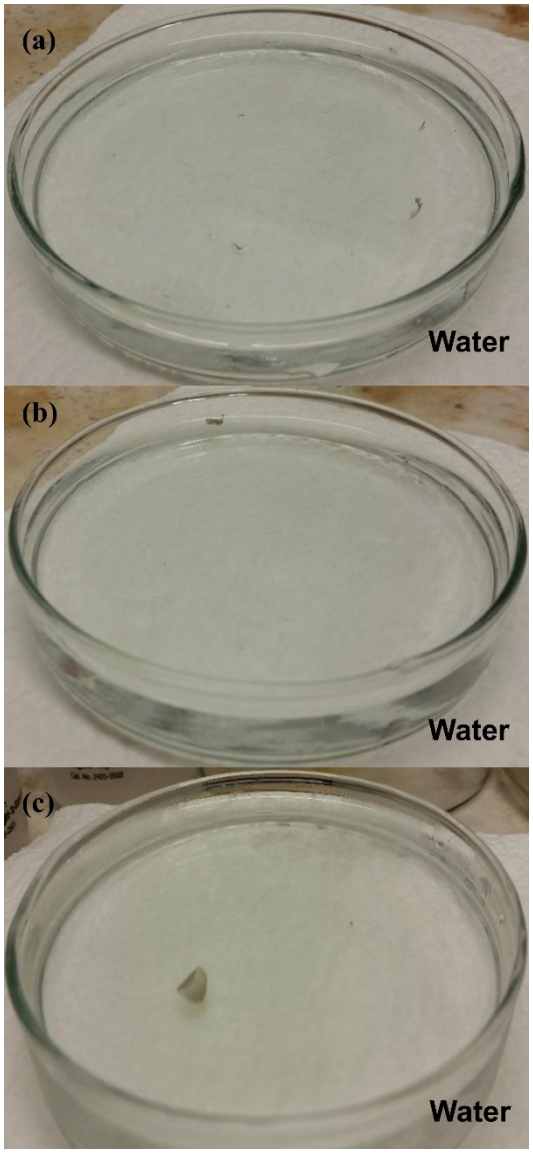
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Application of a hole transporting organic interlayer in graphene oxide/single walled carbon nanotube-silicon heterojunction solar cells

LePing Yu, Munkhbayar Batmunkh, Tom Grace, Mahnaz Dadkhah, Cameron Shearer, and Joseph Shapter*

Centre for Nanoscale Science and Technology, School of Chemical and Physical Sciences, Flinders University, Bedford Park, South Australia 5042 (Australia)



*E-mail: joe.shapter@flinders.edu.au

Fig. S1: (a) Pure CNT films broken into pieces and (b) shrunk after transfer from acetone to deionized water and (c) GOCNT films which is pressed down into water phase.

Fig. S1 (a) shows a pure CNT film broken into small pieces once it comes into contact with deionized water from acetone and Fig. S1 (b) shows a pure CNT film crumpling upon itself after the transfer from acetone to deionized water. These two figures indicate a poor compatibility of pure CNT film with

deionized water due to its highly hydrophobic nature. Fig. S1 (c) shows that a GOCNT film can move into the water phase after being pressed down from the surface of the deionized water, which is evidence of the improved wettability and mechanical properties provided by the addition of GO into CNT film.

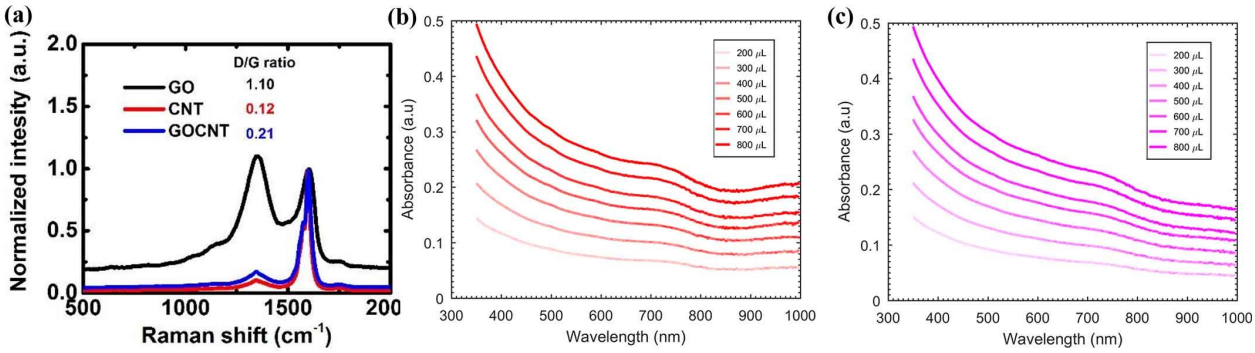


Fig. S2: (a) The Raman spectrum of pure GO, CNT and GOCNT films. (b,c) UV-Vis spectra of (b) GOCNT films and (c) GOCNT/$AuCl_3$ films created with varying volume of GOCNT suspension.

Fig. S2 shows the Raman intensity versus wavenumber for pure GO, pure CNT and GOCNT films before $AuCl_3$ doping. D/G ratio has been estimated for each of these films. Pure GO film has the highest value while pure CNT film has the lowest value. The value of GOCNT electrode (0.21) indicates the successful fabrication of a hybrid electrode by vacuum filtration.

Equation S1: $T = 92.64 - 0.052V$ (R^2 = 0.98)

Equation S1 is the linear fit between the T of GOCNT films at 550 nm and the volume of stock suspension used in vacuum filtration.

Equation S2: $R_{Sheet} = 4.82 \times 10^{-1}\, e^{\frac{T}{10.59}} + 99.67$ (R^2 = 0.92)

Equation S3: $R_{Sheet} = 7.49 \times 10^{-4}\, e^{\frac{T}{6.09}} + 136.8$ (R^2 = 0.99)

Equation S2 and Equation S3 are the exponential fits between the R_{Sheet} and T of the original and $AuCl_3$ doped GOCNT films respectively.

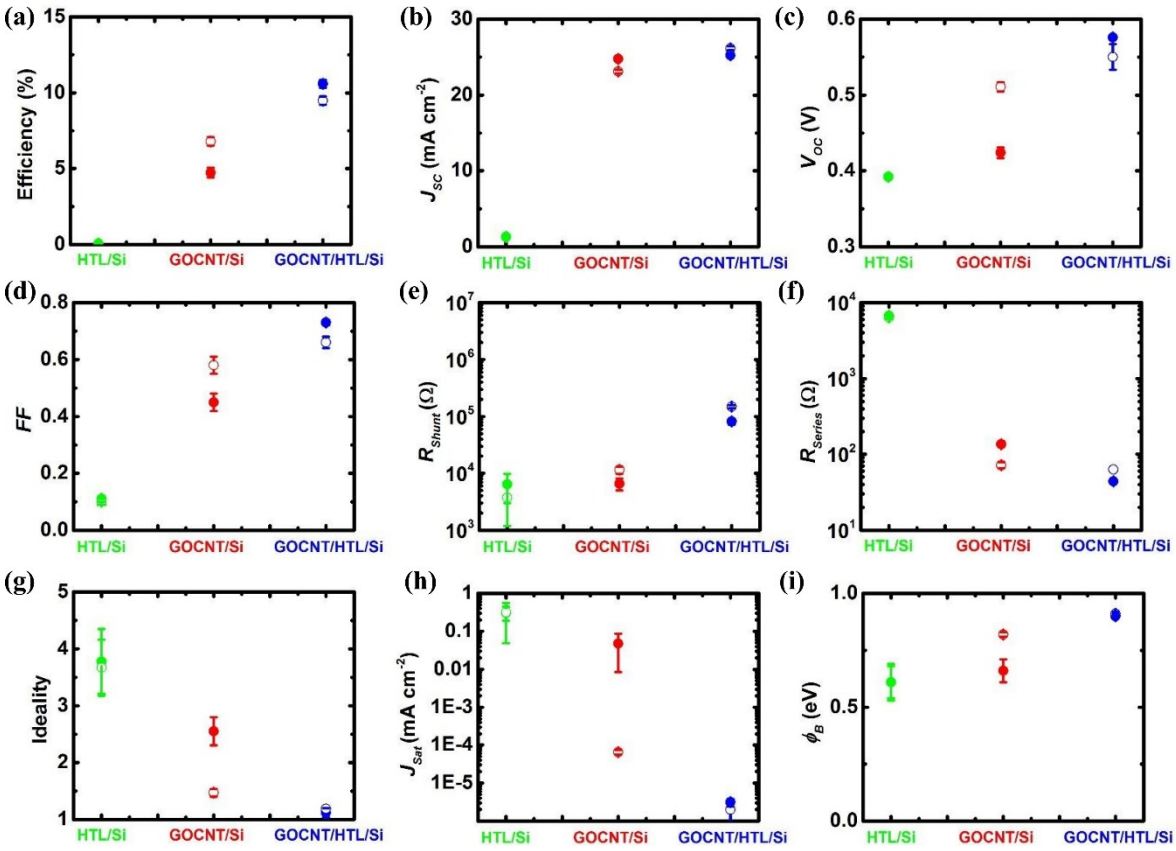


Fig. S3: The details of light and dark curves of spiro-OMeTAD/Si, GOCNT/Si and GOCNT/spiro-OMeTAD/Si devices, (a) Efficiency, (b) J_{SC}, (c) V_{OC}, (d) FF, (e) R_{Shunt}, (f) R_{Series}, (g) ideality, (h) J_{Sat} and (i) ϕ_B before (hollow points) and after (solid points) $AuCl_3$ doping. In the devices in this figure, the T of GOCNT films is 77 % before $AuCl_3$ and the thickness of spiro-OMeTAD layers is 90 nm. HTL stands for spiro-OMeTAD.

Fig. S3 compares the performance of three type of solar cells (spiro-OMeTAD/Si, GOCNT/Si and GOCNT/spiro-OMeTAD/Si), including the details of the *J-V* curves in light and dark conditions before and after $AuCl_3$ doping. Among these three, GOCNT/spiro-OMeTAD/Si devices have the best performance while the spiro-OMeTAD/Si devices have the poorest performance before and after $AuCl_3$ doping. $AuCl_3$ doping does not improve the performance of the spiro-OMeTAD/Si devices. After $AuCl_3$ doping, Au nanoparticles can cause shorts between GOCNT films and Si surface in GOCNT/Si devices which leads to a worse performance. $AuCl_3$ doping reduces the R_{Sheet} and thus improves the performance of GOCNT/spiro-OMeTAD/Si devices. The role of the GOCNT film is to collect and transport the separated charge carriers swiftly. The spiro-OMeTAD interlayer plays two main roles in these devices. It is working as a HTL and protects the Si surface from contact with the Au nanoparticles as well.

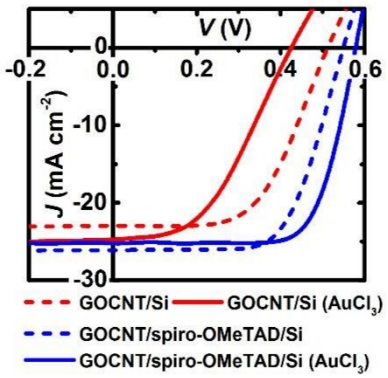


Fig. S4: J-V curves of GOCNT/Si and GOCNT/spiro-OMeTAD/Si before and after $AuCl_3$ doping under light condition. Short dash and solid curves show the performance of the devices before and after $AuCl_3$ doping respectively.

Fig. S4 shows the influence of the $AuCl_3$ doping on the performance of GOCNT/Si and GOCNT/spiro-OMeTAD/Si devices. Due to the shorts caused by Au nanoparticles connecting between GOCNT top electrode and Si surface through the heterojunction, GOCNT/Si device has a decreased V_{OC} and *FF*. On the contrary, the organic interlayer acts as a protection layer which eliminates the shorts but improves the conductivity of the GOCNT films. As a result, the performance of GOCNT/spiro-OMeTAD/Si device is improved.

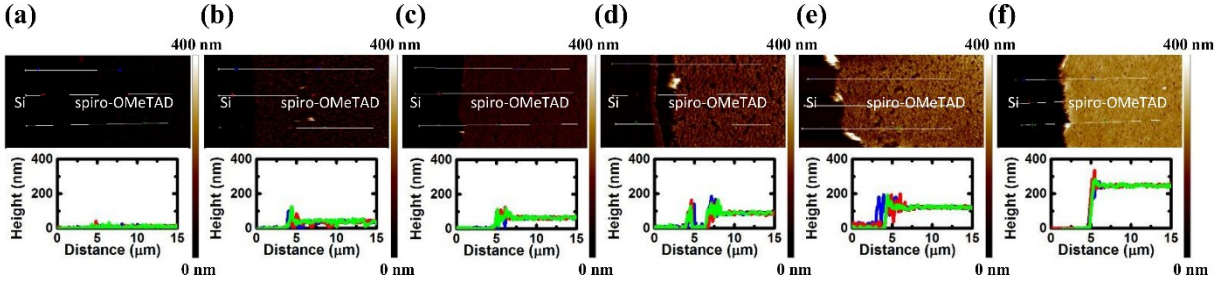


Fig. S5: AFM height images of spiro-OMeTAD films deposited on Si with different volumes of stock solution (a) 2.5 µL, (b) 10 µL, (c) 20 µL, (d) 30 µL, (e) 40 µL and (f) 80 µL.

Fig. S5 shows the AFM height images of spiro-OMeTAD layers on Si surface. The thickness of these layers is determined by scratching the organic layer and measuring the distance between the Si surface and the top of the interlayer. The estimated values for films deposited by 2.5, 10, 20, 30, 40 and 80 µL stock solution are 10, 40, 60, 90, 120, and 240 nm.

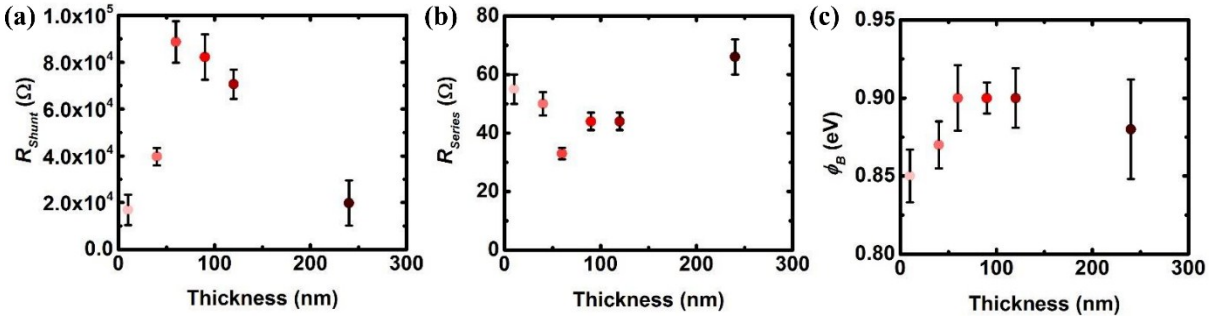


Fig. S6: The performance of $AuCl_3$ doped GOCNT/spiro-OMeTAD/Si as a function of the thickness of the spiro-OMeTAD layer applied on the Si surface (a) R_{Shunt}, (b) R_{Series} and (c) ϕ_B. The devices in this figure are made of GOCNT films with T of 77 % (measured before $AuCl_3$) with spiro-OMeTAD layers of thicknesses ranging from 10 to 240 nm.

Fig. S6 shows the performance details of devices with interlayers of various thicknesses in terms of R_{Shunt}, R_{Series}, and ϕ_B. Devices with an interlayer thickness of 60 nm have the highest R_{Shunt} and lowest R_{Series}, which is line with their highest *FF*. However, due to the large error bars in Fig. S6 (c), it is difficult

to observe a clear trend but devices with interlayer thickness of 60, 90 and 120 nm seem to be the best ones.

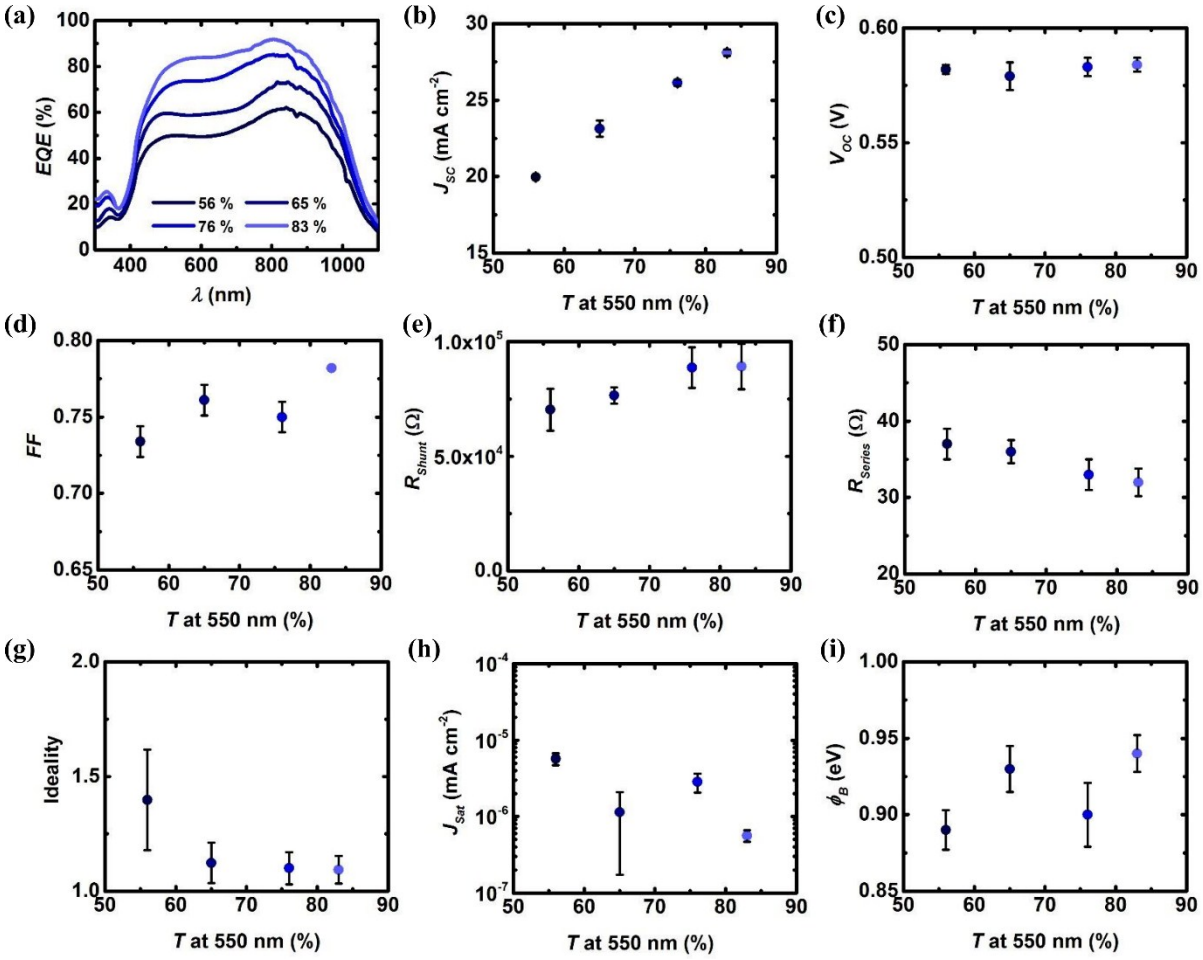


Fig. S7: Performance details of the $AuCl_3$ doped GOCNT/spiro-OMeTAD/Si devices with different GOCNT T (a) EQE (The estimated J_{SC} values of the devices with the GOCNT T of 56 %, 65 %, 76 % and 83 % are 20.68 mA cm^{-2}, 24.58 mA cm^{-2}, 27.18 mA cm^{-2} and 30.17 mA cm^{-2}), (b) J_{SC}, (c) V_{OC}, (d) FF, (e) R_{Shunt}, (f) R_{Series}, (g) Ideality, (h) J_{Sat} and (i) ϕ_B. The thickness of the spiro-OMeTAD in these devices is kept at 60 nm.

Fig. S7 shows the influence of *T* of GOCNT films on the performance of GOCNT/spiro-OMeTAD/Si solar cells with the thickness of spiro-OMeTAD interlayer fixed at 60 nm. The most significant influence of changing the *T* is observed in the change in the photocurrent. The photocurrent increases as the *T* increases, as shown in Fig. S7 (a) and (b). Meantime, all the other factors maintain relatively stable, as shown in Fig. S7 (c)-(i).

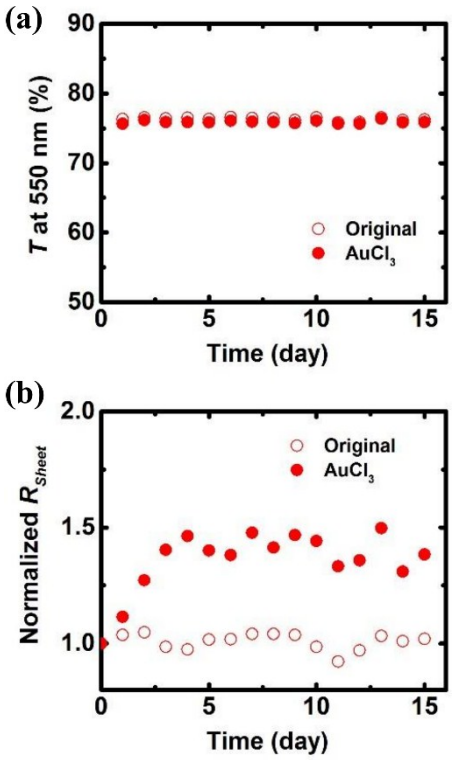


Fig. S8: Degradation of the performance (a) T and (b) R_{Sheet} of the GOCNT films. The hollow and solid data points are used to characterize the properties of the devices or films with and without $AuCl_3$ doping.

Fig. S8 shows the stability of the GOCNT films with and without $AuCl_3$ doping over 15 days in terms of T and R_{Sheet}. T is very stable while the normalized R_{Sheet} of GOCNT films with $AuCl_3$ increases from 1 to 1.5, which is a result of dedoping.