Supporting Information for:

Relationship Between Electroless Pt Nanoparticle Growth and Interconnectivity at the Membrane Interface: Implications for Fuel Cell Applications

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Table S1. Description of model variables and their impact on $M_{Pt\text{-}grain}$

	independent variables			**dependent variable**
case	$\mathbf{N_{Pt\text{-}grains}}$	$\mathbf{r_{Pt\text{-}grain}}$	$\mathbf{Pt_{utilization}}$	$\mathbf{M_{Pt\text{-}grain}}$
A	increasing	constant	constant	$\propto N$
B	constant	increasing	constant	$\propto r^3$
C	constant	increasing	$\propto r$	$\propto r^3$
D	constant	increasing	$\propto r^2$	$\propto r^3$
E	decreasing ($\propto 1/r^2$)	increasing	$\propto r$	$\propto r$
F	decreasing ($\propto 1/r^2$)	increasing	$\propto r^2$	$\propto r$

1. **Floating Electrode Set-up and Cyclic Voltammogram for ECSA Calculation**

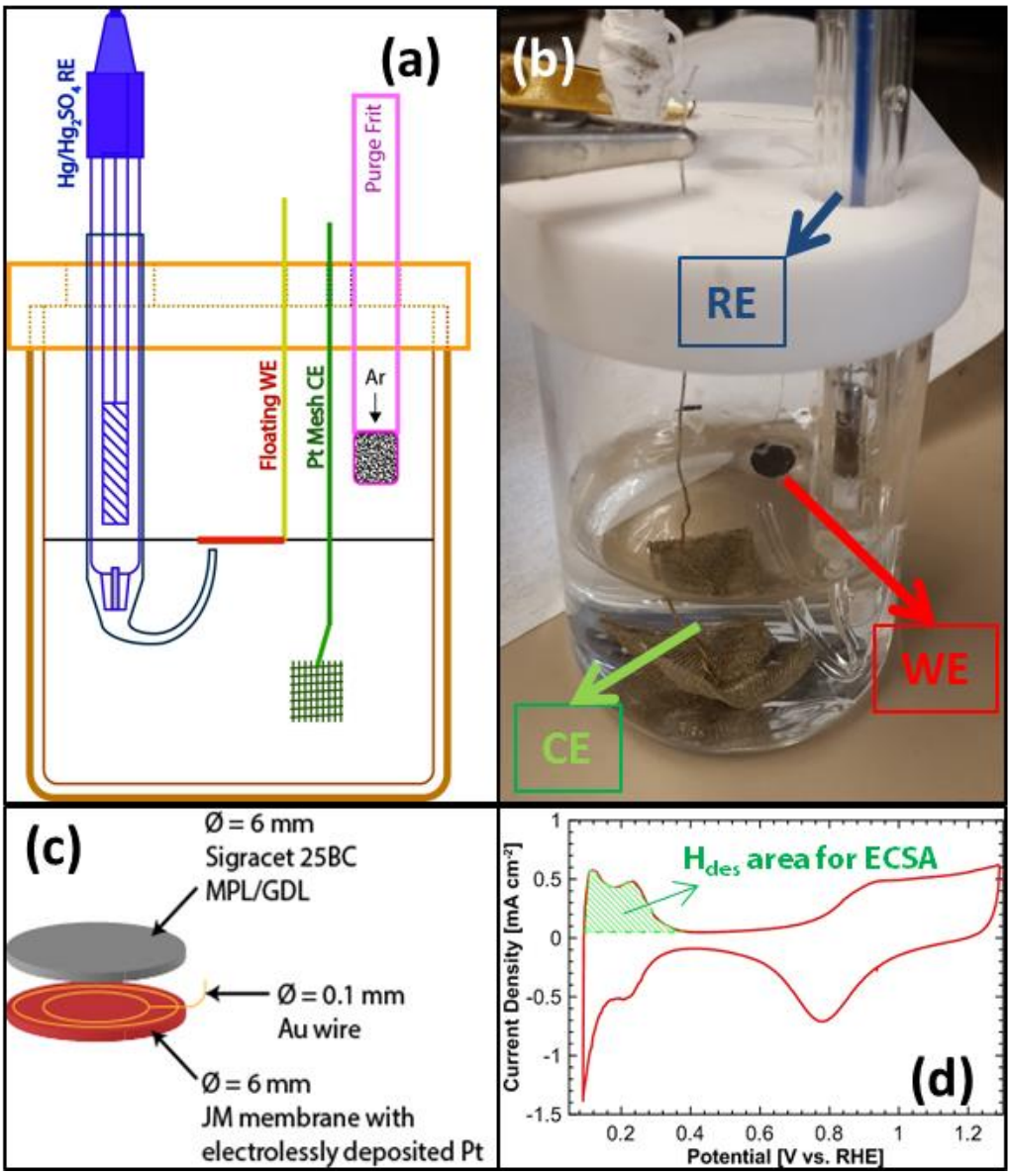

Figure S1. (a) Floating electrode set-up used to determine the electrochemically active surface area, (b) photo of the assembled floating electrode cell, (c) schematics of the components of a floating electrode, and (d) a typical CV of electrolessly deposited Pt and the hydrogen desorption area used for ECSA calculation.

2. Pt Loading Distribution across Nafion Membrane Surface

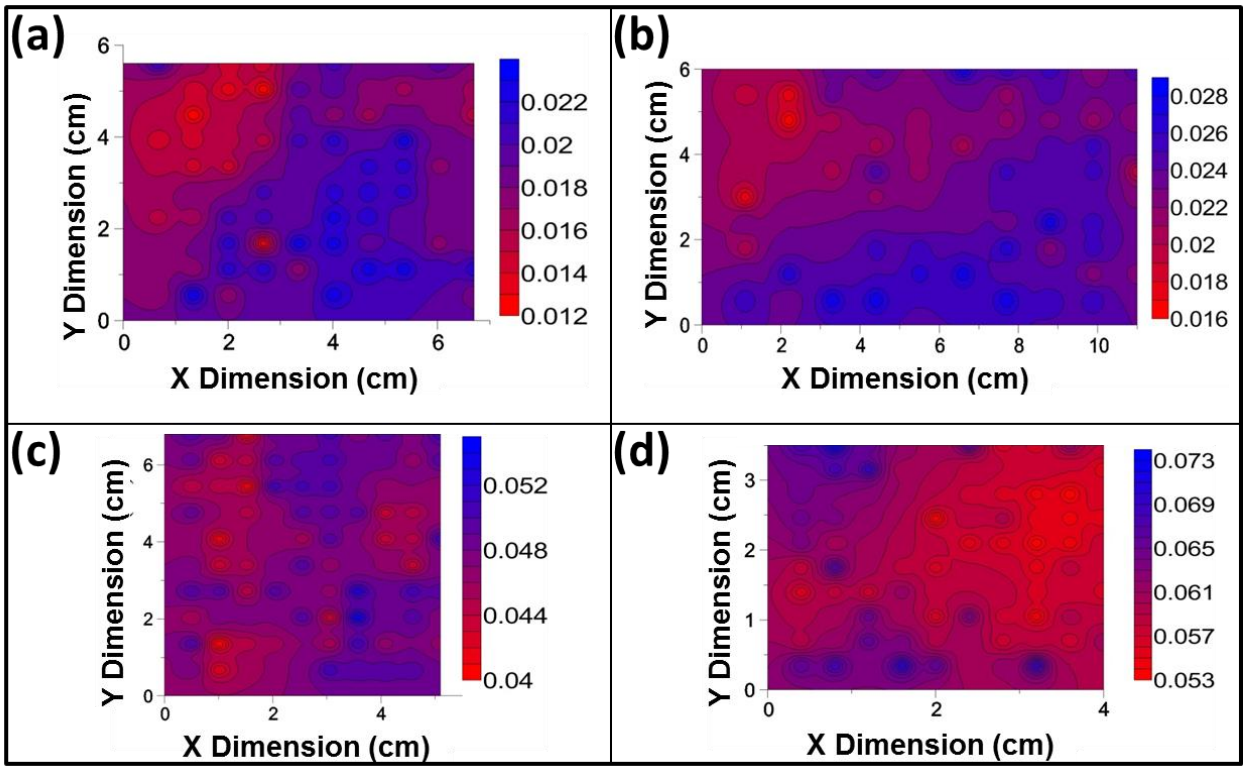

Figure S2. Loading distribution of platinized membrane with a loading of (a) 18.0, (b) 26.2, (c) 45.0, and (d) 63.5 μg_{Pt} cm^{-2} respectively measured by XRF.

3. SEM Cross-sectional Images

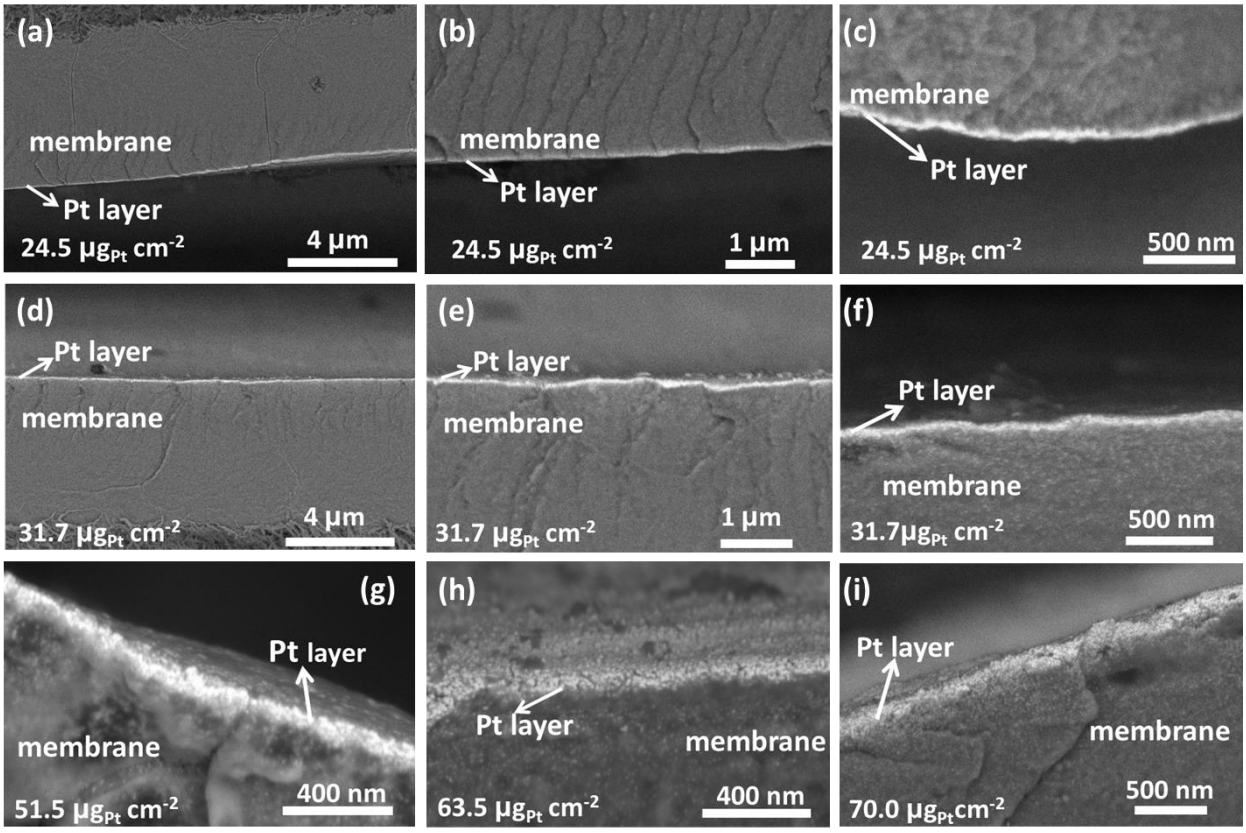

Figure S3. SEM images of electrolessly deposited membrane with different loading: (a-c) 24.5, (d-f) 31.7, (g) 51.5, (h) 63.5, and (i) 70.0 μg_{Pt} cm^{-2}.

4. Optical Reflectivity

As the Pt loading increases, the color of platinized membranes transforms from lighter brown to darker brown to almost black **(Figures S4a-d)** and then finally to a glossy black-gray (**Figures S4e-f**). The transformation from light brown to a glossy black-gray at a loading of 63.5 μg_{Pt} cm^{-2} could suggest a near monolayer coverage, indicating strong Rayleigh scattering and high optical density.[1] This was supported by the reflectance spectra measured in the 400 - 800 nm range of wavelengths. Reflectance measurement in this visible light spectrum shows that the electrolessly deposited membranes with loadings higher than about 52 μg_{Pt} cm^{-2} exhibit significant reflectivity compared to the samples with loadings below about 52 μg_{Pt} cm^{-2} which show no reflectivity for most of the region of the visible light spectrum. The reflectivity of the electrolessly deposited membrane increases with increased Pt loading and reaches ~ 80% for visible light at the near saturated Pt layer achieved in the membrane. The improved reflectivity of a metallic polymer has been linked to its enhanced conductivity,[2,3] which suggested higher conductivity for electrolessly deposited membranes with higher loadings.

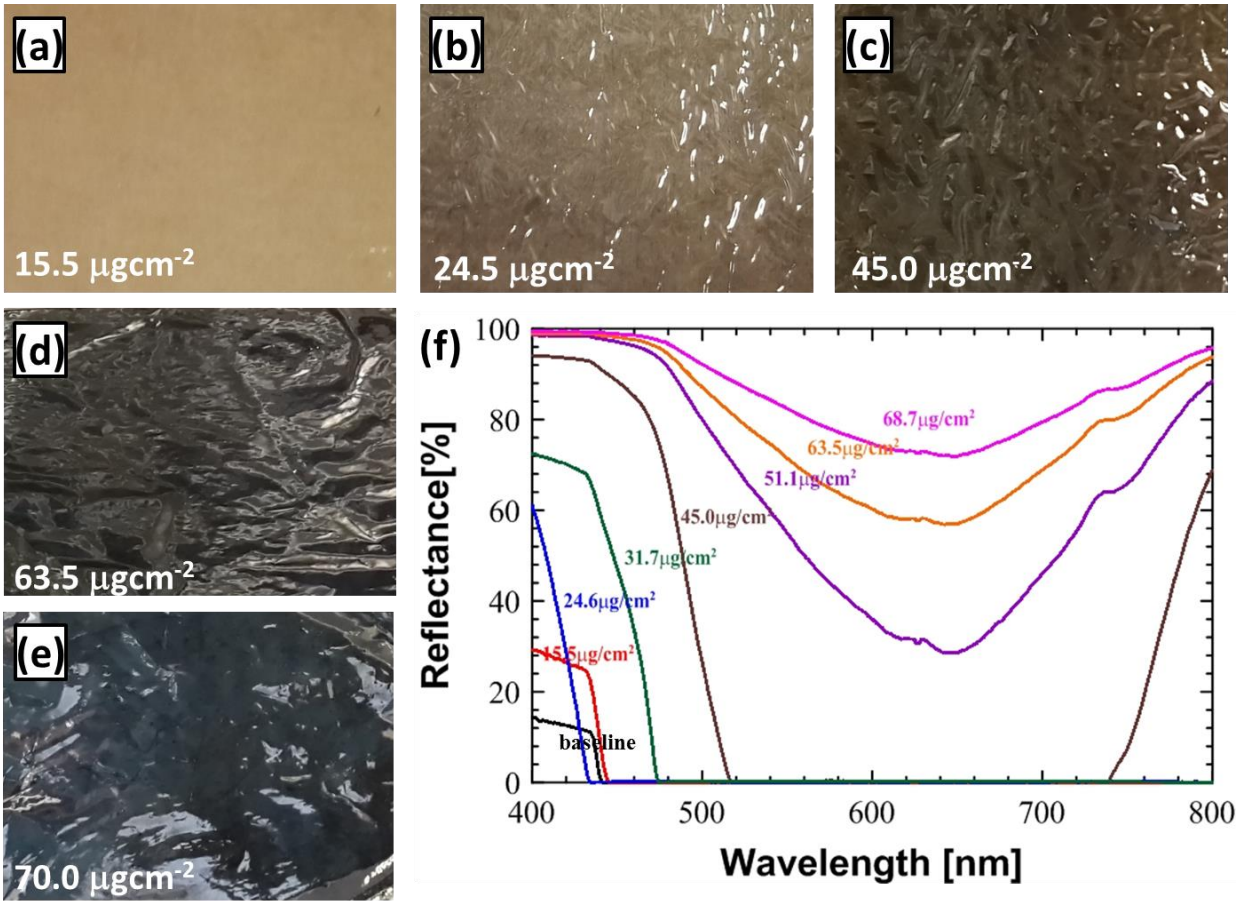

Figure S4. Physical appearance of the electrolessly-deposited membrane with different Pt loadings: (a) 15.5, (b) 24.6, (c) 45.0, (d) 63.5, (e) 68.7 μg_{Pt} cm^{-2}, and (f) profile of reflectance vs. Pt loading with a baseline of blank membrane

5. Ionic and Electronic Conductivity Measurements

Figure S5a shows the in-plane electronic conductivity vs. the electroless Pt loading. The conductivity of the platinized membranes studied here can be classified into three groups: I) membranes with electroless loadings < 35 μg_{Pt} cm^{-2} exhibiting low in-plane conductivity (< 10 mS cm^{-1}), II) membranes with electroless loadings of 35 – 60 μg_{Pt} cm^{-2} in a transition region exhibiting a rapid increase of conductivity with increased loading (10 mS cm^{-1} to over 1 S cm^{-1}), and III) membranes with electroless loadings of > 60 μg_{Pt} cm^{-2} exhibiting significantly higher in-

plane conductivity (~ 4 - 7 S cm^{-1}). The very low conductivity at the loadings below 32 μg_{Pt} cm^{-2} suggests that inter-particle connectivity was very low for the platinized membranes in this region. The inter-particle connectivity is significantly improved for loadings greater than 32 μg_{Pt} cm^{-2} and reaches a constant value (~ 4 - 7 S cm^{-1}) for loadings greater than about 60 μg_{Pt} cm^{-2}. Enhancement of Pt grain connectivity leads to improved electron transfer pathways and leads to an apparent maximum conductivity value (~ 4 - 7 S cm^{-1}) for loadings higher than 60 μg_{Pt} cm^{-2} indicating that Pt grains are essentially almost all connected together. The overall improvement in the electronic conductivity observed here is about three orders of magnitude.

The protonic conductivity of the Pt-deposited membranes under dry condition at room temperature, however, decreases with increased levels of Pt loading (**Figure S5b).** Over the range of Pt loadings studied here (12 – 70 μg_{Pt} cm^{-2}) the protonic conductivity reduces from 0.7 to 0.1 mS cm^{-1} or a factor of 7×. The reduced through-plane proton conductivity may result from formation of denser Pt clusters at the membrane sub-surface which impedes the transfer of protons across the membrane.

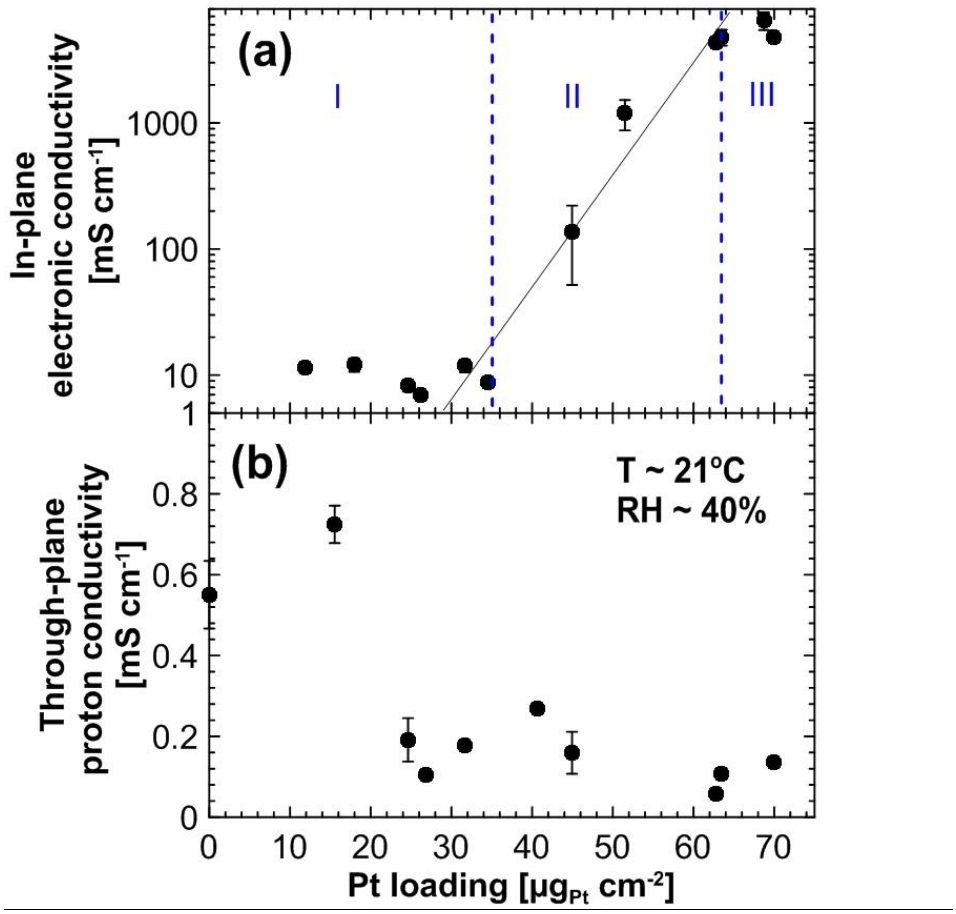

Figure S5. (a) In-plane volume resistivity, and (b) through-plane proton conductivity of the platinized membrane vs. Pt loading. The vertical error bars in (a) indicate the standard deviation from nine different points across the sheet, and in (b) indicate the standard deviation from three different measurements.

6. In-plane Conductivity and Optical Reflectivity

Figure S6 shows the correlation of the in-plane electronic conductivity and reflectance of different electroless Pt loading. The transformation from light brown to glossy black-gray at reflectance values higher than 80% (from a loading of 45.0 to 68.7 μg_{Pt} cm^{-2}) suggests a near monolayer coverage which is closely related to the enhance Pt grains connectivity. Here, the saturation or enhanced Pt grains connectivity is demonstrated by an increase of in-plane

conductivity by almost three orders of magnitude from < 10 mS cm^{-1} to ~ 7000 mS cm^{-1}. It is therefore clear that the Pt interparticle connectivity is improved as the loading increases.

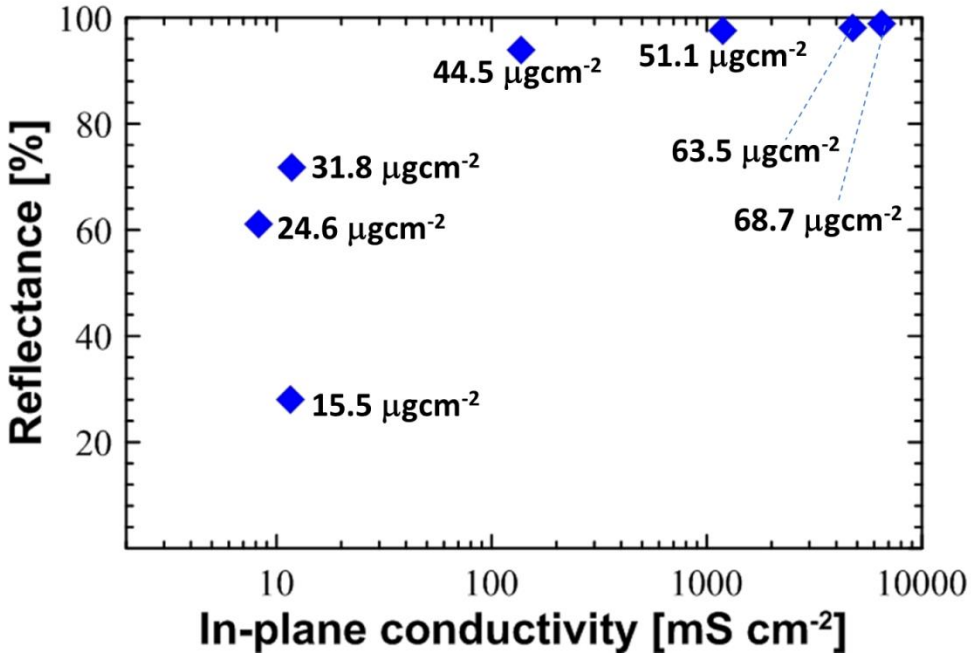

Figure S6. In-plane conductivity vs. reflectance of electroless Pt samples with different loadings in the visible light region.

References

(1) Martens, I.; Pinaud, B. A.; Baxter, L.; Wilkinson, D. P.; Bizzotto, D. Controlling Nanoparticle Interconnectivity in Thin-Film Platinum Catalyst Layers. *J. Phys. Chem. C* **2016**, *120*, 21364–21372.

(2) Zaier, M.; Vidal, L.; Hajjar-Garreau, S.; Balan, L. Generating Highly Reflective and Conductive Metal Layers through a Light-Assisted Synthesis and Assembling of Silver Nanoparticles in a Polymer Matrix. *Sci. Rep.* **2017**, *7*, 1–10.

(3) Liao, Y.; Cao, B.; Wang, W. C.; Zhang, L.; Wu, D.; Jin, R. A Facile Method for Preparing Highly Conductive and Reflective Surface-Silvered Polyimide Films. *Appl. Surf. Sci.* **2009**, *255*, 8207–8212.