

Electronic Supplementary Information (ESI)

Local Reactivity of Metal-Insulator-Semiconductor Photoanodes Imaged by Photoinduced Electrochemiluminescence Microscopy

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1. Experimental section

1.1. 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 M Ω 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(bipyridine)ruthenium(II) chloride hexahydrate (Ru(bpy)₃Cl₂·6H₂O, powder) and tri-*n*-propylamine (TPrA, \geq 98%) were purchased from Sigma Aldrich. Phosphate buffer solution (PBS, 100 mM, pH 7.3) was prepared from potassium phosphate dibasic (\geq 98%, ACS reagent) and sodium phosphate monobasic monohydrate (\geq 99.0%, ReagentPlus[®]) that were purchased from Sigma Aldrich. Photoresist AR-P 5350, and developing solution AR 300-35 were purchased from AllResist.

1.2. Surface preparation

All vials and tweezers used for cleaning silicon were previously decontaminated in 3/1 v/v concentrated H₂SO₄/30% H₂O₂ at 105 °C for 30 min, followed by copious rinsing with ultrapure water. *Caution: the concentrated aqueous H₂SO₄/H₂O₂ (piranha) solution is very dangerous, particularly in contact with organic materials, and should be handled extremely carefully.* The *n*-type silicon wafers (1-10 Ω cm resistivity, phosphorus-doped, single side polished, 475-525 μ m) (100) and the *p*⁺⁺-type silicon wafers (0.001-0.005 Ω cm resistivity, boron-doped, single side polished, 490-510 μ m) (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 Ar flow.

1.3. Photolithography

The Si surfaces were cut to 1.3 x 1.3 cm² squares. Si squares were coated by photoresist AR-P 5350 by spin coating (LabSpin, SUSS MicroTec) (30 s, acceleration: 3000 rpm/s, speed: 4000 rpm). Then, coated Si surfaces were annealed on a 105°C heating plate for 4 min. The annealed Si surfaces were installed on Libro Smart Print (microlight3D) and insulated under UV masked by patterns (**Figure S1**) with an object-glass x5 for 0.75 s. Then the insulated Si surfaces were developed in the solution composed of 2/1 v/v ultrapure water/AR 300-35 for 45 s, followed by rinsing with ultrapure water and dried under N₂ flow. The Ir thin films were deposited on the surfaces by sputtering with a Leica EM ACE600 coating system (Ir target purity: 99.95%). The thickness of the film (\sim 2 nm) was controlled *in-situ* using a quartz crystal microbalance (QCM). The Ir-coated surfaces were immersed into 50°C acetone for 5 min in order to dissolve the rest of photoresist, taking away the above Ir film. Finally, the Ir-patterned Si surfaces were rinsed by ultrapure water and dried under Ar flow.

1.4. Sputtering

The Ir thin film were deposited by sputtering which is a physical vapor deposition (PVD) method. This involve a sputtering target (source of Ir) that was ejected onto a substrate (the silicon wafer) to grow the Ir film on it. The collision between incident particles and the Ir occurs in ionized gas at low pressure, leading to the ejection of Ir particles out of the target.

1.5. Surface characterization

Scanning electron microscopy (SEM) was performed on the Si/SiO_x/Ir patterned surfaces on *n* and *p*⁺⁺ type using a VEGA3 TESCAN in HV at 10 kV with a BSE detector. The SEM revealed the Ir pattern on the Si/SiO_x surface and allowed to measure the bands width.

1.6. Electrode fabrication

The Ir-patterned Si surfaces were processed to fabricate the electrodes. An Ohmic contact was created 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.

1.7. Electrochemical and microscopy experiments

The electrochemical experiments were performed in a 3-electrode configuration using a PalmSens4. The working electrode was an Ir-patterned Si surface with a fixed active area of 0.5 cm², the reference electrode was an Ag/AgCl (3 M) electrode and the counter electrode was a Pt wire. The Si surface electrode was sealed with an O-ring on the backside of a homemade Teflon cell. A transparent glass window on the frontside allowed for transmission of photons. The electrolyte was composed of of 5 mM [Ru(bpy)₃]²⁺, 0.1 M TPrA and 0.1 M PBS at pH 7.4.

The Si electrode was illuminated from the frontside (through the electrolyte) by a 850 nm LED (Thorlabs, M850L3) inclined by about 45°. The PECL emitted from the Si electrode was transmitted through a shortpass filter with a cut-off wavelength at 750 nm (Thorlabs, FESH0750) (**Figure S3**) in order to remove the IR component from the incident light and was imaged with a horizontal microscope OLYMPUS connected to an EMCCD camera (Hamamatsu). A 5x objective (UMPlanFI, NA = 0.15) was used for the low magnification and a 50x objective (LMPlanFLN, NA = 0.5) was used for the high magnification. The PECL spectra was recorded with a spectrometer (Spectra pro 2300i, Princeton Instrument). The pictures were treated by ImageJ software to add the red filter on the PECL pictures and to plot the intensity profiles.

2. Supplementary figures

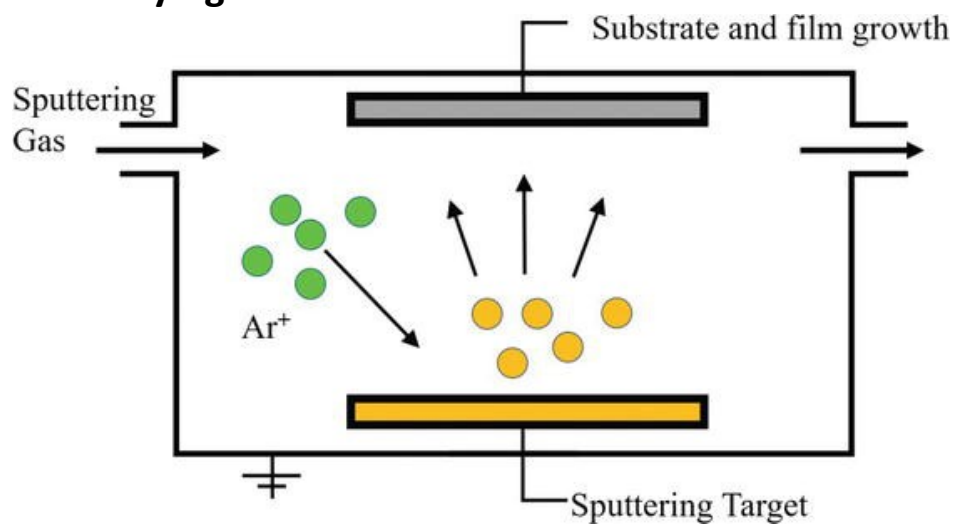


Figure S1. Schematic diagram of magnetron sputtering. Scheme from the reference ¹.

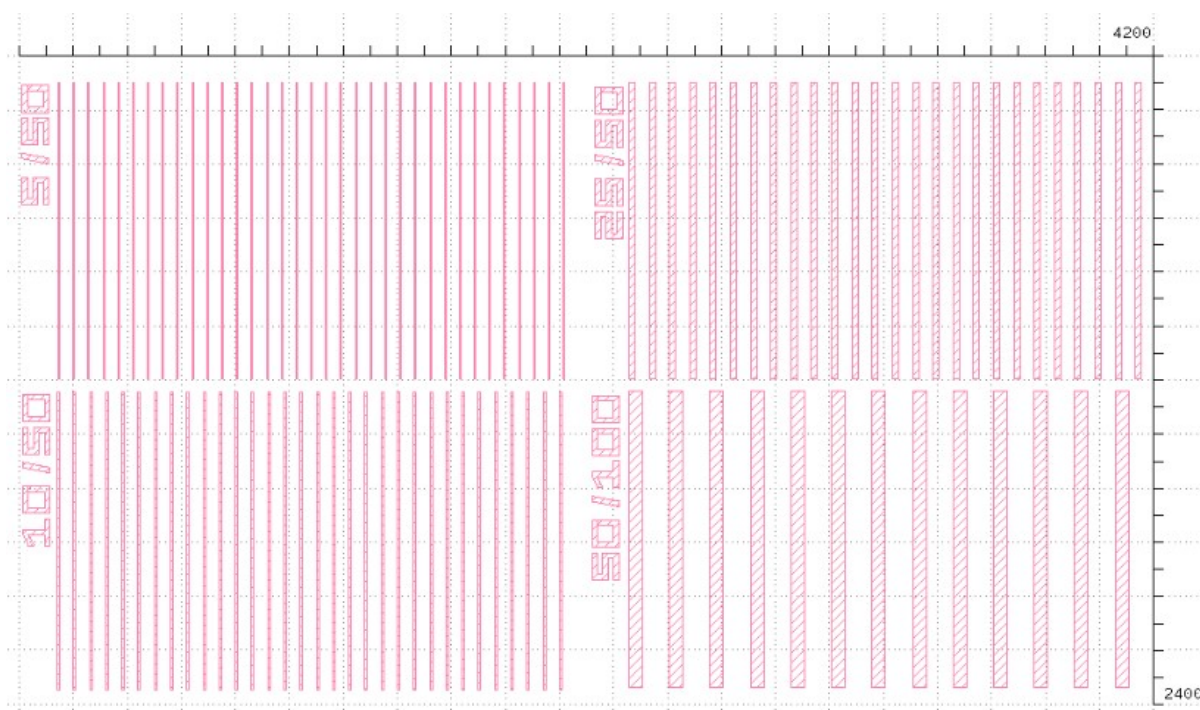


Figure S2. Scheme of the mask used for the Ir patterns manufacturing with different dimensions: 5/50 μm , 10/50 μm , 25/50 μm and 50/100 μm .

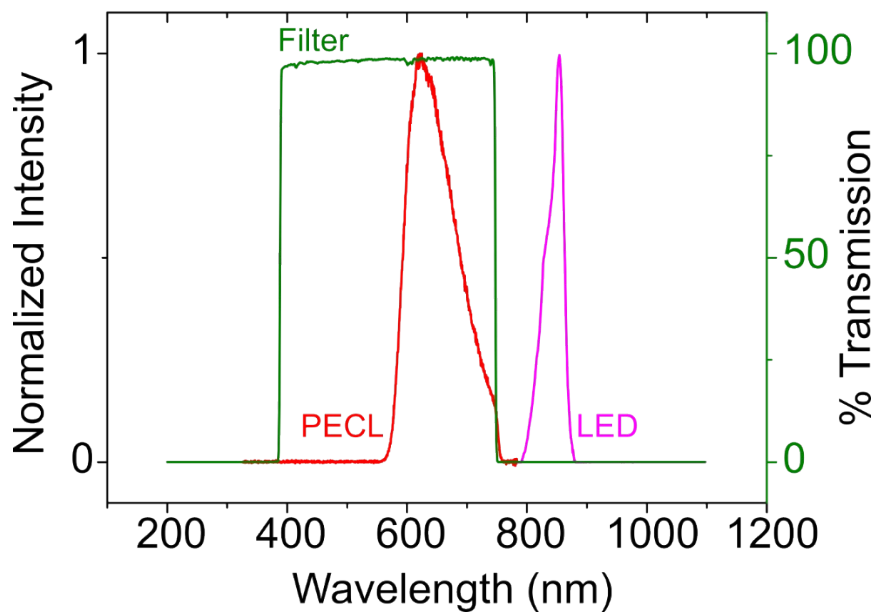


Figure S3. Normalized spectra: PECL emission spectra from the $[\text{Ru}(\text{bpy})_3]^{2+}$ localized on the Ir pattern (red curve) and the infrared LED (pink curve). Overlap with the filter transmission (green curve).

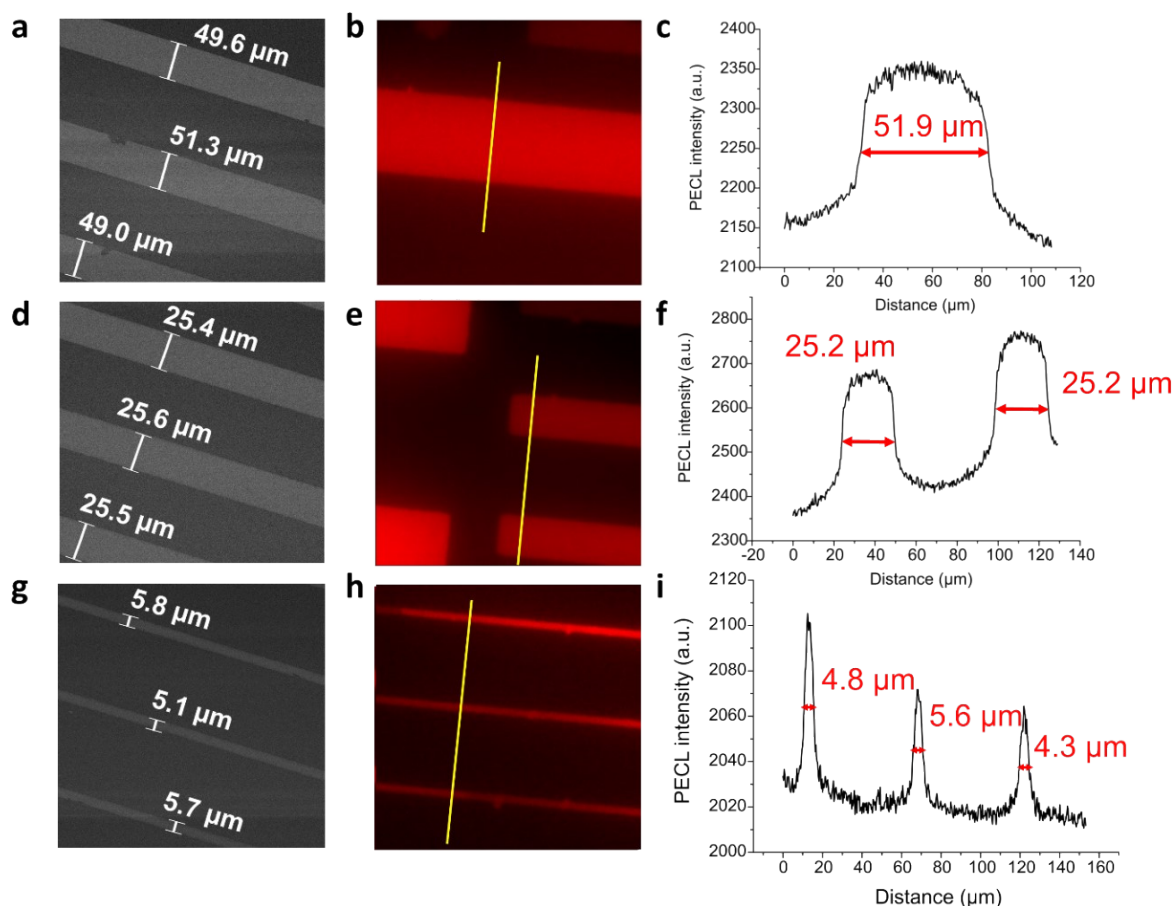


Figure S4. SEM imaging of a) 50 μm , d) 25 μm and g) 5 μm -wide Ir patterns on $n\text{-Si}/\text{SiO}_x$. PECL images and profiles of PECL localized on the b) 50 μm , e) 25 μm , and h) 5 μm -wide Ir patterns using $[\text{Ru}(\text{bpy})_3]^{2+}/\text{TPrA}$ with a potential of 0.8 V (vs Ag/AgCl). The exposure times t_{exp} were 0.5 s, 0.5 s and 1.5 s, respectively. c), f), i) Corresponding PECL intensity profile and FWHM measurements of the patterns with different widths.

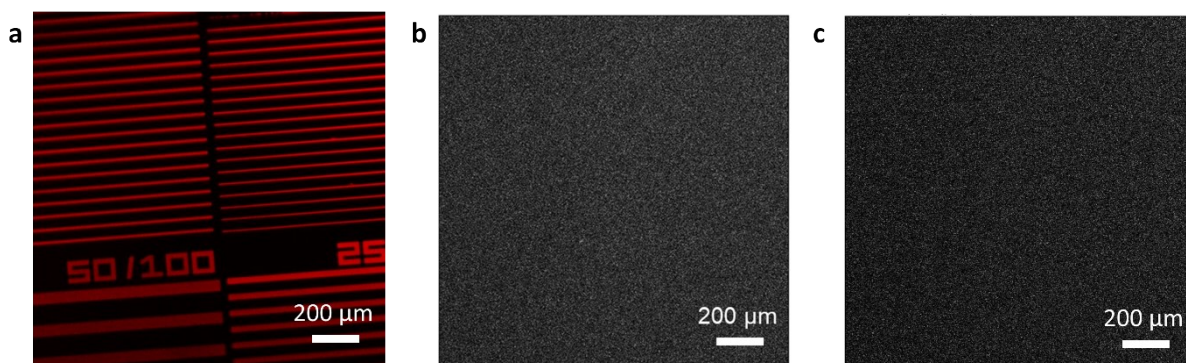


Figure S5. Control experiment with a) PECL imaging of n -Si/SiO_x with Ir patterns at 0.8 V (vs Ag/AgCl) containing the [Ru(bpy)₃]²⁺/TPrA system, b) The same condition as a) at opened circuit voltage under IR illumination and c) The same condition as a) in the dark.

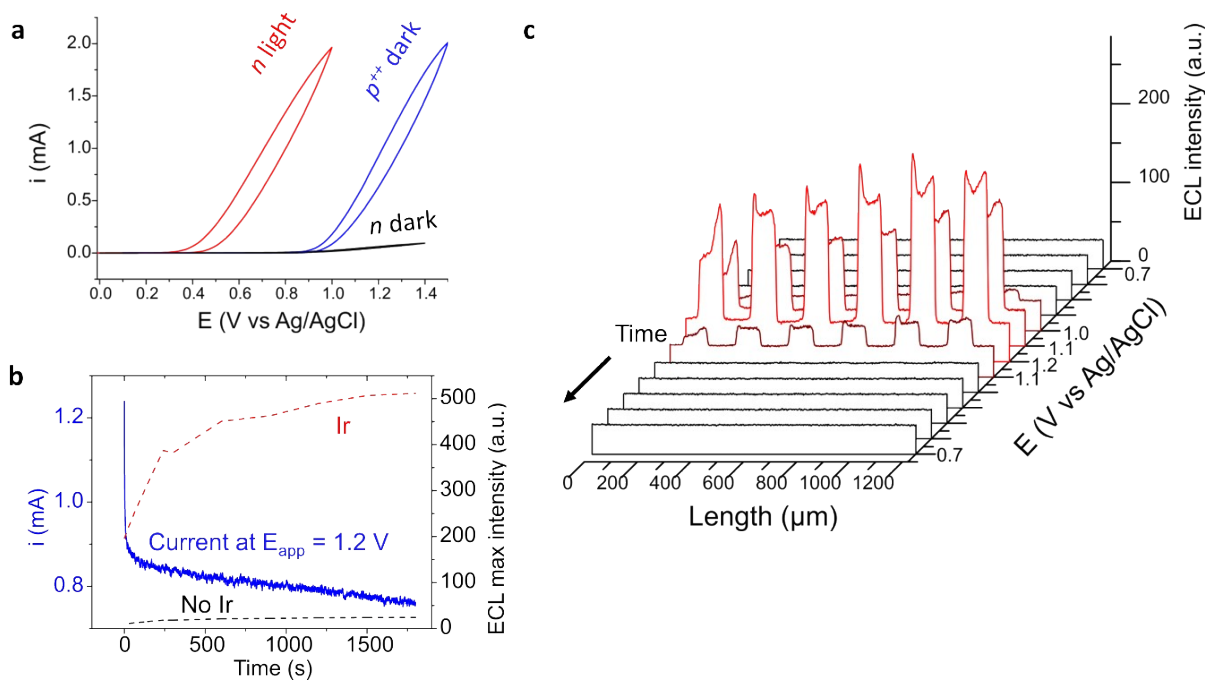


Figure S6. a) CVs recorded on a p^{++} -type electrode patterned with Ir in the dark (blue), on n type electrode patterned with Ir under IR illumination (red) and in the dark (black) in 100 mM TPrA and 5 mM [Ru(bpy)₃]²⁺ in PBS (scan rate: 50 mV/s). b) Chronopotentiostatic measurement on a patterned p^{++} -type electrode in the dark (continuous blue line) and corresponding ECL intensity located on the Ir pattern (red dashed line) and out of the pattern (black dashed line). c) Profile of ECL intensity p^{++} -type electrode during a CV.

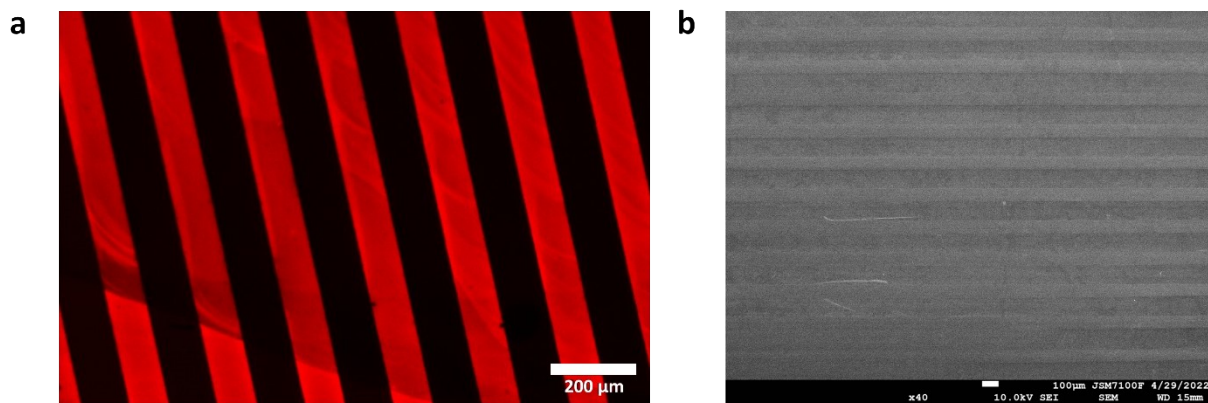


Figure S7. a) Microscope imaging of Ir patterns of 50 μm width on $p^{++}\text{-Si/SiO}_x$ in ECL using $[\text{Ru}(\text{bpy})_3]^{2+}/\text{TPrA}$ system with a potential applied at 1.2 V (vs Ag/AgCl) with a $t_{\text{exp}} = 1.5$ s. b) SEM image of the surface (scale bar: 100 μm).

3. Supplementary table

Table S1. Characteristics of several reported PECL systems.

Reference	Year	PECL type	SC	ECL system	Electrolyte type	E_{app} (V) ^a	λ_{exc} (eV)	λ_{em} (eV)	λ shift (nm)	Operation time (min)
2	1975	upconversion	<i>p</i> -Si & <i>p</i> -InP & <i>p</i> -GaAs	annihilation	organic	- ^b	1.7 ^c	3	-316	≈2
3	1976	upconversion	<i>p,n</i> -GaAs & <i>p,n</i> -InP	annihilation	organic	1.6 ^d	<1.7	2.8 ^e	-293	- ^f
4	2019	upconversion	<i>n</i> -Si/SiO _x /Ni	[Ru(bpy) ₃] ²⁺ TPrA	aqueous	0.5	1.5	1.9	-175	15
5	2019	upconversion	<i>n</i> -Si/1,8-nonadiyne	luminol	aqueous	-0.1	1.7 ^g	2.9	-300	≈3
6	2020	downconversion	<i>n</i> -BiVO ₄	L-012	aqueous	-0.4	3.3	2.5	128	120
7	2021	downconversion	<i>n</i> -α-Fe ₂ O ₃	L-012	aqueous	-0.2	3.3	2.5	123	120
8	2022	upconversion	<i>n</i> -Si/SiO _x /Ir	[Ru(bpy) ₃] ²⁺ -TPrA	aqueous	0.7 ^h	1.46 ^h	1.96 ^h	-220 ^h	2100 ^h
						0.45 ⁱ	1.46 ⁱ	1.96 ⁱ	-485 ⁱ	140 ⁱ
9	2022	upconversion	<i>n</i> -Si/SiO _x /Ir & <i>p</i> -Si	[Ru(bpy) ₃] ²⁺ TPrA	aqueous	1.4 ^j	1.46	1.96	-220	1200
				L-012		0.3 ^j		2.53	-360	- ^f
10	2022	upconversion	<i>p</i> -Si	[Ru(bpy) ₃] ²⁺ BPO	organic	-1.6	1.46	1.96	-220	30
11	2023	upconversion	<i>n</i> -Si/SiO _x /Ni	luminol H ₂ O ₂	aqueous	-0.4	1.46	2.82	-410	180
12	2023	upconversion	Au/ <i>pnn</i> ⁺⁺ Si/Pt	luminol H ₂ O ₂	aqueous	0 ^j	1.46	2.82	-410	30
							1.18 ^k		-610 ^k	- ^{f,k}

^a: potential onset of the PECL emission, vs Ag/AgCl, if not reported otherwise.

^b: the reference electrode was not indicated.

^c: λ_{exc} = 674 nm (1.8 eV) was also reported.

^d: difference between the anodic E_{app} and cathodic E_{app} for *n*-GaAs.

^e: for the TMPD/DPA system on *n*-GaAs.

^f: no duration was reported.

^g: λ_{exc} = 625 nm (2 eV) was also reported.

^h: with Ir coating.

ⁱ: with Pt coating.

^j: bias (V)

^k: microscopy application

4. References

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