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Anti-Stokes Photoinduced Electrochemiluminescence at a Photocathode

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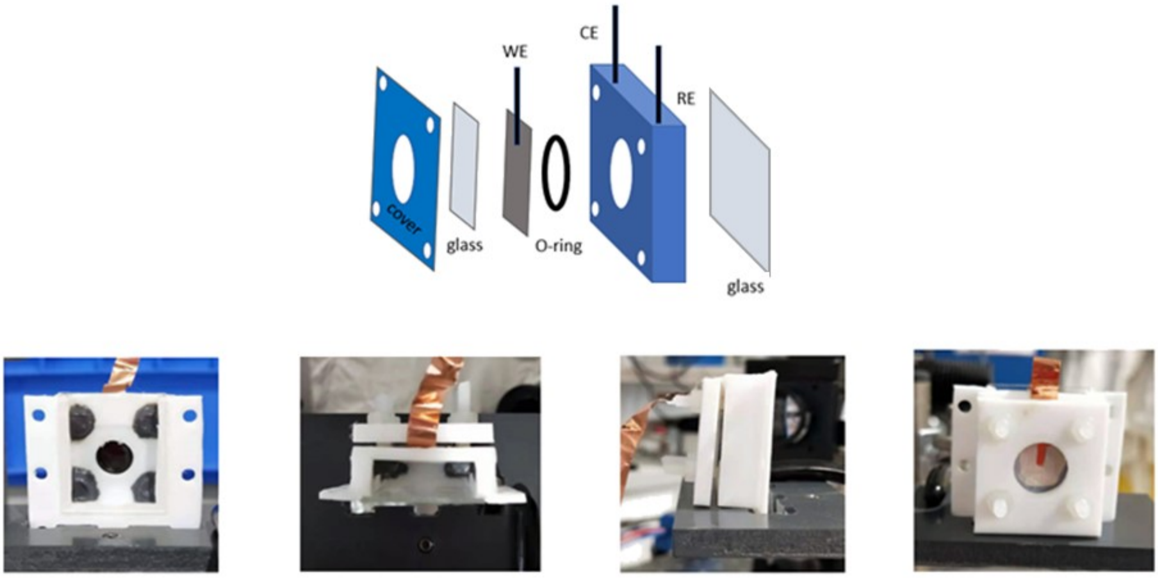
1. Supplementary figures



Front view Top view Side view Back view

Figure S1. Scheme (top) and photographs (bottom) showing the PECL cell design.

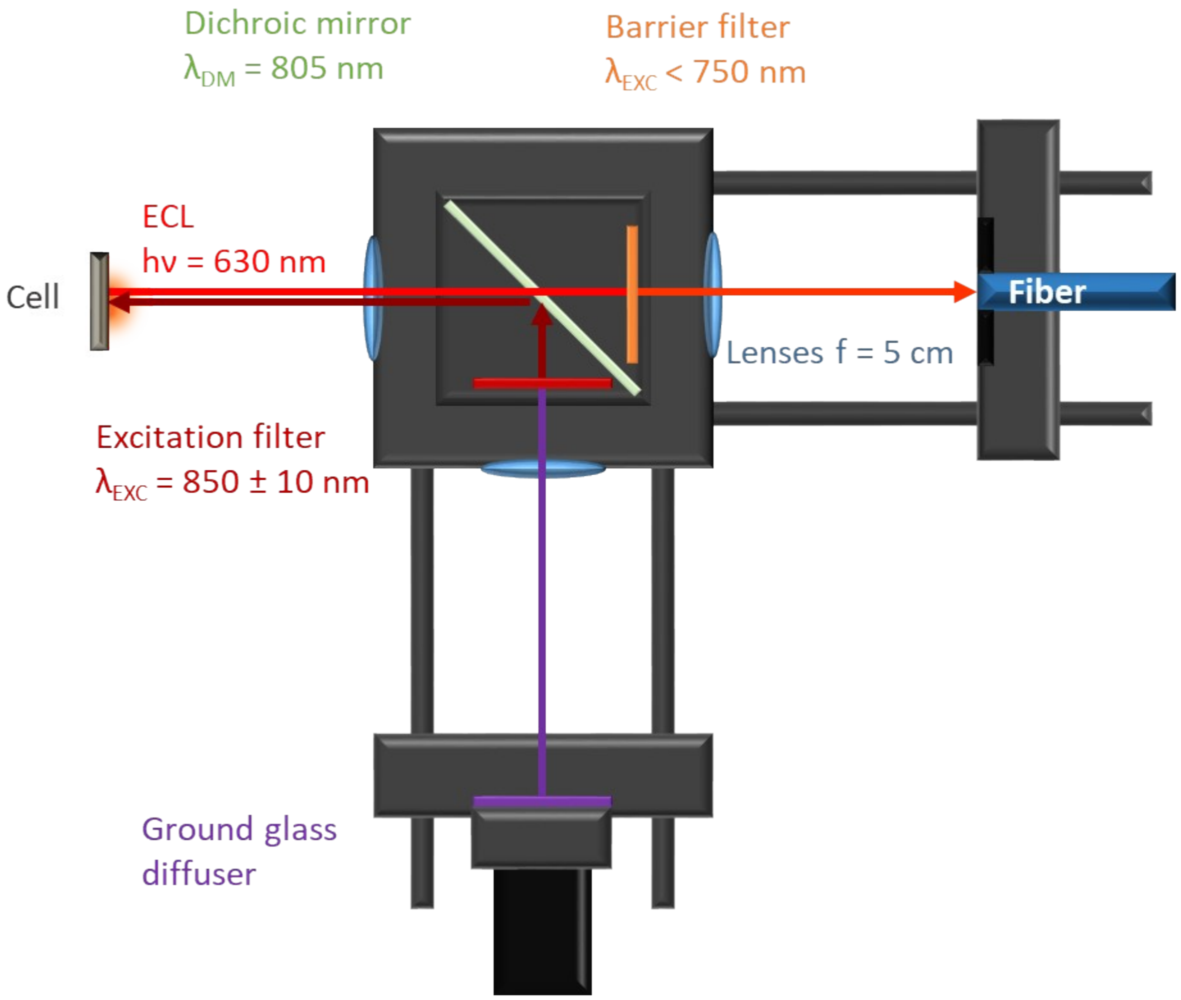


Figure S2. Scheme of the PECL photoelectrochemical setup, with the wavelengths detailed.

2. Materials and methods

Reagents

Acetone (MOS electronic grade, Erbatron from Carlo Erba) and anhydrous ethanol (RSE electronic grade, Erbatron from Carlo Erba) were used without further purification. The ultrapure water had a resistivity of 18.2 MΩ cm (Purelab Classic UV). Sulfuric acid (96%, VLSI grade Selectipur) and hydrogen peroxide (30%, VLSI, Sigma-Aldrich) were purchased from BASF and Sigma Aldrich, respectively. Tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate (97%), benzoyl peroxide (75%, remainder water), tetrabutylammonium hexafluorophosphate (99%) and acetonitrile (99.8%) were purchased from Sigma-Aldrich and used without any further purification.

Surface preparation

All vials and tweezers used for cleaning silicon were previously decontaminated in 3/1 v/v concentrated H_2SO_4/30% H_2O_2 at 105 °C for 30 min, followed by copious rinsing with ultrapure water. *Caution: the concentrated aqueous H_2SO_4/H_2O_2 (piranha) solution is very dangerous, particularly in contact with organic materials, and should be handled extremely carefully.* The *p*-type silicon wafers (1-5 Ω cm resistivity, boron-doped, double side polished, 225-275 µm)

(100) and the n^+-type silicon wafers (0.01-0.05 Ω cm resistivity, phosphorus -doped, single side polished, 240-260 µm) (100) were purchased from University Wafers. All the Si surfaces were degreased by sonication in acetone, ethanol, and ultrapure water for 10 min, respectively. The Si surfaces were then decontaminated and oxidized in piranha solution at 105 °C for 30 min, followed by rinsing with copious amounts of ultrapure water and dried under an Ar flow.

Electrode fabrication

The coated surfaces Si surfaces (1.2 x 1.2 cm^2) were processed to fabricate the electrodes. An Ohmic contact was done on the backside of Si wafer by scratching the surface with a diamond glass cutter; then a droplet of InGa eutectic (Sigma Aldrich, 99.99%, metals basis) and a copper tape was applied on the scratched part. A thin layer of silver paste (Electron Microscopy Sciences) was painted to cover the InGa eutectic contact as well as a part of the copper tape. After the drying of the paste, Kapton tape was deposited to shield the backside for the protection of Ohmic contact. Before their use in electrochemical experiments, the hydrogenated Si electrode (*p*-Si-H and n^+-Si-H) were dipped for 1 min in 10% HF. The electrochemically active electrode surface is 0.5 cm^2, as determined by the O-ring of the cell.

Electrochemical experiments

CV and CA were performed by a Autolab Type II potentiostat connected to a conventional three-electrode cell, consisting of an Ag-wire pseudo-reference electrode, a Pt-wire auxiliary electrode, and hydrogenated Si working electrode, in a N_2-degassed electrolyte comprising 1 mM $[Ru(bpy)_3]^{2+}$, 10 mM BPO and 0.2 M $TBAPF_6$ in acetonitrile. ECL signals were simultaneously recorded by Spectra pro 2300i (Princeton Instrument) spectrometer.