Electronic Supplementary Information (ESI)

Highly Efficient and Stable DSSCs of Wet-chemically Synthesized MoS_2 Counter Electrode†

Supriya A. Patil,[a] Pranav Y. Kalode,[a] Rajaram S. Mane,[a, b] Dipak V.Shinde,[a]An Doyoung, [a]Cho Keumnam, [a] M. M. Sung,[a] Swapnil B. Ambade,[c] Sung-Hwan Han[a]*

[a]Inorganic Nanomaterials Laboratory, Department of Chemistry, Hanyang University, Seongdong -gu, 133791Seoul, Republic of Korea Email: shhan@hanyang.ac.kr,

[b]Centre for Nanomaterials & Energy Devices, School of Physical Sciences, SRTM University, 431606, Nanded, India, Email: rsmane_2000@yahoo.com,

[c]Chonbuk National University, Jeonju, Korea.

S1.Experimental details

A) Synthesis of MoS_2 thin films

For preparation of MoS_2 thin films, cleaned glass and FTO substrates were used. These substrates were placed tilted against the wall in falcon tube containing 0.1M molybdenum (V) chloride and 0.1M thioacetamide in 50 ml ethanol solution. Falcon tube was kept into a hot water bath maintained at 70℃ for 7 h. After completion of the reaction, the films were taken out and washed with ethanol, double-distilled water and dried with flow of argon stream. Synthesized MoS_2 thin films (100 nm thick, see cross sectional view in Fig.S2d for more details) were annealed at 300 ℃ for 30 min under organ environment. After natural cooling, films were taken off from the oven and explored for various characterization and DSSCs application. Detail experimental setup shown in fig.S1.

S1. Experimental setup

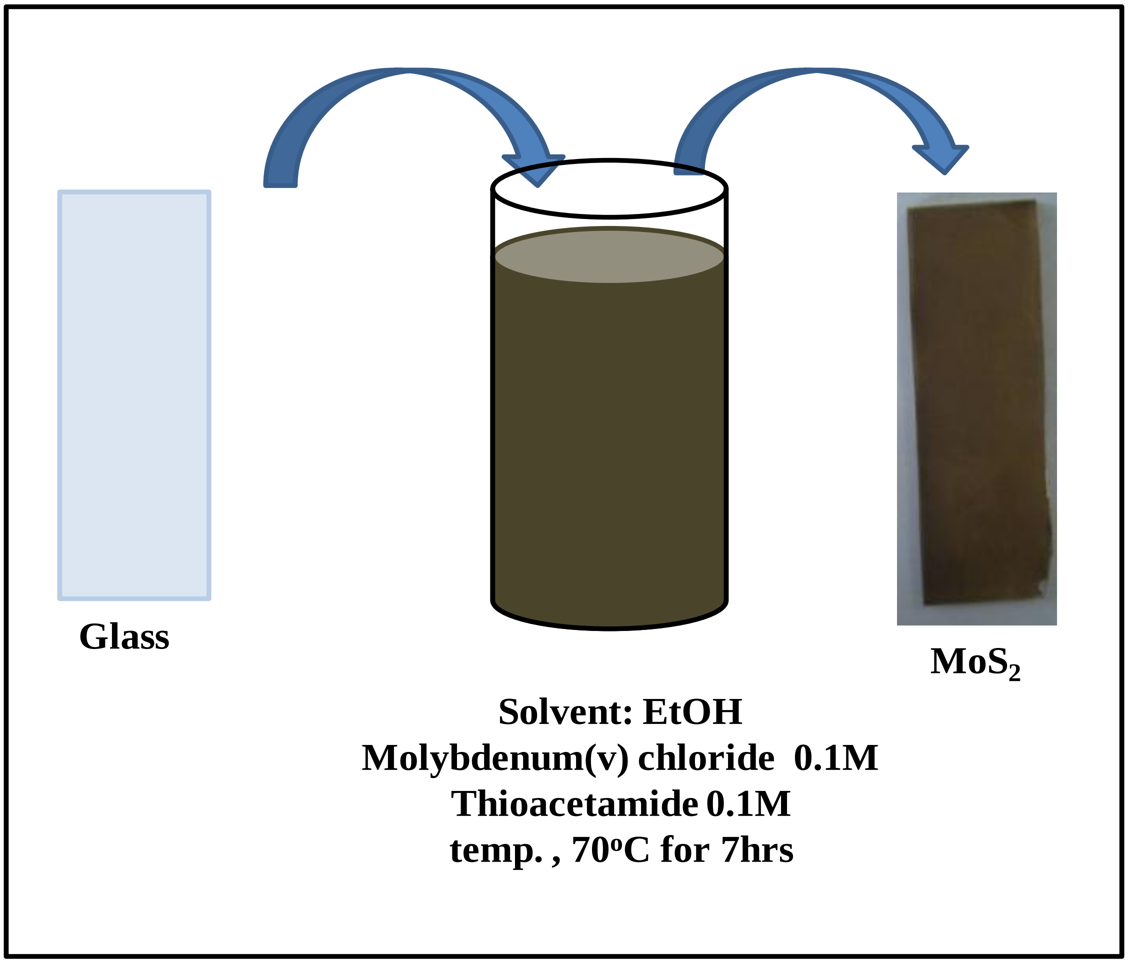


Figure S1. Synthesis protocol for synthesis of MoS_2 CE

Reaction mechanism for MoS_2CE

Based on wet chemical synthesis process, mechanism of MoS_2 thin film formation can be proposed. The kinetic analysis at the initial stage is presented by considering the total concentrations of molybdenum(V) tetrachloride and thioacetamide in the overall deposition reaction as;

$$2\ MoCl_5 + C_2H_5OH \rightarrow 2MoCl_4 + 2\ HCl + CH_3CHO \qquad (1)$$

$$MoCl_4 + 2\ CH_3CSNH_2 \rightarrow MoS_2 + 2\ CH_3CN + 4\ HCl \qquad (2)$$

Depending on the specific process and reaction parameters, the growth of thin film in a wet chemical deposition method occurs in four possible ways; a) ion-by-ion, b) cluster (hydroxide), c) complex-decomposition, and d) complex-decomposition cluster. Out of these, we presumed that the complex-decomposition cluster dominancy because, in the present study Ethanol as solvent medium was used which is based on the formation of solid phase instead of reacting directly with a free anion; it forms an intermediate complex (1) with the anion-forming reagent, continuing with MoS_2 thin film deposition from thioacetamide bath.

The S–C bond of the thioacetamide breaks, leaving the S bond to Mo. It was presumed that Mo $(OH)_4$ forms initially on the substrate and further catalyzes the thioacetamide decomposition. The catalytic effect of the solid surface might decompose thioacetamide to sulphide ion and not necessarily to catalyse the complex-decomposition mechanism.[1,2]

B) Synthesis of Pt CE

To compare DSSCs performance of MoS_2 CE with Pt CE, we also synthesized Pt CE onto the fluorine-doped tin oxide transparent (FTO) glass substrate (8 $\Omega\cdot cm^{-2}$, Hartford Glass Co., USA) was cut into 1 × 2 cm^2carefully. After that, the FTO was ultrasonically cleaned sequentially in detergent, acetone, and distilled water for 10 min in sequence, and the FTO was stored in isopropyl alcohol (IPA). The CE was prepared by drop-cast method; spreading a drop of 2 mM H_2PtCl_6 in isopropanol solvent onto FTO substrate, annealed at 450^0C for 10 min, thus, the CEs were obtained.

C) Characterization details

Crystal structure of MoS_2 thin film was confirmed using X-ray diffractometer (Rigaku D/MAX 2600V, Cu k∝= 0.15418 nm). Raman analysis was carried out using a confocal Raman microscopic system (NT-MDT). The surface topography was examined with a field-emission scanning electron microscopy (FESEM, HITACHI, S-4800) and normal and high-resolution transmission electron microscopy (TEM and HRTEM, Omega EM 912 operated at 200 kV) images. The chemical composition was examined using an energy dispersive X-ray analyzer (EDX) connected to FE-SEM unit. Chemical configuration was determined by X-ray photoelectron (XPS, VG ESCALB) spectrometer equipped with Mg Kα x-ray source, operating at 300 W. The XPS measurements were performed on the sample with Al ∝ X-ray source. The energy calibration was made against the C 1s peak. The specific surface area of MoS_2 powder, scratched from the CE, was obtained by Brunauer–Emmett–Teller (BET) measurement. Nitrogen gas adsorption–desorption method maintained at 77 K using on a (Belsorp II, BET, Korea Inc.) was used for surface area and pore volume analysis. Cyclic voltammetry (CV) curves were obtained from a three-electrode one-compartment cell having Ag/AgCl as reference electrode in the acetonitrile solution consisting of 10.0 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$ and as-prepared MoS_2 and Pt were used as working electrode. The electrochemical impedance spectroscopy (EIS, COMPACTSTATe: 40 IVIUM Technologies in a frequency range of 0.01 Hz to 1.5 MHz with 50 mV amplitude) measurement was carried out with two identical electrodes having an area of 0.36 cm^2 sealed with a thermoplastic hot-melt Surlyn tape. The EIS tests were carried out simulating open-circuit conditions at ambient atmosphere using a Model-100B, series-1488 (obtained from a computer controlled electrochemical analyzer Model-100B, series-1488 BAS-Zahner IM6 Impedance Analyzer was used) electrochemical measurement system at a constant temperature of 20 °C with AC signal amplitude of 10 mV in the frequency range of 0.1 to 10^5 Hz at 0V DC bias in the light (same condition used for J-V measurement). Tafel measurement was carried out with same BAS-ZahnerIM6 Impedance Analyzer (discussed previously). Incident photon-to-current emission (IPCE) measurements of MoS_2 and Pt CEs were measured using a solar simulator (Keithley 2400) under 100 mW cm^{-2} from a 400 W and 150 W Xe short arc lamp filtered by an AM 1.5%G filter, respectively. All photocurrent density-voltage tests were conducted with a Keithley Model 2400 digital source meter under a light intensity of 100 mW cm^{-2} (AM, 1.5) using a solar simulator (PEC-L12, Peccell Technologies). Light intensity was calibrated using a reference Si solar cell. A black mask with aperture area of 0.36cm^2 was applied on the surface of DSSCs to avoid stray light completely. Contact-mode atomic force microscopy was used to obtain two-dimensional images for both MoS_2 and Pt CEs. The scan rate used was 0.95 Hz, and the contact area was 1×1 μm^2.

S2. Surface analysis

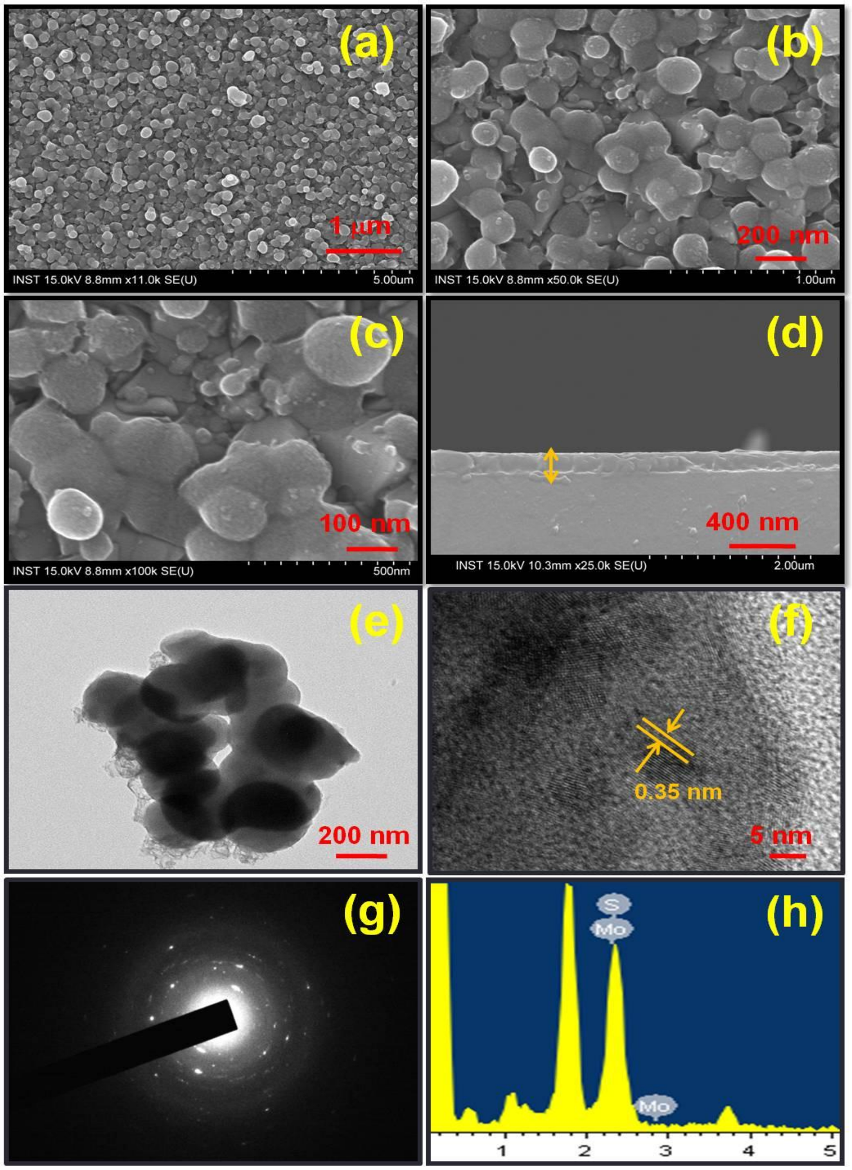


Figure S2. (a-c and d) FESEM surface and cross-sectional views, e-f) TEM and HRTEM images and, g) and h) present SAED and EDX analysis of MoS_2 CE.

S3. Surface area and pore -size distribution measurements

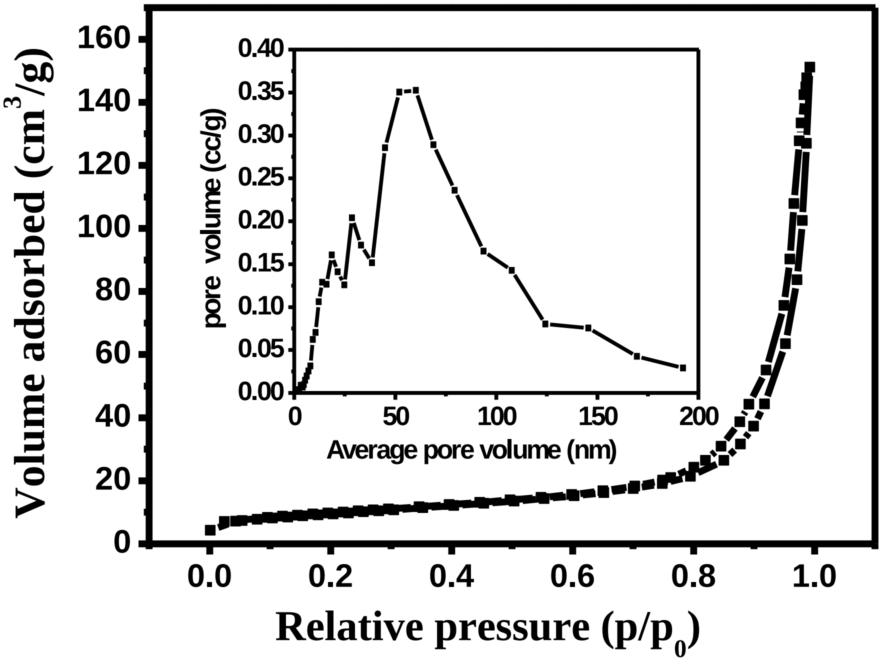
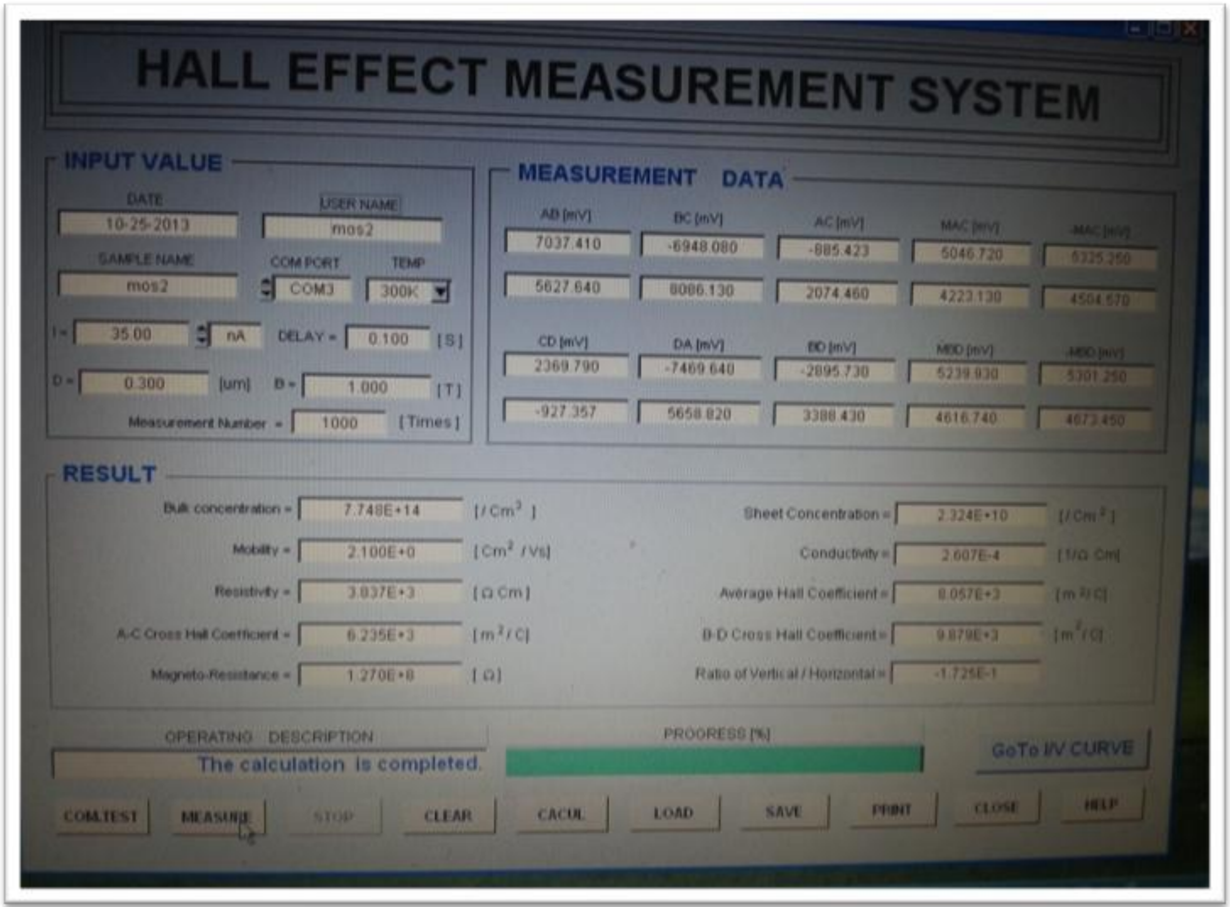


Figure S3. N_2 adsorption and desorption and inset; Barrett-Joyner-Halenda pore size distribution determined from the N_2 adsorption branch isotherm.

S4. Hall effect measurement



HALL EFFECT MEASUREMENT SYSTEM

INPUT VALUE

DATE: 10-25-2013
USER NAME: mos2
SAMPLE NAME: mos2
COM PORT: COM3
TEMP: 300K
I = 35.00 nA
DELAY = 0.100 [S]
D = 0.300 [um]
B = 1.000 [T]
Measurement Number = 1000 [Times]

MEASUREMENT DATA

AB [mV]	BC [mV]	AC [mV]	MAC [mV]	-MAC [mV]
7037.410	-6948.080	-885.423	5046.720	5325.250
5627.640	8086.130	2074.460	4223.130	4504.570

CD [mV]	DA [mV]	BD [mV]	MBD [mV]	-MBD [mV]
2369.790	-7469.640	-2895.730	5239.930	5301.250
-927.357	5658.820	3388.430	4616.740	4673.450

RESULT

Bulk concentration = 7.748E+14 [/Cm³]
Mobility = 2.100E+0 [Cm² /Vs]
Resistivity = 3.837E+3 [Ω Cm]
A-C Cross Hall Coefficient = 6.235E+3 [m²/C]
Magneto-Resistance = 1.270E+8 [Ω]
Sheet Concentration = 2.324E+10 [/Cm²]
Conductivity = 2.607E-4 [1/Ω Cm]
Average Hall Coefficient = 8.057E+3 [m²/C]
B-D Cross Hall Coefficient = 9.879E+3 [m²/C]
Ratio of Vertical / Horizontal = -1.725E-1

OPERATING DESCRIPTION: The calculation is completed.

Name	Conductivity 1/ohm-cm	Surface concentration /cm^2	Mobility cm^2/Vs	Hall coefficient m^2/C	Type	Reference Type
MoS_2	2.607X10^{-4}	2.32X10^{10}	2.1	8.057X10^3	p-Type	p-Type

Figure S4. Digital photoimages of computer display after Hall effect measurement with interested electronic parameters (table at bottom) affiliated to MoS_2 CE.

S5. Circuit and electronic parameter obtain from electrochemical impedance spectroscopy measurement

An equivalent circuit used for fitting the Nyquist plots

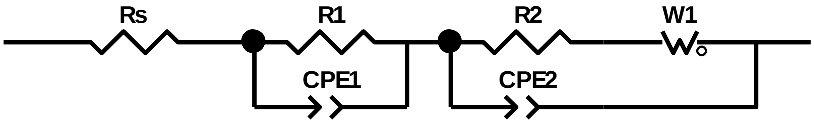


Table S1. Estimated electronic parameters obtained by fitting the Nyquist plots.

Name	**Series resistance (Ωcm^2)**	**R1 (Ωcm-^{2})**	**R2 (Ωcm^2)**	**CPE1-T(F)*10^{-3}**	**CPE1-P(F)**	**CPE2-T(F)*10^{-3}**	**CPE2-P(F)**	**W1-R**	**W1-T**	**W1-P**
Pt	**26.73**	**4.87**	**18.01**	**1.288**	**0.98**	**0.39**	**0.68**	**2.348**	**0.1418**	**0.1649**
MoS_2	**23.51**	**3.25**	**15.25**	**1.011**	**0.94**	**0.26**	**0.62**	**1.801**	**0.1253**	**0.1276**

S6. Atomic force microscopy

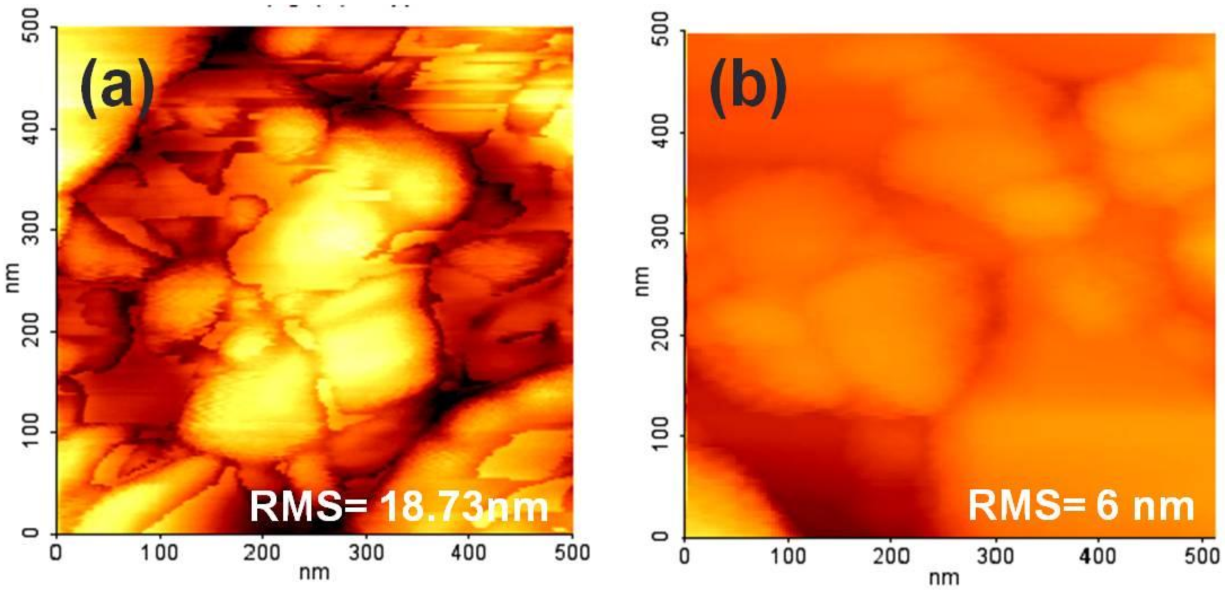


Figure S6. Atomic force microscopy images with 18.73 and 6 nm average roughness values for (a) MoS_2 and, (b) Pt CEs, respectively**,** are measured under a contact mode.

S7. Summarized table

Table S2. Summary of works involving MoS_2 as a counter electrode in DSSCs.

Authors name	**Journal name/ (Year)**	**volume**	**Page no.**	**Composition mixed with MoS_2 for counter electrode**	**Method used for synthesis**	**Temp^{0}C/Time for synthesis hour(h)**	**Obtained efficiency(η%)with dye cell**	**Pristine MoS_2**
Gentian Yue	J. Mater. Chem (2013)	1	1495-1501	**MoS_2+Carbon**	Hydrothermal method	200/48	7.6	5.3
Gentian Yue	Electrochemica acta (2012)	85	162-168	**MoS_2+Graphene**	Slurry coating method	150/24	5.9	---
Mingxing Wu	Phy. Chem. Chem. Phys. (2011)	13	19298-19301	**MoS_2Syntheisized**	Hydrothermal method	200/48	7.5	7.5
Chia-Jui Liu	J. Mater. Chem (2012)	22 (39)	21057-21064	**MoS_2+Graphene**	Coating method	120/12	6.0	5.09
Sheng-Yen Tai	J. Mater. Chem. (2012)	22(47)	24753-24759	**MoS_2+MWCNT**	Hydrothermal method	120/24	6.4	4.99
	Present study (2013)	-	-	**MoS_2**	Wet chemical method	70/7	7.0	7.01

…..Represents results are not mentioned.

References

1. G. Hodes, Chemical solution depostion of semiconductor,2003,91.

2.H. Zeng, J. Dai, W. Yao, D.Xiao, X. Cui, *Nat. Nanotechnology.*,2012,**7,**490-493.