# Supplementary Information

Large-Scale **Fabrication of a Flexible, Highly Conductive Composite Paper Based on** Molybdenum Disulfide-Pt Nanoparticles-Single-Walled Carbon Nanotubes for Efficient Hydrogen Production

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Experimental Section

*Chemicals*. Molybdenum (IV) sulfide ($MoS_2$; 99% metals basis; ~325 mesh powder; Alfa Aesar), imidazole (99%, Acros Organics), tri-sodium citrate (99%, Scharlau), sodium borohydride (98%, Acros Organics), hexachloroplatinate ($H_2PtCl_6$, 99% Acros Organics) and Triton X-100 (Golden Innovation Business Co. Ltd) were used as received. Single-walled carbon nanotubes (SWCNT; CG300-L16) were produced by SouthWest NanoTechnologies Inc.

*Preparation of PtNPs*. All glassware used in the PtNPs synthesis experiments was thoroughly cleaned with aqua regia, rinsed with deionized water (Elga Ltd., HighWycombe, UK) and then dried in an oven before use. The PtNPs were synthesized in glassware with a magnetic stir bar. 1 mL of 16 mM $H_2PtCl_6$,1 mL of 40 mM tri-sodium citrate and 38 mL of deionized water were individually added to a two-necked bottle and stirred for 30 min to obtain a colorless mixture. Then, 200 μL of 50 mM sodium borohydride, a reducing agent, was added drop by drop in the two-necked bottle. The colorless mixture instantly turned to brownish yellow. Finally, the brownish mixture was continuously stirred at room temperature for 1 h.

*Preparation of exfoliated $MoS_2$ nanosheets.* $MoS_2$ powder was exfoliated by organic salts in water and using a Chromtech UP-500 ultrasonic processor with a ½ inch ultrasonic tip. Then, 5g of $MoS_2$ powder, 10g of imidazole and 1000mL of deionized water were added to a 1000mL beaker and sonicated with tip sonication (500W) for 2 h in continuous mode. The exfoliation environment was controlled at 15°C.

*Preparation of the SWCNT dispersion.* 35 mg of SWCNT, 1mL of the dispersant Triton X-100 and 500mL of deionized water were added to a 500mL beaker andsonicated with tip sonication (500W) for 1 h in continuous mode. The exfoliation environment was controlled at 15°C.

*Preparation of the $MoS_2$/PtNPs/SWCNT composite paper*. The suspended $MoS_2$ nanosheets, SWCNT and synthesized PtNPs were filtered through cellulose acetate membranes (0.2 μm diameter pore size, ADVANTEC) then dried in a vacuum at 50°C.

*Electrochemical measurements*. HER activity measurements were performed using a CHI7279E electrochemistry workstation. Electrochemical tests were performed in a three-electrode system using 0.5M $H_2SO_4$ as the electrolyte solution. An Ag/AgCl electrode and a Pt electrode were used as the reference and counter electrode, respectively. Linear sweep voltammetry was performed at a rate of 1 mV/s for the polarization curves. The I-t curve test was done at -0.1 V (V versus RHE). The frequency of impedance measurements was set from 0.001 Hz to 10000 Hz and the amplitude was set at 5 mV. All the samples were degassed using nitrogen for 30 min.

*Material characterization.* The morphology of the $MoS_2$ nanosheets and PtNPs was investigated using TEM (JEOL JEM-1200EX II) with samples directly transferred onto a lacey/carbon coated or formvar/carbon coated copper gird. The morphology of the composite film was investigated using FESEM (JEOL JSM-7600F). Raman mapping was performed using a Raman spectrometer (iHR550, Horiba Jobin Yvon) with a 532 nm excitation laser source; the power of the laser was set at 100 mW, the mapping area was 50 μm x 50 μm and the Raman shift of Si (520.7 $cm^{-1}$) was used for calibration before the test. X-ray photoelectron spectrometry (XPS) measurements were carried out using a Thermo K-Alpha apparatus (VGS) with an Al Kα (1486.6

eV) X-ray source. Atomic force microscope (AFM; Innova/Bruker, Santa Barbara, CA) was used to measure the morphology of the materials. The nominal spring constants of the AFM tips were 20~75 N/m (NSC15, Mikromasch, Tallinn, Estonia).

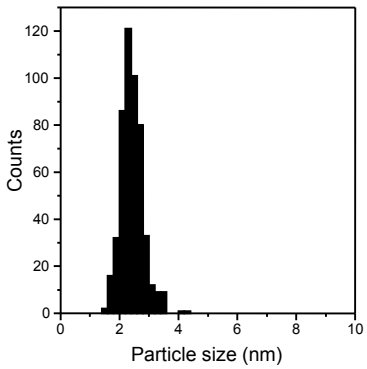


Figure S1. The size distribution of the PtNPs.

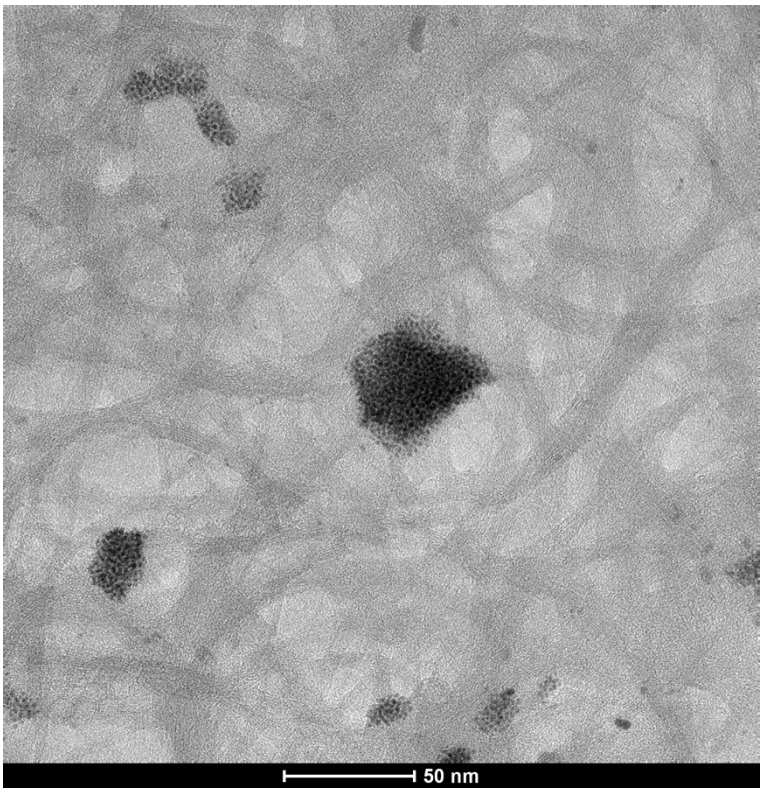


Figure S2. TEM image of the $MoS_2$/PtNPs/SWCNT.

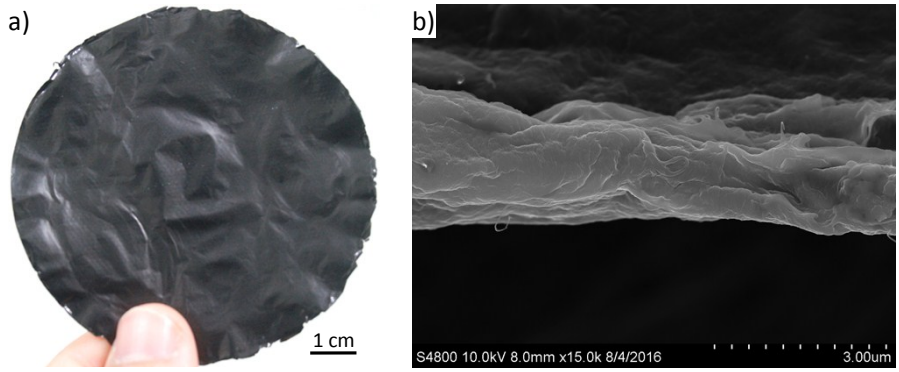


Figure S3. (a) Top view and (b) side view of the free-standing $MoS_2$/PtNPs/SWCNT composite paper.

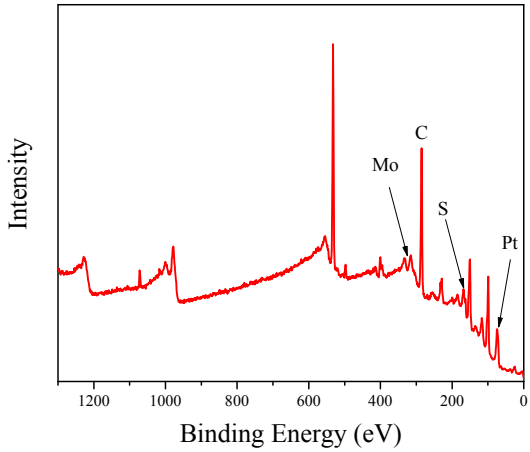


Figure S4. XPS survey spectrum of the $MoS_2$/PtNPs/SWCNT composite paper.

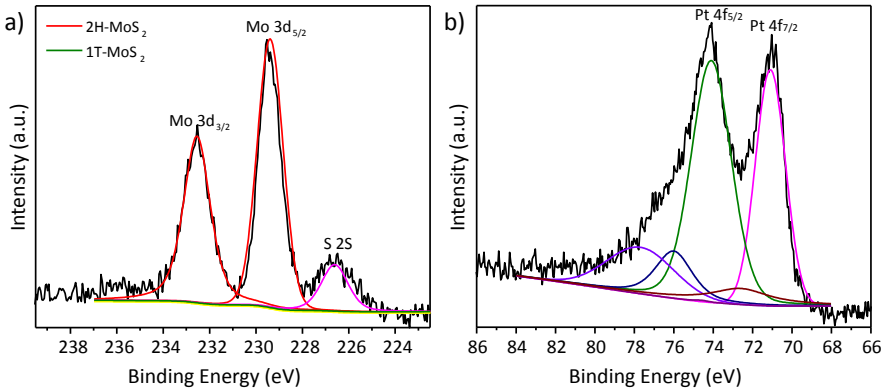


Figure S5. XPS spectra of the $MoS_2$/PtNPs/SWCNT composite paper. a) Core level of Mo 3d and S 2s for the $MoS_2$ nanosheets. b) Core level of Pt for the PtNPs.

Table S1. XPS analysis of the $MoS_2$/PtNPs/SWCNT composite paper.

| Element | Weight (%) |
|---|---|
| S | 6.92 |
| Mo | 2 |
| C | 83.48 |
| N | 6.39 |
| Pt | 1.21 |
| Totals | 100.00 |

Table S2. Comparison of HER performances of $MoS_2$-based hybrid catalyst

| Catalysts | Tafel slope (mV/dec) | Ref. |
|---|---|---|
| $MWMoS_2$@MWCNTs* | 109 mV/dec | *1* |
| Co-doped $MoS_2$/carbon | 101 mV/dec | *2* |
| $MoS_2$ Nanoparticles/CFP** | 62 mV/dec | *3* |
| V-doped $MoS_2$nanosheets | 60-75 mV/dec | *4* |
| $MoS_2$/CNT-GR*** | 58 mV/dec | *5* |
| Core-shell $MoO_3$-$MoS_2$ Nanowires | 50-60 mV/dec | *6* |
| $MoS_2$ Nanoparticles/Au(111) | 55-60 mV/dec | *7* |
| $MoS_x$ Grown on Graphene-Protected 3D Ni Foams | 42.8 mV/dec | *8* |
| $MoS_2$/MGF**** | 42 mV/dec | *9* |
| $MoS_2$/Graphene | 41 mV/dec | *10* |
| SWCNT/PtNPs/$MoS_2$ | 39.6 mV/dec | **This work** |

*$MWMoS_2$: multi-walled $MoS_2$; MWCNTs: multi-walled carbon nanotubes

**CFP: carbon fiber paper

***GR: graphene

****MGF: mesoporous graphene foams

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