

## Shape-controlled synthesis of PtPd alloys as a low-cost and efficient counter electrode for dye-sensitized solar cells

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### Experimental section

#### *Materials*

TiO<sub>2</sub> pastes (series T/SP, series DSL 18NR-AO) and ruthenium based-dye (N719) were purchased from Solaronix, Switzerland. FTO glass for use as a transparent conducting electrode was purchased from Pilkington, USA (~8 Ω/□). The substrates were cleaned in acetone with ultrasonic irradiation, and then, dried in an argon flow. All reagents and chemicals were purchased from Sigma-Aldrich unless otherwise stated, and were ACS grade or higher. The dye was adsorbed from a 0.3 mM solution in a mixed solvent of acetonitrile and tert-butyl alcohol with a volume ratio of 1:1. The electrolyte was a solution of 0.60 M 1-methyl-3-butylimidazolium iodide, 0.03 M I<sub>2</sub>, 0.10 M guanidinium thiocyanate, and 0.50 M 4-tert-butylpyridine in a mixed solvent of acetonitrile and valeronitrile with a volume ratio of 85:15.

#### *Synthesis of Pt NPs, Pd NPs and bimetallic PtPd NPs on FTO glass substrates*

Two solutions containing 10mM  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  in iso-propyl alcohol (IPA) and 10 mM  $\text{PdCl}_2$  in IPA with a small amount of HCl were firstly prepared. After that, seven solutions containing mixed precursor of 10 mM  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  and 10 mM  $\text{PdCl}_2$  in IPA with the volume ratios of 1:0, 9:1, 7:3, 5:5, 3:7, 1:9, and 0:1 were prepared.

A set of bimetallic PtPd NPs on FTO supports was synthesized using prepared precursor solutions with various volume ratios of Pd and Pt precursors. For this purpose, 8  $\mu\text{l}$  of precursor solution was pipetted onto FTO glass with area of 2 x 2  $\text{cm}^2$  and dried in air at 70°C for 10 min. These specimens were then reduced using Ar plasma under atmospheric pressure at a power of 150 W, a gas flow rate of 5 lpm, and a substrate moving speed of 2 mm/s for 10 min.

#### *Preparation of working electrodes, CEs, and assembly of DSCs*

For comparison, seven different CEs were prepared by immobilization of Pt, Pd, and PtPd alloys from the solutions with different volume ratio of Pt to Pd precursors (1:0, 0.9:0.1, 0.7:0.3, 0.5:0.5, 0.3:0.7, 0.1:0.9, and 0:1) on the surface of FTO substrates via DPR. The fabricated CEs are denoted as  $\text{Pt}_1\text{Pd}_0$ ,  $\text{Pt}_{0.9}\text{Pd}_{0.1}$ ,  $\text{Pt}_{0.7}\text{Pd}_{0.3}$ ,  $\text{Pt}_{0.5}\text{Pd}_{0.5}$ ,  $\text{Pt}_{0.3}\text{Pd}_{0.7}$ ,  $\text{Pt}_{0.1}\text{Pd}_{0.9}$  and  $\text{Pt}_0\text{Pd}_1$  CEs.

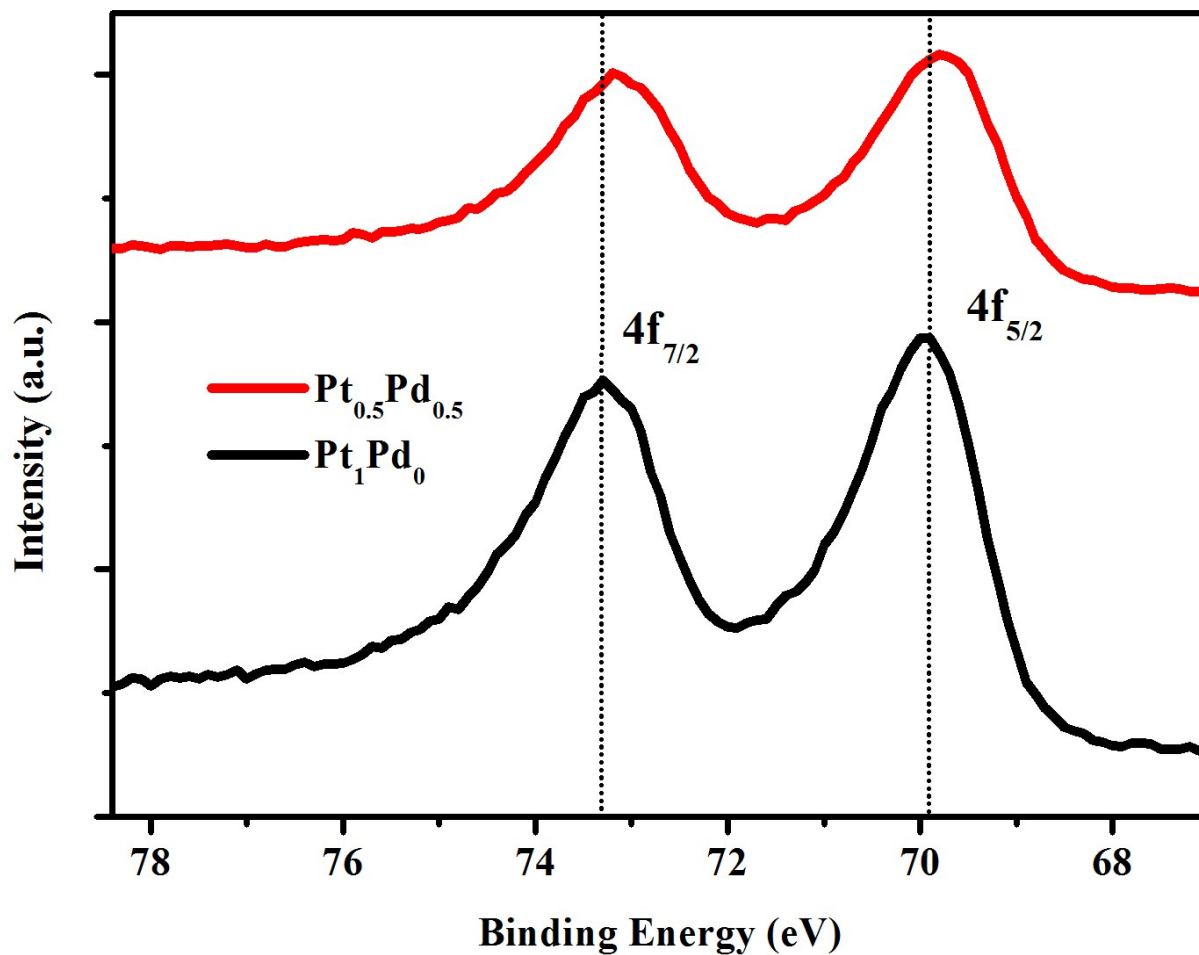
The experimental details on the working electrode fabrication and assembly of DSCs have been described in our previous study [S1].

#### *Measurements*

The morphologies of PtNPs, PdNPs and PtPd bimetallic NPs on FTO glass substrates were observed by means of high resolution scanning electron microscopy (HRSEM) (Jeol JSM 7000F). The chemical states of the bimetallic NPs were analyzed by x-ray photoelectron spectroscopy (XPS) using a spectrometer (Thermo Scientific MultiLab) equipped with a

monochromatic Al K $\alpha$  X – ray source. The core level binding energy positions were defined as the center of the full width at half maximum (FWHM) of the photoemission peak using the XPSpeak41 software package.

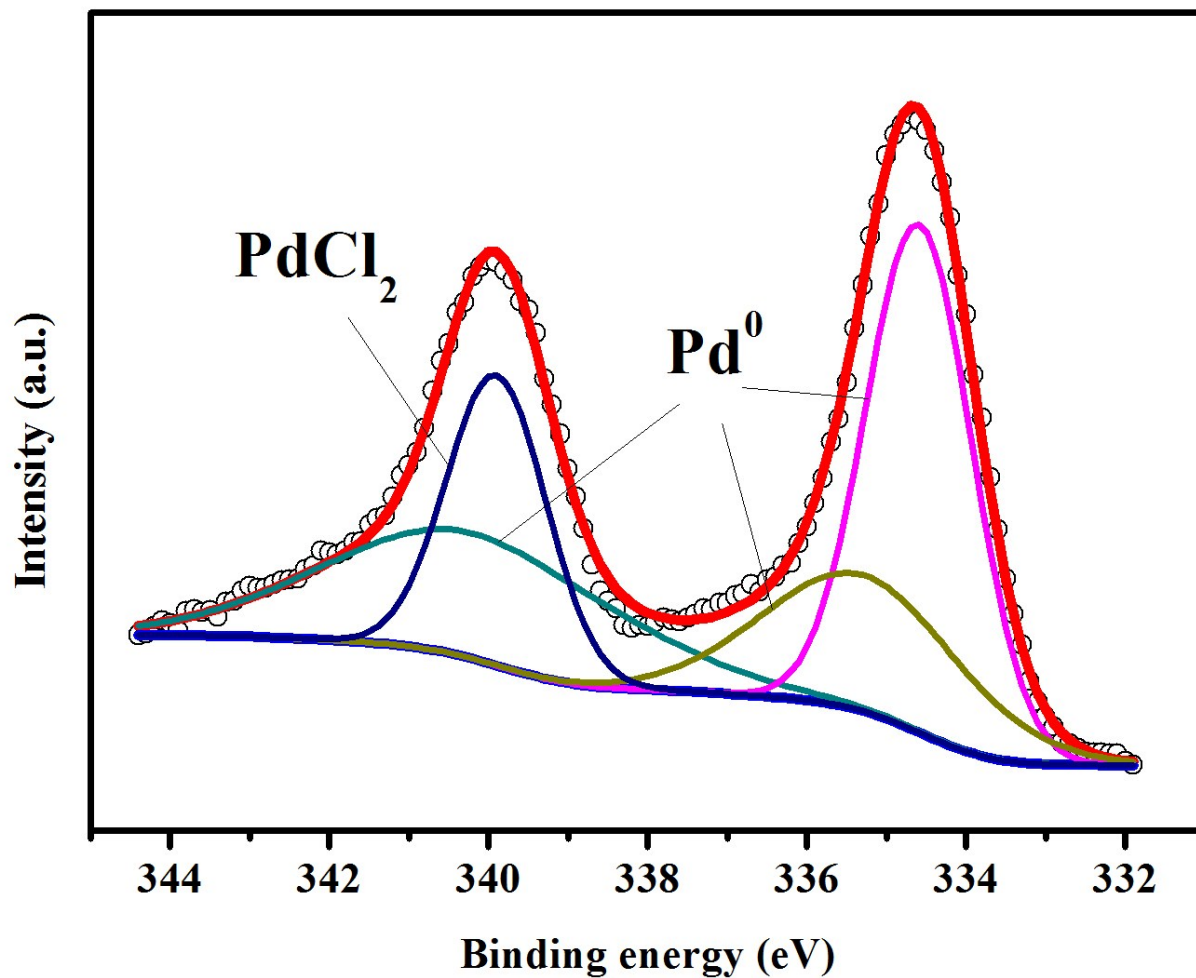
The photocurrent-voltage ( $J - V$ ) characteristics were measured with an IviumStat device under illumination from a Sun 3000 solar simulator consisting of a 1000 W mercury-based Xe arc lamp and AM 1.5-G filters. The redox behaviors of these electrodes were evaluated through a comparative analysis of their cyclic voltamogram (CV). Three electrode electrochemical cells were used. A Pt mesh and Hg/Hg<sup>2+</sup> electrodes were served as the CE and the reference electrodes, respectively. The electrolyte was consisted of 10 mmol L<sup>-1</sup> LiI, 1 mmol L<sup>-1</sup> I<sub>2</sub>, and 1 mmol L<sup>-1</sup> LiClO<sub>4</sub>. The CVs were recorded in a range of 600 to -300 mV at a scan rate of 20 mV s<sup>-1</sup>. The electrochemical impedance spectroscopy (EIS) of a symmetrical dummy cells was performed under open-circuit condition with a frequency range of 100 kHz to 100 mHz and a perturbation amplitude of 5 mV. The obtained spectra were fitted using the Z-view software (v3.2c, Scribner Associates, Inc.) with reference to the proposed equivalent circuit. Tafel measurements were performed with a scanning rate of 5 mVs<sup>-1</sup> in the potential range of 0.6 to -0.6 V. The data were analyzed with the IviumStat device to calculate the exchange current density.



**Figure S1.** Pt4f core-level emissions for the Pt<sub>1</sub>Pd<sub>0</sub> and Pt<sub>0.5</sub>Pd<sub>0.5</sub> samples.

**Table S1.** XPS parameters of the electrodes.

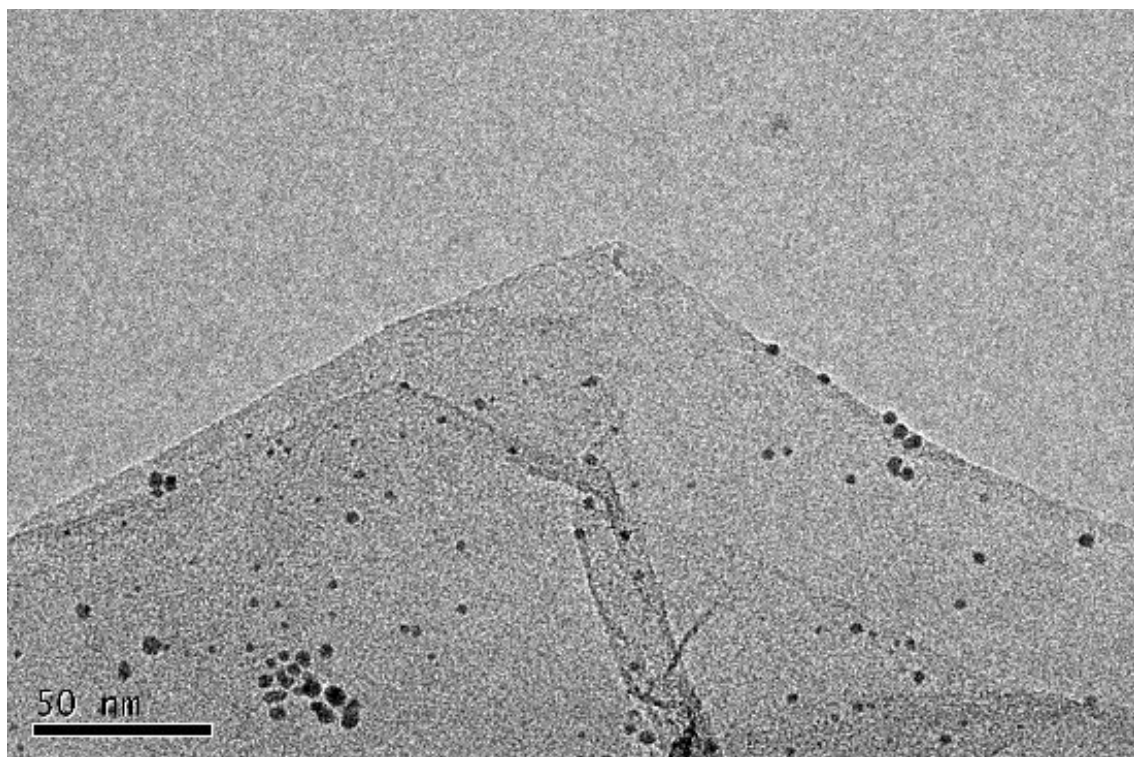
Counter electrode	Binding energy (eV)	
	Pt	Pd
	4f <sub>7/2</sub> /4f <sub>5/2</sub>	3d <sub>5/2</sub> /3d <sub>3/2</sub>
Pt <sub>1</sub> Pd <sub>0</sub>	69.9/73.3	-
Pt <sub>0.5</sub> Pd <sub>0.5</sub>	69.8/73.2	334.3/339.6



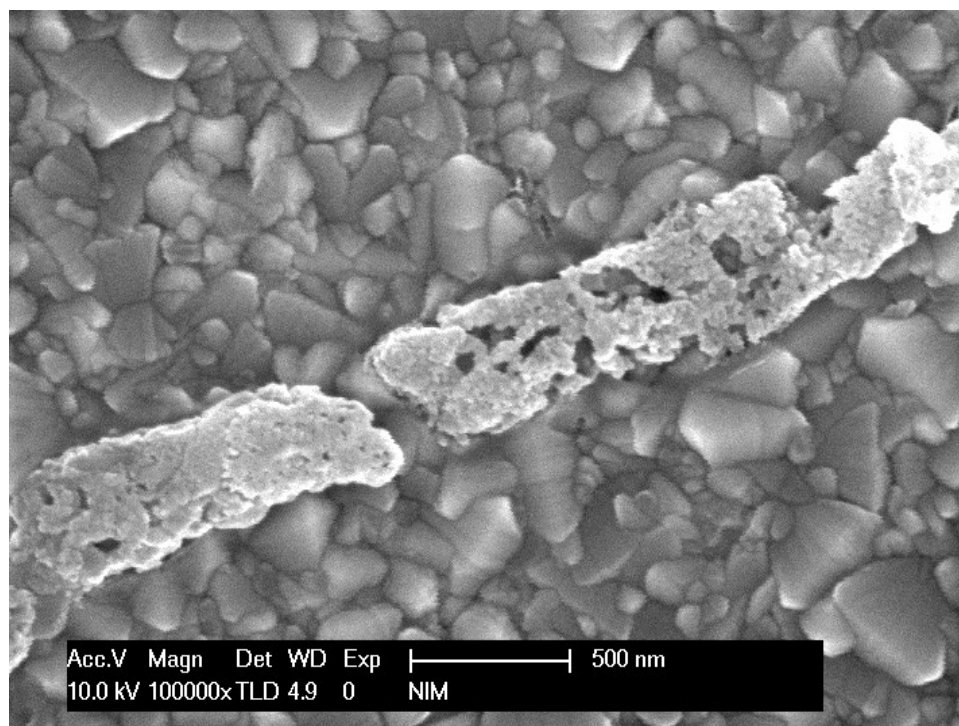
**Figure S2.** Pd3d core-level emission for the Pt<sub>0</sub>Pd<sub>1</sub> sample.

**Table S2.** Data calculated for the Pd3p region of Pt<sub>0</sub>Pd<sub>1</sub>.

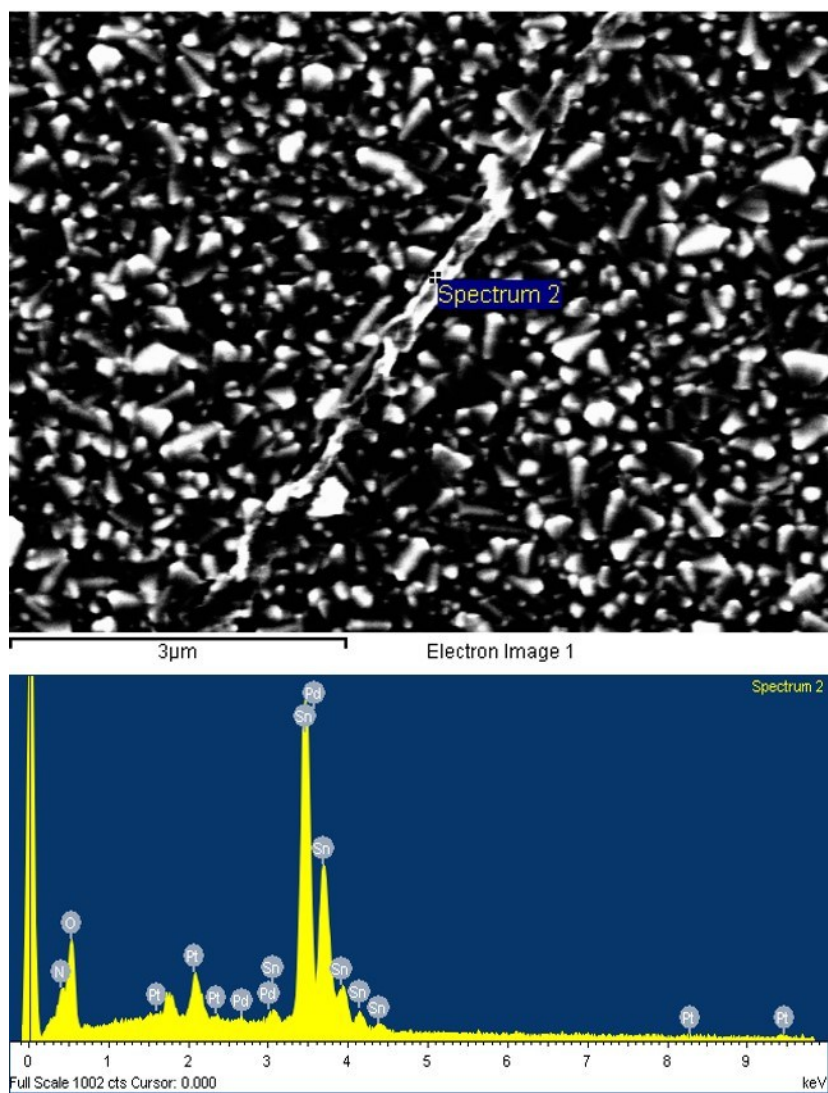
Sample	Binding energy			
	Pd <sup>0</sup>	Pd <sup>0</sup>	PdCl <sub>2</sub>	Pd <sup>0</sup>
Pt <sub>0</sub> Pd <sub>1</sub>	334.59	335.3	339.9	340.2
	Atomic percentage (%)			
Pt <sub>0</sub> Pd <sub>1</sub>	36.8	18.5	19.8	24.9



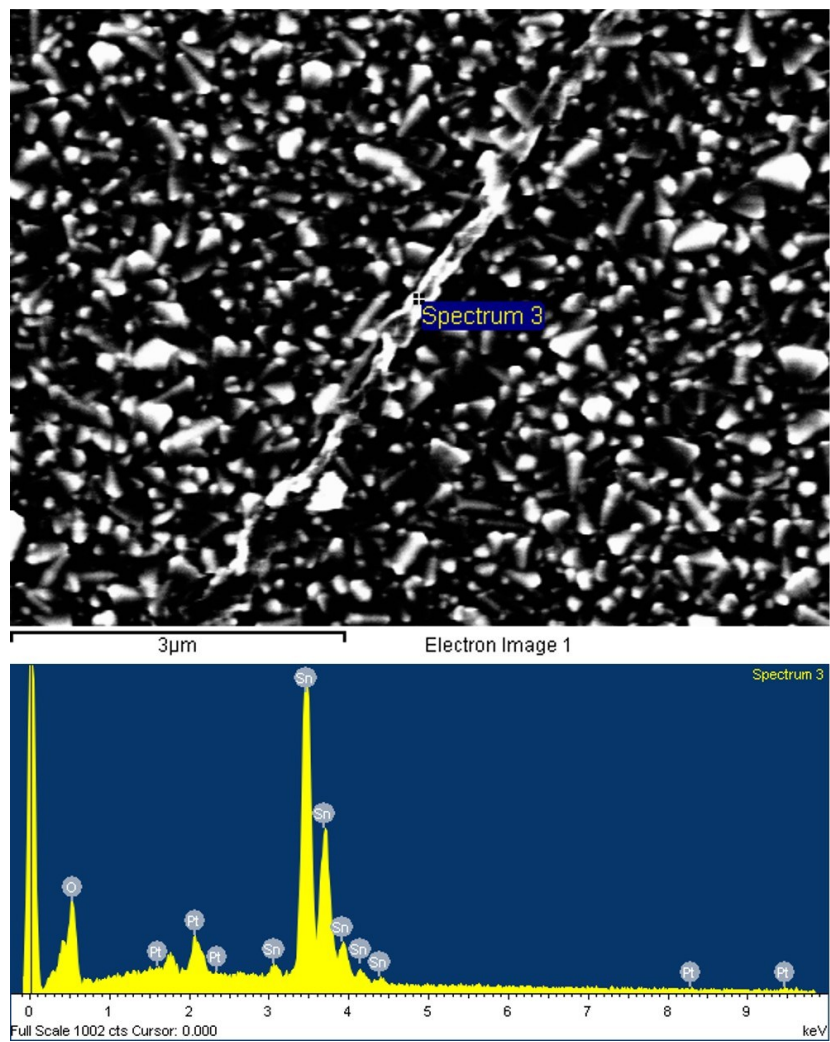
**Figure S3.** TEM image of the Pd NPs/graphene. Note that the Pd/graphene nanohybrid was synthesized using a similar process of immobilizing the Pd NPs on the FTO glass substrate.



**Figure S4.** HRSEM image of Pt<sub>0.1</sub>Pd<sub>0.9</sub> alloy

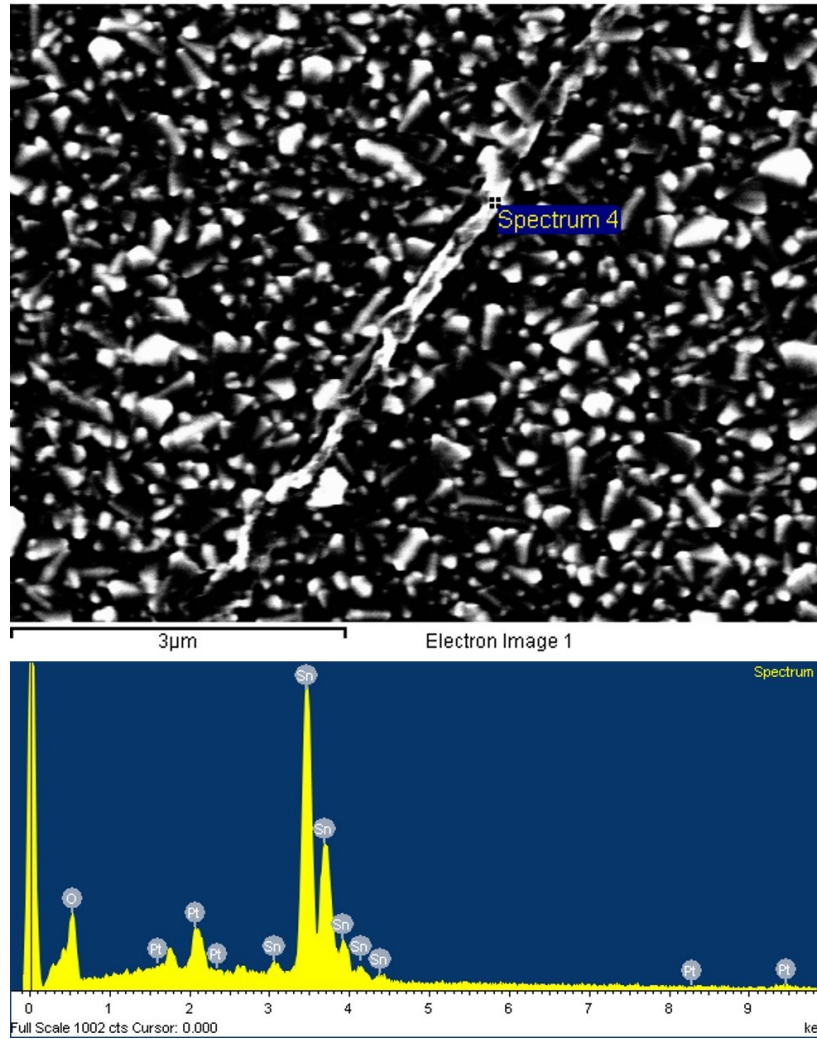


**Figure S5.** SEM-EDS of the  $\text{Pt}_{0.9}\text{Pd}_{0.1}$  sample at spectrum 2.

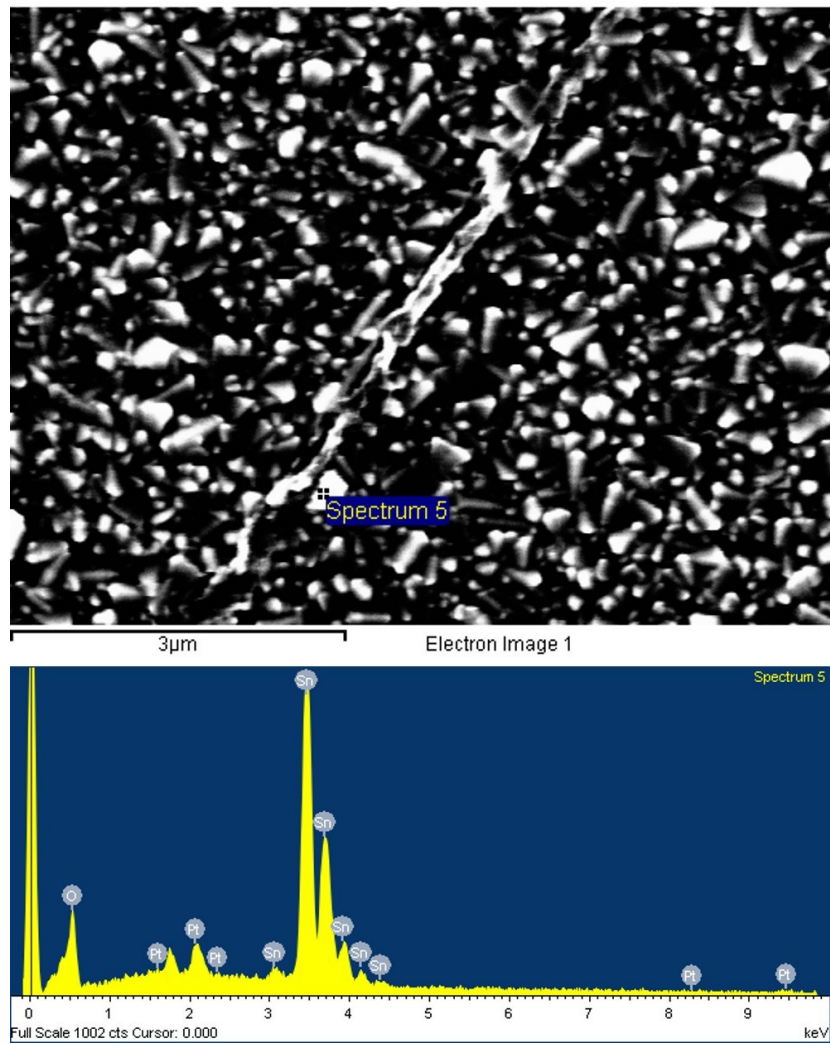


**Figure S6.** SEM-EDS of the  $\text{Pt}_{0.9}\text{Pd}_{0.1}$  sample at spectrum 3.

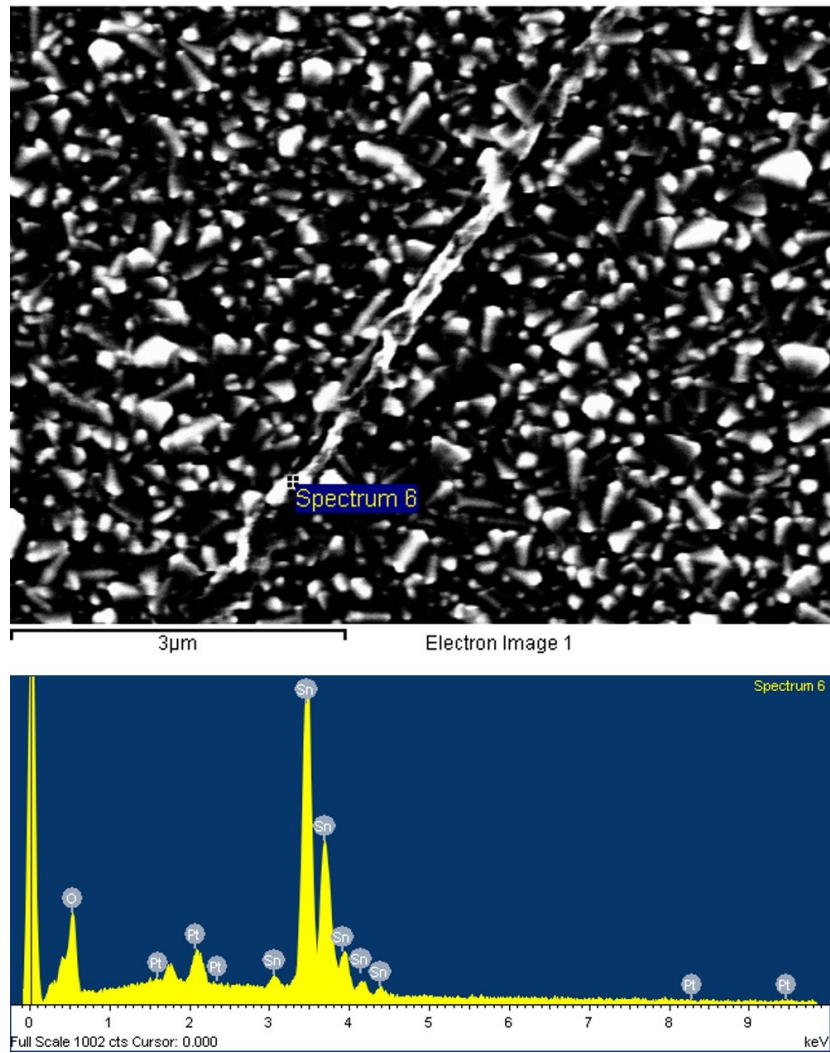




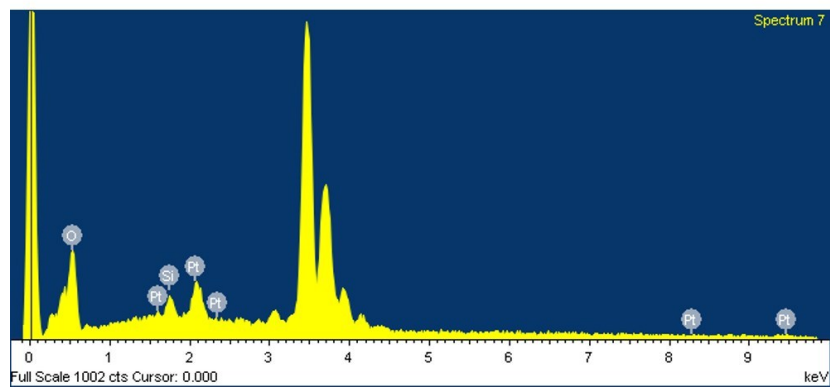
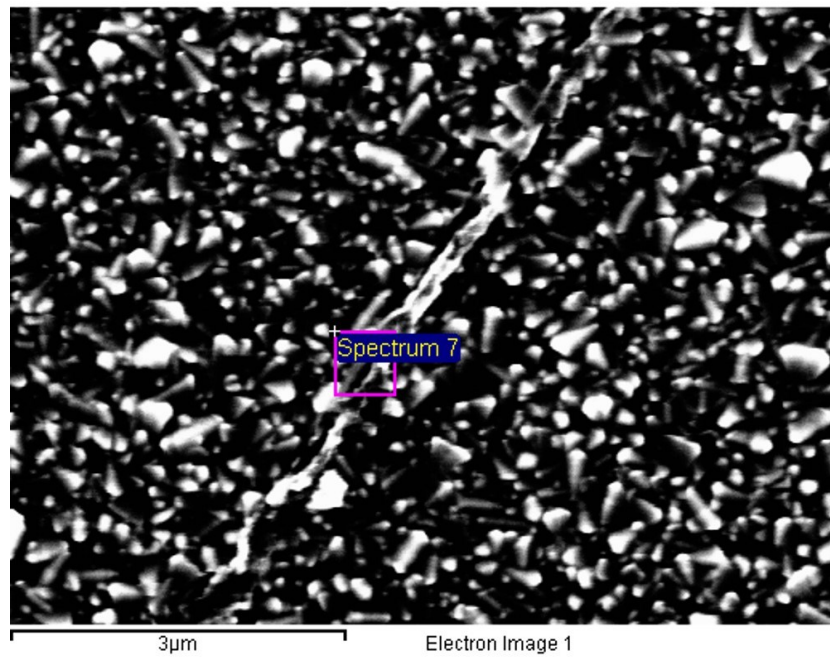
**Figure S7.** SEM-EDS of the  $\text{Pt}_{0.9}\text{Pd}_{0.1}$  sample at spectrum 4.



**Figure S8.** SEM-EDS of the Pt<sub>0.9</sub>Pd<sub>0.1</sub> sample at spectrum 5.



**Figure S9.** SEM-EDS of the  $\text{Pt}_{0.9}\text{Pd}_{0.1}$  sample at spectrum 6.



**Figure S10.** SEM-EDS of the  $\text{Pt}_{0.9}\text{Pd}_{0.1}$  sample at spectrum 7.

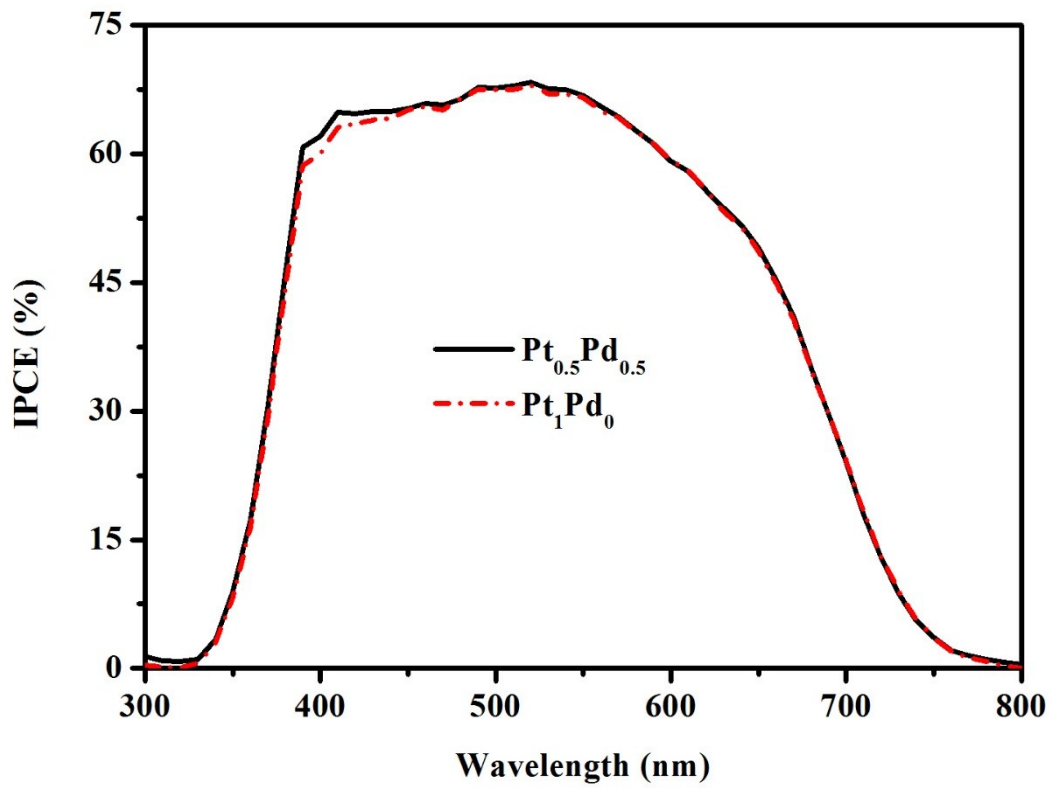
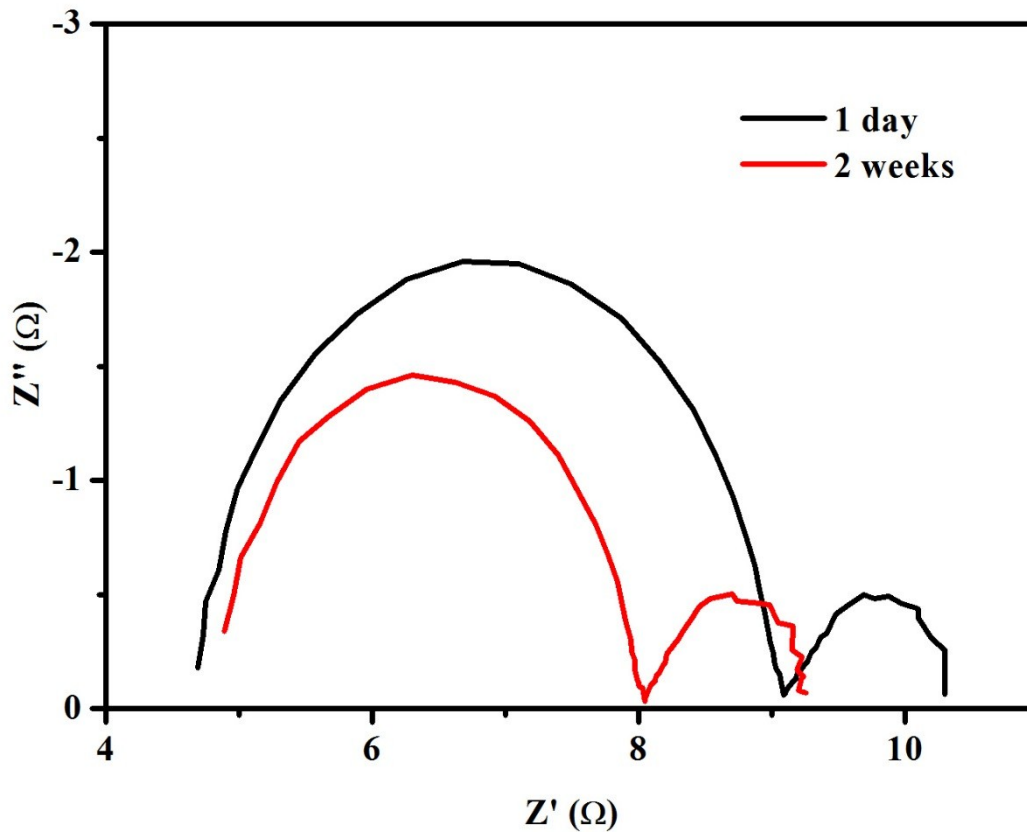


Figure S11. IPCE of DSCs with different CEs



**Figure S12.** Nyquist plot of the Pt<sub>0.5</sub>Pd<sub>0.5</sub> CE measured on the cell assembly day and after 14 days

**Table S3.** The relationship between the Pt volume precursor and absolute efficiency increased and  $\Delta\eta/v$ .

Pt volume%	$\Delta\eta$	$\Delta\eta/v$
10	6.27	0.63
30	7.19	0.24
50	7.29	0.15
70	7.23	0.10
90	7.17	0.08

## References

[S1] V. D. Dao, Q. C. Tran, S. H. Ko, H. S. Choi, *J. Mater. Chem. A* **2013**, 1, 4436.