

Platinum-free dye-sensitized solar cells by flower-like mixed-phase $\text{Co}_x\text{S}_y/\text{Ni}_x\text{S}_y/\text{Mo}_x\text{S}_y$ composites

Vijaya Subbiah,^a Giovanni Landi,^b Jerry J. Wu,^c Sambandam Anandan^{*a}, Muthupandian Ashokkumar^d

^a*Nanomaterials and Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Tiruchirappalli -620015, India. E-mail: sanand@nitt.edu*

^bENEA, Portici Research Center, P.le E. Fermi 1, Portici Naples, 80055, Italy.

^cDepartment of Environmental Engineering and Science, Feng Chia University, Taichung 407, Taiwan.

^dSchool of Chemistry, University of Melbourne, Vic 3010, Australia.

* To whom correspondence should be addressed: E-mail: sanand@nitt.edu

Supplementary Information

Fig. S1 FE-SEM images of (a) CNM10 (b) Ni_3S_4 (c) CoS_2 and d) MoS_2 .

Fig. S2 Ac equivalent circuit of DSSC.

Fig. S3 Dark J - V characteristics of DSSCs fabricated with Pt, CNM10, and CNM25 CEs.

Fig. S4 EQE and integrated J_{SC} of DSSCs fabricated with (a) Pt (b) CNM10 (c) CNM25 CEs respectively.

Experimental Section

Materials

Fluorine doped tin oxide (FTO) glass plates ($8\ \Omega$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexaammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), thiourea (H_2NCSNH_2), hexachloroplatinic acid hexahydrate ($\text{H}_2\text{Pt}(\text{Cl})_6 \cdot 6\text{H}_2\text{O}$), N3 dye (cis-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)), TiO_2 (Degussa P25), polyethylene glycol (PEG; MW = 10000), lithium iodide (LiI), acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$), TiCl_4 (1M in toluene), iodine (I_2), propan-2-ol also called isopropyl alcohol (IPA) were purchased from Sigma Aldrich and used as received without any further purification.

Photoanode preparation

TiO_2 paste was prepared by following the procedure: 0.16 mg of PEG (MW 10000) was dissolved in 1M HNO_3 , 0.21 mL acetylacetone, 0.04 mL Triton-X, and TiO_2 (P25 Degussa) nanopowder were added and the solution mixture was sonicated for 1 h and stirred for 24 h.¹⁻²

FTO glass plates ($8\ \Omega$) were cut into $2\text{ cm} \times 2\text{ cm}$ pieces. The glass plates were washed with a mild alkaline solution, deionized water, acetone, and isopropyl alcohol subsequently for 10 min each using the ultrasonic water bath. Then, these glass plates were blow air dried. The TiO_2 blocking-layer was coated by immersing the cleaned FTO glass plates (facing the conductive side upwards) in a 40 mM aqueous solution of TiCl_4 for 30 min at 70°C . After cooling to room temperature, these TiO_2 layer coated FTO plates were rinsed with distilled water and ethanol; dried at 100°C for 10 min. The mesoporous TiO_2 layer was achieved by the doctor-blade technique. Invisible tape (thickness $55\ \mu\text{m}$) was used as a spacer to maintain a uniform

thickness of the film. These TiO₂ coated FTO glass plates were dried to evaporate the solvents. Finally, these FTO/TiO₂ plates were sintered at 450°C for 30 min and those plates were used as photoanodes.

Counter electrode (CE) preparation

20 mg of CNM10 (or CNM25) was dispersed in 1 mL IPA and sonicated for 30 min. Then, the same solution was drop-casted onto the pre-cleaned FTO glass plates and dried at room temperature (to avoid the oxidation of the sample) to evaporate the solvent overnight.¹

Pt CE preparation

Pt CE was prepared by thermal decomposition of hexachloroplatinic acid hexahydrate (drop-casting 4 mM of H₂Pt(Cl)₆·6H₂O in IPA solution onto a pre-cleaned FTO glass plate) at 450 °C for 30 min¹⁻² and cooled down to room temperature. These Pt electrodes were used as the reference counter electrode in this work.

Fabrication of DSSCs

The dye-sensitization was performed by dipping photoanodes (FTO/TiO₂) at 70 °C in 0.5 mM N3 dye dissolved in tert-butanol/acetonitrile (v/v = 1:1) for 24 h under dark conditions. Then, the dye coated TiO₂ films were taken out from the dye solution and the plates were rinsed with ethanol to remove the excess dye. The excess portion of the dye coated TiO₂ film was scrapped to fix the cell active area (0.25 cm²). Now, both dye adsorbed TiO₂ electrode and counter electrodes were sandwiched with the help of two crocodile clips. Parafilm was used to separate the electrodes from contacting each other to avoid the short circuit between two conductive surfaces of the electrodes. Finally, the electrolyte (liquid iodine/iodide) was injected in the space

between the two electrodes. The liquid electrolyte was composed of 0.05 M I₂/0.5 M LiI/0.5 M 4-tert-butylpyridine in 3-methoxypropionitrile.

Characterization and measurements

Bruker D8 diffractometer using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at a scan rate of $0.02^\circ \text{ min}^{-1}$ was involved to perform X-ray diffraction (XRD) analysis. The morphology and EDX (Energy-dispersive X-ray spectroscopy) analysis of the samples were analyzed by field emission scanning electron microscopic (FE-SEM) technique with the help of a JEOL 7401F Scanning electron microscope. A JEOL JEM 2010 microscope was employed to record the high-resolution transmission electron spectroscopy (HR-TEM). The surface electronic state of the elements were analyzed by Thermo Scientific X-ray photoelectron spectroscopic (XPS) technique. The electrochemical studies were performed by using Metrohm AUTOLAB12/FRA2 PGSTAT302N electrochemical analyzer assembly with NOVA software version 1.10 version. 0.05 M LiI, 0.01 M I₂, and 0.5 M LiClO₄ in acetonitrile solution were used to measure CVs of Pt and CNM CEs at the potential range -0.4 V to 0.8 V at the scan rate of 10 mV s^{-1} using 3 electrode system (Ag/AgCl as reference electrode and Pt wire as a counter electrode). For this, samples were prepared by drop-casting CNM10 or CNM25 dispersed in IPA solution onto a pre-cleaned 4×1 FTO glass plates. These glass plates were dried at room temperature overnight and used as the working electrode (WE). Dummy cells were fabricated using two identical electrodes (Pt and CNM electrodes) which were clipped together to study the electrochemical impedance spectroscopy (EIS) studies and parafilm was used to separate the electrodes from contacting each other. The exposure area of 0.25 cm^2 was fixed during the fabrication of dummy cells. To complete the fabrication, the liquid electrolyte was injected into space between the two electrodes. The measurement was recorded at the frequency range of 0.1 to 10^5 Hz and the

amplitude of the sinusoidal AC voltage was fixed to 10 mV. The J - V measurement of the fabricated DSSCs was characterized by AUTOLAB12/FRA2 PGSTAT302N associated with a solar simulator (85 mW cm^{-2} , AM 1.5 G). QE-T (Enlitech, Taiwan) was used to record the incident photon to electron conversion efficiency (IPCE) spectra of the devices using Oriel 300 W Xe Arc lamp in combination with an Oriel Cornerstone 260 $\frac{1}{4}$ m monochromator. The reference monocrystalline silicon diode was calibrated to calculate the number of incident photons for each wavelength. ZSimpWin software was used for equivalent circuit fitting of the EIS data.

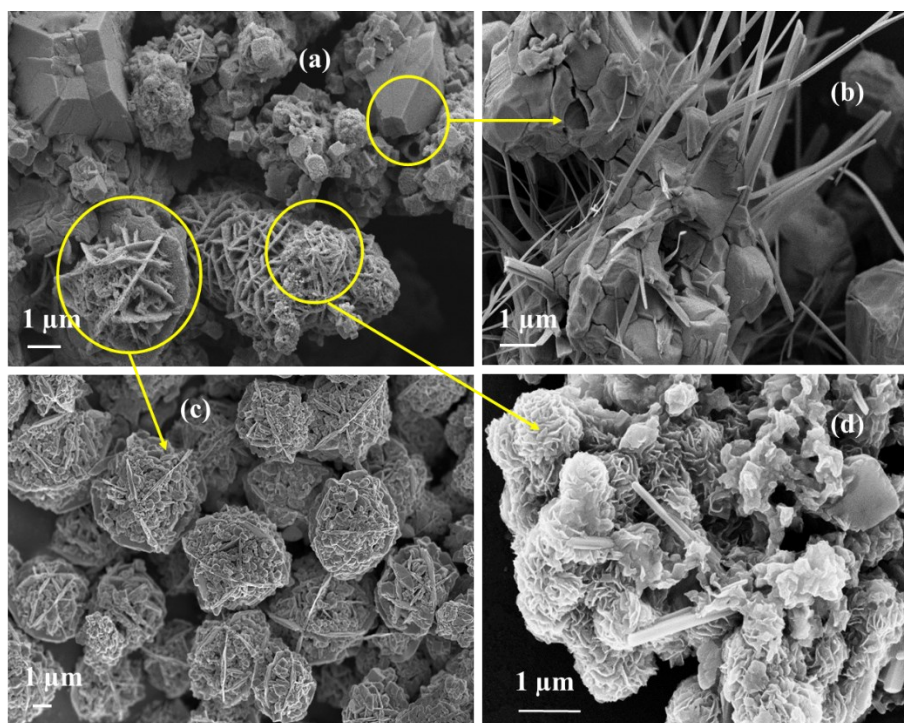


Fig. S1 FE-SEM images of (a) CNM10 (b) Ni_3S_4 (c) CoS_2 (d) MoS_2

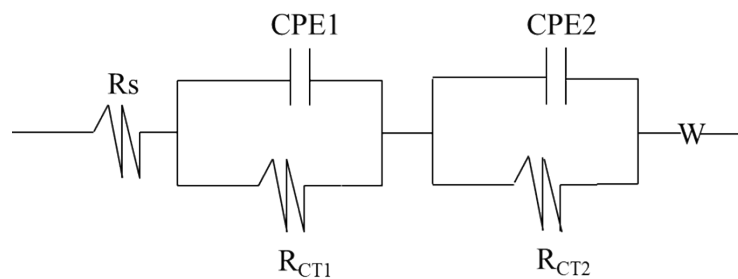


Fig. S2 Ac equivalent circuit of DSSC

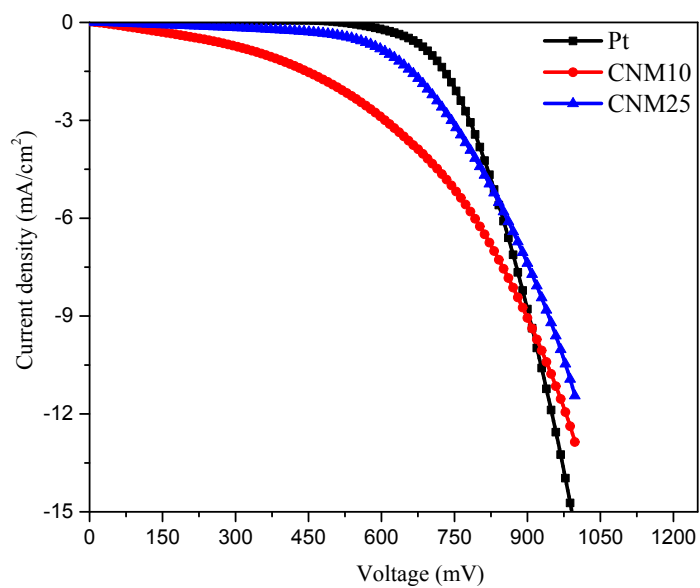


Fig. S3 Dark $J-V$ characteristics of DSSCs fabricated with Pt, CNM10, and CNM25 CEs respectively.

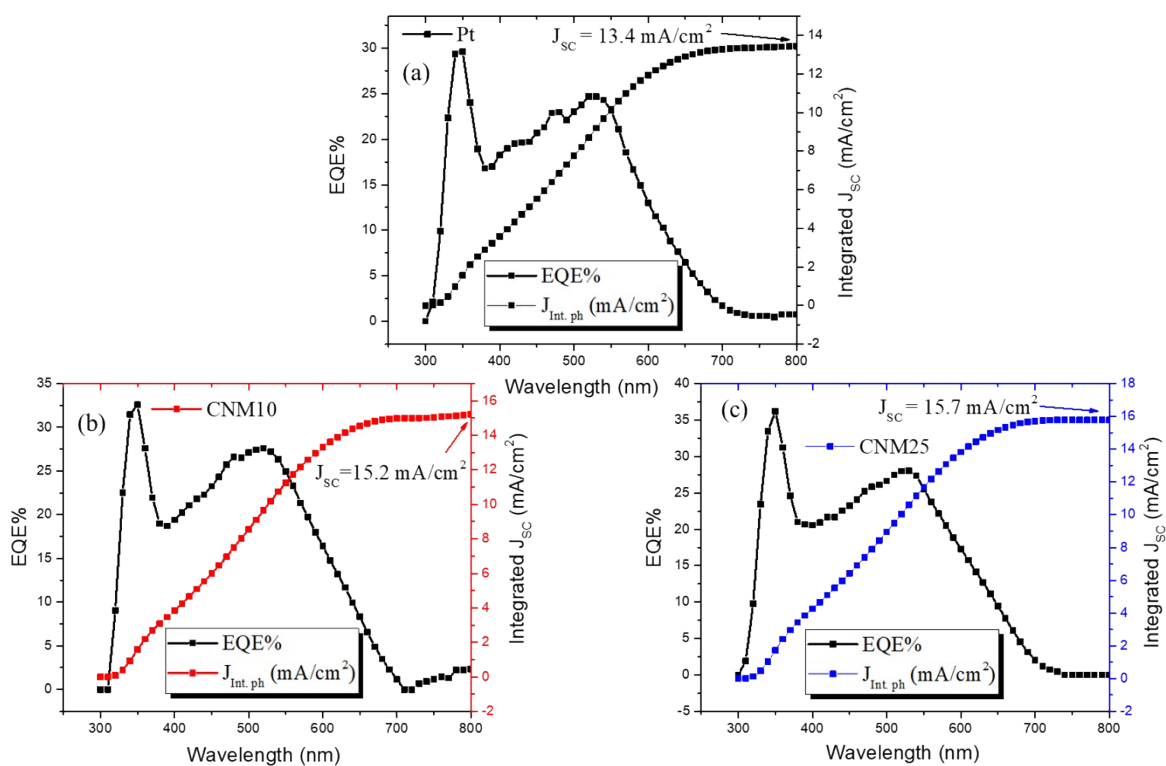


Fig. S4 EQE and integrated J_{sc} of DSSCs fabricated with (a) Pt (b) CNM10 (c) CNM25 CEs respectively.

References

1. S. Vijaya, G. Landi, J. J. Wu, S. Anandan, *Phys. Chem. Chem. Phys*, 2019, **21**, 25474-25483.
2. S. Vijaya, G. Landi, J. J. Wu, S. Anandan, *Electrochimica Acta*, 2019, **294**, 134-141.