Supporting Information

Carbon-Coated Hollow Mesoporous FeP Microcubes: An Efficient and Stable Electrocatalyst for Hydrogen Evolution

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Experimental Section

Chemicals

Polyvinylpirrolydone (PVP, K30, MW ≈ 40 000), potassium ferrocyanide $K_4Fe(CN)_6$, hydrochloric acid (HCl), Diammonium phosphate $(NH_4)_2HPO_4\cdot H_2O$ were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Pt/C (20 % Pt on Vulcan XC-72R) and Nafion (5 %) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. All solutions were prepared with double distilled water.

Synthesis of Prussian blue microcubes

Prussian blue (PB) microcubes were prepared according a facile solution method.[1] In a typical procedure, PVP (10.0 g) and $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.55 g) were added to a HCl solution (0.1 M, 200 mL) under magnetic stirring. After the mixture was stirred for 30 min, a clear solution was obtained. The bottle was then placed into an electric oven and heated at 80 ^oC for 24 h. The obtained blue product was separated by centrifugation and washed several times with distilled water and absolute ethanol and finally dried in a vacuum oven at 60 ^oC for 12 h.

Preparation of Fe_3O_4 microcubes and HMFeP@C

To convert the PB microcubes into Fe_3O_4 microcubes, the as-synthesized PB was heated at 500 °C with a temperate ramp of 2 °C min^{-1} for 6 h in N_2. To prepare HMFeP@C, the obtained Fe_3O_4 microcubes and $(NH_4)_2HPO_4\cdot H_2O$ were put at two separate positions in a porcelain boat with $(NH_4)_2HPO_4\cdot H_2O$ at the upstream side of the furnace. The molar ratio for Fe to P was 1:50. Subsequently, the samples were heated at 350 °C for 120 min in a static Ar atmosphere, and then naturally cooled to ambient temperature under Ar.[2]

Characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advanced X-ray diffractometer with Ni filtered Cu Kα radiation ($\lambda = 1.5406$ Å) at a voltage of 40 kV and a current of 40 mA. Field-emission scanning electron microscope (FESEM) images were acquired on a JEOL JSM-6700F microscope operated at 5 kV. Transmission electron microscopy (TEM) images were taken on JEM-2010 and JEOL JEM-2100F microscopes. Energy-dispersive X-ray (EDX) analysis and elemental mapping were performed using the energy-dispersive X-ray spectroscope attached to the JSM-6700F and JEM-2100F, respectively. Nitrogen sorption measurements were performed on an Autosorb 6B apparatus at liquid N_2 temperature. Raman spectroscopy was performed on a Renishaw RM2000 microscopic confocal Raman spectrometer (Gloucestershire, United Kingdom) using green (514 nm) laser excitation.

Preparation of Working Electrodes

Catalyst ink was prepared by dispersing 10 mg of catalyst into 900 μL of ethanol solvent containing 100 μL of 5 wt % Nafion and sonicated for 30 min. Then 5 μL of the catalyst ink (containing 50 μg of catalyst) was loaded onto a glassy carbon electrode (GCE) of 3 mm in diameter (loading ca. 0.72 mg cm^{-2}).

Electrochemical Measurements

All the electrochemical measurements were conducted using a CHI1011 electrochemical workstation (CH Instruments, China) in a typical three-electrode setup with an electrolyte solution of 0.5 M H_2SO_4, a Pt wire as the counter electrode, and an Ag/AgCl-saturated KCl as the reference electrode. Linear sweep voltammetry (LSV) was conducted in 0.5 M H_2SO_4 with a scan rate of 5 mV s^{-1}. Onset overpotentials were determined based on the beginning of the linear regime in the Tafel plot. The time dependency of catalytic currents during electrolysis for the catalyst was tested in 0.5 M H_2SO_4 at $\eta = 150$ mV after equilibrium. Electrochemical impedance spectroscopy (EIS, PARSTAT 2273, Princeton Applied Research, USA) measurements were carried out in the frequency range of 100 kHz-0.1 Hz. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.197 + 0.059pH) V.[3]

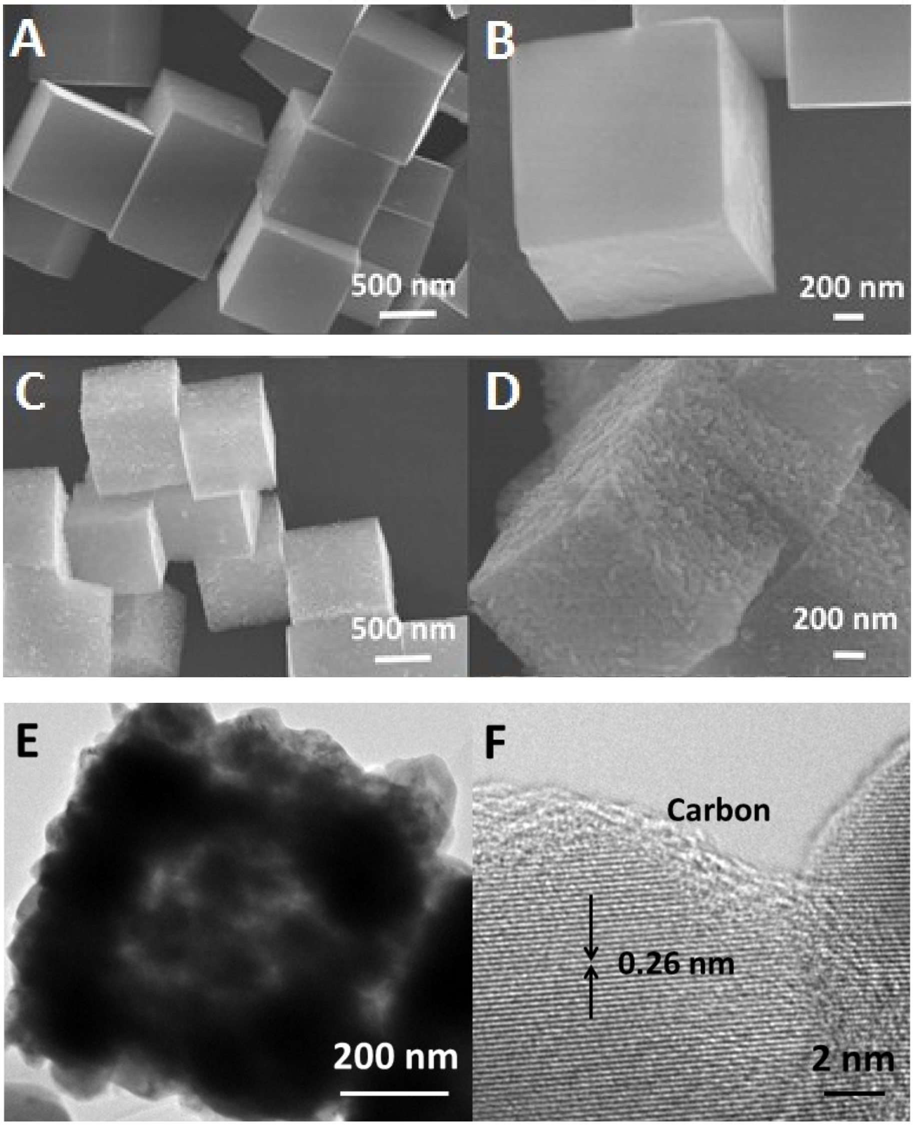


Figure S1 SEM images of PB microcubes (A, B) and HFe$_3$O$_4$@C microcubes (C, D). TEM images of HFe$_3$O$_4$@C microcubes (E, F).

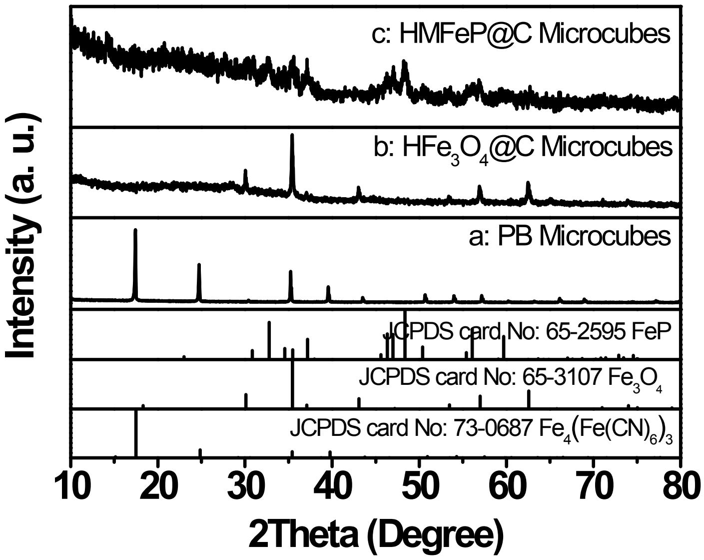
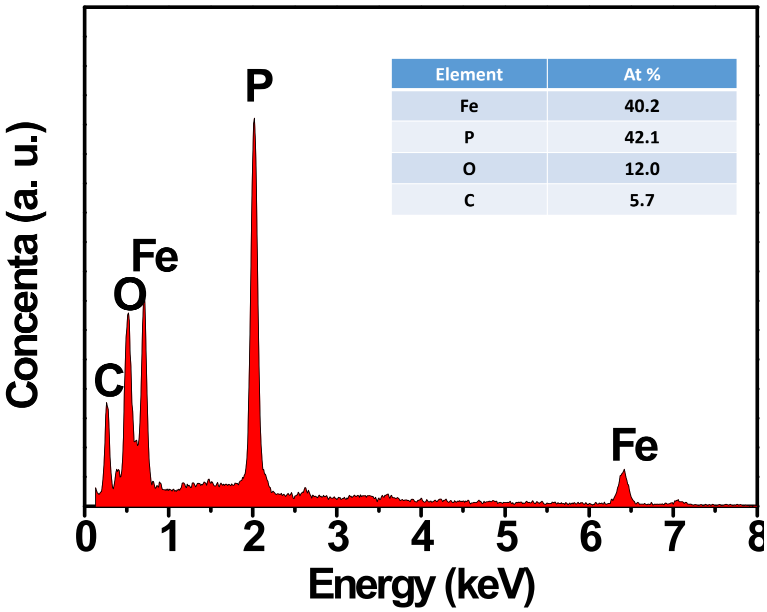


Figure S2 XRD patterns of PB microcubes, HFe_3O_4@C microcubes and HMFeP@C.



Element	At %
Fe	40.2
P	42.1
O	12.0
C	5.7

Figure S3. EDX of HMFeP@C.

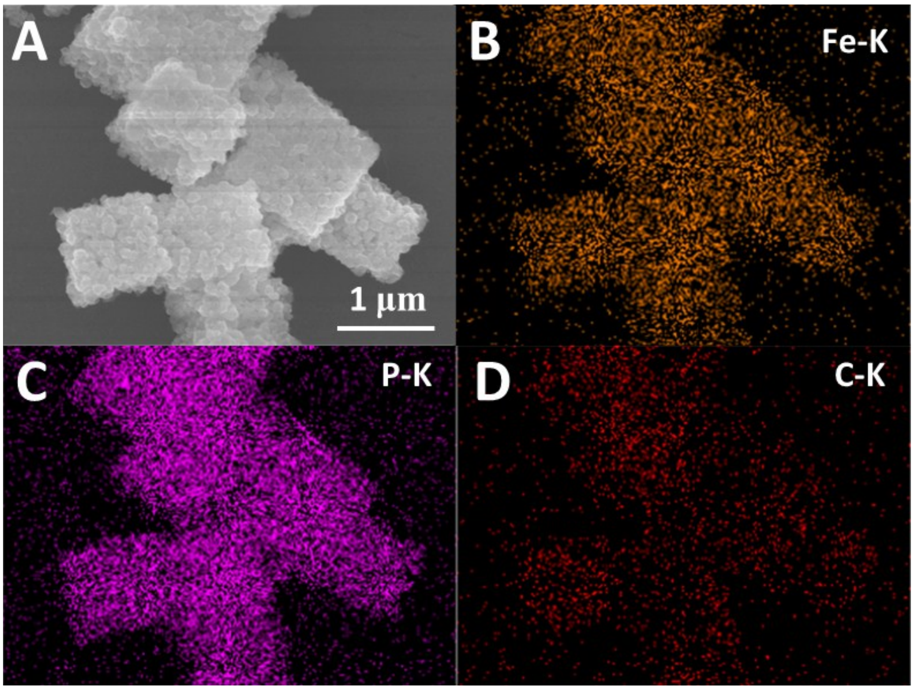


Figure S4. EDX mapping on SEM for HMFeP@C.

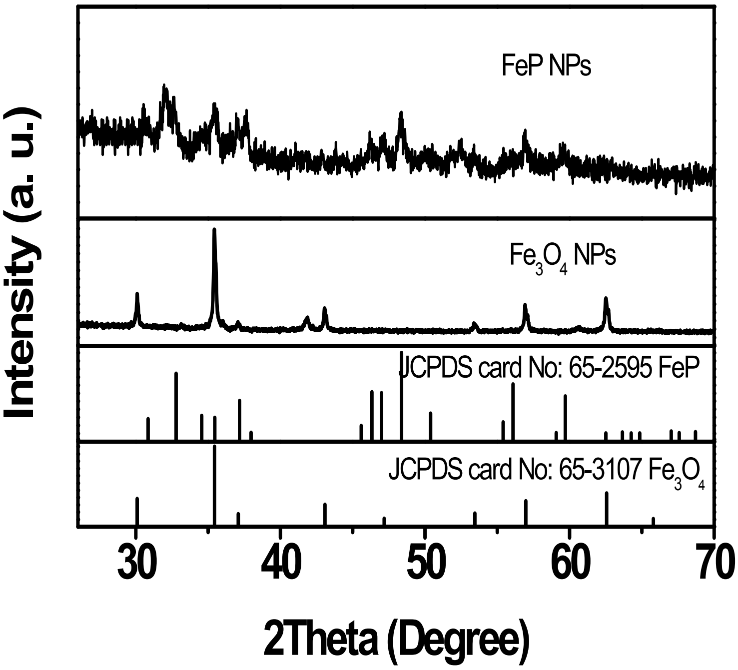


Figure S5. XRD patterns of Fe_3O_4 NPs and FeP NPs.

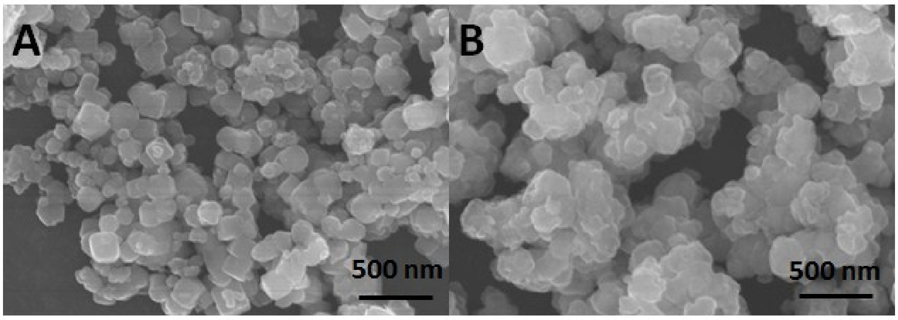


Figure S6. SEM images of Fe_3O_4 NPs (A) and FeP NPs (B).

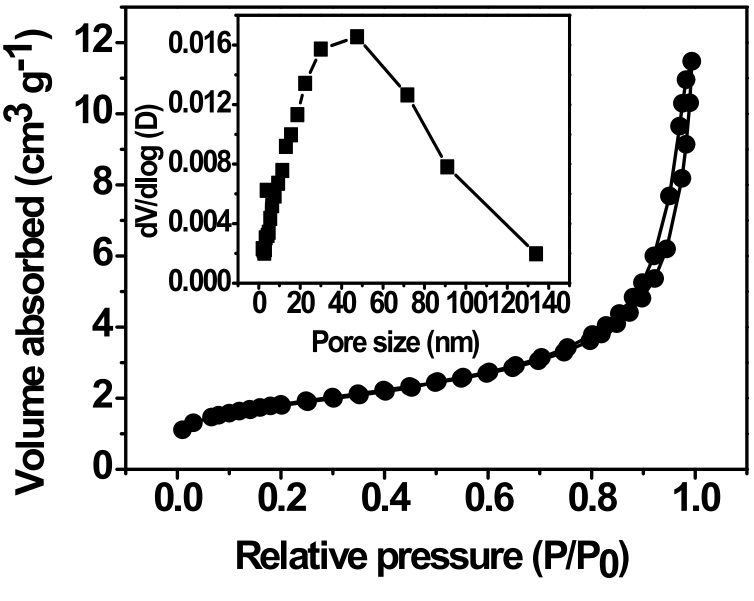
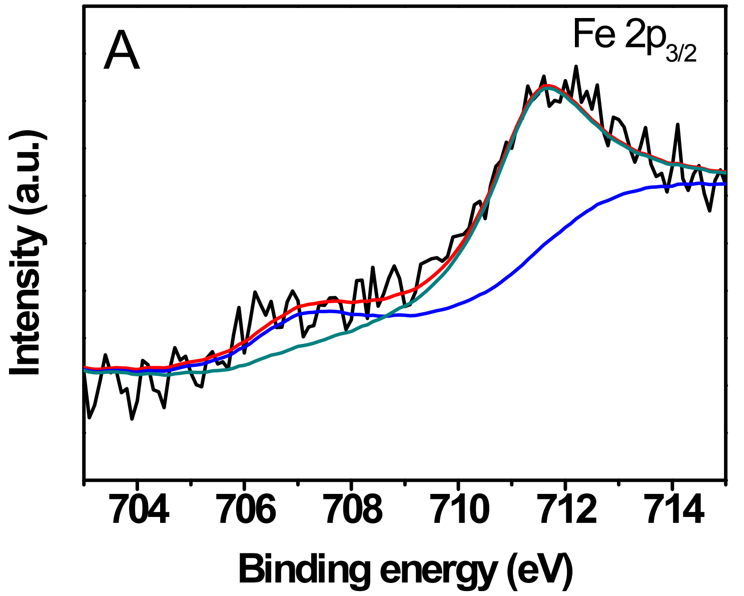


Figure S7. Nitrogen adsorption-desorption isotherms of porous FeP NPs. Inset: the BJH pore-size distribution of the nanocomposite calculated from the desorption branch of N_2 isotherm.



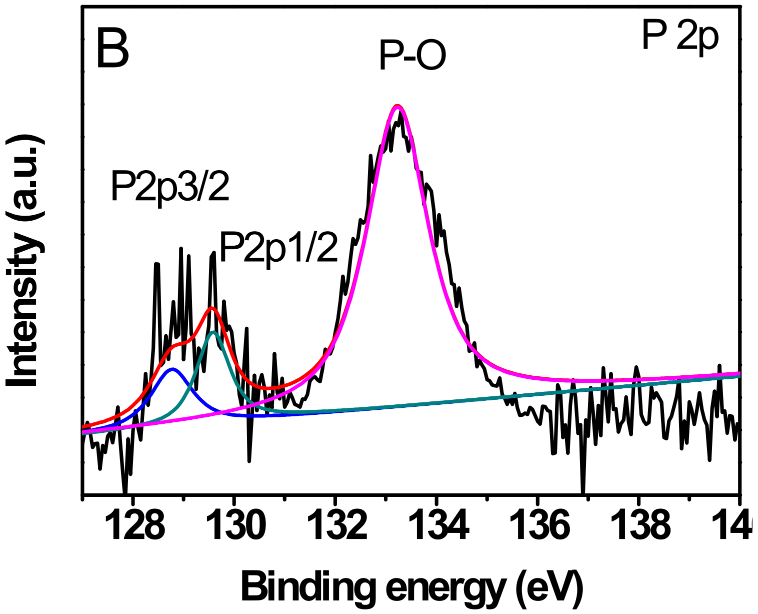


Figure S8. XPS spectrum of Fe ($2p_{3/2}$) (A) and regions for FeP NPs (B).

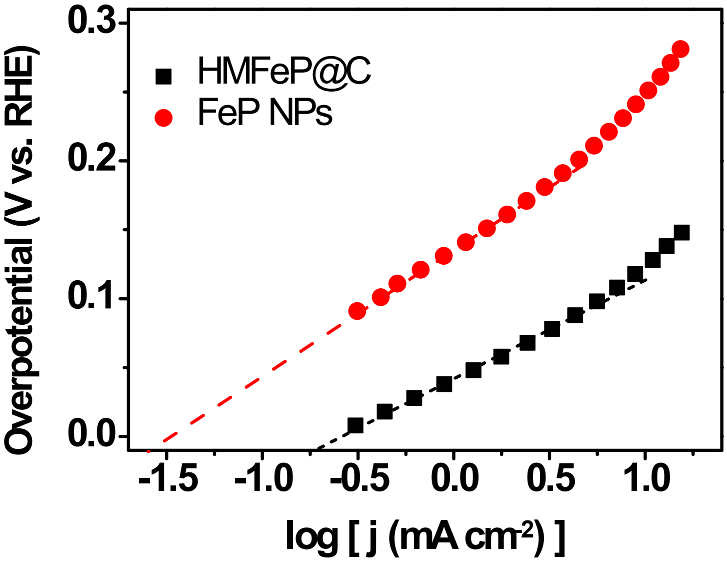


Figure S9. Tafel plots used for calculating j0 of the HMFeP@C and FeP NPs.

The exchange current density (j_0) was calculated using extrapolation methods. When the overpotential value is 0, the log j values for HMFeP@C and FeP NPs are -0.72 and -1.60, respectively. Based on Tafel equations, j_0 for HMFeP@C and FeP NPs was calculated to be 0.191 mA cm^{-2} and 0.025 mA cm^{-2}, respectively.

Table S1. Comparison of HER performance in acidic media of HMFeP@C with other non-noble metal electrocatalysts ([a] catalysts directly grown on current collectors; rGO: reduced graphene oxide; --: not given; NRs: nanorod arrays NAs: nanowire arrays, GN: graphene nanosheets; CNTs: carbon nanotubes; CC: carbon cloth; CF: carbon fiber; CFP: carbon fiber paper)

Catalysts	Onset η (mV)	Overpotential (mV vs. RHE) at 10 mA/cm^2	Tafel slope	Reference
MoS_2/Ti[a]	150	--	51	Adv. Mater. 2014, 26, 2683
MoS_2-rGO/GCE	--	~150	41	J. Am. Chem. Soc. 2011, 133, 7296
MoS_2 NSs/GCE	120	--	50	Adv. Mater. 2013, 25, 5807
$MoSe_2$/GN	50	159	61	Small 2015, 11, 414
MoP/GCE	40	125	54	Adv. Mater. 2014, 26, 5702
WP/GCE	54	161	57	ACS Catal. 2015, 5, 145
Cu_3P NAs/CF[a]	62	143	67	Angew. Chem. Int. Ed. 2014, 53, 9577
Ni_2P/Ti[a]	130	180	81	J. Am. Chem. Soc. 2013, 135, 9267
CoP-CNTs/GCE	40	122	54	Angew. Chem. Int. Ed. 2014, 53, 6710
CoP NAs /CC[a]	38	67	51	J. Am. Chem. Soc. 2014, 136, 7587
FeP NRs/CC[a]	20	45	58	ACS Catal. 2014, 4, 4065
FeP NAs/Ti[a]	16	55	38	Angew. Chem. Int. Ed. 2014, 53, 12855
FeP graphene/GCE	30	123	50	Chem. Commun., 2014, 50, 11554
FeP nanosheet/GCE	100	~240	67	Chem. Commun., 2013, 49, 6656
FeP Nanotubes/CF[a]	35	88	35.5	Chem. Eur. J., 2015, 21,18062
FeP NAs/Fe[a]	--	96	39	Chem. Commun., 2016, 52, 2819
FeP NRs/CFP[a]	--	31	48	*J. Mater. Chem. A*, 2016, **4**, 1454
FeP NR/GCE	45	120	55	Int. J. Hydrogen Energ., 2015, 40, 14272
Rugae-like FeP/CC[a]	--	34	29.2	Nanoscale, 2015,7, 10974
HMFeP@C	25	115	56	This work

References

[1] L. Zhang, H. B. Wu, X. W. Lou, *J. Am. Chem. Soc.* **2013**, *135*, 10664.

[2] J. Tian, Q. Liu, A. M. Asiri, X. Sun, *J. Am. Chem. Soc.* **2014**, *136*, 7587.

[3] M. Liu, J. Li, *ACS Appl. Mater. Interfaces* **2016**, *8*, 2158.