Supplementary Information

Detailed Methods

Corning 1737 display grade glass was solvent cleaned and blown dry with a particle-filtered N_2 stream. A thin (2.0 nm) Ge film was evaporated from a W boat under 5 x10^{-7} Torr vacuum at a rate of 0.01 nm/s. The Ge film serves as an adhesion layer for and reduces the roughness of the subsequent Ag film (38 nm, 0.05 nm/s) deposited from a Mo boat without breaking vacuum.[1] The films are annealed overnight under flowing Ar at 450°C (2°C deg/min ramp rates, 30 min soak). After fully cooling, the samples are promptly transferred to the 60°C sample stage of an ALD tool (Savannah 200, Cambridge Nanotech). Metal oxides (Al_2O_3, ZnO or TiO_2) were deposited by dosing trimethyl aluminum (TMA), diethyl zinc (DEZ), or titanium isopropoxide (TTIP), respectively, alternately with water. The (metal precursor)-(N_2 purge)-(H_2O)-(N_2 purge) timings were x-60-0.015-60 where x = 0.015 s for DEZ and TMA or 0.15 s for TTIP. Two cycles of Al_2O_3 were first deposited to improve adhesion and promote oxide nucleation. Subsequently, 4 nm of ZnO was deposited to further protect the Ag film before ramping the temperature up to 140°C for ZnO and finally 225°C for TiO_2. The remainder of each film thickness was deposited at these higher temperatures with purge times reduced to 20 s for ZnO or 7 s for TiO_2. After cooling back to 80°C the samples were removed, transferred to a quartz tube furnace and annealed overnight under flowing O_2 at 400°C (2°C deg/min ramp rates, 10 min soak). Both the Ag and metal oxide film quality and thickness were monitored by ex-situ variable angle spectroscopic ellipsometry (VASE) throughout the fabrication procedure. It should be noted that the

entire photoelectrode fabrication is a careful balance between preserving the ultra-smooth Ag film and sufficiently oxidizing the overlying metal oxide for efficient DSSC operation. Once optimized, batch yields greater than 80% were found to be of device quality pinhole free. Finally, each sample was soaked in an ethanoic solution of 0.5 mM $(Bu_4N)_2$[Ru(4-(COOH),4′-(COO)-2,2′-bipyridine)$_2$(NCS)$_2$] ("N719", Dyesol, B2 dye) for 30 min (ZnO) or 2.5 hours (bilayer ZnO/TiO_2) and rinsed with dry acetonitrile before the devices were assembled according to established methods.[2] Briefly, a 25 μm Surlyn spacer (Solaronix SX1170-25) was sandwiched between the photoelectrode and a platinized fluorine doped tin oxide (FTO) dark electrode. A 0.07 cm^2 active area was defined by a spacer, which softens at 80°C to seal the device. Planar control devices without cavity mode enhancement were constructed on FTO without Ge or Ag layers. Nanoparticle control devices were constructed on FTO by doctor-blading a transparent and opaque nanoparticle paste and firing to 500°C under flowing O_2. The total nanoparticle film thickness was ~8 um.

A solution of 0.6 M butylmethylimidizolium iodide (TCI America), 0.1 M lithium iodide, 0.03 M I_2, and 0.25 M tert-butylpyridine in acetonitrile was introduced into the cell via vacuum backfilling through a hole in the platinized FTO electrode. A second Surlyn spacer and microscope coverslip were sealed over the hole with a soldering iron. All chemicals were used as received from Sigma-Aldrich unless otherwise specified.

Normal incidence illumination for spectral response experiments was achieved with an IPCE measurement kit (Newport) that consists of an excitation monochromator coupled to a 300W Xe lamp with AM1.5 filter and calibrated with a Si photodiode. IPCE and broadband (I_{int} = 83 mW/cm^2) normal incidence J-V data were measured with a

potentiostat (Metrohm, Autolab III) in a two-electrode configuration. Reflectivity measurements were conducted by prism-coupling the 543 nm line of a HeNe laser into the device, which was mounted on a computer controlled rotation stage, with a Si photodiode and lock-in amplifier used for detection.

The light harvesting efficiency (LHE) of dyed photoelectrodes was derived from the subtraction of absorption spectra acquired before and after dye removal (with 0.1 M KOH in H_2O) on a UV-Vis-NIR spectrophotometer (Varian Cary 5000).

Light Harvesting Efficiency and Spectral Response

The light harvesting efficiency (LHE) of N719 on planar photoanodes is less than 1%, Figure SI-2. When light is normally incident upon control devices with TCO anode (no Ag) IPCEs are similar to the LHE. The Ag anode in cavity mode enhanced DSSC acts as a broadband neutral density filter resulting in lower IPCEs under normal incidence. The shape of each spectrum is characteristic of the Ru-based dye (N719).

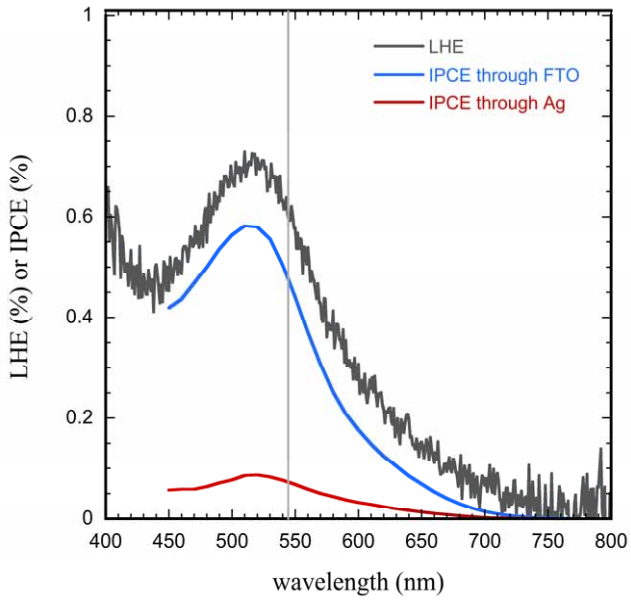

Figure SI-1: The light harvesting efficiency of N719 on planar photoanodes (gray) is compared to IPCE spectra of a control device without Ag (blue) and cavity mode enhanced DSSC (red) at normal incidence. The HeNe wavelength used for resonance measurements (λ = 543 nm) is highlighted for reference.

J-V Fitting

Dark currents were rigorously fit according to the diode equation that also includes a small capacitive offset current to account for the non-origin crossing that is treated equivalently to a photocurrent in the dark.

$$J = Offset_{cap} - J_{sat}(e^{q(V+JAR_s)/mkT} - 1) + \frac{V + JAR_s}{R_{sh}}$$

The dark parameters were fixed when fitting the photocurrent, only the photogenerated current, J_{photo} was fit. Table SI-1 summaries the fit parameters used in the fits plotted below as Fig. SI-2.

Table SI-1

	J_{sat}	R_{shunt}	R_{series}	m (ideality)	$Offset_{cap}$	J_{photo}
Units	mA cm^{-2}	kOhm cm^2	kOhm	unitless	mA cm^{-2}	mA cm^{-2}
Nanoparticle	9E-7	13000	0.009	1.81	5E-5	3.6
Planar	11.7E-14	760	0.036	1.35	6.5E-4	0.4

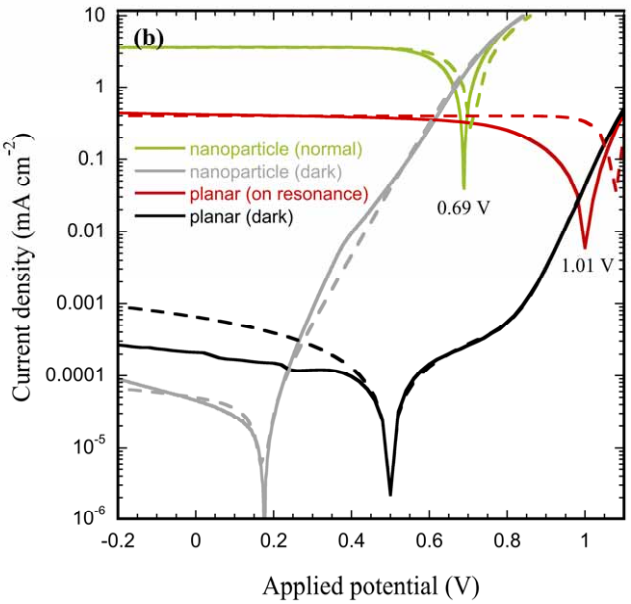

Figure SI-2: Current density vs. applied voltage in the dark and light for planar (black and red) and nanoparticle (gray and green) DSSC. Best fits to the diode equation are shown as dashed lines.

References

(1) Vj, L.; Kobayashi, N. P.; Islam, M. S.; Wu, W.; Chaturvedi, P.; Fang, N. X.; Wang, S. Y.; Williams, R. S. *Nano Lett.* **2009**, *9*, 178.

(2) Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Bessho, T.; Gratzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835.