Electronic Supplementary information (ESI) *for*

Heterogeneous Junction Engineering on Core-Shell Nanocatalysts Boost the Dye-Sensitized Solar Cell

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1. Synthetic procedure of Co–Pt core–shell CNCs and the preparation of CNCs/FTO cathode.

The synthesis of Co_{core}-Pt_{shell} NCs (denoted as Pt_s/Co_c) with a precisely controlled thickness around 1.5 atomic layers was conducted by combining chemical reduction and poylol reaction. In the first step, cobalt core NPs was grown by wet chemical reduction method. It was conducted by adding 10 ml of 300 mM sodium borohydride [$NaBH_4$] water solution into 40 grams of 20 mM cobalt acetate tetrahydrate [$C_4H_6CoO_4{\cdot}4H_2O$] ethylene glycol (EG) solution in a presence of 10 wt% of polyvinylpyrrolidone stabilizer (PVP-40, MW = 40 k). The solution of PVP blended Co NPs (Co-PVP) was re-dispersed in EG into a metal contain of 10 mM and then heated to 160℃ to dehydrate for 2 h. After dehydration and cooling to room temperature, the Pt shell crystal was grown by mixing Co-PVP with hexachloroplatinic acid [$H_2PtCl_6{\cdot}6H_2O$] then treated at 160℃ for another 2 h. The Pt shell thickness was adjusted by changing the Pt/Co ratio. The entire procedure was conducted under an ambient atmosphere. After the NPs were synthesized, the entire solution (sample) was mixed with 9 times or high of acetone solvent. This procedure will induce the condensation of polymer blended NPs from the product. These NPs was then redispersed into adequate amount of ethanol to form the slurry. The cathode was prepared by spin coating the slurry onto FTO glass followed by the annealing at 300^{o}C for 30 min (see Figure S1).

2. DSSC assembling procedure

The anode and cathode of DSSC were synthesized by coating the slurries of commercial ~25 nm titanium oxide powder paste and polymer blended Co-Pt core-shell nanoparticle on the FTO glass, respectively. The resulting anode is a porous ~21 – 22 nm thick P25@FTO thin-film. It was annealed at 450oC for 30 min, cooled down to room temperature, and then immersed into the TiO_2 precursor (50 mM $TiCl_4$/EtOH). The immersion improves the packing density (roughness factor) and thus increasing the specific number density of arched dye on anode for harvesting sun radiation. After immersion, the anode was annealed and then immersed into the dye solution for 24h. The spacer was made by a ~80 μm thick surlyn thin film with the flow channel patterns. The DSSC module was assembled by hot pressing the P25/FTO anode, the patterned surlyn, and the NPs/FTO cathode at 80°C for 5 min. As shown in the Figure S1, the electrolyte was injected into the DSSC channel by syringe pump for the PV measurement.

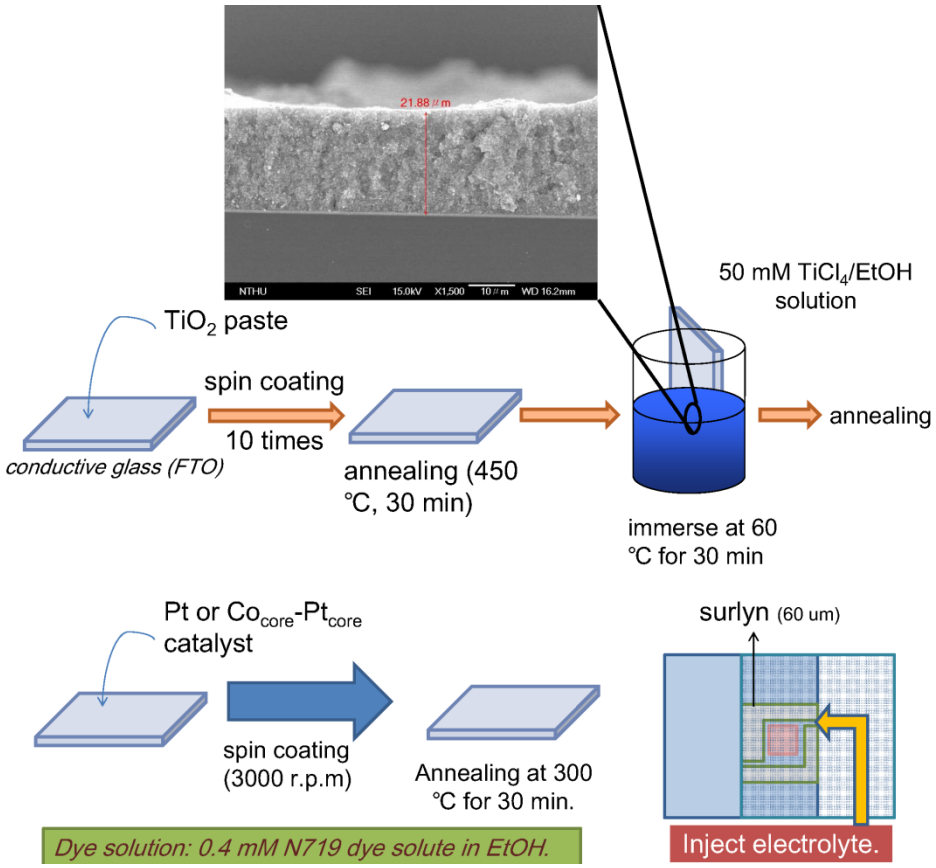

Figure S1. Schematic representation for the fabrication of NPs coated cathode and anode in a DSSC module.

3. SAXS characterization

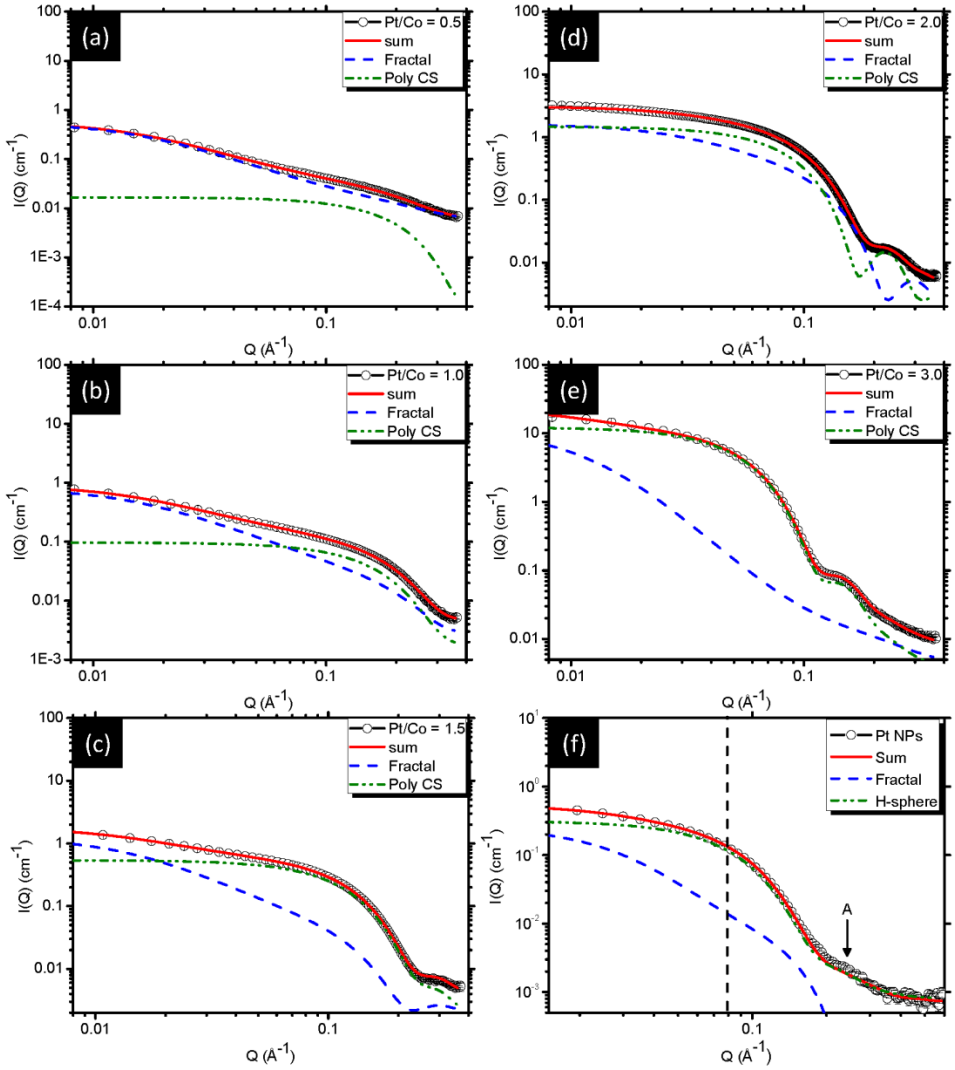

Figure S2: SAXS spectra with fitting Curve of Co-Pt core-shell NPs. Model labels, Poly CS: polydispersed core-shell particle model; Fractal: fractal aggregation, H-sphere: hard sphere with Shultz distribution of particle size.

Table S1 SAXS determined structure parameters of core-shell NPs.

NPs	Structure parameters						Applied fitting model
	Interparticle*				Intraparticle**		
	D_F	R_B (Å)	ξ (Å)	W/D_{all} (%)	D_C (Å)	T_S (Å)	
Pt/Co = 0.5	1.78	9.55	61.65	9.9	10.8	2.12	Fractal + poly CS
Pt/Co = 1.0	1.75	11.87	65.49	8.9	10.46	2.35	
Pt/Co = 1.5	1.95	18.52	67.31	8.9	15.78	4.11	
Pt/Co = 2.0	1.95	19.39	62.72	9.1	17.02	9.23	
Pt/Co = 3.0	2.51	8.15	75.61	15.0	24.10	23.93	
Pt NPs***	3.04	18.15	25.93	27.1	41.91	NA	Fractal + H-sphere

* D_F: fractal dimension (particle packing dimension), R_B: bulk radius (radius of individual particle in a fractal aggregate), ξ: coherent length (dimension of an fractal aggregate), W/D_{all}: polydispersity of particle size

** D_C: dimension of core crystallite

*** D_C for Pt NPs refer to the average particle (D_{avg})

4. XAS characterization

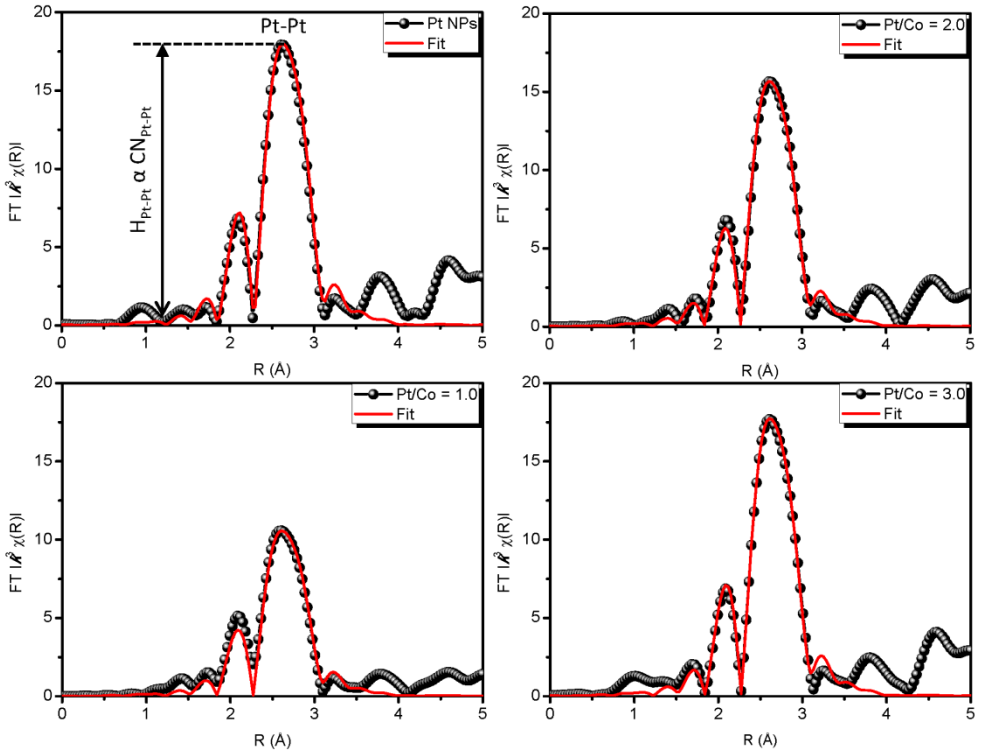

Figure S3. Pt L_3-edge Fourier transformed EXAFS spectra with the fitting curves for CNCs of (a) Pt NPs and C/P CNCs of the Pt/Co ratios of (a) 1.0, (b) 2.0, and (c) 3.0, respectively.

Table S2. Pt L_3-edge XAS determined structure parameters of Pt NPs and C/P CNCs of different Pt/Co ratios.

CNCs	Bond pair	*R* (Å)	*CN**
PtNPs	Pt-Pt	2.765	9.5
Pt/Co = 1.0	Pt-Pt	2.749	5.5
Pt/Co = 2.0	Pt-Pt	2.751	8.2
Pt/Co = 3.0	Pt-Pt	2.751	9.2

*coordination number

The extent of Co oxidation on C/P CNCs was determined by Co K-edge XAS analysis including the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The normalized Co K-edge XANES structure at room temperature for C/P CNCs of different Pt/Co ratios is shown in Fig. S4a. The energy is calibrated by using a Co metal foil with threshold energy of E_0 = 7709 eV at the inflection point of the edge (region A, 1s-4d transition). The E_0 for the

standard Coacac (Co 3+) indicates a substantial shift of the edge energy with increasing Pt/Co ratio. The almost identical threshold edge energy E_0 at 7720 eV for the C/P CNCs indicates that all samples are very close to the stoichiometric composition with trivalent Co3+. The *K*-edge XANES main edge absorption is attributed to the 1s-4p dipole transition to the Co 4p states. The *K*-edge XANES main edge absorption is attributed to the 1s-4p dipole transition to the Co 4p states. The main edge features, labeled as B, C, and D, can be reasonably explained by the Co 4p partial density of states, their broadening reflects the finite lifetime of the 1s core hole [I. S. El_mov, V. I. Anisimov, and G. A. Sawatzky, Phys. Rev. Lett. 82, 4264 (1999).]. Feature B is attributed to the hybridization between the Co 4p states with the neighboring Pt 5d orbitals, C 2s, and O 2p, feature C is the Co 4p states split by the crystal field. Here, the increased feature C intensity suggesting that the strengthened heteroatomic orbital coupling at Co with neighboring atoms (i.e., C and O atoms). This coupling goes maximum extent due to the substantial Pt-to-Co transmetalation by increasing the Pt/Co ratio to 2.0. In this case, a considerate amount of Co atoms is transformed into metallic complex and then interacts with the CHO: radicals during polyol reduction. It triggers to the heterogeneous nucleation - growth pathways to form the heteroatomic $Pt_{(1-x)}Co_x$ alloys at the CNCs surface ($x << 1$) and results in a certain amount of retained Co-complex. The surface Co atoms and retained Co-complexes will be stabilized by pyridine ligands and thus resulting in the Co carbide and oxides during the subsequent annealing. Further increasing the Pt/Co ratio to 3.0 suppresses the coupling of between Co and neighboring O atoms. This is due to the embedment of Co atoms by certain extent in the rapidly grown Pt shell.

The suppression of Co-O bondings by increasing Pt shell (Co embedment) can be further revealed by the EXAFS analysis. The radial structure function curves of C/P CNCs of different Pt/Co ratios with the corresponding model simulation curves are compared in Figure S4b, S4c, and S4d. As indicated, the radial peak at ~1.6 Å refers to the interferences of first nearest shell (R^{1st}) bond pairs of Co atom. The simulation curves of bond pairs are presented, which indicating that the 1^{st} radial peak is originated from the combination of Co-O (A) and Co-O (B, C, and D) bonds in the crystalline Co carbide phase (Co_3O_4) and the Co-C^C, respectively. Quantitative structure parameters are given by the model simulation and results are summarized in the Table S3. As clearly can be seen, the coordination number of Pt-C bond pair "CN(Pt-C)" is increased with the Pt/Co ratios which consistent with the XRD results suggesting the growth of Co-C^C crystalline. On the other hand, the decreasing of peak A intensity (i.e., CN(Pt-O)) could be rationalized by the embedment of Co atoms by growing the Pt shell crystalline.

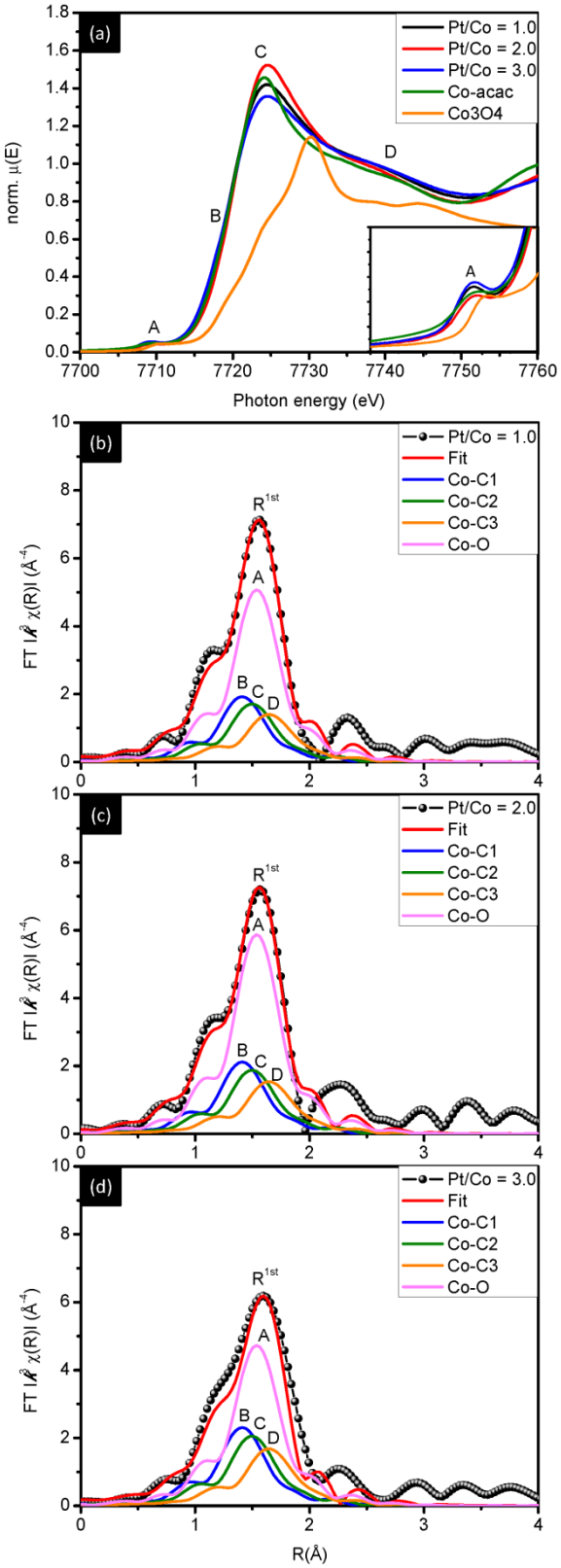

Figure S4. (a) XANES spectra of C/P CNCs of different Pt/Co ratios and Radial structure functions of C/P CNCs with the Pt/Co ratios of (b) 1.0, (c) 2.0, and (d) 3.0, respectively.

Table S3. EXAFS determined structure parameters of C/P CNCs of different Pt/Co ratios.

CNCs	phase*	path	R	CN	σ^2	r factor
Pt/Co = 1.0	Co-C^C	Co-C1	1.86	1	0.002	0.013
		Co-C2	1.95	1		
		Co-C3	2.11	1		
	Co_3O_4	Co-O	1.99	3.1		
Pt/Co = 2.0	Co-C^C	Co-C1	1.86	1.1	0.002	0.02
		Co-C2	1.95	1.1		
		Co-C3	2.11	1.1		
	Co_3O_4	Co-O	1.99	3.3		
Pt/Co = 3.0	Co-C^C	Co-C1	1.88	1.2	0.002	0.011
		Co-C2	1.97	1.2		
		Co-C3	2.13	1.2		
	Co_3O_4	Co-O	2.01	2.6		

* Co-C^C: crystalline cobalt carbide including CoC_2, CoC_8, and $Co_2(CO)_8$.

5. UPS characterization

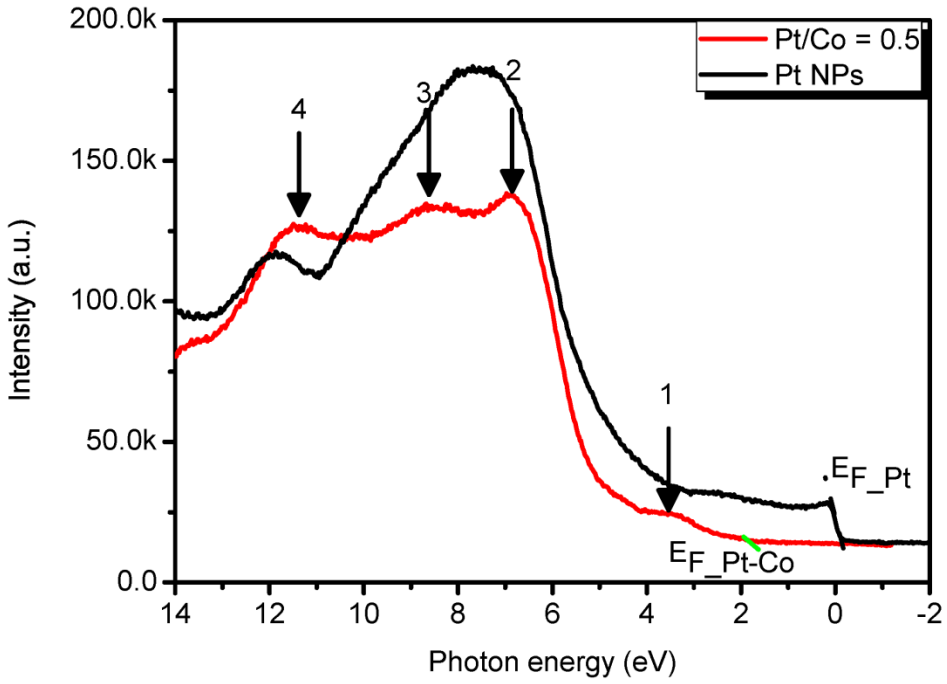

Figure S5. VB spectrum of C/P CNCs capping with uncompleted Pt shell (Pt/Co = 0.5).