Flexible dye-sensitized solar cells containing multiple dyes in discrete layers

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DSC assembly and characterization

1. Cell fabrication: The dye sensitized working electrode on the ITO-PEN substrate was sandwiched with a Pt-sputtered ITO-PEN counter electrode. A 25 μm thick surlyn (DuPont) was used as a spacer. The electrolyte, comprising of 0.4 M LiI, 0.4 M tetrabutylammonium iodide, 0.04 M I_2, 0.3 M *N*-methylbenzimidazole in a mixture of acetonitrile and 3-methoxypropionitrile (1:1, by volume) was injected into the devices. Then the cell was put into a jig with screws to tighten the device avoiding leakage of electrolyte during testing.

2. Characterization: I-V curves of the DSCs were obtained by using a Keithley 2400 Source Meter under illumination of simulated sunlight (100 mW/cm^2) provided by an Oriel solar simulator with an AM1.5 filter. A black metal with a circle aperture (4.5 mm in diameter) was placed on top of the device during photovoltaic testing. IPCE spectra were recorded on a Keithley 2400 Source Meter under the irradiation of a 300 W xenon lamp with an Oriel Cornerstone™ 260 1/4 m monochromator. The electrochemical impedance spectroscopy (EIS) measurements of the DSCs were recorded on a potentiostat (BioLogic VSP) with a frequency range of 0.05 – 10^5 Hz. The magnitude of the alternative signal was 10 mV. The EIS measurements were carried out under AM 1.5 solar radiation with a voltage bias of V_{oc}.

Stamping Process

In the stamping process, there are three different adhesions: TiO_2 layer with ITO, TiO_2 layer with TiO_2 layer and TiO_2 layer with PEN. The TiO_2 layer with TiO_2 layer has the strongest adhesion, the high pressure applied during stamping would induce strong connections between the TiO_2 particles to facilitate electron transportation. Similarly, the TiO_2 nanoparticles would also form strong connections with the ITO particles. However, the TiO_2 nanoparticles cannot form an effective connection with the PEN. Therefore, the TiO_2 layer on the PEN was transferred to the TiO_2 layer on the ITO. The different adhesion properties may be due to the different surface free energy. The TiO_2 and ITO layers are composed of metal oxide nanoparticles, which have a high surface free energy, ~89 dynes/cm. While the PEN substrate has a relatively low surface free energy (~44 dynes/cm. *Note: the well known non-stick polytetrafluoroethylene (TEFLON) coating has a surface free energy of ~20 dynes/cm*). The higher surface free energy would help the adhesion.

The surface roughness also attributes to the different adhesion properties. The surface of the ITO layer (as shown in Fig. S1) and TiO_2 layer are much rougher than that of PEN, due to their nanoparticulate structure. The increased roughness means a higher contact surface area and a larger number of connections at the interface. Actually, other plastic materials, such as a plastic bag (PE/PA, with a surface free energy ~44 dynes/cm), can also be used to create a weak bonding with the TiO_2 film for the stamping process.

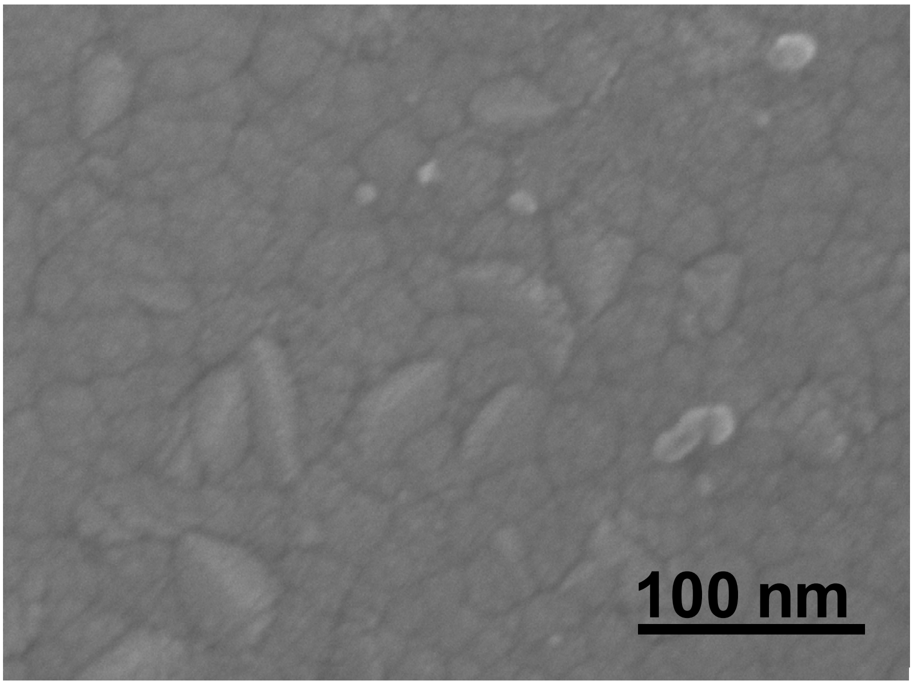

Figure S1 SEM image of the surface of ITO-PEN substrate.

Table S1. The photovoltaic characteristics of two DSC cells. The NN-Stamping sample contained an electrode composed of two layers of N719 sensitized TiO_2 formed via the stamping process. The NN sample contained a single layered N719 sensitized TiO_2 film of similar total thickness to that in the NN-Stamping sample.

Sample name	V_{oc} (mV)	J_{sc} (mA/cm^2)	Fill Factor	PCE (%)
NN-Stamping	748	10.55	0.68	5.36
NN	757	11.17	0.65	5.44

Table S2. Dye loading for the electrodes of N719, GD3, NG-Stamping, and NG-Cocktail.

	N719 (x 10^{-8} mol/cm^2)	GD3 (x 10^{-8} mol/cm^2)
N719	3.65	-
GD3	-	7.03
NG-Stamping	3.57	6.23
NG-Cocktail	4.69	3.91

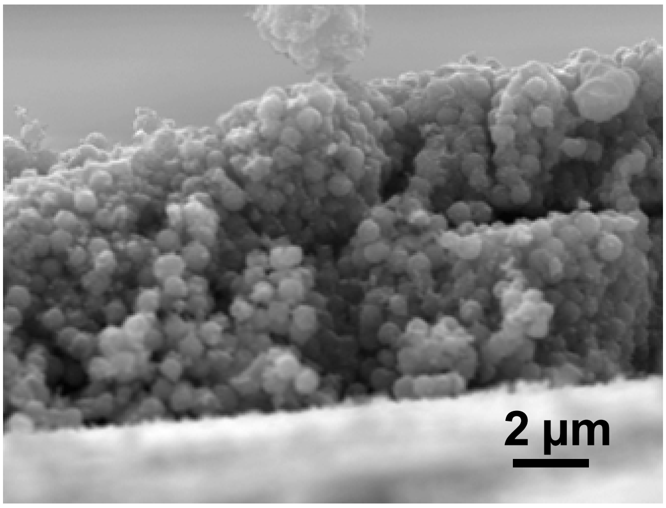

Figure S2 Cross-section SEM image of a stamped two-layer electrode.

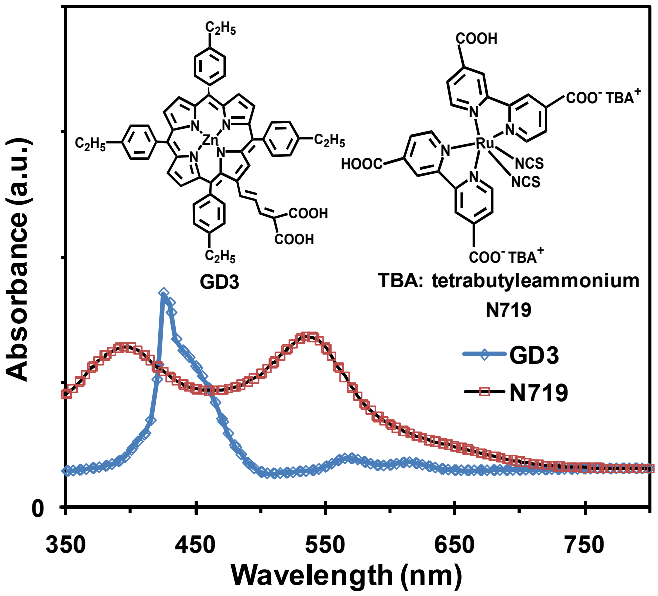

Figure S3 UV-Vis absorption spectra of GD3 and N719 dye solutions.

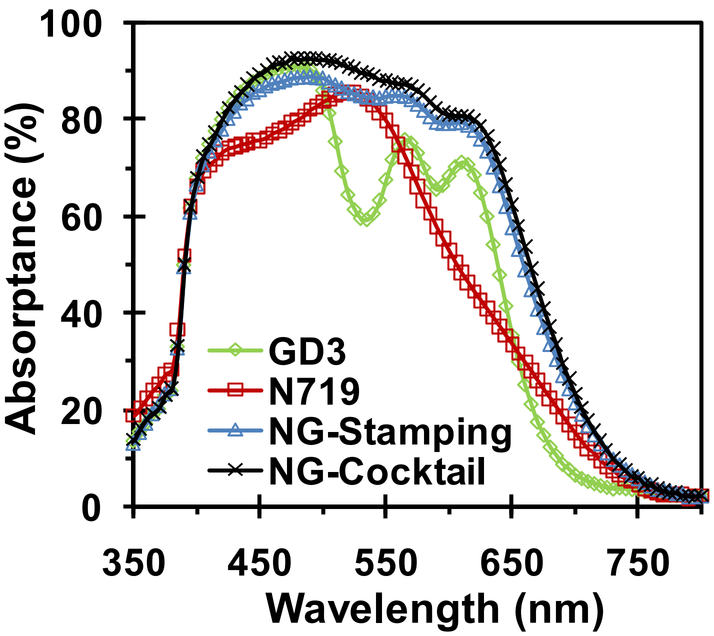

Figure S4 UV-Vis absorption spectra of the dye sensitized GD3, N719, NG-Stamping, and NG-Cocktail electrodes.

Note: The spectra were calculated from the following equation:

$$A(\lambda) = 1 - R(\lambda) - T(\lambda) \qquad \text{(S1)}$$

Here λ is the wavelength, $A(\lambda)$ is the absorptance (fraction of light absorbed by a sample at a specified wavelength), $R(\lambda)$ is the diffuse reflectance (the fraction of incident radiation scattered and reflected by a surface at a specified wavelength), $T(\lambda)$ is the diffuse transmittance (the fraction of incident light at a specified wavelength that passes through a sample). First, the diffuse reflectance and transmittance spectra of the films were measured on a Cary 5000 UV-Vis-NIR spectrophotometer via integrating sphere (Internal DRA-2500). Then the absorption spectra were calculated from equation S1. Finally, the absorption spectra were corrected by subtraction of the absorbance of the ITO-PEN substrate.

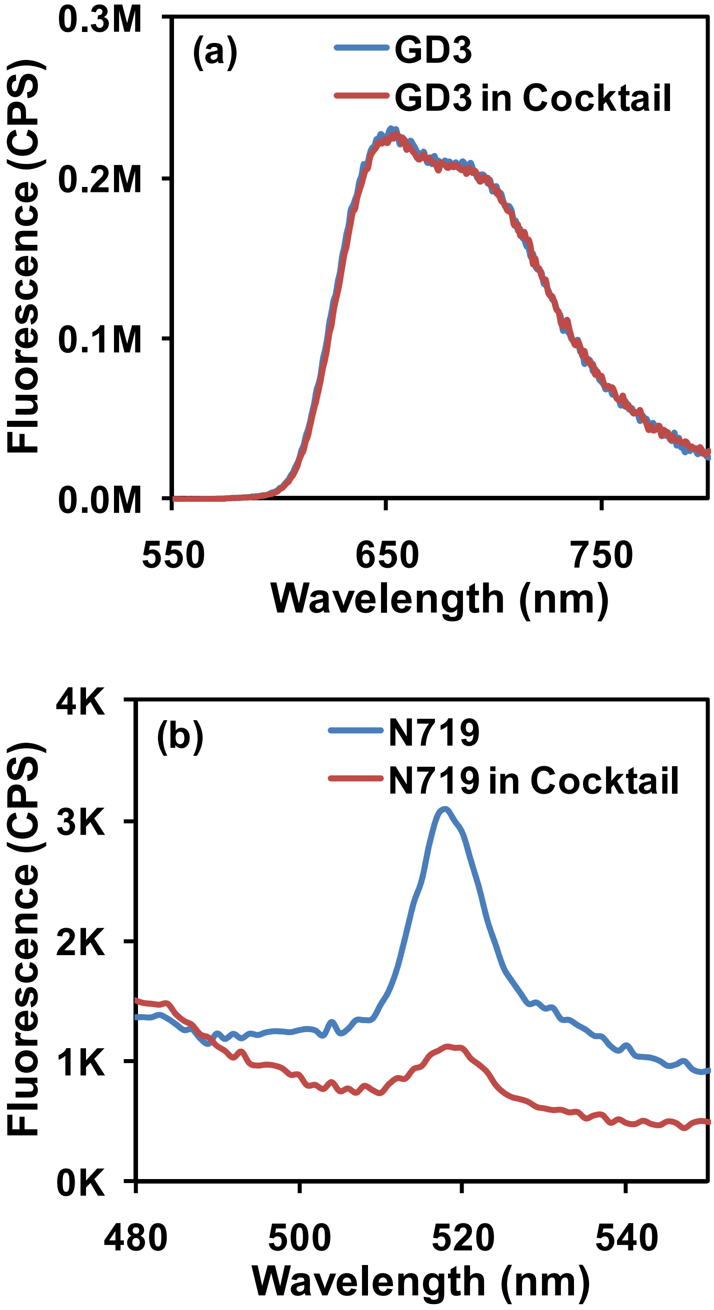

Figure S5 The fluorescence spectra of (a) GD3 and (b) N719 in solution and the mixed cocktail solution with the same individual dye concentrations.

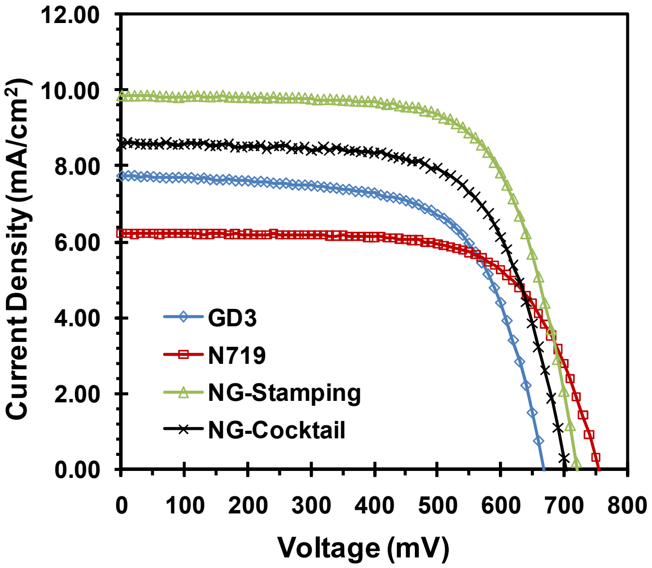

Figure S6 I-V curves of the DSCs made from GD3, N719, NG-Stamping, and NG-Cocktail electrodes.