Improved Efficiency of Perovskite Solar Cell Using Reduced Graphene Oxide Modified SnO$_2$

Xinchen Dai[1], Pramod Koshy[1], Charles Christopher Sorrell[1], Jae Sung Yun[2]
[1]*School of Materials Science and Engineering, UNSW Sydney, Sydney, NSW 2052, Australia*
[2]*Australian Centre for Advanced Photovoltaics (ACAP), School of Photovoltaics and Renewable Energy Engineering, UNSW Sydney, Sydney, NSW 2052, Australia*

Introduction

Tin oxide (SnO$_2$) is widely employed as an electron transport layer (ETL) in perovskite solar cells (PSCs) because of its high electron mobility, excellent optical transmission, deep conduction level, and low-temperature processability. However, the SnO$_2$ fabricated from low-temperature processing suffers from low crystallinity and the resultant ETL layer has a high density of surface defects / trap states, which would reduce the performance of PSC devices and result in significant hysteresis. To enable the development of highly efficient SnO$_2$ ETL in PSCs, it is necessary to passivate the surface trap states and facilitate the electron extraction and transportation in the SnO$_2$. For this purpose, a reduced graphene oxide (RGO)-modified SnO$_2$ (RGO:SnO$_2$) is proposed as a solution with superior electronic properties which can contribute to the development of high-performance PSC devices. Mixing of graphene oxide nanocolloids with tin chloride precursor can allow for the development of the RGO and simultaneously the graphene oxide nanocolloids act as an oxidising agent to oxidise Sn^{2+} to Sn^{4+}.

Results
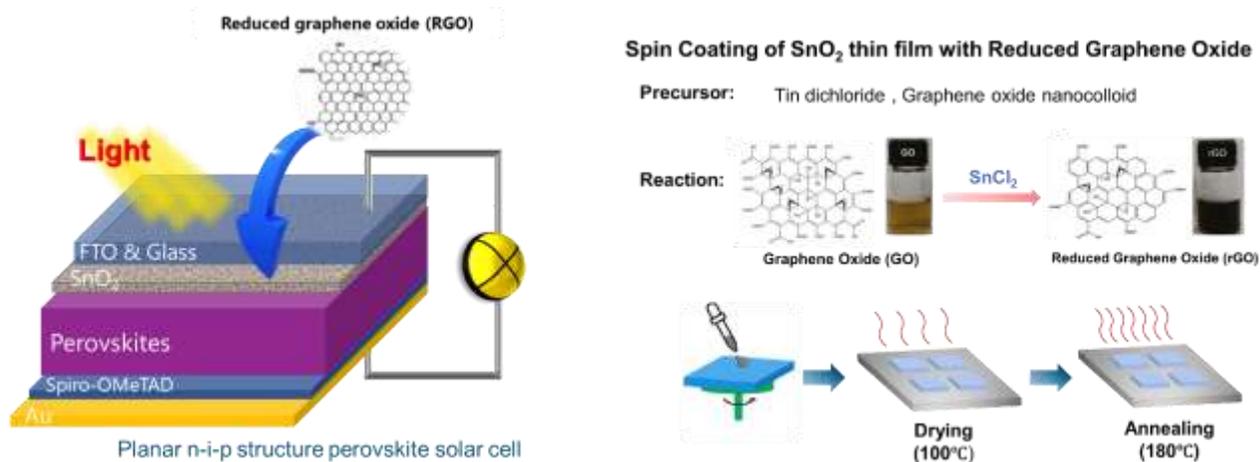
Figure 1. Illustration of our PSC structure and the deposition of reduced graphene oxide-modified SnO$_2$ ETL layer

Several techniques were used to characterise the composite materials including grazing incidence X-ray diffraction (GIXRD), Raman spectroscopy, transmission electron microscopy (TEM) and selective area electron diffraction (SAED), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), UV-Vis spectroscopy, Hall measurement, conductive atomic force microscopy (c-AFM), I-V and J-V analysis, incident photon-to-current efficiency (IPCE) spectra, steady-state photoluminescence (PL), time-resolved photoluminescence (TRPL), and electrochemical impedance spectroscopy (EIS).

RGO:SnO_2 thin film was fabricated via spin coating. For this purpose, graphene oxide nanocolloids dispersion was mixed with tin chloride ($SnCl_2$) precursor in ethanol followed by stirring at room temperature; this results in the reduction of the graphene oxide to form reduced graphene oxide. The successful reduction of GO to RGO was observed in terms of the change in colour from deep brown to dark in a few minutes. XPS and Raman spectra also confirmed the formation of RGO. Further, there was expectedly a higher amount of Sn^{4+} in the film after the RGO doping. This precursor was then deposited on the fluorine-doped tin oxide (FTO) substrate by spin coating followed by drying at 100°C for 1 h and subsequent annealing at 180°C for 1 h.

The successful mixing of RGO with SnO_2 was confirmed by XPS. The XRD results showed a nanocrystalline of SnO_2 film with RGO, and this was confirmed by TEM and selective area electron diffraction (SAED). The film showed good optical transparency and a large bandgap as determined using UV-Vis spectroscopy. SEM analysis showed smooth coverage on the substrate without pinholes and uniform morphology; the EDX data also revealed uniform dispersion of RGO in the SnO_2 ETL layer. The film thickness was ~45 nm as determined via FIB and AFM. The effects of RGO:SnO_2 on the morphology and topography of perovskite layer were also investigated. The surface roughness of the perovskite film became smoother due to the hydrophilicity of the graphene while the crystal size showed negligible change.

A large improvement in the efficiency of electron extraction and transportation was observed while attenuated charge recombination is achieved. The energy levels were determined from the data from UPS and UV-Vis spectroscopy and further calculations. RGO contributed to a lower HOMO level and higher Fermi level of the SnO_2 film. The I-V characterization of the ETL-only device showed that the RGO:SnO_2 film has better conductivity than the pristine SnO_2 film. The c-AFM also confirmed a larger increment of conductivity after RGO doping. Enhanced electron mobility was confirmed by dark-IV. PL spectra showed a larger PL quenching in RGO:SnO_2 ETL while its TRPL showed a faster PL decay, indicating more efficient electron extraction and transportation of the RGO-based devices. EIS measurements showed that a small volume of RGO contributed to decreased series resistance (R_s) and larger recombination resistance (R_{rec}) in the PSCs compared to those undoped.

To study the performance and repeatability of the devices, multiple devices were fabricated. These shows a better average power conversion efficiency (PCE) with reduced hysteresis of RGO-based PSCs compared to those of the control devices. IPCE results showed a variation between the doped and undoped devices in J_{sc}, which corresponded with the results of J-V curves. The stability of the devices was also investigated.

Conclusions

The introduction of RGO in the SnO_2 layer is a facile way to passivate the surface defects and enhance the performance of PSCs. The enhanced performance was attributed to the excellent electronic properties of RGO and the high oxidation state of Sn due to the rection between RGO and $SnCl_2$. Although the kinetics were not fully discussed, the successful employment of RGO in SnO_2 can pave the way for the utilization of RGO to boost the performance of PSCs.