Supporting Information

Realizing the Ultimate Goal of Fully Solution-processed Organic Solar Cells: A Compatible Self-sintering Method to Achieve Silver Back Electrode

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Ag NPs are synthesized using a fast AgNO₃ thermal reduction method and the reaction finishes in 10 minutes (details in experimental section).¹ X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the crystal structure and morphology of the synthesized nanoparticles. As shown in Figure S1a in supporting information, four broad peaks sited at $2\theta = 38.1^{\circ}$, 44.3° , 64.4° and 77.5° have been captured. These peaks can be well indexed to cubic Ag (JCPDS#04-0783) with a space group of Fm-3m (225), which suggests the synthesized product is highly pure. Compared to the XRD pattern of bulk silver, the peaks in Figure S1a show a broadening which can be ascribed to the small size of the product. The TEM image confirms that the Ag nanoparticles have a diameter around 6-10 nm (Figure S1b, supporting information). The corresponding selected area electron diffraction (SAED) exhibits four bright circles which can be assigned to (111), (200), (220) and (311) planes of cubic silver. In summary, the synthesized product is pure cubic silver nanoparticles with a diameter around 6-10 nm.



Figure S1. (a) XRD pattern and (b) TEM image of the synthesized Ag nanoparticles. The inset in (b) showing the corresponding SAED image.



Figure S2. AFM images of (a) pristine Ag electrode (without treatment) and (b) its corresponding surface height histogram figure.



Figure S3. XPS survey spectrum of Ag electrode in pristine and sintered states.



Figure S4. Atom ratio of different elements of pristine and sintered electrodes.



Figure S5. Extended high-resolution core-level N 1s XPS spectra of the electrodes in pristine and sintered states.



Figure S6. Core-level (a) C 1s and (b) O1s XPS spectra of the electrodes in pristine and sintered state.



Figure S7. The magnified cross-sectional SEM image of the fully solution processed device. A boundary is well defined between the Ag NPs electrode and carrier transport layer.



Figure S8. The equivalent circuit for EIS analysis and the corresponding fitted results.



Figure S9. The comparison of power conversion efficiencies between this work and other reported devices with a directly solution processed silver back electrode using P3HT:PCBM as active layer.

Solvent	Relative polarity*	Sheet resistance (Ω /sq)	_
Methanol	0.762	1.78	_
Ethanol	0.654	0.91	
1-butabol	0.586	1.38	
Isopropanol	0.546	1.57	
DMF	0.386	4.49	
Ethyl acetate	0.228	2	
Anisole	0.198	1.7	

Table S1. Relative polarity and sheet resistance table for different solvents.

The sheet resistance is the average value of 5 different pieces. *Steve Murov. (2010, April 10). *Solvent polarity table*. Retrieved from <u>https://sites.google.com/site/miller00828/in/solvent-polarity-table</u>

	Pristine	Sintered
Ag (0)	91.4%	96.5%
Ag-N	8.6%	3.5%

 Table S2. The ratio of Ag in different chemical state.

	Sintering method	Jsc/mA cm ⁻²	Voc/V	FF/%	PCE/%
Ref 1 ²	UV curing followed by 150°C 2 min annealing	10.9	0.585	41.4	2.65
Ref 2 ³	Thermal annealing 120 °C 20 min	8.39	0.51	45.45	1.96
Ref 3 ⁴	Thermal annealing 130 °C 20 min	8.7	0.561	58.1	2.8
Ref 4 ⁵	Not available	7.05	0.56	47.5	1.9
Ref 5 ⁶	Thermal annealing 140 °C 2 min	9.21	0.61	51.36	2.89
Ref 6 ⁷	Thermal annealing 130 °C 30 min	7.93	0.539	59.6	2.6
Ref 7 ⁸	Thermal annealing 120-140 °C 3 min	7.52	0.564	59.3	2.50
Ref 89	Thermal annealing 140 °C 5 min	9.30	0.52	53.13	2.58
Ref 9 ¹⁰	Thermal annealing 130 °C 10 min	8.60	0.524	57.9	2.80
Ref 10 ¹¹	Thermal annealing 150 °C 10 min	7.90	0.60	54.3	2.58
This work	Chemical sintering	8.36	0.59	60.5	2.98

Table S3. Comparison of PCE between this work and other reported devices with a directlysolution-processed silver back electrode (P3HT:PCBM as active layer).

Table S4. Photovoltaic performance parameters of the PBDB-T:IT-M based devices with a solution processed or evaporated electrode (the average values with error range for 10 individual devices in the brackets).

	Jsc (mA/cm ²)	Voc (V)	FF	PCE (%)
Solution process	17.17	0.87	0.65	9.73 (9.42 ± 0.24)
Evaporation	16.55	0.90	0.68	10.19 (9.87 ± 0.20)

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