

PHOTOCURRENT ENHANCEMENT OF CdS QUANTUM DOT SENSITIZED TiO₂ ELECTRODE IN THE PRESENCE OF GOLD NANOPARTICLES

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ABSTRACT

PHOTOCURRENT ENHANCEMENT OF CdS QUANTUM DOT SENSITIZED TiO₂ ELECTRODE IN THE PRESENCE OF GOLD NANOPARTICLES. Photocurrent enhancement of CdS Quantum Dot (CdS-QD) sensitized TiO₂ electrode in the presence of gold nanoparticles had been investigated. CdS quantum dots were prepared by successive ionic layer adsorption and reaction (SILAR) method, in which solution containing Cd(CH₃COO)₂ and Na₂S were used as a precursor. Whereas, gold nanoparticles was synthesized using solution containing HAuCl₄ as a precursor, NaBH₄ as a reducing agent and polyvinyl pyrrolidone (PVP) as a stabilizer. The film of CdS quantum dots and Au nanoparticles were characterized by UV-Vis spectrophotometer, Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), and electrochemical working station. Photoelectrochemical study revealed that CdS-sensitized TiO₂ electrode with gold nanoparticles have been able to increase photocurrent of 54 μA/cm² to 68 μA/cm², so the photocurrent enhancement of approximately 25% was observed. This observation indicates that the gold nanoparticles is potentially applicable to enhance photocurrent in a CdS-QD sensitized TiO₂ electrode, which may lead to the development of more efficient solar cell.

Keywords: Photocurrent, TiO₂, CdS quantum dot, Gold nanoparticles.

ABSTRAK

PENINGKATAN ARUS CAHAYA PADA ELEKTRODA TiO₂ TERSENSITASI CdS QUANTUM DOT DENGAN ADANYA NANOPARTIKEL EMAS. Peningkatan arus cahaya pada elektroda TiO₂ yang tersensitasi CdS *Quantum Dot* (CdS-QD) dengan adanya nanopartikel emas telah diselidiki. CdS *quantum dot* dibuat dengan metode *Successive Ionic Layer Adsorption and Reaction* (SILAR), di mana larutan yang mengandung Cd(CH₃COO)₂ dan Na₂S digunakan sebagai prekursor. Sedangkan nanopartikel emas dibuat menggunakan larutan HAuCl₄ sebagai *precursor*, NaBH₄ sebagai reduktor dan polivinilpirolidon (PVP) sebagai penstabil. Lapisan CdS *quantum dot* dan nanopartikel Au dikarakterisasi dengan spektrofotometer UV-Vis, *Scanning Electron Microscope* (SEM), *X-Ray Diffraction* (XRD), dan perangkat kerja elektrokimia. Pada uji fotoelektrokimia menunjukkan bahwa adanya nanopartikel emas pada elektroda TiO₂ yang tersensitasi CdS mampu meningkatkan arus cahaya dari 54 μA/cm² menjadi 68 μA/cm², sehingga terjadi peningkatan arus cahaya sebesar 25%. Dari pengamatan ini menunjukkan bahwa nanopartikel emas berpotensi meningkatkan arus cahaya pada elektroda TiO₂ yang tersensitasi CdS-QD, sehingga dapat untuk pengembangan sel surya yang lebih efisien.

Kata kunci: Arus cahaya, TiO₂, CdS *quantum dot*, Nanopartikel emas

INTRODUCTION

The use of fossil fuels on a large scale gives an impact on global climate change (global warming).

Therefore it is necessary to switch from fossil fuels to a renewable energy sources by two main reasons, (i) the

earth's natural resources are limited and cannot be regenerated in a short time, and (ii) burning of fossil fuels causes the formation of CO₂ thus causing the greenhouse effect.

Solar cells as an alternative energy, is a promising way as a source of CO₂ emission-free energy. Since the invention of nano structured Dye-Sensitized Solar Cell (DSSC), many experiments have been done to enhance cell efficiency [1]. The ruthenium based dyes proved to be the best dye so far. However due to the expensive price of ruthenium dye, it is necessary to find another alternative dye type as photosensitizer for future development. The quantum dot (QD) has been showed potential candidate as a photo sensitizer to replace ruthenium dyes. QD offers some significant advantages compared to the other dye. QD is more suited to the solar spectrum due to the absorption spectrum that can be adjusted according to the size of the particle. QD can also generate multiple electron-hole pairs per photon, thus increasing the efficiency of the solar cell [2].

In addition, although the mechanism is not yet fully understood, it was reported that photocurrents of solar cell have also been enhanced by the presence of metal nanoparticles (NP), such as gold (Au) and silver (Ag), in the photo sensitizer matrix. It seems that NP acts as an electron trap to help separating the photogenerated charge and increase the interface charge transfer [3]. Several studies have shown that the presence of metal nano particles such as gold nanoparticles [2,4-7] and silver nanoparticles [8-9], can improve the performance of the DSSC, enhance hydrogen production via photo catalytic water splitting [10-11], and can accelerate the decomposition of organic compounds [12].

Au nanoparticles undergo charge equilibration with TiO₂ nanoparticles and shift the apparent Fermi level to more negative potentials. As a result, presence of Au nanoparticles cause an increase in photo voltage [3,13-14]

In this paper, the investigation of photocurrent enhancement of the CdS-QD sensitized TiO₂ photoanode in the presence of Au nanoparticles will be reported and discussed.

EXPERIMENTAL METHOD

Materials and Instrumentation

All chemicals and solvents used in this study were of reagent grade. Titanium (IV) isopropoxide, polyethylene glycol (Mr = 1000), triethanolamine, Na₂S were purchased from Sigma Aldrich. While methanol, ethanol, Cd(CH₃COO)₂ · 2H₂O, HAuCl₄ 1000 mg/L, NaBH₄, polyvinylpyrrolidone (PVP), thio glycolic acid (TGA), CHCl₃, toluene were purchased from Merck. Distilled water produced from a BioPure purification system was used throughout the

experiments and homemade FTO (75X25X1,4 mm³, sheet resistance = 21Ω/sq) were made by spray pyrolysis method.

XRD patterns of the prepared film were obtained by X-Ray Diffractometer XRD 7000 Shimadzu Cu Kα radiation (α = 0.154184 nm) that operated at 40 kV and 30 mA. FESEM images were taken using Field Emission Scanning Electron Microscope (FESEM) (FEI-Inspect F50). The percentage of Ti, Cd, S, and Au in composite film was calculated from energy dispersive spectra (EDS) measurements recorder on FESEM (EDAX, Apollo X). A UV-Vis spectrophotometer (Specord-200, Analytic Jena) was used to characterize Au nanoparticles. Photocurrent was measured with a standard three-electrode configuration, which was connected to a computer-controlled potentiostat (e-DAQ/e-corder 401) to record the generated photocurrent. TiO₂ photoanode was placed as working electrode, while a Pt wire and Ag/AgCl was placed as counter and reference electrode, respectively. The supporting electrolyte was 0.3 M Na₂S. TiO₂ photoanodes were illuminated with 15W UV lamp (2.80 mW/cm²) and visible light (60W tungsten lamp, 2.2 mW/cm²). Linear sweep voltammetry was done at a scan rate of 40 mV/s from -1200 mV to 500 mV under UV/visible illumination, while multi pulse amperometry was done in 100 second with potential = 0 volt.

Procedure

Preparation of FTO/TiO₂ Film

Titanium tetraisopropoxide (TTIP), polyethylene glycol (PEG, Mr= 1000), triethanolamine, ethanol, home made FTO (fluorine tin oxide) glass having sheet resistance of 21 Ω/sq [15] and distilled water were used in this experiment. TiO₂ sol was prepared by mixing of 7.5 mL TTIP, 2.4 mL triethanolamine, and 36 mL of ethanol. The mixture was stirred with a magnetic stirrer at room temperature for 1.5 hours, then was added by adequate ethanol-water (4.5:0.5) and 2 grams of PEG, and stirred with a magnetic stirrer for 1.5 hours. The resulting sol then was used to coat the FTO glass by a dip coating method, and then annealed at 500 °C for 1 hour, to obtain TiO₂ film on the surface of FTO (FTO/TiO₂).

Preparation of FTO/TiO₂/CdS Film

QD-CdS was prepared by a Successive Ionic Layer Adsorption and Reaction (SILAR) method. Individual solution containing Cd(CH₃COO)₂ and Na₂S were used as a Cd and S precursor to obtain QD-CdS. The QD-CdS was deposited directly by immersing the FTO/TiO₂ glass into an aqueous solution of 0.3M Cd(CH₃COO)₂ for 2 minutes, then rinsed with distilled water. Then was immersed in aqueous solution of 0.3M Na₂S for 2 minutes, then rinsed with distilled water. This step was repeated 3 times until enough CdS layer was

formed. The QD-CdS layer on FTO/TiO₂ surface then was dried for few minute in an oven at 100°C to obtain FTO/TiO₂/CdS film [16].

Preparation of Au Nanoparticles (Au-NP)

Au NP was synthesized using HAuCl₄ as a precursor, NaBH₄ as a reducing agent and polyvinyl pyrrolidone (PVP) as a stabilizer. 100 mL of 0.2M HAuCl₄ was added with the 5 mL of 1% PVP and stirred with a magnetic stirrer vigorously, then 2 mL of 0.5% NaBH₄ was added to the solution drop by drop. The color of the solution changes from yellow to ruby red which indicates the formation of Au nanoparticles[17]

Preparation of FTO/TiO₂/Au/CdS Composite Film

Thio glycolic acid (TGA) was used as molecular linkers between FTO/TiO₂ to the Au NP. TiO₂ has a strong affinity to the carboxylic group of the linker molecule, whereas the sulfur atom of TGA bind to Au NP through surface interactions. FTO/TiO₂ films were dried in an oven at 100 °C for 1 hour to remove excess H₂O. The dried FTO/TiO₂ then was soaked in a solution of 70% TGA in CHCl₃ for 2 hours, then rinsed with toluene to remove excess TGA, and then soaked in a solution containing Au NP for 2 hours. While, subsequently, the QD-CdS was deposited by SILAR method as mentioned in the previous paragraph. Only the Au component is tied up with the TGA, while the next component, QD-CDS enters as a uniform layer.

RESULTS AND DISCUSSION

FTO/TiO₂ Film

Figure 1 shows the Field Emission Scanning Electron Microscope (FESEM) image of TiO₂ film (FTO/TiO₂) prepared by a sol-gel method in the presence of PEG 1000 as the structure-directing agent. As can be seen, the TiO₂ aggregate lies on top of FTO substrate and was likely not a highly ordered. The TiO₂ framework organized by PEG might have been partly destroyed after calcination because of the poor thermal stability of TiO₂

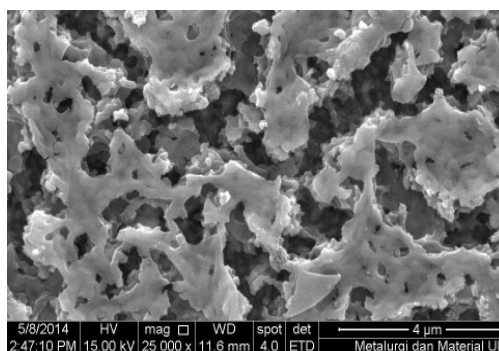


Figure 1. FESEM image of the porous TiO₂ on the top of FTO substrate

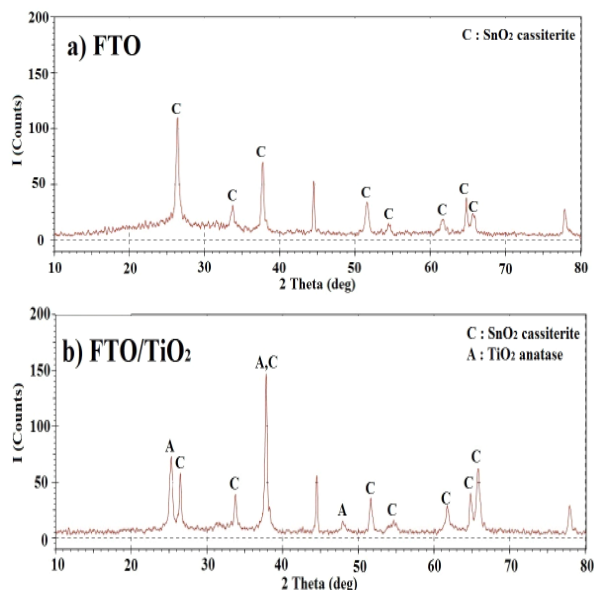


Figure 2. (a). XRD patterns of FTO film and (b). FTO/TiO₂ film

network. Despite this, a number of porous still exist in the film after calcination, which increases the surface area of TiO₂ film. This results indicate that the TiO₂ porous film, although not very dense, was formed on top of FTO surface.

The X-Ray Diffractometer (XRD) patterns of typical obtained TiO₂ films on top of FTO glass (FTO/TiO₂) calcined at 500 °C (Figure 2) shows the characteristic of anatase structure (JCPDS No. 21-1272) and no rutile diffraction lines were observed. The dominant of SnO₂ peaks observed was due to low thickness of TiO₂ film and by the cracking of the film structure.

The anatase crystallite size of TiO₂ was estimated using the Scherrer equation as equation (1)

$$D = k\lambda / (\beta \cos\theta) \dots\dots\dots (1)$$

where the constant k is a shape factor usually ~0.9, λ is the wave length of X-ray (0.15418 nm), β is the full-width at half-maximum (FWHM) in radians and θ is the Bragg's angle. The crystallite size calculated by equation (1) from anatase peaks was found about 30-60 nm.

Photocurrent Generation on the FTO/TiO₂ Film Anode

TiO₂ is a semiconductor with a band gap of 3.2 eV, (it is equivalent to a wavelength of 388 nm), therefore when it was illuminated by UV light, a photocurrent will be generated. It can be seen from Figure 3, under UV illumination quite significant photocurrent evolved due to photo activity of TiO₂.

This is also reinforced by the amperometric data in Figure 4, where the photocurrent under the dark is nearly zero and only very small current observed under visible light illumination. On the other hand the

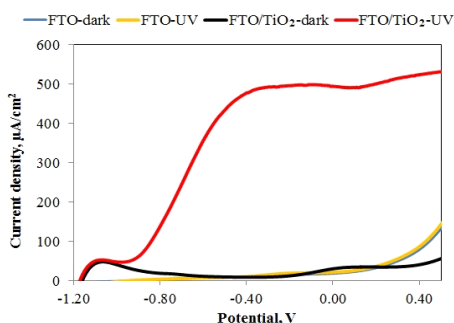


Figure 3. Linear sweep voltammograms, collected at a scan rate of 40 mV/s at applied potential from -1.2 V to +0.5 V, in the dark and with UV illumination of 2.80 mW/cm²

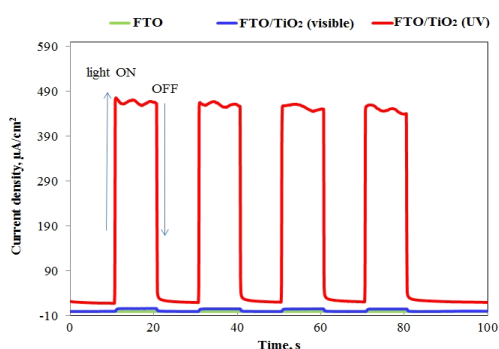


Figure 4. Photocurrent curve of FTO/TiO₂ film at constant potential of 0 V (under UV and visible illumination, with intensity 2.80 mW/cm² and 2.20 mW/cm² respectively)

photocurrent under UV light as much as 450 µA/cm² was observed. Meanwhile, if only the FTO substrate, did not give a photocurrent, both in the dark and under UV illumination. This is because the FTO has a larger band gap than TiO₂ is 3.8 eV so that the ordinary UV light is unable to produce photocurrent.

FTO/TiO₂/CdS Film

Under visible light, the presence of QD-CdS on the surface of TiO₂ was able to increase up to 10 times of photocurrent compared to that of solely TiO₂ film (Figure 5). This is due to the fact that QD-CdS has a

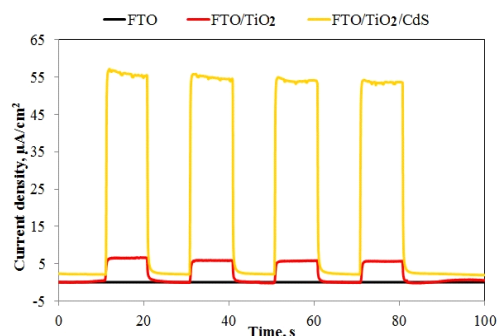
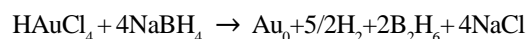


Figure 5. Photocurrent curve of FTO, FTO/TiO₂ and FTO/TiO₂/CdS films at constant potential of 0 V (under visible illumination, 2.20 mW/cm²)

smaller band gap than TiO₂. Band gap of QD-CdS is 2.25 eV which is equivalent to a wavelength of 550 nm, therefore it can be activated by visible light.

Au Nanoparticles(Au-NP)

In the synthesis of Au nanoparticles, it was used HAuCl₄ as source of Au, NaBH₄ as a reducing agent and polyvinylpyrrolidone as a stabilizer, with the reaction as follow:



In general, the SPR (surface plasmon resonance) of Au nanoparticles ranged from 510 to 550 nm, depending on the particle size. The larger particle size the absorption shifts to the infrared region (red shift). From the color and spectrum of Au nanoparticles (Figure 6), compared with the color and spectrum of Au nanoparticles standard [18], it can be concluded that size of Au nanoparticles was around 5 nm.

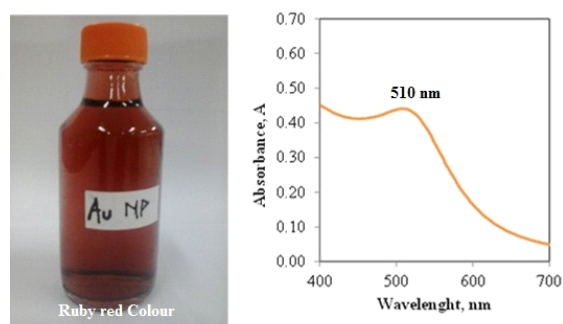


Figure 6. Left : Color of Au nanoparticles Right : Spectrum of Au nanoparticles

FTO/TiO₂/Au/CdS Composite Film

The surface morphology of the layer of TiO₂/Au/CdS can be seen in Figure 7. This porous layer had more surface area, and it would give more contact with electrolyte.

From SEM-EDS spectrum (Figure 8) shows that FTO/TiO₂/Au/CdS was already well-arranged with a gold content of 1%.

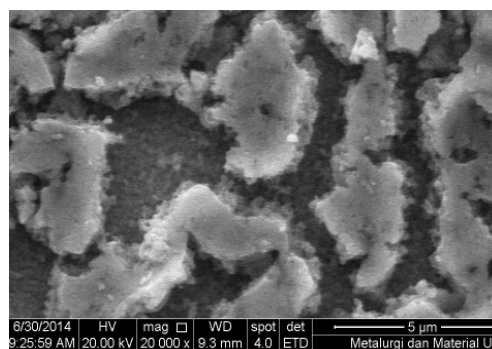


Figure 7. Surface morphology of the FTO/TiO₂/Au/CdS layer

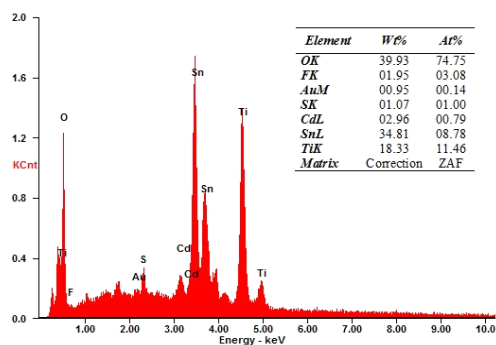


Figure 8. EDS spectrum and elemental composition of FTO/TiO₂/Au/CdS electrode

Photocurrent Enhancement on FTO/TiO₂/Au/CdS Film Anode

Photoelectrochemical test was conducted by using linear sweep voltammetry (LSV) and amperometry, in the dark and under visible illumination.

A 60 watt tungsten lamp with intensity 2.20 mW/cm² was used as source of visible light. Figure 9 shows that in the dark, photocurrent of all configurations are nearly zero, but under visible illumination FTO/TiO₂/CdS and FTO/TiO₂/Au/CdS give high photocurrent response. This is due to the fact that TiO₂ has a bandgap in the UV region is 3.2 eV, which is equivalent to a wavelength of 388 nm, so that TiO₂ can only produce a photocurrent when illuminated by UV

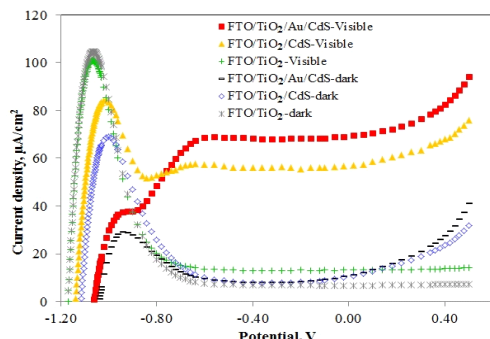


Figure 9. Linear sweep voltammograms, collected at a scan rate of 40 mV/s at applied potential from -1.2 V to +0.5 V, in the dark and with visible illumination of 2.20 mW/cm²

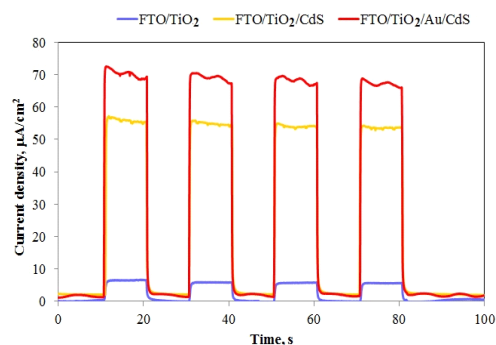


Figure 10. Photocurrent curve of FTO/TiO₂, FTO/TiO₂/CdS and FTO/TiO₂/Au/CdS films at constant potential of 0 V (under visible illumination, 2.20 mW/cm²)

light. While CdS and Au has an absorption in the visible light region. CdS has a bandgap of 2.25 eV, which is equivalent to a wavelength of 550 nm and Au have the SPR at about 510-550 nm, so that both CdS and Au-CdS will produce high photocurrent when illuminated by visible light.

From Figure 10, it can be seen that under visible illumination, FTO/TiO₂ only resulted 5 μA/cm², while FTO/TiO₂/CdS and FTO/TiO₂/Au/CdS resulted the photocurrent, 54 μA/cm² and 68 μA/cm², respectively. TiO₂ had band gap 3.2 eV (equivalent with 388 nm), while CdS had band gap 2.25 eV (equivalent with 550 nm) so the presence of CdS quantum dot improved the photocurrent of FTO/TiO₂ up to 10 fold, from 5 μA/cm² become 54 μA/cm². The presence of Au nanoparticles has also improved photocurrent of FTO/TiO₂/CdS from 54 μA/cm² become 68 μA/cm². It caused by surface plasmon resonance of Au nanoparticles lies on visible region and finally the presence of Au nanoparticles had successfully enhanced photocurrent of FTO/TiO₂/CdS up to 25%.

CONCLUSION

Thin layer of porous TiO₂ was successfully prepared by sol gel method and deposited into FTO glass by dip coating method. CdS quantum dot was successfully synthesized by SILAR method, and under visible illumination, TiO₂-CdS able to generate photocurrent up to 10 fold from TiO₂ only. Au nanoparticles was successfully synthesized and Au-CdS able to improve photocurrent up to 25% compared with solely CdS (from 54 μA/cm² become 68 μA/cm²) Finally it can be concluded that FTO/TiO₂/Au/CdS electrode has a great opportunity to be used in solar cells with better efficiency

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