Annexure A
Materials and Methods

A.1 MATERIALS

A.1.1 Synthesis

Titanium(IV) isopropoxide and titanium tetrachloride (>99%) were purchased from Spectrochem. Hydrochloric acid (>37%) and nitric acid (68–70%) were acquired from Fisher Scientific. Ethanol (absolute > 99.8%), terpineol (>98%), acetic acid (glacial > 96%) and ethyl cellulose (44–51%) were obtained from Changshu Yangyuan, Alfa Aesar, Qualigens and Himedia respectively. P25 commercial TiO_2 nanoparticles was purchased from Degussa. HDA, KCl and liquid ammonia were purchased from Sigma-Aldrich, Fisher Scientific respectively. Methylene blue, methyl orange, cresol rad, thymol blue, solochrome black, tritonix and potassium dichromate were acquired from SRL, Acros and Fisher Scientific respectively. All other chemicals used in this synthesis were procured commercially and used without further purification.

A.1.2 Solar cell

Fluorine doped tin oxide glass, electrolyte solution Iodolyte Z-50, Meltonix (Surlyn), Platisol-T and N719 Ruthenizer 535-bis TBA were purchased from Solaronix. Silver conductive paste (Pelco-colloidal Silver liquid) was acquired from Ted Pella, Inc.

A.2 METHODS

A.2.1 Material synthesis

(a) Sub-zero temperature TiO_2

TiO_2 nanoparticles of different morphologies and size were prepared using reactor chamber (Radley). Overhead stirrer mounted on the reactor (Heldoph RZR 2102 control) was used to maintain the stirring speed at 350 rpm. The thermoregulatory (Huber unistat 705) was connected to the reactor ready chamber to obtain the desired reaction temperature. By controlling the reaction temperatures from -40°C to -10°C, mixture of 80 mL TTIP, 1000 mL ethanol and 400 mL distilled water were stirred for 24 hours in the reactor. Nitric acid was used to control reaction pH up to 1.5. The resultant solution was dried and annealed at 100°C for 12 hours. To optimize results, three samples S1, S2 and S3 were prepared consisting of 0%, 40% and 100% of TiO_2 prepared at -40°C and the remaining amount was made up with TiO_2 prepared at -40°C that is 100%, 60% and 0% respectively.

(b) ZnO-TiO_2 heterojunction solid nanospheres

In a typical synthesis of the ZnO-TiO_2 solid nanosphere, 1.97 g of hexadecylamine was added to 200 mL absolute ethanol, 0.8 mL of 0.1 M KCl, and then the solution was vigorously stirred to dissolve HDA completely. Next, 4 mL of TTIP was added dropwise. For doping, 1%, 5%, and 10 wt% of ZnO\TTIP was mixed followed by sonication for 10 min. The mixture was kept static overnight and then filtered. The filtrate was washed with distilled water and absolute ethanol several times followed by drying in air at room temperature to obtain a powder. A portion of the above powder (0.8 g) was dispersed in 10 mL absolute ethanol having 0.45 M liquid ammonia and transferred to a Teflon-lined autoclave (20 mL). It was kept in an oven at 180°C for 16 h for complete reaction. The filtrate was collected by washing with distilled water and ethanol and air annealed at 500°C for 2 h.

(b) H-TiO_2/HfO_2 nanospheres

The samples of TiO_2, HfO_2/TiO_2, H-TiO_2 and H-HfO_2/TiO_2 nanospheres were first prepared via a slightly modified sol–gel hydrothermal method. Then 70 mM titanium isopropoxide and 4 mM hafnium isopropoxide (HIP) were added dropwise to a mixture of 200 mL ethanol and 1.975 g HDA with vigorous stirring. The mixture was kept undisturbed for 18 h to form a gel and then filtered using a vacuum filter followed by drying at room temperature. 0.8 g sample was dispersed in 10 mL ethanol, 5 mL deionized water and 0.25 mL liquor ammonia. The obtained mixture was transferred to a 20 mL Teflon-lined stainless steel autoclave and kept at 160°C for 8 h in an oven. After the completion of the reaction, the resultant product was washed three times with deionized water (DI) and absolute ethanol before drying overnight in a vacuum oven at 70°C and subsequently calcined at 500°C for 2 h to obtain HfO_2/TiO_2 nanospheres. The same procedure was repeated without the addition of HIP, resulting in the synthesis of a white powder of TiO_2 nanospheres. These were placed in a quartz boat and heated in a tube furnace under a gas flow of 10% H_2 and 90% N_2 for 2 h at 500°C. Hydrogen annealing of TiO_2 and HfO_2/TiO_2 was performed at a heating rate of 2.5°C min^{-1} under a constant hydrogen flow, resulting in H-TiO_2 and H-HfO_2/TiO_2, respectively. The graphene was synthesized by exfoliation of graphite using hydrazine hydrate by modified Hummer's method.

A.2.2 Solar cell preparation

(a) Preparation of electrodes

Photoanode: FTO glass slides were ultrasonically cleaned for 15 min individually with soap solution, D/W, 0.1% HCl–ethanol and acetone. The cleaned FTO were treated with 40 mM aqueous $TiCl_4$ solution at 70°C for 30 min then washed with D/W and ethanol. Photoanodes were fabricated by screen printing method keeping the area of the photoanode film precisely controlled by screen printing mesh size dimension. The prepared samples were mixed with P25 at a ratio 4:6 (weight ratio) using which screen printing paste was prepared with the addition of ethanol, terpineol, acetic acid and ethyl cellulose.

In case of ZnO–TiO_2 and H-HfO_2/TiO_2 nanospheres, mixed in 4:6 ratio in the form of a paste with TiO_2 (P25) powders and uniformly grinded with ethyl cellulose in a-terpinol and ethanol (wt% ratio: 2.7:1:3.38). The paste (25 mg) was screen printed onto the FTO substrates and dried at 120°C for 6 min and repeatedly printed several times to increase the layer thickness.

Firstly, sintered at 500°C for 15 min and after post treating with 40 mM $TiCl_4$ aqueous solution for 30 min at 70°C, the photoanodes were sintered again at 520°C for 30 min. The sample photoanodes were then immersed into 0.5 mM N719 dye for 20 hours.

Counter electrode: FTO glass slides were cleaned by the same process as mentioned earlier. Pt counter electrode were prepared by brush painting Platisol-T onto the FTO. Then the films were annealed at 450°C for 30 min.

(b) Device assembly

The dye loaded photoanode and counter electrode were assembled into a sandwich type of structure and after that sealed with 25 mm thick spacer made up of Surlyn. Then the cell was thermally treated at 110°C for 30 min. After sealing, few drops of electrolyte Iodolyte Z-50 were added to fill the space between two electrodes. Silver conductive paste was applied on both sides of the cell and then dried at room temperature.

A.2.3 Water treatment

The contaminated water solution was prepared with methyl orange, methylene blue, cresol red, solochrome black and thymol blue, where concertation for every contaminate was kept as 2×10^{-5} M. Titania decorated filter membrane was prepared by filtration of solution contains titania prepared at subzero temperatures, distilled water and surfactant. This composite membrane was washed with distilled water for several times and dried at 60°C under

air condition for 12 hours and used as photo-assisted membrane to remove organic impurities and toxic materials as chromium from water (80 ppm). Photo-catalytic was performed under one sun irradiation.