Thiolate Capped Noble Metal Particles as Novel Sensitizers for Solar Cells

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Abstract

MPA (3-Mercaptopropionic acid) capped noble metal particles (Ag, Au) are studied in this project as sensitizers for solar cells. TiO_2 nanotube arrays were fabricated via etching anodization method. The MPA capped noble metal sensitizer was deposited onto the surface of the TNAs using in-situ hydrothermal method. Different initial molar ratios of Ag and Au were investigated. The specimens were characterized using FE-SEM, HRTEM, XRD, XPS and UV-vis spectroscopy. Photoelectrochemical measurements, including *J-V* curves, stability test and electron lifetime assessment, were conducted to examine the performance of the sensitized TiO_2 materials. It is found that the Ag (0) @ Ag (+) – MPA nanocluster showed the best performance in light energy conversion. Better stability was also achieved compared to previous works.

Keywords: *Nano-photocatalyst, visible-light activation, nano metal clusters, solar cell sensitization.*

1. Introduction

Metal-cluster-sensitized solar cell uses silver glutathione (Au-GSH) nanoclusters deposited on the mesoporous TiO_2 film as the photoanode (Kamat et al. 2014). The light-electricity conversion efficiency reached about 2.3% under AM 1.5 illumination. The mechanism of the excitation of the Au-GSH nanoclusters was characterized and reported in the literature (Linic et al. 2011). The excitation behavior of the Au-GSH nanoclusters is size-dependent and similar to that of dye molecules rather than plasmonic particles. The small nanoclusters composed of metal atoms behave as big molecules.

Recently, investigators studied the use of hybrid nanomaterials as sensitizers in liquid-junction solar cells illustrated in Fig. 1 (Chen et al. 2013, Fan et al. 2014). When there are incident photons with energy exceeding the semiconductor's bandgap energy, the electrons of the semiconductor can absorb the photon energy and be excited to the conduction band, leaving positively charged holes in the valence band. The excited free electrons will migrate through the circuit under the built-in potential difference. The holes capture electrons from the electrolyte so some species are oxidized. Meanwhile, when the free electrons reached the cathode, they reduce the oxidized species in the electrolyte. The chemical state of the electrolyte remains unchanged and the net effect of the cell is converting the photon energy to electricity. On the other hand, the excited free electrons may simply recombine with the holes without producing any useful electricity.

In liquid-junction solar cell, the hybrid nanomaterial consists of noble metal particles and organic compound. The metal-organic hybrid nanomaterials can absorb long-wavelength photons and inject charge carriers to the electrode, which is same as the roles played by traditional dye and quantum dots. The hybrid materials have shown some very intriguing and promising features and good chance to a step-forward in the field. The main objective of this research is to develop noble metal (silver and gold) based hybrid nanomaterials for enhancing solar photovoltaic performance.
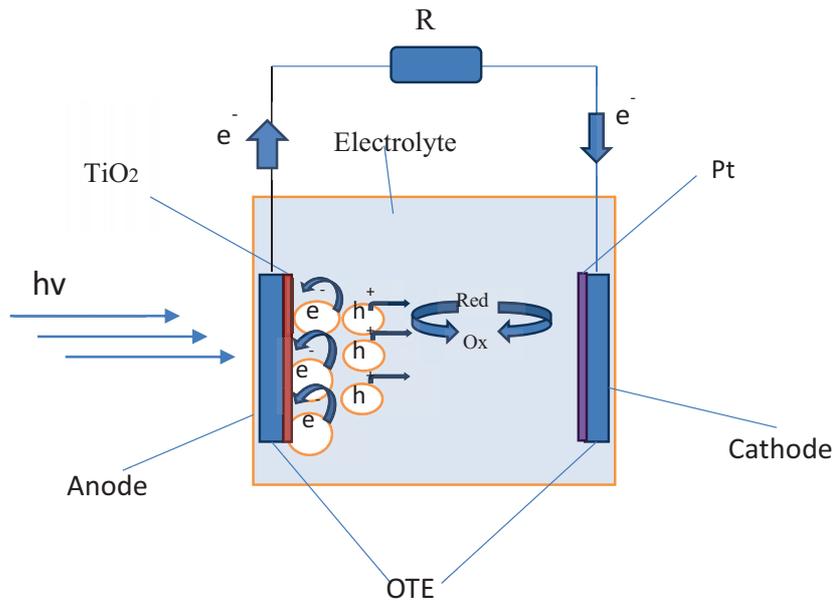
Fig. 1: Mechanism of liquid-junction solar cell

2. Experimental

2.1. Sample fabrication

Etching anodization method is a commonly employed fabrication approach of self-ordered titanium nanotube arrays (TNAs) and has been a relatively mature means. Although the first nanotubes did not show very neat morphology, it demonstrated the effect of F^- ions on fabricating TNAs. A series of studies explored the impacts of pH value, the water content, the organic electrolyte system (such as ethylene glycol), constant voltage, duration and so on. Under the existence of anodic voltage and conductive electrolyte, the metallic titanium is firstly oxidized to TiO_2 and the H^+ in the electrolyte is reduced to H_2. If there was no etching ions (e.g. F^-) in the electrolyte, the reactions lead to formation of a compact oxide layer on the surface of Ti. Addition of F^- ions leads to formation of $[TiF_6]^{2-}$. The $[TiF_6]^{2-}$ species is water soluble, therefore reaction (eq. 1) represents an etching process of the as-formed TiO_2. During the anodization process, the F^- ions are driven to the anode under the electrical field, penetrate the as-formed amorphous TiO_2, and undergo reaction (eq. 1). If all the parameters are within a certain range, the combination of above mentioned processes lead to the formation of independent tube array (Roy et al. 2011). After anodization, a post-annealing treatment converts the amorphous TiO_2 into crystalline structures. The crystal phase can be determined by the annealing temperature.

$$TiO_2 + 4H^+ + 6F^- \rightarrow [TiF_6]^{2-} + 2H_2O \qquad \text{(eq. 1)}$$
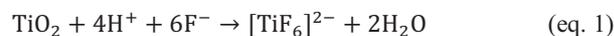
The deposition of noble metal (Ag) onto the TiO_2 nanotube arrays occurs in dark condition. Silver nitrate (Strem, 99.9%) aqueous solution was mixed with 3-Mercaptopropionic acid in a glass vial. Then, 1 M NaOH (Sigma Aldrich, 97%) was added drop by drop into the vial till the mixture returned to clear and then the pH value was adjusted to 9.0. deionized (DI) water was added into the solution till the solution reached 15 mL. One piece of TNAs foil was placed into the vial with the TNA facet facing down. A dose of 5 mL ethylene glycol (Sigma Aldrich, 99%) was added into the vial. The solution was then purged with N_2 gas for 20 minutes. The vial was placed in a Teflon vessel with 25 ml DI water. The Teflon vessel was fixed and sealed into a stainless steel autoclave. The whole system was then heated in a 120 ºC oven for 4 hours. The autoclave was then taken out of the oven and cooled down to room temperature. The sample was washed with DI water, and dried in nitrogen steam. We fabricated samples of different Ag:Au molar ratios: 3:1, 1:1 and 1:3 as shown in Fig. 2.

Au-GSH nanoclusters was deposited onto titanium dioxide fluorine-doped tin oxide (TiO_2-FTO) glass electrodes. The deposition followed a modified in-situ hydrothermal approach. Basically, 0.06g of gold (III) chloride trihydrate (Aldrich, ≥99% trace metal basis) and 0.07g of L-glutathione reduced, was mixed in 75 ml of DI water in a round bottom flask. TiO_2-FTO-glass electrodes were immersed into the solution and the solution was purged with N_2 gas. Then the flask was heated and refluxed at 70 °C for 24 hours. During the entire experiment, the solution kept being bubbled with N_2 gas.
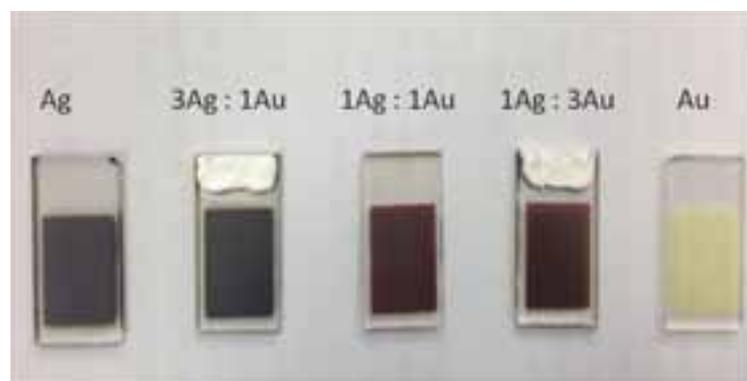

Fig. 2: TiO$_2$-nanoparticle-FTO samples

2.2. Material characterization

The light absorption ability of the sensitizers was examined using UV-Vis spectroscopy, where a small aliquot was taken from the remaining liquid after the in-situ hydrothermal deposition. Characterization of the morphology was carried out using field-emission scanning electron microscopy (FE-SEM) with acceleration voltage of 5.0 kV, and high-resolution transmission electron microscope (HRTEM) at 200 keV. For FE-SEM, the sample was cut into small pieces and attached to an aluminum plate with conductive silicon tapes and then subjected to observation. For HR-TEM, the sample was scratched off from the foil and dispersed onto a copper mesh with the help of ethanol. Elemental composition of the samples was analyzed using energy dispersive X-ray spectroscopy (EDX) equipped on the FE-SEM. The crystalline structure of the samples was scanned using X-ray diffraction (XRD), with Cu Kα radiation, from 2θ of 20° to 80° with steps of 0.02°. The surface energy state and chemical composition was analyzed with X-ray photoelectron spectroscopy (XPS) with Al Kα as the excitation source.

2.3. Photoelectrochemical performance

The photoelectrochemical (PEC) measurements were conducted using the three-electrode cell setup. The sample was assigned as the working electrode. The other two electrodes, the counter electrode and reference electrode, was a platinum plate and a saturated calomel electrode (SCE), respectively. A 2-cm diameter quartz window is located in one wall of the cell and its distance from the working electrode was kept at 2 mm to minimize the light absorption by the electrolyte in the spacing. A redox electrolyte was filled into the cell which was prepared through mixing 0.5M sulfur powders and 0.5 M sodium sulfide solution. The experiment was carried out under exposure to artificial sunlight obtained mounting a neutral density metallic filter and an AM 1.5G filter on a 300-W Xe lamp (Newport). The incident power density at the working electrode was adjusted to approximately 100 mW/cm^2 and was kept the same for every measurements. A potentiostat instrument (Solartron) was used to conduct the measurements and collect the data.

3. Results and discussion

3.1. Material properties

In the SEM and TEM images (Figs. 3 and 4) of samples fabricated show the deposition of nanoparticles onto the TiO_2 nanostructures. The EDX measurements (Table 1) indicate that the nanoparticles are Ag and Au.
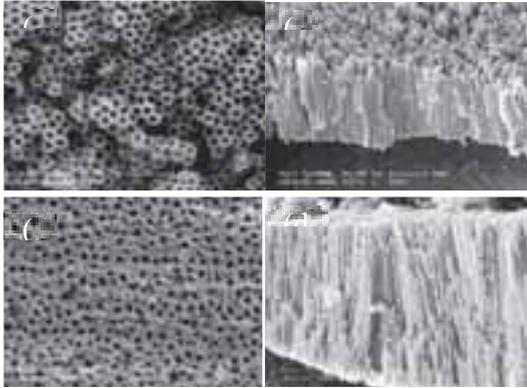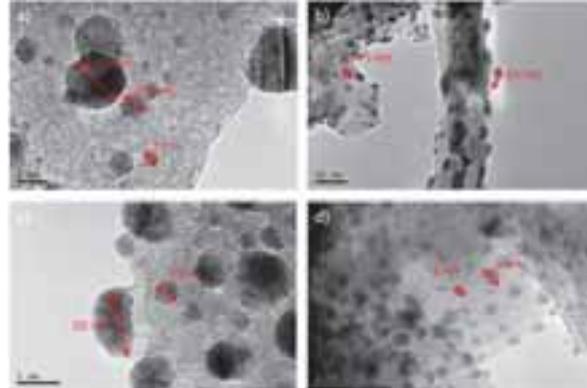

Fig. 3: SEM images of TNAs   **Fig. 4: TEM of TNAs with Ag and Au deposition**

Table 1: Atom percentage from EDX analyses

Element	Sample 1 Ag	Sample 2 3Ag:1Au	Sample 3 1Ag:1Au	Sample 4 1Ag:3Au	Sample 5 Au
O	59.06	51.41	52.18	57.98	61.57
Ti	31.73	29.58	28.19	31.02	31.5
S	1.21	3.86	3.73	1.86	0.48
Ag	2.39	4.45	3.1	0.9	0
C	5.6	7.1	8.59	6.43	5.6
Au	0	1.31	1.13	1.81	0.85

3.2. PEC performance

Figure 5 shows the UV-Vis absorption of the five samples. The Au modification yields better visible-light absorption. The *J-V* curves of the samples are shown in Fig. 6. Ag-MPA sensitized TNAs exhibits the best performance. The short-circuit current density is 1.5 mA/cm^2, which is 38 times greater than that of bare TNAs electrode (0.04 A/cm^2).). On the other hand, the Au Sample 5 is not satisfactory. The sample sensitized by Au-MPA nanoclusters did not show much increase in performance compared to bare TNA. The overall trend shows that Ag-based sensitizers exhibit higher photo-activity than the Au-based counterpart.
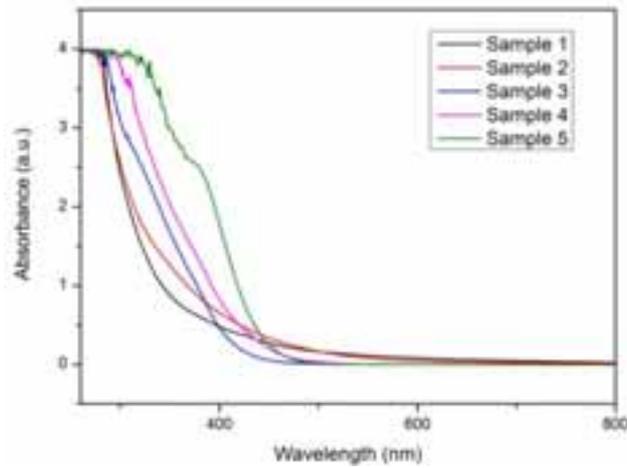
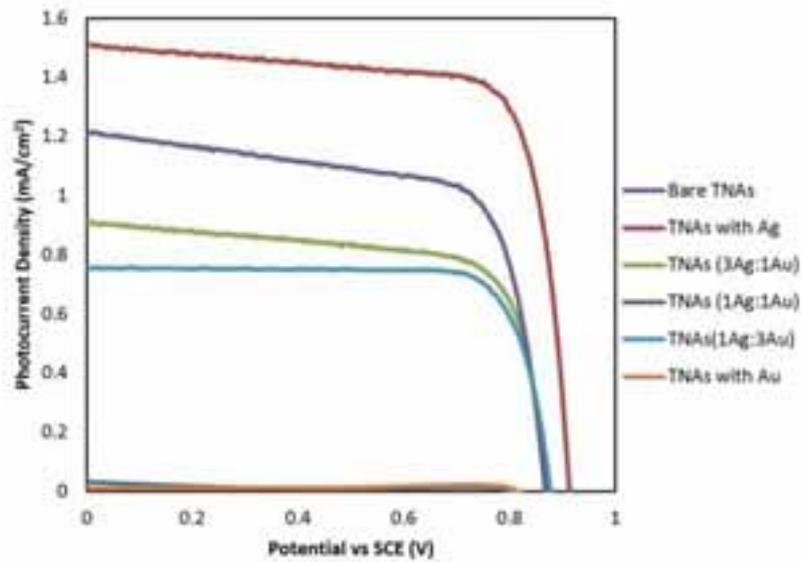**Fig 5: Ultraviolet-Visible spectral absorption**

Fig. 6. PEC performance of samples fabricated

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4. Conclusion

TiO_2 nanotube arrays fabricated by anodization have uniform morphology with pore diameter of ~100 nm and tube length of ~6 μm. After annealing, the TNAs are transformed into Anatase phase with a trace amount of Rutile. MPA capped Ag nanoparticles are deposited onto the surface of TNAs through the in situ-hydrothermal method. The nanoparticle diameter is 6~7 nm. The nanoparticles are classified as nano-clusters. The deposition of the Ag-MPA nanoclusters onto TNA can boost the PEC performance for significant increase in solar conversion efficiency.

5. Acknowledgment

6. References

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