Supplementary Information(SI) for Inorganic Chemistry Frontiers.

Synthesis and Photocatalytic Evaluation of First Nickel Dioxo-Haloselenate Complexes Immobilized on Mesoporous TiO₂ for Enhanced Solar-Driven Hydrogen Production

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based on the maximum absorbance peaks observed in the diffuse reflectance spectra (DRS)31
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1. Experimental section

1.1 Instrumentation

1.1.1 Single-crystal X-ray Diffraction

Single-crystal data of 1-3 were collected using a Bruker D8 Venture diffractometer operating with an Incoatec IµS high brilliance Mo-K α , λ = 0.71073 Å, X-ray tube with twodimensional Montel micro-focusing optics and a Photon 100 detector. Each structure was solved by dual space methods with Bruker XT^1 and refined with Bruker XL^2 on F^2 using anisotropic parameters for all non-hydrogen atoms. The hydrogen atoms positions were calculated starting from the idealized positions. The crystalline structure of complex 2 shows positional disorder of the Br2 atom. The disordered atoms were named Br2A and Br2B. After finding how positions of the disordered atoms, the solution of the disorder was performed through of the PART 1 and PART 2 commands, using the XL/SHELXL-2015 program.² The disorder positional found in complex **2** for the Br2 atom, shows occupations for the named atoms Br2A and Br2B of 48% and 52%, respectively. Drawings were done using Crystal Impact Diamond 4.³ Anisotropic thermal ellipsoid plots can be found in the supplementary material (Figs. S1–S3). Crystal data and further details regarding the data collection and refinement for 1-3 are shown in Table S1. CCDC 2261474, 2261475 and 2261478 contain the supplementary crystallographic data for 1-3. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk; from the Cambridge Crystallographic Data Centre at 12 Union Road, Cambridge CB2 1EZ, UK; via fax: (+44) 1223-336-033; or via e-mail: deposit@ccdc.cam.ac.uk.

1.1.2 Powder X-ray Diffraction

Powder X-ray diffraction data for 1-3, m-TiO₂, 1@m-TiO₂, 2@m-TiO₂, and 3@m-TiO₂ photocatalysts were obtained using a Bruker AXS D8 Advance diffractometer equipped with Ni-filtered, Cu-Ka radiation (K α 1 = 1.5406 Å) and a LynxEye detector. The samples were scanned from 4 to 60 degrees in a 2-theta angle, with a slit width of 0.2 degrees, a step size of 0.01 degrees, 600 ms per step, and a rotation speed of 50 rpm (Figs. S4–S8).

1.1.3 Elemental Analysis

Elemental analyses (CHN) were determined using a Perkin Elmer 2400 series II.

1.1.4 FT-IR Spectroscopy

FT-IR spectra were recorded using the attenuated total reflectance (ATR) sampling mode on a Bruker VERTEX 70 spectrophotometer with a Platinum ATR accessory featuring a diamond crystal. A total of 32 scans were performed at 4 cm⁻¹ resolution across the spectral range of 4000-30 cm⁻¹ (Figs. S9 and S10). Legend for attribution of vibrational modes: v_s = symmetric stretching; v_{as} = asymmetric stretching; δ_{ip} = in-plane deformation; δ_{op} = out-ofplane deformation; τ = twist ring.

1.1.5 Raman Spectroscopy

The confocal Raman spectra were obtained with a Bruker Senterra confocal Raman microscope fitted with a thermo-electrically cooled CCD camera (Bruker/Andor, 1024 × 256 pixels) and coupled to an Olympus Microscope (BX-51). The spectra were produced using a 785 nm laser line (diode laser), which was focused onto the sample by a $20 \times Olympus$ objective (NA 0.40). The exposition time was set to 5 seconds operating at 10mW of power (Fig. S11).

1.1.6 Mass Spectrometry

Electrospray ionization mass spectrometry (ESI MS) was carried out for complexes 1-3 using an Agilent 6210 TOF LC/MS system, in ESI⁺ mode (cationic fragment detection) and the samples were prepared in ethanol (Figs. S12-S14).

1.1.7 UV-Visible Spectroscopy

The UV-Vis spectra in the solid-state of **1–3** were measured using a UV-2600 Shimadzu UV-Vis spectrometer equipped with a diffuse reflectance integration sphere model ISR-2600Plus, covering the range of 250 to 800 nm. $BaSO_4$ was used as the reference material (Fig. 5). The UV-Vis absorption spectra in solution were recorded on the same spectrometer within the same spectral window for the determination of the molar absorptivity of complexes **1–3** and the supernatant solutions after 6 hours of photocatalytic reaction using **2**@m-TiO₂ as photocatalyst (Figs. S15-S21).

1.1.8 Scanning Electron Microscopy

For $1@m-TiO_2$, $2@m-TiO_2$, and $3@m-TiO_2$ photocatalysts, a Bruker Quantax 200 spectrometer device coupled with a JEOL 55 M6360 microscope was utilized in a scanning electron microscope (SEM) operating at 20 kV. Prior to the analysis (Figs. 8 and S25-S27), the samples were coated with a layer of gold using a Denton II magnetron sputter.

1.1.9 Nitrogen adsorption and desorption (BET and BJH methods)

The adsorption and desorption isotherms of mesoporous TiO_2 were obtained using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer with a liquid nitrogen bath at 77 K. The sample was dried and degassed under vacuum at 250 °C for 10 hours. The adsorption/desorption isotherms for N₂ were acquired within a relative pressure range from 0.01 to 0.99, and the specific surface area was calculated using the multi-point Brunauer-Teller method (B.E.T.), with a relative pressure range from 0.06 to 0.30 (Fig. S28-S30).

1.1.10 Cyclic Voltammetry

Voltammograms were acquired using a Metrohm Eco Chemie AutoLab PGSTAT128N potentiostat in dry EtOH as the solvent, at room temperature and under ambient conditions. A scanning speed of 100 mV/s was applied, and tetrabutylammonium perchlorate (TBACIO₄) was used as the supporting electrolyte. The redox potentials were adjusted using ferrocene (Fc/Fc⁺) as an internal calibration standard and convert to the normal hydrogen electrode (NHE = +0.63 V) (Fig. S22).

1.1.11 X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) analysis was performed using a solid sample of m-TiO₂, **1**@m-TiO₂, **2**@m-TiO₂ and **3**@m-TiO₂ in a Thermo K-Alpha spectrometer equipped with a monochromatic Al K α X-ray source (h ν = 1486.6 eV) (Figs. S23-S24). The XPS data was recorded using a constant pass energy of 50 eV and 200 eV for high resolution and survey spectra, respectively, with a step size of 0.10 eV. For data calibration, the adventitious C 1s peak in 284.8 eV was used.^{4–6}

1.1.12 Solid-state photoluminescence spectroscopy (PL)

The PL spectra were recorded using a Horiba FluoroMax Plus spectrofluorometer in the spectral range of 325–500 nm, with excitation and emission slit widths of 5.0 nm (Figs. S38-S40).

1.2 Synthetic Procedures

All analytical grade reagents and solvents were obtained commercially and performed in an open atmosphere.

1.2.1 Synthesis of $[NiBr(SeO_2Br)(bipy)_2]$ (1), $[NiBr(SeO_2Br)(phen)_2]$ (2) and $[NiCl(SeO_2Cl)(bipy)_2]$ (3): In a test tube, 0.022 g (0.10 mmol) of NiBr₂ (for 1 and 2) or 0.013 g (0.10 mmol) of NiCl₂ (for 3), 0.013 g (0.10 mmol) of H₂SeO₃ and 0.032 g (0.20 mmol) of 2,2'-bipy (for 1 and 3) or 0.036 g (0.20 mmol) of 1,10-phen (for 2) were suspended in 5 mL of acetonitrile. The test tube was placed in a stainless-steel reactor (Fig. S31) and the reactor was closed. The system was then heated using an Oxylab OXY-E – 1 oven equipped with a NOVUS N1200 temperature controller, following the parameters outlined in Table S3. Upon the oven temperature dropping below 30 °C, the reactor was opened, and the green crystals (blocks) were obtained. Yield: 53% (0.017 g for 1), 47% (0.016 g for 2), and 41% (0.011 g for 3), based on H₂SeO₃.

Properties of **1**: air stable, green crystalline solid. Elemental analysis: Calcd. for $C_{20}H_{16}Br_2N_4NiO_2Se$ (641.86 g·mol⁻¹): C: 37.43%, H: 2.51%, N: 8.73%. Found: C: 36.92%, H: 2.51%, N: 8.12%. FT-IR (ATR, cm⁻¹)⁷⁻⁹: 3410 (br) [vO–H]; 3104 (w), 3086 (w), 3072 (w), 3030 (w) [v_s(C–H)_{Ar}]; 1597 (s), 1573 (m), 1564 (m), 1490 (w), 1475 (m), 1467 (vs) [v_s(C=C/C=N)]; 1316 (m), 1248 (m), 1220 (w) [v_s(C–N)]; 1174 (w), 1157 (m), 1147 (m), 1118 (w), 1100 (w), 1056 (w), 1041 (m) [δ_{ip} (C=C–H)]; 975 (s) [v_{as} O–Se–O]; 889 (s), 809 (s), 759 (s), 734 (m) [v_s O–Se–O]; 652 (w), 632 (w)[δ_{op} (C=C–H)]; 550 (w) [v(Se–O)]; 467 (w), 440 (w), 410 (w) [δ_{op} (C=C–C)_{Ar}]; 383 (w), 328 (w) [τ (C–C)(C-N)]; 281 (w) [v(Ni–O)]; 264 (w), 253 (w) [v(Ni–N)]; 226 (w) [v(Se–Br)]; 211 (w) [v(Ni–Br)]. Raman (cm⁻¹)^{8,10–14}: 3073 (m), 3054 (w) [vO–H]; 1678 (s), 1598 (m), 1565 (m), 1494 (w), 1489 (w), 1434 (w), 1421 (s) [v_s (C=C/C=N)]; 1317 (w), 1290 (w), 1265 (w), 1249 (w) [v_s (C–N)]; 1175 (w), 1155 (w), 1103 (w), 1041 (w), 1025 (vs) [δ_{ip} (C=C–H)]; 960 (w), 893 (m), 812 (m), 767 (w), 735 (w) [v_s O–Se–O]; 654 (w), 633 (w) [δ_{op} (C=C–H)]; 552 (w) [v_s (Se–O)]; 466 (w), 422 (w)

[δ_{op}(C=C-C)_{Ar}]; 386 (w), 362 (w) [τ(C-C)(C-N)]; 256 (w) [ν(Ni-O)]; 239 (w) [ν(Ni-N)]; 225 (w) [ν(Se-Br)]; 194 (w) [ν(Ni-Br)]. ESI⁺ MS (*m/z*): [C₂₀H₁₆N₄NiBr₂O₂Se + H]⁺ 642.854 (found), 642.822 (calcd.). UV-Vis: ε (H₂O) = 28,425.5 L·mol⁻¹·cm⁻¹ for λ = 306 nm. The molecular structure of **1** in 50% probability ellipsoids is depicted in Fig. S1.

Properties of 2: air stable, green crystalline solid. Elemental analysis: Calcd. for C₂₄H₁₆Br₂N₄NiO₂Se (689.89 g·mol⁻¹): C: 41.78%, H: 2.34%, N: 8.12%. Found: C: 41.66%, H: 2.37%, N: 7.80%. FT-IR (ATR, cm⁻¹)^{8,15,16}: 3399 (br) [vO-H]; 3055 (w), 3000 (w) [v_s(C-H)_{Ar}]; 1623 (w), 1603 (w), 1580 (m), 1513 (s), 1492 (w), 1424 (s), 1413 (w) [v_s(C=C/C=N)]; 1342 (w), 1319 (w), 1308 (w), 1273 (w), 1255 (w), 1209 (w) [V₃(C–N)]; 1193 (w), 1139 (w), 1100 (w), 1050 (w) [δ_{ip}(C=C–H)]; 997 (w), 982 (w), 962 (s) [v_{as}O–Se–O]; 908 (w), 844 (s), 816 (s), 771 (w), 722 (s) [v_sO-Se-O]; 642 (m), 621 (w), 607 (w) [δ_{op}(C=C-H)]; 548 (w), 502 (w) $[v(Se-O)]; 485 (w), 423 (m) [\delta_{op}(C=C-C)_{Ar}]; 296 (m), 274 (m) [v(Ni-O)]; 233 (m) [v(Ni-N)];$ 196 (w) [v(Ni-Br)]. Raman (cm⁻¹)^{8,10-13,15}: 3062 (w), 3030 (w) [vO-H]; 1625 (w), 1604 (w), 1582 (w), 1515 (w), 1452 (m), 1424 (m) [v_s(C=C/C=N)]; 1346 (w), 1321 (w), 1310 (w), 1257 (w) $[v_s(C-N)]$; 1196 (w), 1138 (w), 1106 (w), 1094 (w), 1051 (m) $[\delta_{ip}(C=C-H)]$; 972 (w), 910 (m), 870 (w), 844 (w), 817 (m), 733 (m) $[v_sO-Se-O]$; 559 (w) $[v_s(Se-O)]$; 510 (w), 483 (w), 448 (w), 425 (w), 420 (w) [δ_{op}(C=C-C)_{Ar}]; 293 (w), 276 (w) [ν(Ni–O)]; 234 (m) [ν(Ni–N)]; 215 (m), 194 (vs) [v(Ni-Br)]. ESI⁺ MS (m/z): [C₂₄H₁₆N₄NiBr₂O₂Se + H]⁺ 688.8226 (found), 688.8231 (calcd.). UV-Vis: ϵ (H₂O) = 66,822.5 L·mol⁻¹·cm⁻¹ for λ = 270 nm. The molecular structure of **2** in 50% probability ellipsoids is depicted in Fig. S2.

Properties of 3: air stable, green crystalline solid. Elemental analysis: Calcd. for C₂₀H₁₆Cl₂N₄NiO₂Se (552.93 g·mol⁻¹): C: 43.44%, H: 2.92%, N: 10.13%. Found: C: 42.46%, H: 2.91%, N: 9.93%. FT-IR (ATR, cm⁻¹)^{7,8,11,17}: 3322 (br) [vO-H]; 3106 (w), 3085 (w), 3052 (w), 3031 (w) [v_s(C–H)_{Ar}]; 1597 (s), 1573 (m), 1464 (m), 1493 (w), 1475 (m), 1467 (m), 1437 (s) [v_s(C=C/C=N)]; 1316 (m), 1306 (w), 1287 (w), 1248 (m), 1220 (w) [v_s(C-N)]; 1174 (w), 1157 (m), 1146 (m), 1100 (w), 1075 (w), 1056 (w), 1041 (m), 1021 (w) $[\delta_{ip}(C=C-H)];$ 977 (m) [v_{as}O–Se–O]; 918 (m), 906 (s), 893 (s), 817 (m), 761 (m), 734 (w) [v_sO–Se–O]; 651 (w), 631 (w), 602 (w) $[\delta_{op}(C=C-H)]; 550$ (w) $[v_s(Se-O)]; 472$ (w), 442 (w), 414 (w) $[\delta_{op}(C=C-C)Ar.];$ 389 (w) [r(C-C)(C-N)]; 336 (w) [v(Se-Cl)]; 269 (w) [v(Ni-O)]; 237 (w) [v(Ni-Cl)]; 217 (w) [v(Ni–N)]. Raman (cm⁻¹)^{8,10,11,13,14}: 3075 (m), 3054 (w) [vO–H]; 1598 (vs), 1565 (m), 1489 (m), 1423 (w) $[v_s(C=C/C=N)]$; 1362 (w), 1318 (s), 1266 (w) $[v_s(C-N)]$; 1177 (w), 1157 (w), 1120 (w), 1103 (w), 1026 (vs) $[\delta_{ip}(C=C-H)]$; 919 (w), 901 (m), 818 (m), 769 (w), 743 (w) $[v_sO-Se-O]; 655$ (w), 633 (w) $[\delta_{op}(C=C-H)]; 553$ (w) [v(Se-O)]; 473 (w), 423 (w), 411 (w) $[\delta_{op}(C=C-C)Ar.];$ 363 (w) [v(Se-Cl)]; 264 (w) [v(Ni-O)]; 251 (w) [v(Ni-Cl)]; 239 (m) [v(Ni–N)]. ESI⁺ MS (m/z): [C₂₀H₁₆N₄NiCl₂O₂Se + H]⁺ 552.965 (found), 552.924 (calcd.). UV-Vis: ε (H₂O) = 26,244.5 L·mol⁻¹·cm⁻¹ for λ = 295 nm. The molecular structure of **3** in 50% probability ellipsoids is depicted in Fig. S3.

1.2.2 Synthetic procedures for the new photocatalysts: The synthesis of the photocatalysts $1@m-TiO_2$, $2@m-TiO_2$, and $3@m-TiO_2$ involved a methodology adapted from the literature.¹⁸10 mg of complexes **1–3** were dissolved in 1 mL of water. After complete dissolution, 200 mg of m-TiO₂ was added to the solution and kept under stirring at room temperature for 72 hours. The proportion was 5% w/w of the complexes in relation to the solid support for all photocatalysts. The solid obtained during the synthesis was filtered, washed with water, and centrifuged several times, then dried for later use. This procedure was conducted to eliminate remnants of complexes 1-3 that were not impregnated in the solid supports, ensuring greater reliability in the results obtained during the application of the photocatalysts. To determine the actual percentage of impregnated complex and the respective loading values, the solutions obtained from washing the photocatalysts were collected in 50 mL volumetric flasks (solution M) for analysis of the complex concentration in the solution. Impregnation was calculated through an indirect calculation, utilizing data from the UV-Vis analysis in solution. Photocatalyst 1@m-TiO₂: Immobilization yield: 18.1% (1.81 mg of complex 1), Loading: 1.36x10⁻⁵ mol·g⁻¹; Photocatalyst 2@m-TiO₂: Immobilization yield: 15.2% (1.52 mg of complex **2**), Loading: 1.11x10⁻⁵ mol·g⁻¹; Photocatalyst **3**@m-TiO₂: Immobilization yield: 3.40% (0.34 mg of complex 3), Loading: 2.97x10⁻⁶ mol·g⁻¹. The syntheses of the new photocatalysts are easily reproducible. Furthermore, understanding the main properties of these synthesized materials, such as light absorption, charge separation, and stability, is essential for improving solar energy devices. This knowledge helps in choosing the right

materials, improving charge separation, and ensuring long-term performance. It directly contributes to the development of more efficient systems for applications like photocatalytic hydrogen production and solar cells. Therefore, our findings not only demonstrate the utility of nickel dioxo-haloselenate complexes in enhancing H₂ generation but also provide a foundation for the rational design of future materials and devices aimed at scalable solar energy conversion applications, including photocatalytic water splitting.¹⁹

1.3 Photocatalytic H2 evolution test

The experiments on H₂ generation were assessed utilizing a dual-layered quartz reactor, where the temperature was maintained at 23°C via water circulation. Within the reactor, 20 mL of 10 v% TEOA (triethanolamine) aqueous solution, where TEOA acts as the sacrificial electron donor (SED). The solution was continuously stirred magnetically, and 10 mg photocatalyst sample (1@m-TiO₂, 2@m-TiO₂, or 3@m-TiO₂) was introduced. Argon gas was bubbled into the mixture for 10 minutes to remove other gases, particularly O₂. Before initiating the reaction, a 300 µL gas sample was withdrawn from the reactor using a Hamilton syringe and subjected to gas chromatography analysis (Shimadzu GC-2014 gas chromatograph with a 4.6 m long, 2.10 mm internal diameter Carboxem 1000 column and a thermal conductivity detector) to confirm the absence of gaseous H₂ (t=0 min). Subsequently, the reactor containing the suspension was exposed to UV-Vis light radiation from a 300 W Hg/Xe lamp and intensity of 1470 W/m² with continuous magnetic stirring for 6 hours. The evolution of H₂ gas was observed by collecting 300 µL gas samples at 1-hour intervals.

		•	•
	1	2	3
Formula	$C_{20}H_{16}Br_2N_4NiO_2Se$	$C_{24}H_{16}Br_2N_4NiO_2Se$	$C_{20}H_{16}CI_2N_4NiO_2Se$
F.W. (g.mol-1)	641.86	689.89	552.94
Т (К)	295(2)	296(2)	296(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P21/c	Pbca	P21/c
<i>a</i> (Å)	14.0502(5)	10.5766(4)	13.8108(7)
b (Å)	10.1635(3)	16.8520(6)	10.0814(5)
c (Å)	15.1056(5)	26.1453(9)	14.8966(7)
α (°)	90	90	90
eta (°)	94.4760(10)	90	94,414(2)
γ(°)	90	90	90
V (ų)	2150.49(12)	4660.11(3)	2067.98(18)
Ζ;	4	2	4
$r_{\rm calc}$ (g cm ⁻³)	1.982	1.967	1.776
μ (mm⁻¹)	3.374	3.120	1.571
F(000)	1248	2688	1104
Refl. Collected	77378	139739	63586
Refl. unique (R _{int})	6551 [0.0649]	7125 [0.0810]	6340 [0.1289]

Table S1. Crystallographic and structure refinement data for complexes 1–3.

$R_1\left[l>2\sigma(l)\right]$	$R_1 = 0.0353$	$R_1 = 0.0346$	$R_1 = 0.0466$
$wR_2[l > 2\sigma(l)]$	$wR_2 = 0.0648$	$wR_2 = 0.0607$	$wR_2 = 0.0743$
<i>R</i> ¹ (all data) ^[a]	$R_1 = 0.0580$	$R_1 = 0.0594$	$R_1 = 0.0936$
wR ₂ (all data) ^[b]	$wR_2 = 0.0719$	$wR_2 = 0.0682$	$wR_2 = 0.0865$
<i>Goodness-of-fit</i> em <i>F</i> ²	1.077	1.077	1.036
Largest diff. peak and hole	0.598 e -0.834	0.344 e -0.541	0.410 e -0.437
(e Å ⁻³)			

(e Å⁻³) $[a]R_1 = |F_o - F_c|/|F_o|; [b]wR_2 = [w(F_o^2 - F_c^2)^2/(wF_o^2)]^{1/2}.$

Table S2. Selected bond lengths (Å) and angles (°) for complexes 1-3.

Bond lengths (Å)		Bond angles (°)	
1			
Ni1-N1	2.081(2)	N1-Ni1-N2	78.85(9)
Ni1–N2	2.075(2)	N3-Ni1-N4	78.57(9)
Ni1-N3	2.082(2)	N1-Ni1-01	90.55(9)
Ni1-N4	2.072(2)	N2-Ni1-01	89.86(8)
Ni1-01	2.116(2)	N3-Ni1-01	173.10(9)
Ni1–Br1	2.5606(4)	N4-Ni1-01	94.57(9)
Se1-01	1.659(2)	O1-Ni1-Br1	97.35(8)
Se1-02	1.622(3)	01–Se1–O2	107.58(11)
Se1-Br2	2.6097(5)	O2-Se1-Br2	101.46(9)
Se1…Br1	3.0264(1)	O1–Se1–Br2	97.35(8)
2			
Ni1-N1	2.087(2)	N1-Ni1-N2	79.98(8)
Ni1–N2	2.084(2)	N3-Ni1-N4	80.00(8)
Ni1-N3	2.071(2)	N1-Ni1-01	91.19(8)
Ni1-N4	2.094(2)	N2-Ni1-01	87.75(8)
Ni1-01	2.1078(18)	N3-Ni1-01	93.41(8)
Ni1-Br2	2.5464(4)	N4-Ni1-01	173.14(9)
Se1–O1	1.6504(18)	O1–Ni1–Br2	91.52(5)
Se1–O2	1.606(3)	01–Se1–O2	105.94(13)
Se1–Br1A	2.590(4)	O1–Se1–Br1A	102.71(10)
Se1-Br1B	2.574(4)	O1–Se1–Br1B	101.43(13)
		O2–Se1–Br1A	98.20(2)
		O2–Se1–Br1B	107.7(3)

3			
Ni1-N1	2.077(2)	N1-Ni1-N2	78.76(10)
Ni1-N2	2.085(2)	N3-Ni1-N4	78.63(10)
Ni1-N3	2.074(2)	N1-Ni1-01	94.43(10)
Ni1-N4	2.085(2)	N2-Ni1-01	173.19(9)
Ni1-01	2.124(2)	N3-Ni1-01	90.63(9)
Ni1–Cl1	2.4035(8)	N4-Ni1-01	88.92(9)
Se1-01	1.656(2)	O1-Ni1-Cl1	87.91(6)
Se1-02	1.618(2)	01–Se1–O2	107.82(12)
Se1–Cl2	2.4253(10)	01–Se1–Cl2	100.89(10)
Se1…Cl1	2.944(1)	O2–Se1–Cl2	96.63(8)
		Cl1…Se1–Cl2	158.26(2)
		Cl1…Se1–O1	81.17(2)
		Cl1…Se1–O2	100.33(2)

Table S3. Time (t) and temperature (T) used to obtain 1–3.

n ^c	t _n (min)	T _n (°C)
0	-	70
1	60	90
2	60	110
3	60	120
4	240	120
5	120	110
6	120	100
7	120	80
8	120	60
9	180	40

Total time: 18 h, with 4 h at 120 °C.

a) time required for the oven to reach Tn; b) temperature in the reactor.

Table S4. Values of ε	(molar absorptivity	coefficient) for complexes 1 -	- 3.
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Complex	1	2	3
Values of ϵ	28,425.5	62,822.5	26,244.5

Complex	1 @mTiO ₂	2 @mTiO ₂	3 @mTiO ₂
Mean absorbance	0.725	0.772	0.917
Impregnation (mg)	1.81	1.52	0.34
Impregnation (mol)	2.82 x 10 ⁻⁶	2.29 x 10 ⁻⁶	6.13 x 10 ⁻⁷
Immobilization yield (%)	18.1	15.2	3.40
Impregnation (%) (m/m TiO ₂)	0.905	0.760	0.170
Loading (mol.g ⁻¹)	1.36 x 10 ⁻⁵	1.11 x 10 ⁻⁵	2.97 x 10 ⁻⁶



Figure S1. ORTEP²⁰ representation of the molecular structure of $[NiBr(SeO_2Br)(bipy)_2]$ (1). The thermal ellipsoids indicate the 50% probability level.

Table S5. Mean absorbance values, impregnations in milligrams, moles and percentage and loading values found for photocatalysts $1@m-TiO_2$, $2@m-TiO_2$ and $3@m-TiO_2$.



Figure S2. ORTEP²⁰ representation of the molecular structure of $[NiBr(SeO_2Br)(phen)_2]$ (2). The thermal ellipsoids indicate the 50% probability level



Figure S3. $ORTEP^{20}$ representation of the molecular structure of $[NiCl(SeO_2Cl)(bipy)_2]$ (**3**). The thermal ellipsoids indicate the 50% probability level.



Figure S4. Simulated and experimental PXRD pattern for [NiBr(SeO₂Br)(bipy)₂] (1).



Figure S5. Simulated and experimental PXRD pattern for [NiBr(SeO₂Br)(phen)₂] (2).



Figure S6. Simulated and experimental PXRD pattern for [NiCl(SeO₂Cl)(bipy)₂] (3).



Figure S7. Simulated and experimental PXRD pattern for m-TiO₂.



Figure S8. Experimental PXRD pattern for m-TiO₂ and photocatalysts 1@m-TiO₂, 2@m-TiO₂ and 3@m-TiO₂.



Figure S9. FT-IR spectra for complexes 1–3.



Figure S10. FT-IR spectra for m-TiO₂ and photocatalysts 1@m-TiO₂, 2@m-TiO₂ and 3@m-TiO₂.



Figure S11. Confocal Raman spectra for complexes 1–3.



Figure S12. ESI⁺ MS spectrum for complex 1. The sample was prepared in ethanol.



Figure S13. ESI⁺ MS spectrum for complex 2. The sample was prepared in ethanol.



Figure S14. ESI⁺ MS spectrum for complex 3. The sample was prepared in ethanol.



Figure S15. Dilutions for calculating molar absorptivity coefficient of complex **1** measured in duplicate. Water was used as solvent.



Figure S16. Dilutions for calculating molar absorptivity coefficient of complex **2** measured in duplicate. Water was used as solvent.



Figure S17. Dilutions for calculating molar absorptivity coefficient of complex **3** measured in duplicate. Water was used as solvent.



Figure S18. Linear equation for molar absorptivity coefficient for complex **1**, where ε is the average of the angular coefficient (28,425.5 L mol⁻¹ cm⁻¹).



Figure S19. Linear equation for molar absorptivity coefficient for complex **2**, where ε is the average of the angular coefficient (66,822.5 L mol⁻¹ cm⁻¹).



Figure S20. Linear equation for molar absorptivity coefficient for complex **3**, where ε is the average of the angular coefficient (26,244.5 L mol⁻¹ cm⁻¹).



Figure S21. Qualitative UV-Vis spectra of the supernatant solution after 6 h of photocatalytic reaction using $2@m-TiO_2$ as photocatalyst.



Figure S22. Voltammograms for complexes 1–3.



Figure S23. Survey XPS spectra of (A) Ti 2p, (B) C 1s and (C) O 1s for the m-TiO₂, 1@m-TiO₂, 2@m-TiO₂ and 3@m-TiO₂.



Figure S24. High-resolution XPS spectra in the regions of (A) Ti 2p, (B) C 1s and (C) O 1s for the m-TiO₂, **1**@m-TiO₂, **2**@m-TiO₂ and **3**@m-TiO₂.



Figure S25. Particle size distribution for the photocatalyst 1@m-TiO₂.



Figure S26. Particle size distribution for the photocatalyst 2@m-TiO₂.



Figure S27. Particle size distribution for the photocatalyst 3@m-TiO₂.



Figure S28. Adsorption and desorption isotherm of mesoporous TiO₂.



Figure S29. BJH analysis of the adsorption branch of mesoporous TiO₂.



Figure S30. BJH analysis of the desorption branch of mesoporous TiO₂.



Figure S31. Hydrogen evolution over the time for complexes 1–3.



Figure S32. Stability test in H₂O for 6 hours for complexes 1–3.



Figure S33. Reactor used in syntheses of 1–3.



Figure S34. SEM images of the photocatalysts $1@m-TiO_2$, $2@m-TiO_2$ and $3@m-TiO_2$ after the photocatalytic testing.



Figure S35. EDS analysis for $1@m-TiO_2$ after the photocatalytic testing.



Figure S36. EDS analysis for 2@m-TiO₂ after the photocatalytic testing



Figure S37. EDS analysis for 3@m-TiO₂ after the photocatalytic testing



Figure S38. Solid-state photoluminescence (PL) emission spectra of complex 1, m-TiO₂, and 1@m-TiO₂, recorded at their respective excitation wavelengths (λ_{exc}). The λ_{exc} values were selected based on the maximum absorbance peaks observed in the diffuse reflectance spectra (DRS).



Figure S39. Solid-state photoluminescence (PL) emission spectra of complex **2**, m-TiO₂, and **2**@m-TiO₂, recorded at their respective excitation wavelengths (λ_{exc}). The λ_{exc} values were selected based on the maximum absorbance peaks observed in the diffuse reflectance spectra (DRS).



Figure S40. Solid-state photoluminescence (PL) emission spectra of complex **3**, m-TiO₂, and **3**@m-TiO₂, recorded at their respective excitation wavelengths (λ_{exc}). The λ_{exc} values were selected based on the maximum absorbance peaks observed in the diffuse reflectance spectra (DRS).

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