Supplementary Information

[(Ph₃P)₂Ag(μ-SeCH₂Ph)₂In(SeCH₂Ph)₂]: A New Heterobimetallic Single Source Precursor As a Springboard to Bulk, Nano and Thin Film of Ternary AgInSe₂ Material

Gourab Karmakar,*[a] Adish Tyagi,*[a] Deepak Tyagi,[a] Alpa Y. Shah,[a] A. P. Wadawale,[a] Harish Donthula,[b] Vishal Singh[b]

[a]*Chemistry Division, Bhabha Atomic Research Centre, Mumbai- 400 085 (India),*

[b]*Materials Science Division, Bhabha Atomic Research Centre, Mumbai- 400 085 (India).*

Email: gourabk@barc.gov.in, tyagia@barc.gov.in.

Experimental:

Materials and methods:

InCl₃, AgNO₃, oleylamine (OAm), and analytical grade solvents were procured from commercial sources. The dimer of the ligand (dibenzyldiselenide) was prepared according to the literature method with modifications.[1] Elemental analyses were carried out on a Thermo Fischer Flash EA-1112 CHNS analyser. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Advance-II NMR spectrometer operating at 300 and 75.47 MHz, respectively. Chemical shifts are relative to internal chloroform peak for ^1H and $^{13}C\{^1H\}$ NMR spectra.

Thermogravimetric analyses (TGA) were carried out on a Nitzsch STA 409 PC-Luxx TG-DTA instrument, which was calibrated with $CaC_2O_4.H_2O$. The TG curves were recorded at a heating rate of 10°C min^{-1} under a flow of argon. X-ray powder diffraction patterns were obtained on a Philips PW-1820 diffractometer using Cu-Kα radiation. XPS measurements were carried out using Mg-K$_\alpha$ (1253.6 eV) source and DESA-150 electron analyzer (Staib Instruments, Germany). For XPS analysis, a film was prepared by drop coating the sample on glass substrate and drying under the IR lamp. The binding energy scale in XPS was calibrated to C-1s line of 284.5 eV. All the deconvolutions and fittings were done by the CasaXPS software. Optical diffuse reflectance measurements in the range 200-1100 nm (1.12 eV to 6.2 eV) were performed on a JASCO V-670 two-beam spectrometer with a diffuse

reflectance (DR) attachment consisting of an integration sphere coated with $BaSO_4$ which was used as a reference material. Measured reflectance data were converted to absorption (A) using Kubelka-Munk remission function.[2] The band gaps of the samples were estimated by extrapolating the linear portion of the plot to X (energy) axis. SEM and EDS measurements were carried out on ULTRA 55 FESEM of Zeiss and Oxford Inca instruments, respectively. A Zeiss Libra 200 FE Transmission electron microscope (TEM) operating at accelerating voltage of 200 kV was used for TEM studies. The samples for TEM and SAED were prepared by placing a drop of sample dispersed in toluene on a carbon coated copper grid.

Intensity data for $[(Ph_3P)_2Ag(\mu\text{-}SeCH_2Ph)_2In(SeCH_2Ph)_2]$ (**1**) was collected from a single crystal at 298(2) K on a XtaLAB Synergy, Dualflex, HyPix four-circle diffractometer with a micro-focus sealed X-ray tube using a mirror as a monochromator and a HyPix detector. The diffractometer was equipped with a low-temperature device and used Mo-K_α radiation (λ = 0.71073 Å). The unit cell parameters (Table S1) were determined from 25 reflections measured by a random search routine. All data were integrated with CrysAlis PRO and a multi-scan absorption correction using SCALE3 ABSPACK was applied.[3] The structures were solved by iterative methods using OLEX 1.2 and refined by full-matrix least-squares methods against F^2 using SHELXL-2017/1.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond length restraints and displacement parameter restraints. Molecular structures were drawn using ORTEP.[5]

Synthesis of $[(Ph_3P)_2Ag(\mu\text{-}SeCH_2Ph)_2In(SeCH_2Ph)_2]$ (1)

To a freshly prepared $NaSeCH_2C_6H_5$ (from $(C_6H_5CH_2Se)_2$ (142 mg, 0.42 mmol) and $NaBH_4$ (33 mg, 0.87 mmol) in toluene/methanol (20 mL)) was added solid $InCl_3$ (46 mg, 0.21 mmol) and stirred for 1 h (solution **A**). A second solution (solution **B**) was prepared by dissolving $AgNO_3$ (35 mg, 0.21 mmol) and PPh_3 (110 mg, 0.42 mmol) in 20 mL CH_3CN. Then solution **B** was added to solution **A** and the stirring was continued for 4 h. The reaction mixture was dried under vacuum, the powder thus obtained, was washed with H_2O and dried in vacuum to give the title complex (yield 217 mg, 73%), m.p. 98°C. Anal. Calcd. for

$C_{64}H_{58}AgInP_2Se_4$: C, 53.84; H, 4.09%. Found: C, 53.71; H, 4.09%. $^{31}P\{^1H\}$ NMR (CDCl$_3$): d = 3.5 (br, s) ppm.

Preparation of silver Indium Selenide

The silver indium selenide materials were prepared using [(Ph$_3$P)$_2$Ag(μ-SeCH$_2$Ph)$_2$In(SeCH$_2$Ph)$_2$] (**1**) as molecular precursor. For synthesizing bulk AgInSe$_2$, **1** was taken in a quartz boat and heated in a tubular furnace at 400°C for 2 hours under Ar flow. For the synthesis of nanostructured AgInSe$_2$, hot injection method employing OAm as high boiling solvent was chosen. In a typical hot injection method, 9 mL OAm was taken in a three-necked round bottom flask and degassed at 110°C under nitrogen flow for 30 min. Subsequently, the temperature was raised to 300°C. In the pre-heated solvent, 200 mg of the precursor **1**, dispersed in OAm (1 mL) was rapidly injected. The reaction temperature dropped by around 20°C upon injection; however, the set temperature was attained in no time. The temperature was maintained for 5 minutes after which the heat source was removed and the reaction mixture was allowed to cool to 60°C and methanol was added to ensure complete precipitation of nanostructures. The synthesized material was collected after repeated washing with methanol and toluene mixture followed by centrifugation to remove excess capping agent. Finally, for the deposition of AgInSe$_2$ thin film, AACVD experiment was performed. In a typical experiment, the precursor **1** (~100 mg) was dissolved in 25 ml of toluene in a three-necked round bottom flask. Aerosol droplets of the solution were generated by an ultrasonic humidifier and were transported using argon as a carrier gas (flow rate of 180 sccm) to a hot glass substrate placed in a turbo furnace at 400°C for 1h.

Photo electrochemical cell experiment

Photo responsiveness of the AgInSe$_2$ nanostructures was measured in a photo electrochemical cell prepared by using silicon/AgInSe$_2$ nanostructures geometry as the working electrode, Pt wire as counter and pseudo reference electrodes, respectively and Na$_2$S (0.6 M):Na$_2$SO$_3$ (0.8 M) (1:2) as the electrolyte. Working electrodes of silicon/AgInSe$_2$ was prepared by drop casting a colloidal solution of AgInSe$_2$ nanostructures in chloroform on the rough surface of n-type Si wafer of (100) orientation having thickness of 200 μm and resistivity of 1-10 Ωcm. The drop casted film was dried at 140°C for 2 h. The process was repeated many times till a uniform coating was obtained on the silicon surface. The prototype PEC cell (Height

= 3 cm, Internal diameter = 2 cm, Si wafer diameter = 1 cm, Radius = 0.5 cm, Effective Area of illumination = 0.785 cm^2) (Fig. S6) was illuminated with fluorescent white lamp (36 W, UV content < 3%) as radiation source with light intensity at the cell being 200 μWcm^{-2} with a bias voltage of -1.5 V.

Table S1. Selected bond lengths (Å) and angles (°) for [(Ph$_3$P)$_2$Ag(μ-SeCH$_2$Ph)$_2$In(SeCH$_2$Ph)$_2$] (**1**)

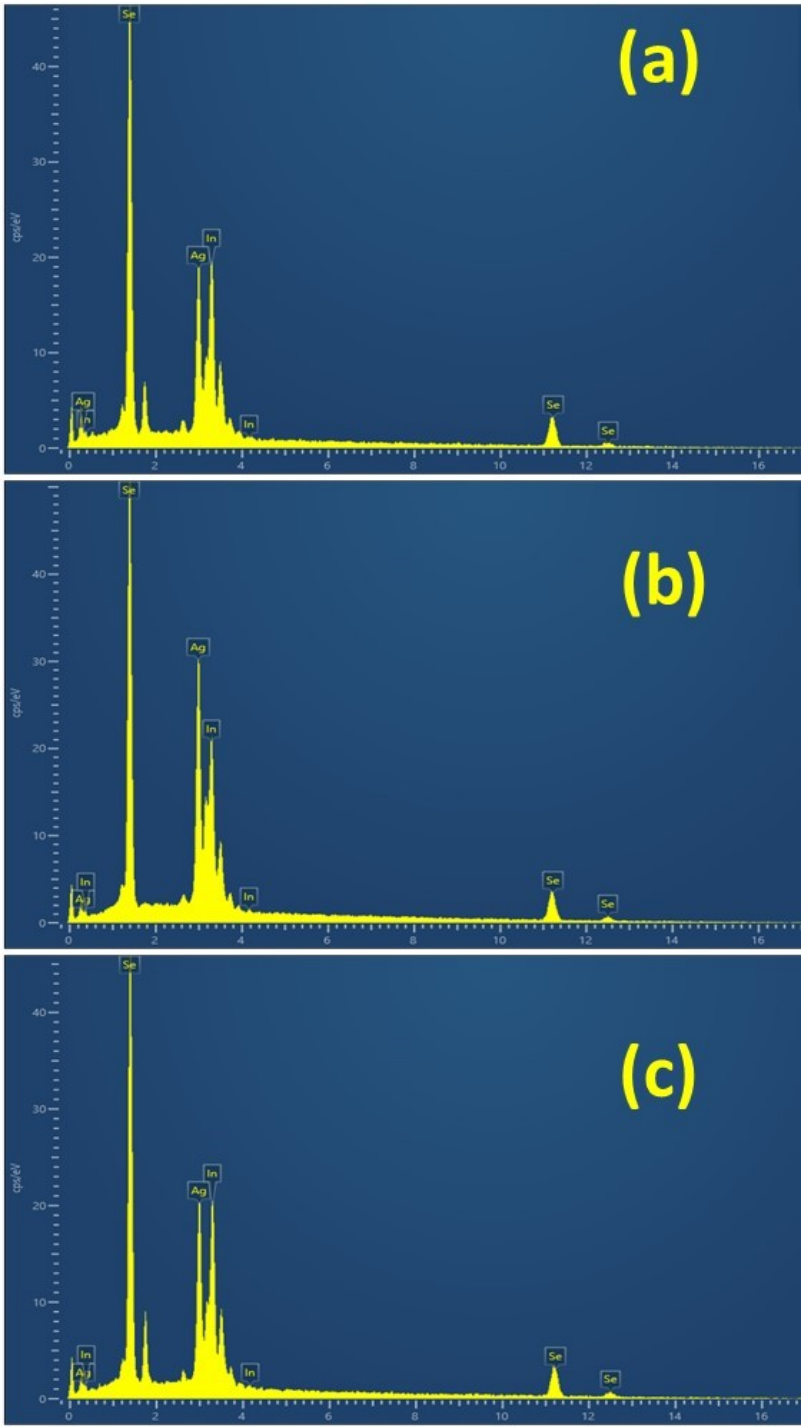| Bond length (Å)		Bond angle (°)	
In(1)-Se(1)	2.6169(3)	Se(1)-In(1)-Se(1)	102.701(14)
In(1)-Se(2)	2.5484(3)	Se(1)-In(1)-Se(2)	113.614(10)
Ag(1)-Se(1)	2.7763(3)	Se(2)-In(1)-Se(2)	111.748(18)
Se(1)-C(1)	1.985(3)	Se(1)-Ag(1)-Se(1)	94.810(13)
Ag(1)-P(2)	2.4696(6)	In(1)-Se(1)-Ag(1)	81.243(10)
Ag(1)···In(1)	3.513	P(2)-Ag(1)-Se(1)	116.540(16)
		P(2)-Ag(1)-Se(1)	102.897(16)
		P(2)-Ag(1)-P(2)	120.66(3)

Figure Captions:

Fig. S1. EDS analysis of (a) bulk, (b) nanostructures and (c) thin film of AgInSe$_2$.

Fig. S2. XPS survey scan of (a) bulk, (b) nanostructures and (c) thin film of AgInSe$_2$.

Fig. S3. Particle size distribution histogram for AgInSe$_2$ nanostructures.

Fig. S4. SAED patterns of (a) bulk powder and (b) nanostructured AgInSe$_2$ respectively.

Fig. S5. 2D elemental mapping of (a) bulk powder and (b) nanostructured AgInSe$_2$ respectively.

Fig. S6. Actual photograph of the prototype PEC cell used for measurements.

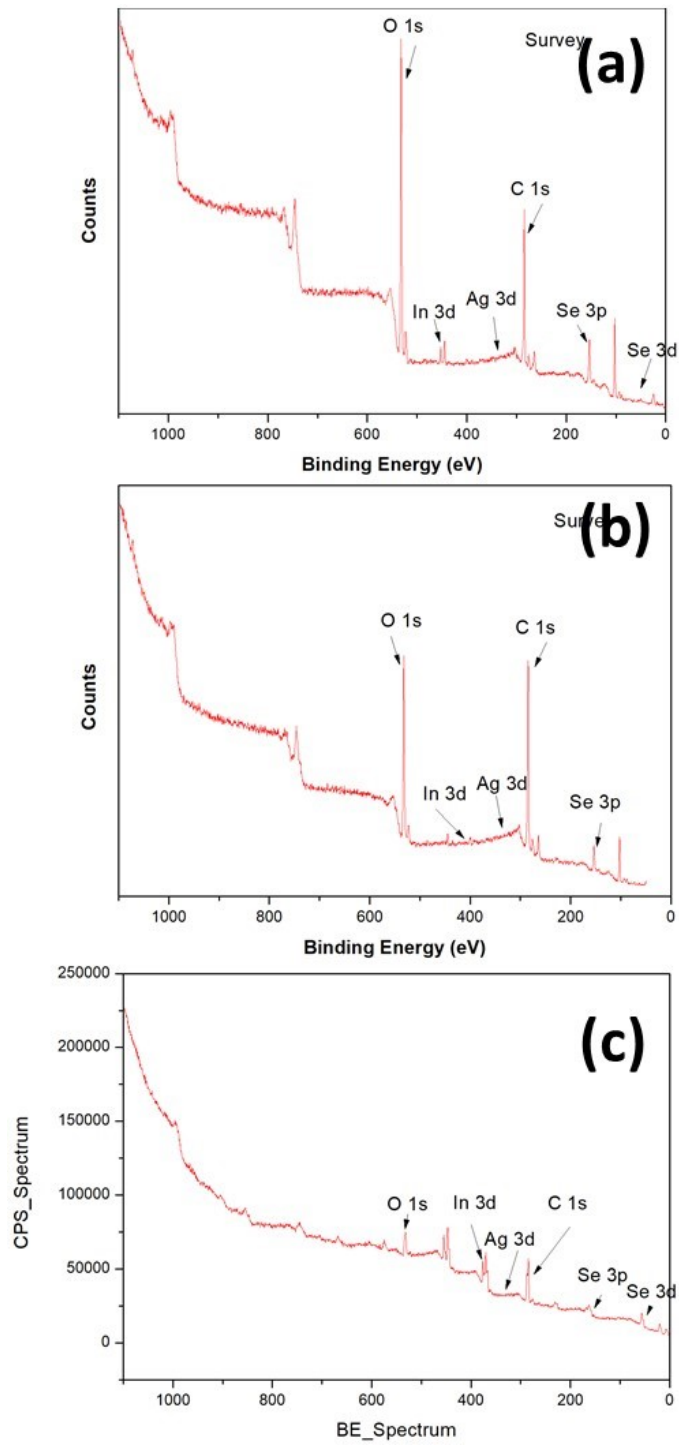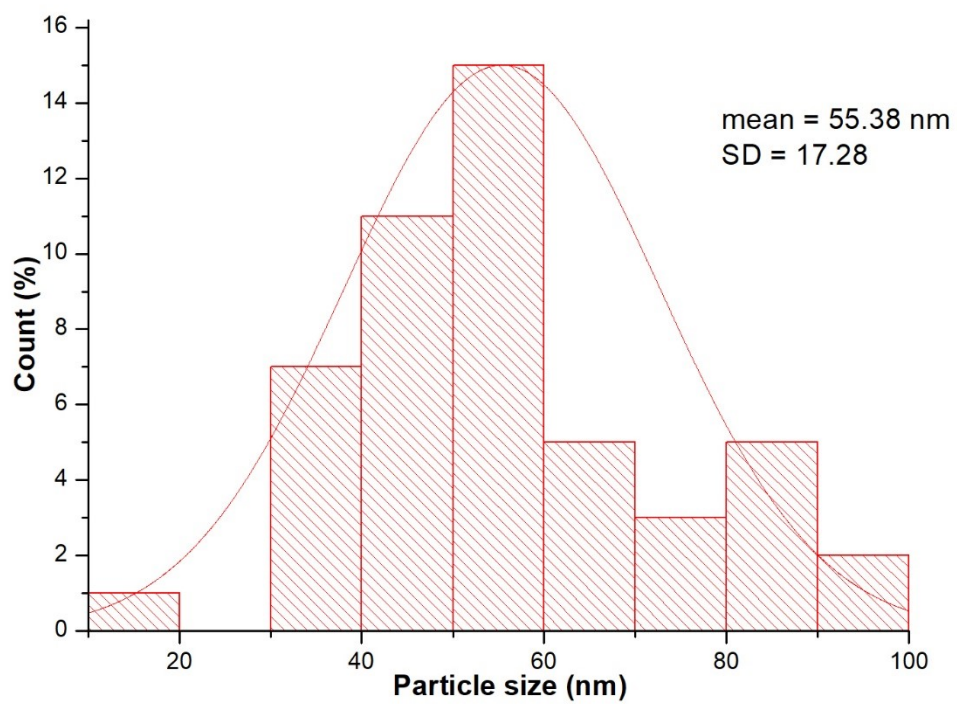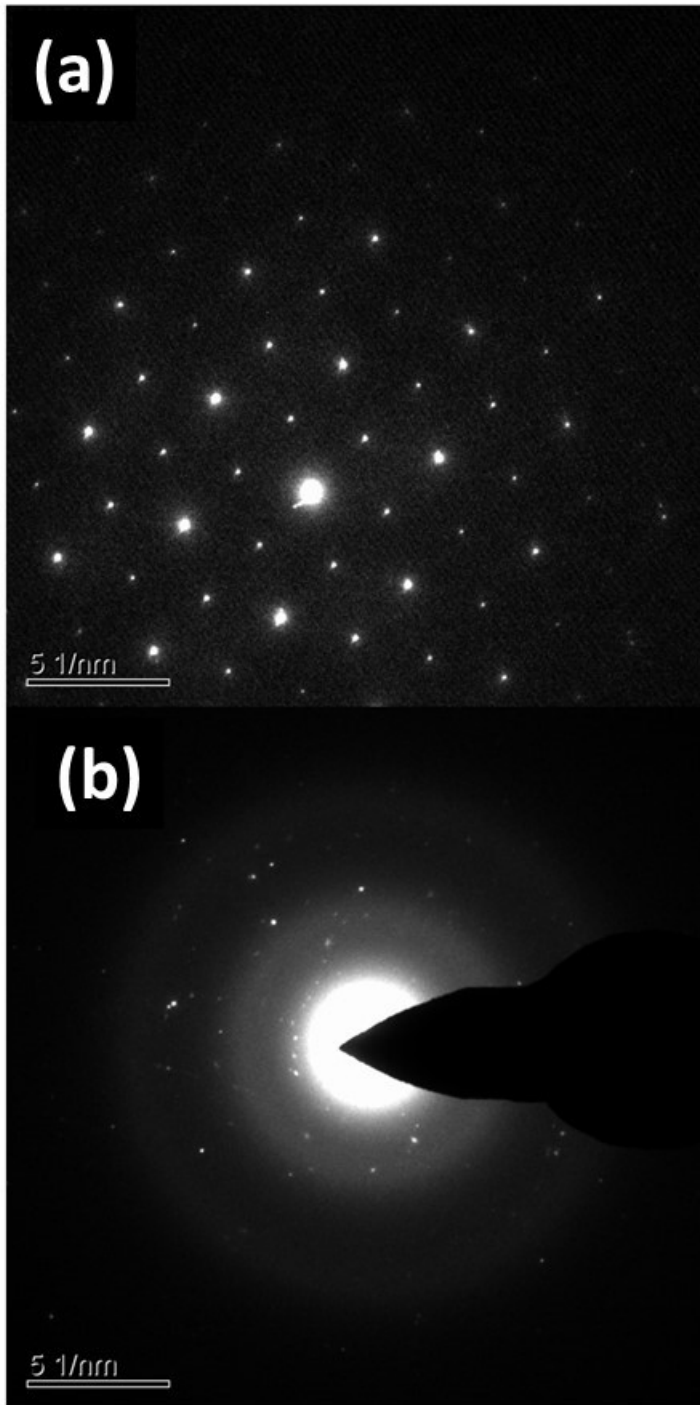**Fig. S1.** EDS analysis of (a) bulk, (b) nanostructures and (c) thin film of $AgInSe_2$.

Fig. S2. XPS survey scan of (a) bulk, (b) nanostructures and (c) thin film of AgInSe$_2$.

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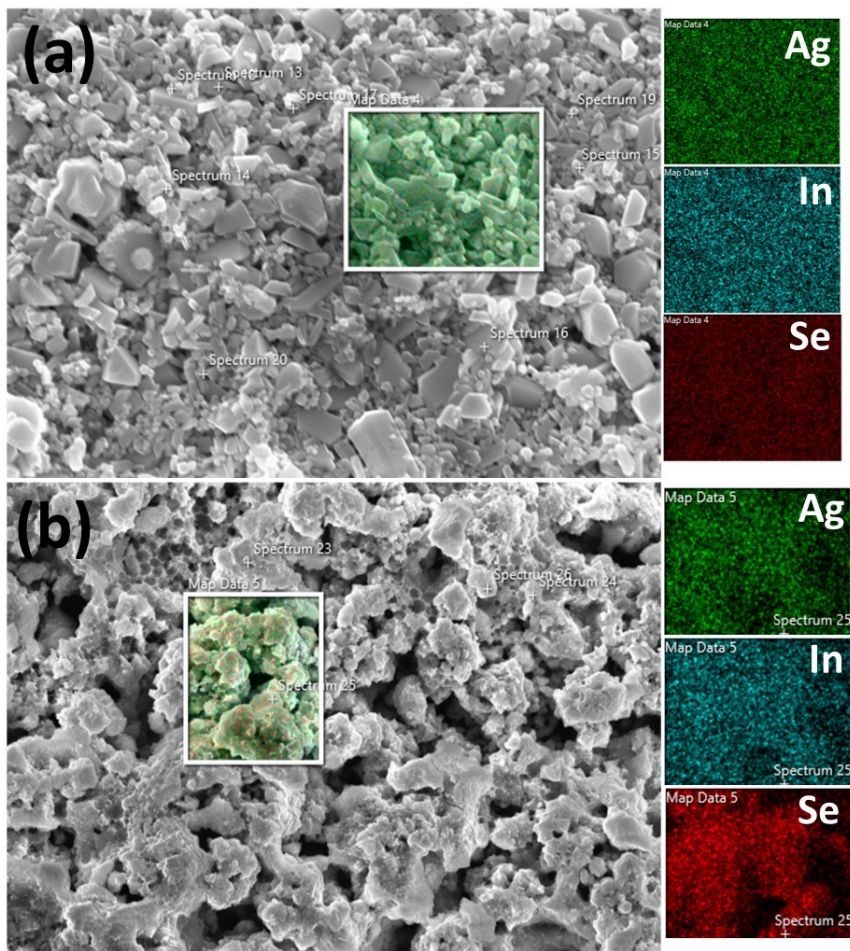
Fig. S5. 2D elemental mapping of (a) bulk powder and (b) nanostructured AgInSe$_2$ respectively.
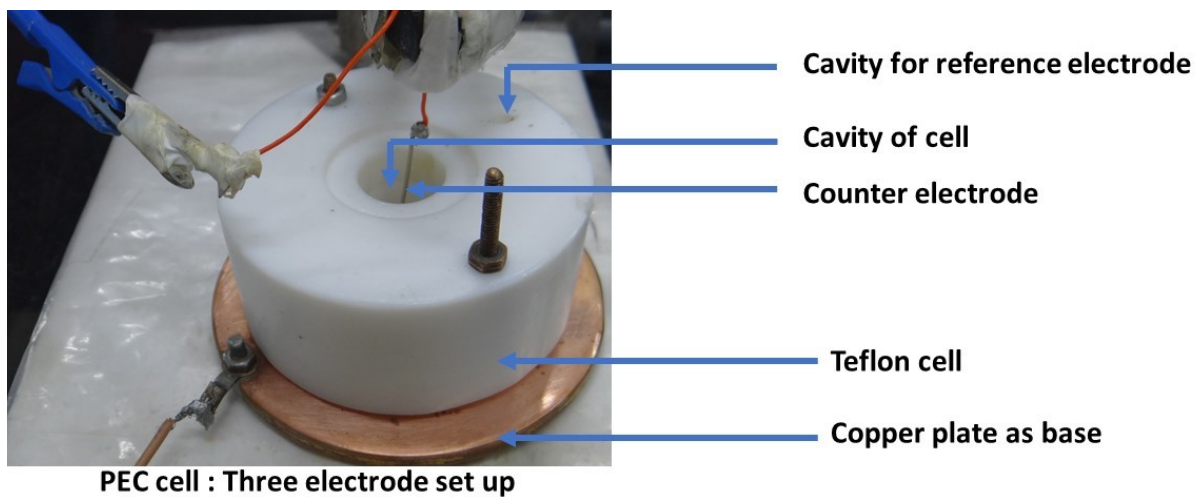

Fig. S6. Actual photograph of the prototype PEC cell used for measurements.

References:

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