Different methods of introduction gold NPs into Perovskite Solar Cells with their efficiencies

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Abstract. The introduction of gold nanoparticles (Au NPs) into Perovskite Solar Cells doesn’t bring a higher enhancement in efficiency than fullerene like C60 or PCBM (phenyl C61-butyric acid methylester) or graphene introduced into the PSCs which have improved the efficiency more than 15%. In this work, the Au NPs prepared by sol-gel method using Turkevish method have been introduced into PSCs by three different ways and their efficiencies have been investigated for looking for the best method. This adding of the Au NPs is done firstly by doping the TiO$_2$, secondly by depositing Au NPs layer into the TiO$_2$ layer and thirdly by depositing the Au NPs doped TiO$_2$ layer into TiO$_2$ layer. All of them have given some results but still significantly low compared to other materials used. Even though the Au NPs could improve the short-circuit photocurrent density $J_{sc}$, the contact between Au NPs or TiO$_2$ and spiro-OMeTAD may also have decreased the PCE.

1. Introduction

The perovskite deposition can vary from sensitising the TiO$_2$ electron transporting (called mesoporous perovskite solar cells sensitised), to filling the pores (mesoporous perovskite solar cells with capping layer) where it acts as both light absorber and hole transporting material in one[1]. There is also planar-structured without TiO$_2$ mesoporous used. Solar cell architectures which have given the best power conversion efficiency are TiO$_2$-mesoporousperovskite solar cell (mesostructured device) and planar heterojunction perovskite solar cell (planar-structured device). In this paper, only mesoporous perovskite solar cells were discussed. Perovskite solar cells (PSCs) using Perovskite as light absorbers in photovoltaic has been developed more during these decade years starting with one deposition of Perovskite, the lead iodide and methylammonium mixed before deposition with different concentration mixture. The crystallography, the absorption, the diffusion length have investigated minutely[2, 3]. The big growth has been bringing in a sequential deposition with its ease synthesis allows bringing up forward this research[4]. During these last years, the improving of PCE has also reached high efficiency by the knowledge of the proprieties of these materials[5, 6]. But also by introducing different materials [7, 8, 9,10, 11] as P3HT (poly(3-hexylthiophene)), PCBM, fullerene, graphite, or metal nanoparticles[12, 13, 14] for enhancing the PCE, FF, $J_{sc}$ or $V_{oc}$. 
2. Experimental

2.1 Fabrication and Synthesis

The synthesis of Au NPs has been carried out using a citrate reduction method[15]. A 16 ml aqueous solution of 4.5 mg HAuCl₄·3H₂O (hydrogen tetrachloroaurate (III) trihydrate) was brought to boil on a hot plate, and about 0.5ml of 1% w/w trisodium citrate aqueous solution was added. The solution was stirred for 30 min, and finally, a wine red- coloured solution was obtained. The same procedure has been done, with different concentrations of HAuCl₄·3H₂O and different concentrations of trisodium citrate solution. Immediately after Au NPs have been synthesized, the TiO₂ paste (TiO₂ (18NR-T) or (30NR-D) with ethanol w/w 1:3.5) was added to the solution of Au NPs. Also the TiO₂ made with Titanium isopropoxide is used instead of TiO₂ paste (18NR-T) added to the solution of Au NPs.

The synthesis of TiO₂ paste

The synthesis procedure for nano-TiO₂ is as follows: titanium (IV) isopropoxide, nitric acid, ethanol and distilled water mixed under vigorous stirring between half or one hour and at 70 °C. After that, the solution was kept for one day for the ageing process.

Fabrication of Perovskite Solar Cells

Solar cells fabricated on fluorine-doped tin oxide glass substrates with a sheet resistance of 15Ω/square (Pilkington). Chemical etching patterned FTO substrate with Zinc powder and HCl aqueous solution. The conductive substrates cleaned with a detergent solution, de-ionised water and ethanol. A thin dense, compact TiO₂ layer (c-TiO₂) was deposited on the etched FTO substrate by spin coating (3000 rpm, 30s) using a titanium diisopropoxidebis(acetylacetonate) solution in ethanol and HCl at a volumetric ratio of 0.35:5:1 followed by annealing at 500°C. Porous TiO₂ films got by commercially available TiO₂ paste (18-NR-T, Dyesol, average particle size ~ 20 nm) diluted in ethanol (1:3.5 weight ratio) were directly deposited on top of the c-TiO₂ by spin coating at 5000 rpm for 30s and annealed at 500°C. PbI₂ solution is diluted in DMF (dimethylformamide) (462mg/ml) and was kept at 70°C. Thus, the prepared mesoporousTiO₂ films were loaded with PbI₂ for 30s and then spin-coated at 6000 rpm for 30s after that dried 2min and finally annealed at 70°C during 30min. After drying, the films were spin coated at 6000 rpm at 30s after were loaded a solution of CH₃NH₃I in 2-propanol (13mg/ml) for 30s. The HTM (hole-transporting material) was deposited by spin-coating a solution of spiro-MeOTAD, tert-butylypyridine, lithium bis(trifluoromethylsulphonylimide) and tris(2-(1H-pyrazol-1-yl)-4-tert-butylypyridine)cobalt(III) bis(tri-fluoromethylsulphonylimide) in chlorobenzene. Silver (Ag) (66nm) was thermally evaporated on top of the device to form the back contact.

![Figure 1. Schematic view of perovskite solar cell with introducing Au NPs](image)

The same fabrication described above used, only the anode has modified by introducing the Au NPs. Firstly, TiO₂ paste (TiO₂ (18NR-T) with ethanol w/w 1:3.5) was added to solution of Au NPs allowing to get Au NPs doped TiO₂. Secondly the Au NPs layer has been deposited into TiO₂ paste (18NR-T) or (30NR-D). Thirdly, the Au NPs doped TiO₂ layer has been deposited into TiO₂ paste (18NR-T) or (30NR-D).

When the deposition of Au-TiO₂ done at 6000 rpm into the TiO₂; the efficiency became insignificant which could be explained by the increasing of thickness. The Jₑₑ varies between 8 to 10 mA/cm² and 10 to 13mA/cm² for Au NPs doped TiO₂ at 2mM HAuCl₄·3H₂O added 1.2mL citrate and at 1mM HAuCl₄·3H₂O added 2ml citrate respectively.
2.2. Characterization
The photocurrent density –voltage characteristics of the perovskite solar cells were evaluated by a source meter (Keithley 2400) under a solar simulator (Oriel 92250A-1000, Newport, 100 mW cm\(^{-2}\)). The absorption of different films was measured using a UV-visible Spectrophotometer (UV-2450, Shimadzu).

3. RESULTS AND DISCUSSION

3.1. First method

**Figure 2.** J-V curve for a photovoltaic device (FTO/c-TiO\(_2\)/Au-TiO\(_2\)/perov/HTM/Ag)

**Figure 3.** J-V curve for a photovoltaic device (FTO/c-TiO\(_2\)/Au-TiO\(_2\)/perov/HTM/Ag) with Au nanoparticle (Au NPs made with an 18ml aqueous solution and 20mg of HAuCl\(_4\) · 3H\(_2\)O)

The short-circuit photocurrent (J\(_{sc}\)) decreases with increasing the concentration of HAuCl\(_4\) · 3H\(_2\)O with different citrate volume adding due to increasing the thickness of the Au doped TiO\(_2\) or due to increasing the carrier concentration.

3.2. Second method

Absorption

Figure 4 shows the absorption of perovskite; the speed coating used is same for TiO\(_2\) deposition and TiO\(_2\)/Au NPs bilayers, but two ways could explain the increasing of perovskite absorption, the first one is due by increasing the infiltration of PbI\(_2\) by adding the Au NPs layer, Plasmon effect could give the second explanation.

**Figure 4.** Absorbance spectra of perovskite deposited into TiO\(_2\), Au-TiO\(_2\) and TiO\(_2\)/Au
3.2.1. Difference between different adding of citrate

Table 1. Data of J-V characteristic at different volume

| Devices               | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|-----------------------|----------------------|--------------|--------|---------|
| 1mM+2ml citrate       | 14.35                | 0.79         | 60     | 6.8     |
| 1mM+3ml citrate       | 14.79                | 0.8          | 68.8   | 8.2     |

Figure 5. Reverse curve with different volume of citrate

3.2.2. Au NPs synthesised with 45 ml solvent with 11 mg of HAuCl4 3H2O added 3ml of citrate

Table 2. Data of J-V characteristic

| Device                  | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|-------------------------|----------------------|--------------|--------|---------|
| 11mg/45ml HAuCl4+3ml citrate | 16.7                | 0.73         | 64.5   | 7.8     |

Figure 6. Reverse curve of J-V characteristic

The majority of devices have short circuit density ($J_{sc}$) between 10 to 15 mA/cm$^2$ at different citrate solution volume add to solution aqueous of HAuCl$_4$.3H$_2$O at 10ml of3mM HAuCl$_4$.3H$_2$O for improving the distribution of Au NPs on the surface and approaching the Au NPs between them. However increasing the concentration of HAuCl$_4$.3H$_2$O and decreasing the citrate solution volume for getting the big size of Au NPs, the solution became less bright and unstable. Increasing the precursor solvent has allowed improving the short-circuit photocurrent ($J_{sc}$). Therefore this study could be improved by finding the best rate volume between HAuCl$_4$.3H$_2$O and citrate for increasing the size for getting a Plasmon effect allowing the enhancing the PCE.

3.3. Third method

FTO/c-TiO$_2$/m-TiO$_2$/AuNPs-TiO$_2$synthesised /CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Ag.

Au NPs used to dope TiO$_2$ is made with 11mg/45ml HAuCl$_4$.3ml citrate.

Au NPs-TiO$_2$ layer is deposited into mesoporous TiO$_2$ by spin coating at 3000 rpm during 30s.
Table 2. Data of J-V characteristic

| Device           | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF(%) | PCE(%) |
|------------------|----------------------|--------------|--------|--------|
| Forward curve    | 14.55                | 0.63         | 52.5   | 4.8    |

Figure 7. J-V characteristic

The short-circuit photocurrent ($J_{sc}$) has improved with the deposition a layer of Au-TiO$_2$ into TiO$_2$ at 6000 rpm with TiO$_2$ synthesized with Titanium isopropoxide. This layer should be thin for improving the $J_{sc}$.

4. Conclusion

This study about introducing Au Nanoparticles by different ways into PSCs is allowed to improve the $J_{sc}$ that is following the literature. However the enhancement of PCE still low compared to improvement excepted in all of the methods used. At the third method the thickness of the second layer of Au NPs doped TiO$_2$ should be thin for improving the efficiency; therefore the synthesis of Au NPs doped TiO$_2$ should be improved. Perhaps this study could be developed by using different techniques for more enhancements. In all cases the Plasmon effect need more investigations for looking for a best device of PSC using Au NPs.

5. References

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