Supporting Information

Energy efficient, one-step microwave-solvothermal synthesis of highly electro-catalytic thiospinel $NiCo_2S_4$/graphene nanohybrid as a novel sustainable counter electrode material for Pt-free dye-sensitized solar cells

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Note: This supplementary information contains Synthesis procedure used for the preparation of GO, DSSC fabrication and characterization procedure with supplementary Figure S1

Preparation of GO

The Graphene oxide (GO) used in this process was prepared from graphite natural flake using 'modified Hummers' method as reported in earlier work.[1,2] In brief, 1.25 g each of graphite powder and KNO_3 were added gradually into 58 mL of concentrated H_2SO_4 (98% Fisher Scientific) at room temperature. The mixture was stirred for 10 min towards the addition of 7.5 g of $KMnO_4$, then heated to 35°C and constantly stirred for 6 h. Subsequently, 20 mL of H_2O was added drop wise under constant stirring, bringing about a quick temperature rise to 90-95 °C for 30 min. Later, 50 mL of H_2O and 1.5 mL of H_2O_2 (30 wt %) (Fischer Scientific) was added drop by drop to dissolve insoluble manganese species. A yellow colored GO suspension was obtained which was washed until pH reached nearly 5. The resulting suspension was sonicated for 30 min using Ti-Horn probe Vibra Cell (VCX 750), Sonics and Materials, Inc., USA. The obtained GO suspension was finally dried at 60 °C in vacuum oven.

DSSC Device Fabrication.

The photoanodes for DSSCs were prepared using doctor-blade technique, referring to our earlier works.[3,4] 0.5 g of the TiO_2 sample prepared by MW-HT was dispersed into 4 mL ethanol by ultrasonication for 10 min. Then 1.5 g terpineol and 0.1g ethyl cellulose were added and the solution was again subjected to sonication to form a homogenous viscous paste. The obtained paste was spread over a well-cleaned fluorine-doped tin oxide (FTO) glass substrate (Sigma Aldrich) by doctor-blade method to obtain a thickness of ~17 – 22 µm using 3M scotch adhesive tape into an area of 0.25 cm^2 (with suitable mask). After air-drying, sintering was done at 450 °C for 1 h with temperature ramping rate of 5°C min^{-1}. When room temperature was attained, the coated substrates were sensitized by soaking into a 0.5 mM N719 dye solution (Sigma-Aldrich) for 12 h. Later the sensitized photoanodes were rinsed with ethanol to remove the excess dye molecules on the photoanode surface.

The $NiCo_2S_4$ and $NiCo_2S_4$/GNS-hybrid CEs were prepared on FTO by a facile drop-casting technique. In detail, 1 mg of the synthesized $NiCo_2S_4$ or $NiCo_2S_4$/GNS hybrid was dispersed in 4 mL of ethanol by ultrasonication for few minutes to form a homogenous CE ink solution. 1 or 2 drops of this ink solution was spread over cleaned FTO by drop-casting method. The resultant CE film was dried in vacuum oven at 80°C for 6 h. As a reference for comparison studies, Pt CE was fabricated by drop-casting 5 mM H_2PtCl_6 (in isopropanol) upon a pre-cleaned FTO and successively annealed at 400°C for 20 min. While assembling the DSSCs, two electrodes were sandwiched together with Surlyn film (30µm) as spacer by two binder clips. The redox electrolyte containing 0.06 M 1-butyl-3-methyl imidazolium iodide, 0.03 M of iodine solution (I_2), 0.10 M guanidiniumthiocyanate, 0.5 M 4-tert-butylpyridine in a solvent mixture of acetonitrile and valeronitrile (v/v, 85:15) was introduced between the two electrodes.

2.5 DSSC Device Characterization

Photovoltaic (PV) measurements were implemented by a Newport® 150W 96000 solar simulator set at 100 $mWcm^{-2}$ full spectrum power using AM1.5G filter. Current density-voltage (*J-V*) curves were generated using a Keithley 2400 source meter. The light intensity of the xenon light source was calibrated using a standard silicon photodiode (New Port, USA). The spectral response of the fabricated DSSCs were characterized by determining the wavelength dependence of the incident photon-to-current efficiency (IPCE) *via* focusing light using a xenon lamp with a monochromator on to the cell using Bentham PVE300 system. Electrochemical Impedance spectroscopy (EIS) and Cyclic Voltammetry (CV) measurements were executed on Biologic potentiostat-galvanostat (SP-150). CV measurements were done in a three-electrode system with different $NiCo_2S_4$ CEs as working electrode, Ag/Ag^+ as reference electrode and a Pt wire as the counter electrode at a scan rate of 50 mVs^{-1}. The electrolyte solution containing 0.1 M $LiClO_4$, 1mM I_2 and 10 mM LiI in an anhydrous acetonitrile was used.

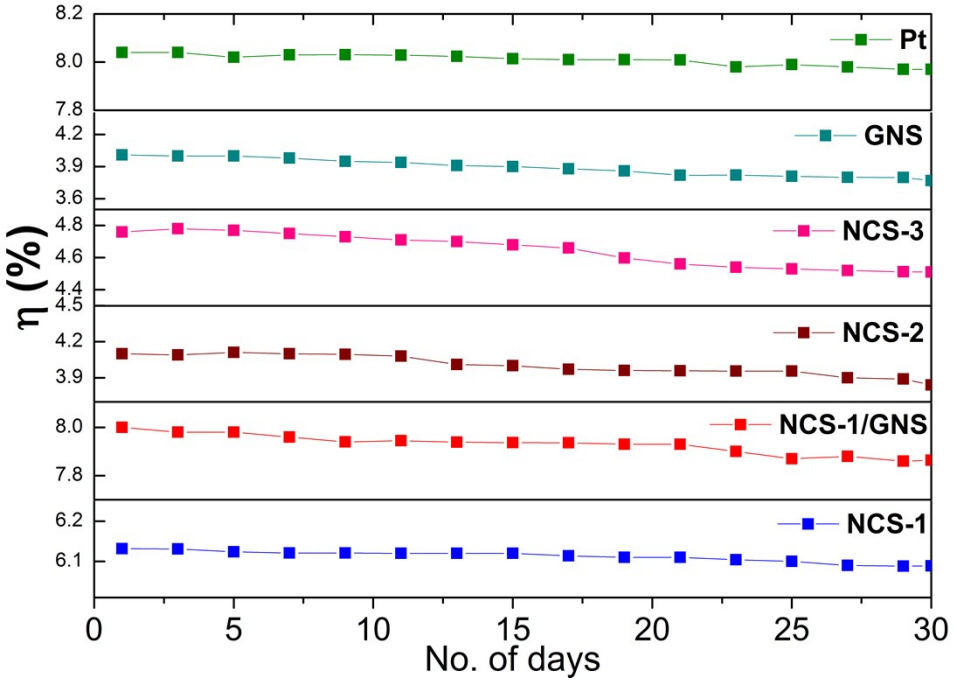

Figure S1 The stability of PCE DSSCs assembled with different CEs studied over a period of 30 days under ambient conditions.

REFERENCES

1. A. VadivelMurugan, T. Muraliganth, A. Manthiram, *Chem. Mater*. 2009, **21**, 5004-5006.

2. S. Praneetha, A. VadivelMurugan, *RSC Adv.,* 2013, **3**, 25403-25409.

3. R. Krishnapriya, S. Praneetha, A. VadivelMurugan, *CrystEngComm.*2015, **17**, 8353-8367.

4. R. Krishnapriya, S. Praneetha, A. VadivelMurugan, *New. J. Chem*., 2016, **40,** 5080-5089

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