaded TiO$_2$ nanoparticles was examined by energy dispersive X-ray spectrophotometry (EDXS, ISIS300, Oxford, England). Specific surface area (SSA$_{BET}$) of the samples was investigated by the Brunauer-Emmett-Teller (BET, Micromeritics Tristar 3000). An average particle diameter (d$_{BET}$) of TiO$_2$ and Au-loaded TiO$_2$ nanoparticles was calculated using the following formula: 

\[ d_{BET} = \frac{6}{(\rho_{TiO_2} \times SSA_{BET} \times wt.\%TiO_2) + (\rho_{Au} \times SSA_{BET} \times wt.\%Au)} \]

where \( \rho_{TiO_2} \) and \( \rho_{Au} \) are the weight densities of TiO$_2$ (3.84 g cm$^{-3}$) and Au (19.30 g cm$^{-3}$), respectively.

2.4. Fabrication of DSSCs. DSSCs were fabricated by TiO$_2$ and Au-loaded TiO$_2$ nanoparticles for comparison of the efficiency performance. ITO glass substrate with a sheet resistance of 10 Ω/sq was used as an anode. Dish washing liquid solution, water, distilled water, and DI water were used for cleaning of ITO substrate. After cleaning process, squeegee technique was used to deposit TiO$_2$ or Au-loaded TiO$_2$ layers as follows: TiO$_2$ or Au-loaded TiO$_2$ nanoparticles were dispersed in ethanol with the concentration of 2, 3, 4, or 5 M in order to optimize the appropriate thickness. Then, TiO$_2$ or Au-loaded TiO$_2$ pastes were coated on ITO substrates by squeegee technique. TiO$_2$ or Au-loaded TiO$_2$ films were then calcined at 450°C for 90 min. To prevent the corrosion of Au particles by iodine electrolyte, Au-loaded TiO$_2$ films were immersed in 0.001 M 1-octadecanethiol (CH$_3$(CH$_2$)$_{17}$SH, Aldrich, England) for 15 h after calcination step. N-719 (di-tetrabutylammonium cis-bis (isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium (II), Sigma-Aldrich) was used as a photosensitized dye. TiO$_2$ or Au-loaded TiO$_2$ films were immersed in 0.5 mM N-719 dye for 12 h. DSSCs were fabricated as shown in Figure 2.
2.5. Characterization of the Fabricated DSSCs. The absorption of TiO$_2$ and Au-loaded TiO$_2$ films was observed by UV-vis spectroscopy technique (UV-vis spectrometer, V-650, JASCO). Photovaltaic properties were studied by irradiating a solar simulator (HAL-C100, 100W compact xenon light source, ASAHI SPECTRA) to the fabricated DSSCs.

3. Results and Discussion

3.1. Synthesis and Characterization of Au-Loaded TiO$_2$ Nanoparticles. In this research, the TiO$_2$ and Au-loaded TiO$_2$ nanoparticles were prepared by the modified sol-gel method and the modified sol-gel method together with the impregnation method, respectively. The preparation of the TiO$_2$ was followed from our previous reported research [30, 31]. The sol-gel method consists of hydrolysis and condensation of titanium alkoxides, Ti(OR)$_n$, to form oxopolymers, which are converted to an oxide complex as equation mentioned in our previous report [30].

The rates of hydrolysis and condensation are important factors that might affect characteristic of Au-loaded TiO$_2$. Smaller particle sizes were obtained from hydrolysis and condensation rates which are controlled by basic solution [34–37]. Consequently, cellophane membrane was used to control the hydrolysis and condensation rates in the reaction to acquire the nanosized particles [30, 31]. Moreover, TiO$_2$ loading with Au was produced by the impregnation method which is a very simple technique and does not require expensive equipment. The homogeneous powders of TiO$_2$ show white color, while increase of Au ions changed the color to grayish purple.

The structure confirmation of TiO$_2$ and Au-loaded TiO$_2$ nanoparticles was obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) Card Files numbers 21-1272 and 04-0784. Figure 3 shows the XRD patterns of the TiO$_2$ and 1.0 mol% Au-loaded TiO$_2$ nanoparticles. The results of the TiO$_2$ and 1.0 mol% Au-loaded TiO$_2$ nanoparticles confirmed anatase structures according to JCPDS file number 21-1272 [30, 31]. The Au-loading might not affect the phase of TiO$_2$ nanoparticles. The diffraction peaks of Au were found on Au-loaded TiO$_2$ nanoparticles at 2θ value of 38.2° and 44.4° according to JCPDS file number 04-0784. The high intensity value of the XRD peaks shows that all of the samples have well crystalline structure and the broad peaks at 2θ value of 25.2° show that the particles have a small average crystallite size.

The specific surface area (SSABET) of the TiO$_2$ and Au-loaded TiO$_2$ nanoparticles was found to be in the range of 69–109 m$^2$ g$^{-1}$ with the particle diameter in the range of 14–21 nm, corresponding well with the XRD results. It was reported that high surface area of TiO$_2$ active layer has many advantages such as large amount of dye adsorption, high light-harvesting efficiency, rapid electron transport, and low electron recombination [38–40]. Therefore, high photoefficiency could be expected.

Morphologies, particle sizes, and element chemical compositions were investigated by scanning electron microscopy (SEM) as shown in Figure 4(a). The SEM result shows the rough morphology and the presence of agglomerated nanoparticles with an average diameter of 50–100 nm. From the EDS spectra as shown in Figure 4(e), the chemical compositions of 1.0 mol% Au-loaded TiO$_2$ showed the characteristic X-ray energy level of titanium, oxygen. The characteristic peaks of Au were observed to confirm the presence of Au corresponding to the XRD results. Furthermore, element composition of Au-loaded TiO$_2$ was investigated by EDS mapping mode. Figures 4(b), 4(c), and 4(d) show element composition of Ti, O, and Au in 1.0 mol% Au-loaded TiO$_2$ nanoparticles. The presence of Au in the sample was confirmed. Further analysis for the accurate sizes and morphology of the nanoparticles was carried out by TEM observation. The average particle diameter of TiO$_2$ and Au-loaded TiO$_2$ nanoparticles was in the range of 15–20 nm as shown in Figure 5.
Figure 4: (a) SEM micrographs and EDS mapping mode of (b) Ti, (c) O, (d) Au, and (e) EDS spectra of 1.0 mol% Au-loaded TiO$_2$ nanoparticles.

Figure 5: TEM micrograph of 1.0 mol% Au-loaded TiO$_2$ nanoparticles.
3.2. Characterization and Optimization of Au-Loaded TiO₂ Films. Figure 6 shows the UV-vis absorption spectra of TiO₂ and 0.50–3.0 mol% Au-loaded TiO₂ films deposited on ITO substrate. A broad peak of Au appeared in the wavelength of 530–580 nm and increased intensity with increasing the Au loading amount on the TiO₂ nanoparticles. This result indicated that the localized surface plasmon resonance could be excited on Au-loaded TiO₂ nanoparticles [41]. As mentioned in the previously reported research by many groups, the film thickness is one of the most important factor effects on the performance of DSSCs [42, 43]. The film thickness was optimized by varying the concentration of 3.0 mol% Au-loaded TiO₂ paste in the squeegee process. The thickness of 3.0% Au-loaded TiO₂ films was increased with increasing the concentration of Au-loaded TiO₂ paste, as shown in Figure 7(a). Figure 7(b) shows the effect of 3.0% Au-loaded TiO₂ film thickness on short-circuit photocurrent properties of DSSCs. It was found that the short-circuit
photocurrent increased with increasing film thickness up to 8 μm (Figure 7(c)). However, the photocurrent decreased with the film thickness more than 8 μm.

3.3. Photovoltaic Properties of the Fabricated DSSCs Using TiO2 and Au-Loaded TiO2 Nanoparticles. Photovoltaic properties of the fabricated DSSCs using TiO2 and different nominal 0.50–3.0 mol% of Au-loaded TiO2 nanoparticles were studied to compare the enhancement of photovoltaic performance of DSSCs. Figure 8 shows current density versus voltage \((J-V)\) curves of fabricated DSSCs using TiO2 and 0.50–3.0 mol% Au-loaded TiO2 nanoparticles. Photovoltaic performances were calculated from these \(J-V\) curves as shown in Table I. The open circuit voltage \(V_{oc}\) is almost constant value with Au-loading amount. This indicates that the Au-loading to TiO2 does not affect the Fermi level because the \(V_{oc}\) is originated from the energy difference between Fermi level of TiO2 layer and the oxidation/reduction potential of the electrolyte [44]. The results show that the short-circuit current densities \(J_{sc}\) of the fabricated DSSCs with TiO2, 0.50, 1.0, 2.0, and 3.0 mol% Au-loaded TiO2 nanoparticles were 10.04, 12.48, 13.06, 8.27, and 7.02 mA/cm², corresponding to the efficiency \(\eta\) of 4.34, 5.40, 5.52, 4.13, and 3.33%, respectively. These results confirmed that Au-loading could enhance the performances of DSSCs with the loading amount up to 1.0 mol%. However, the short-circuit current density and the efficiency of the fabricated DSSCs were decreased upon the increasing amount of 2.0 mol% Au loading. These effects might be possibly due to the fact that the active site was shielded by the large amount of Au loading or rougher morphology of the Au-loaded TiO2 layers.

4. Conclusion

In this research, the Au-loaded TiO2 nanoparticles were successfully synthesized by the modified sol-gel method together with the impregnation method. Anatase phase of TiO2 was obtained in all samples with an average particle size of 20 nm. The DSSC was improved by an effect of the Au-loaded titanium dioxide (Au-loaded TiO2). For the enhancement of DSSCs, the fabricated cell with up to 1.0 mol% Au-loaded TiO2 could enhance the performance by localized surface plasmon effect and scattering property.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This research was supported by a Grant-in-Aid for Young Scientists (B) (23760010) and Grant-in-Aid for Scientific Research (C) (25390051) from the Japan Society for the Promotion of Science (JSPS), the Thailand Research Fund, The Royal Golden Jubilee Ph.D. Program (PHD/0358/2551), the National Science and Technology Department Agency (NSTDA), Thailand Graduate Institute of Science and Technology, through its program of Center of Excellence in Nanotechnology (NANOTEC), NSTDA, Ministry of Science and Technology, through its program of Center of Excellence Network, Thailand, and the Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand. Sukon Phanicphont wishes to thank the National Research University Project under Thailand’s Office of the Higher Education Commission for financial support.

References


