Annexure A
Materials and Methods

A.1 Reagents

To conduct the experiments and reactions the following list of chemicals were procured from various sources and is listed below:

Chemicals/Reagents	Make/Source
Hafnium isopropoxide	Alfa Aesar
Titanium tetra isopropoxide	Acros
Hexadecylamine	Sigma Aldrich
Absolute ethanol	Changshu Hongsheng Fine Chemical Co., Ltd, China
Methyl orange	Acros
Methylene blue	SRL
Cresol red	Sigma
Thymol blue	Qualigens
Solochrome black	Qualigens
Liquor ammonia	Qualigens
Ethanol	Shangzu, China
Carbon soot	Degussa
Resorcinol	Qualigens
Formaldehyde	Fischer
Ethylenediamine	Sigma Aldrich
Tetraethylorthosilicate	Sigma Aldrich
Hydrofluoric acid	Sigma Aldrich
N3 dye	Solaronix
Iodolyte	Solaronix
Nickel (II) nitrate hexahydrate	Alpha Aesarco
Cobalt nitrate hexahydrate	Sigma Aldrich
Nitric acid	Fischer Scientific
Liquor ammonia	Fischer Scientific
Oleic Acid	Acros
Oleylamine	Sigma Aldrich
Lead Bromide	Alfa Aesar
Cesium carbonate	Acros
1-Octadecene	Sigma Aldrich

A.2 Solar cell fabrication

A.2.1 Photoanode Preparation for DSSC

FTOs glasses were cleaned with soap solution, distilled water and acetone successively in order in a an ultrasonicator for 15 mins each. Afterwards, in a mixture of 0.1% HCl and

ethanol mixture, the glasses were cleaned similarly for 10 mins. The synthesized nanomaterials were mixed in a mortar pestle in a terpineol, ethanol, acetic acid and ethyl cellulose mixture until the formation of a sticky paste. The paste was then screen printed into an FTO repeatedly for three times. The prepared photoanodes were then annealed at 500 °C for 30 min. In order to sensitized the photoanodes with dye, the annealed photoanodes were dipped and soaked in 0.5 mM N_3 ruthenium-based dye solution for 20 h.

A.2.2 Counter electrode preparation for DSSC

FTO glasses were cleaned as mentioned in A.2.1. The cleaned photoanodes were dried and platinic acid (H_2PtCl_6) were paint brushed over it. Afterwards, the electrodes were annealed at 450 °C temperature for 30 min.

A2.3 DSSC device fabrication

The dyed photoanode and counter electrode are sandwiched together with the active area facing each other with a surlyn separator in between. Then the electrolyte was filled using an injection in the space between the two.

A.3 Instrumentation Techniques

The synthesized nanomaterials were subjected to powder X-ray diffraction (XRD) analysis using a Bruker D8 Advance Diffractometer equipped with a Cu Kα wavelength of 1.54 Å. TEM imaging was performed by transmission electron microscope (FEI Tecnai-G2 T20). For imaging, ~10 mg of the sample was dispersed in ethanol and drop coated on a copper grid and allowed to dry before imaging. Diffuse reflectance spectra (DRS) were recorded using a UV−vis spectrophotometer (Varian Cary 4000) over a wavelength range of 200−800 nm. Here, PTFE (poly tetrafluoroethylene) was used as the standard material for baseline correction. HRTEM images were analyzed with ImageJ and Gatan Digital Micrograph software. The surface composition and chemical states were measured with an Omicron Nanotechnology (Oxford Instruments) X-ray photoelectron spectroscope (XPS) equipped with monochromatic Al Kα radiation. The peak correction with respect to the adventitious carbon peak is done for Hf 4f and O 1s by a shift correction factor of 4.8 eV with reference to a standard carbon 1s peak obtained at 284.6 eV.30 The XPS spectra were fitted by means of a Gaussian function after a Shirley background subtraction. A BET adsorption−desorption isotherm was performed to understand the porosity of the nanomaterials. The specific surface area was analyzed by BET, and the pore volume and geometry were analyzed by BJH analysis using an N_2 adsorption−desorption isotherm (Quantachrome Autosorb iQ3) with 0.05 error values for all of the measurements. Temperature-programmed desorption (TPD) experiments were performed using an Autochem 2920 Micromeritics Chemisorption Analyzer. TG Analysis was carried out in a PerkinElmer, Simultaneous Thermal Analyzer (STA) from room temperature to 900 °C at 10 C/min under N_2 atmosphere. IV for the DSSC and other electrochemical measurements were recorded using the CHI660e from CH Instruments under one sun irradiation by PET Photo Emission Tech. SS50AAA solar simulator The supercapacitor performance was estimated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge techniques (0.1 mM Na_2SO_4 as an electrolyte, scan rate 100 mV/s and applied voltage 0-1 V) in an electrochemical workstation from CH Instruments Model No. CHI660e. CO_2 adsorption measurements of the synthesized materials were carried out after outgassing the materials for 12 h at 200 °C using Quantachrome Autosorb iQ3 at 298 K.

A.4 Software Used

Origin, Gatan Micrograph, Image J, CASA XPS, CHI660e and Chem Draw.

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