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Nanostructured IrO_x Coatings for Efficient Oxygen Evolution Reactions in PV-EC Setup

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Abstract: New heteroleptic iridium compounds exhibiting high volatility and defined thermal decomposition behavior were developed and tested in plasma-enhanced chemical vapor deposition (PECVD). The iridium precur-[(COD)Ir(TFB-TFEA)] (COD = 1,5-cyclooctadiene; TFB-TFEA = N-(4,4,4sor Trifluorobut-1-en-3-on)-6,6,6-trifluoroethylamin) unifies both reactivity and sufficient stability through its heteroleptic constitution to offer a step-by-step elimination of ligands to provide high compositional purity in CVD deposits. The substitution of neutral COD ligands against CO groups further increased the volatility of the precursor. PECVD experiments with unambiguously characterized Ir compounds (single crystal X-ray diffraction analysis) demonstrated their suitability for an atom-efficient (high molecule-to-precursor yield) gas phase deposition of amorphous iridium oxide (IrO_x) phases. Thin films of IrO_x were well suited as electrocatalyst in oxygen evolution reaction so that an efficient coupled system in combination with solar cells is viable to perform water-splitting reaction without external bias.

Keywords: advanced materials; CVD; iridium oxide; iridium precursor; nanos-tructured films.

1 Introduction

Iridium oxide is one of the most efficient electrocatalysts used in oxygen evolution reaction (OER) because of its favorable combination of properties including

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high corrosion resistance and the low overpotential (ca. 0.3 V) required for proceeding the reaction [1–14]. Research on water splitting reaction has focused mainly on catalysis of the oxygen evolution reaction because of the sluggish kinetics compared with hydrogen evolution reaction (HER) [15, 16]. Although in the natural photosystems the OER is catalyzed by a manganese oxide cluster, iridium-based materials offer promising opportunities to perform this kinetically challenging OER in the laboratories [17]. One of the key experimental findings about the relationship between activity and stability of iridium-based electrodes is the identification of transient surface states characterized by the formation of nonstoichiometric IrO_x species that lead to an enhanced OER performance [5, 18–20]. Water splitting, coupled with wind or solar energy generators, produces hydrogen which is an attractive alternative energy source. Furthermore pure H_2 is generated at the cathode that can be used as a fuel, with O_2 as the only waste by-product, which makes water splitting an attractive route for producing an environmentally clean fuel [21–23]. In this context plasma-enhanced chemical vapor deposition (PECVD) processes enable reproducible synthesis of catalytically active IrO_x thin films, which however requires molecular compounds with substantial vapor pressure essential to achieve iridium feedstock in the gas phase [24, 25]. In the context of iridium precursor chemistry, known metal-organic compounds like metal alkoxide, carbonyl or β -diketonate complexes are used that suffer from low vapor pressure and high decomposition temperatures thereby providing little control over film growth conditions [26]. Moreover, in many cases, use of reactive gases is necessary to accelerate the precursor flow in the reactor that results in compositional gradients due to limited ad-atom mobilities. Since the volatility of precursors strongly depends on inter- and intramolecular interactions as well as the molecular weight of the compound, one of the synthetic challenges is to find strategies to decrease molecular weight and nuclearity of precursors to render them kinetically labile. We demonstrate here that application of neutral chelating ligands increases the stability of complexes and allows a careful design of heteroleptic precursors showing sufficient volatility and adequate reactivity and accessibility to modify precursor properties (Figure 1) [27-34].

We report herein the solid-state and solution phase structure of new heteroleptic iridium(I) precursor $[(CO)_2Ir(TFB-TFEA)]$ (5) demonstrate its intrinsic advantages as molecular precursor for synthesis of iridium-based films via PECVD at low temperatures. Furthermore, quantitative conversion of amorphous iridium oxide films into phase-pure iridium dioxide films and electrocatalytic OER behavior in PV-EC coupled systems is described.



Fig. 1: Synthesis of *Janus*-headed iridium precursors by ligand modification to manipulate volatility and electronic properties of molecular complexes.

2 Results and discussion

2.1 Precursor synthesis

The bidentate ligand **2** was prepared by reacting ethyl vinyl ether with trifluoroacetic acid anhydride in presence of pyridine under elimination of pyridinium trifluoroacetate to get 1-Ethoxy-4,4,4-trifluorobut-1-en-3-on (ETFB **1**). Addition of the fluorinated amine in toluene led to *N*-(4,4,4-Trifluorobut-1-en-3-on)-6,6,6trifluoroethylamin (HTFB-TFEA **2**) under elimination of EtOH. The heteroleptic iridium(I) precursor [(CO)₂Ir(TFB-TFEA)] (**5**) was synthesized via salt metathesis reaction by reacting dimeric [(COD)IrCl]₂ (**4**) and the sodium salts of **2** (**2b**, Scheme 1) [27, 35]. Afterwards CO was passed through the reaction mixture to obtain precursor **5**.



Scheme 1: Synthetic route to heteroleptic monomeric Ir(l) compound (5) from a dimeric compound (3).

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The heteroleptic iridium(I) complex (**5**) was isolated as air-stable crystalline red solid by sublimation in dynamic vacuum. The sublimation temperature of **5** (45 °C, 10^{-3} mbar) could be significantly lowered compared to similar compounds such as [(COD)Ir(ThTFP)] (110 °C, 10^{-3} mbar) [27], [Ir(acac)₃] and [(COD)Ir(MeCp)] (180 °C, 100 °C, 10^{-3} mbar) [26, 27] which are conventionally used as precursors in the CVD of iridium-based films. The higher volatility of [(COD)Ir(TFB-TFEA)] compounds is attributed to the lower molecular weight and higher covalent character verified by the bond lengths determined through single crystal structure analysis.

2.2 Structural characterization of [(CO)₂Ir(TFB-TFEA)]

¹H NMR spectra (see Supporting Information) of compound (5) displayed two doublets for vinylic protons of the TFB-TFEA ligand at $\delta = 7.91$ ppm (³J = 6.9 Hz) and $\delta = 6.04$ ppm (³J = 6.9 Hz). CH₂ protons of TFB-TFEA compounds appeared at $\delta = 4.66$ ppm as a quartet due to coupling to C8-F₃ group. Furthermore, no COD signals could be detected for compound (5) but carbonyl ligands could be detected in the ¹³C DEPT spectrum at $\delta = 171.6$ ppm and $\delta = 169.5$ ppm (C1/2). ¹⁹F NMR spectra (see Supporting Information) of compound (5) revealed that the compound is pure and no secondary impurities coexist.

Single crystal X-ray diffraction analysis of heteroleptic iridium(I) complex (5) showed a distorted square planar coordination around iridium, as observed in other iridium(I) compounds such as [(COD)Ir(ThTFP)] (Figure 2) [27, 36]. The distorted geometry of compound (5) originated from the angle between C1 and nitrogen atom N1 (C1–Ir01–N1) (95.4 \pm 0.2)° that is larger than the C2–Ir01–O3 angle



 $[(CO)_2 Ir(TFB-TFEA)] (5)$

Fig. 2: Molecular structures of $[(CO)_2 Ir(TFB-TFEA)]$ (5). Thermal ellipsoids are drawn at 50% probability level.



Fig. 3: Thermogravimetric analysis of heteroleptic Ir(I) compound (5).

with (87.5 \pm 0.2)° and C1–Ir01–C2 angle (87.4 \pm 0.2)° due to higher steric profile of –CH₂CF₃ group present at the amine.

Compound **5** was investigated by EI mass spectrometry at an ionization energy of 70 eV and evaporation temperatures of 30 °C (10^{-6} mbar). The mass spectrum was dominated by the molecular ion $[M]^{+\bullet}$ base peaks. Thermal behavior of the precursor investigated by thermogravimetric (TG) analysis (Figure 3) showed a complete evaporation of compound **5** without any decomposition in the temperature range 100–200 °C. This demonstrated high volatility of the new precursors compared to conventionally used Ir-precursors and an enhanced feedstock in the gas phase. This also indicated the challenges associated with high volatility that can influence the growth rate and materials yield due to intact transport of precursor to the cold trap.

2.3 Plasma-enhanced chemical vapor deposition of [(CO)₂Ir(TFB-TFEA)]

Amorphous iridium oxide (IrO_{2-x}) thin films were deposited by decomposition of $[(CO)_2Ir(TFB-TFEA)]$ (5) by radio frequency PECVD onto silicon, aluminum oxide, FTO, Au and Au@Cu substrates with pure O_2 gas as the reactive gas and maintaining the precursor reservoir at the room temperature. In X-ray diffraction of as deposited thin films no peaks of crystalline materials could be detected to conclude that those films are amorphous. XPS analysis showed that as deposited iridium oxide films for deposition time periods of 60 min

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Fig. 4: High resolution Ir 4f (left) and O 1s (right) XPS spectra of as deposited iridium oxide films (above) and annealed iridium dioxide films (below) deposited on Si substrates.

(Figure 4, above), whereas annealing of iridium-based films produced iridium dioxide films that exhibited hydroxide groups on the surface (Figure 4, below) [37]. Additionally disproportionation reactions of subvalent Ir(I) precursor to elemental iridium and iridium (IV) oxides could possibly occur in as-deposited films.

The successful deposition of iridium oxide films on single crystal (Si), amorphous (SiO₂) and polycrystalline (Al₂O₃) substrates showed the universal applicability of the precursor and its chemically-controlled decomposition irrespective of the surface chemistry of the substrate material. Obtained XPS spectra revealed the formation of iridium oxide and dioxide deposits as a function of the deposition and post-treatment conditions [38]. XRD patterns of annealed IrO₂ thin films at Si substrates are depicted in supporting information. Sublimation at room temperature (25 °C) using compound **5** and deposition of iridium-based coating has been reported for the first time and enriches the family of precursors due to its high volatility and defined deposition in gas phase deposition processes.

2.4 Application of iridium-based coatings in oxygen evolution

The electrochemical activity of iridium layers on different kind of substrates was evaluated in a three electrode system in alkaline media. To analyze the potential of IrO_{2-x} films in the electrochemical water splitting, they have been analyzed regarding they morphology by SEM (Figure 5, additional micrographs see supporting information). $IrO_x@Au@Cu$ (deposited by PECVD) and Ir@Au (MOCVD) are representatively depicted in Figure 5.

They were deposited onto different conductive substrates (FTO, Au@Cu and Au) to obtain rough nanotopographies of iridium-based materials in the size range of ~50 nm and below. Their electrochemical performances were comparatively analyzed. A platinum mesh was used as counter electrode while Ag|AgCl served as reference electrode. Figure 6 demonstrates high electrochemical activity of all iridium-based thin films obtained from different deposition methods (MOCVD, PECVD; Figure 6, left) with overpotential values in the range of 0.35–0.60 V (measured potentials: 1.58–1.83 V) at 10 mA/cm² (vs. Ag/AgCl). The lowest overpotential values of ~1.6 mV was found for IrO_x@Au@Cu (PECVD) and IrO_x@Au (PECVD), show a stabile behavior under the applied measurement conditions (900 s in 1 M KOH) (Figure 6, right).

Figure 6 reveals that films deposited by PECVD (Figure 6; right; black and blue lines) showed highest potentials lowest stability in alkaline media. Furthermore, as deposited films also showed increased current densities at lower potentials (Figure 6; left; green, blue and light blue lines). The most active layers offering lowest overpotentials (Ir@FTO (MOCVD); IrO_x@Au (PECVD); IrO_x@Au@Cu



Fig. 5: SEM micrographs of as deposited Ir-based films by PECVD (left) and MOCVD (right) on different kind of Au-based substrates.





Fig. 6: Current densities / of different prepared electrodes against applied potential *E* (left) and time dependent potentials *E* of iridium-based substrates at different deposition condition at 10 mA/cm² (1 M KOH, right).

(PECVD)) were investigated in a customized two electrode setup [39, 40] as OER catalyst in combination with an a-Si:H/a-Si:H/ μ c-Si:H (a-Si:H = hydrogenated amorphous silicon, μ c-Si:H = hydrogenated microcrystalline silicon) thin film silicon solar cell that operate at $V_{OC} \approx 2.2$ V with a platinum plate as HER (Figure 7, right) [41, 42]. Furthermore a heat-treated oxide film (IrO₂@Au (MOCVD-annealed) as well as a crystalline metallic film (Ir@Au (MOCVD)[27]) were investigated towards their light induced water splitting potential. In all the experiments, bias



Fig. 7: Schematic overview of a-Si:H/a-Si:H/ μ c-Si:H (a-Si:H = hydrogenated amorphous silicon, μ c-Si:H = hydrogenated microcrystalline silicon) thin film silicon solar cell with Pt as HER catalyst [40] in a two electrode setup with iridium-based thin films as OER catalyst (left). Current densities-voltage curves (*J*-*V*) measured for different PV-EC devices employing the shown solar cell + HER catalyst combination (left side) and different OER catalysts under illumination using 1 M KOH as electrolyte. Bias free water splitting is enabled at 0 V.

free solar driven water splitting was possible and the generation of H₂ and O₂ was observed by eye (Figure 7, right). A current density of -3 mA/cm^2 at 0 V was observed for as-deposited Ir(0) films on FTO substrates. Other samples showed an increased activity of \sim -3.5 mA/cm² at 0 V.

3 Conclusion

A new class of heteroleptic iridium(I) complexes containing both anionic and neutral multidentate ligands demonstrated a synergistic interplay of reactivity and stability while pointing new possibilities of ligand modification and precursor design (Figure 1). Through the availability of a new class of iridium precursors for an efficient gas phase transport, the efficiency of thin film deposition processes was enhanced. The controlled deposition of metallic (Ir) and oxide (IrO_{2-x}) films on various substrate materials underlines the potential of new precursor chemistries enabling low-temperature deposition of catalytically active coatings with high reproducibility. Application of the Ir-based coatings in an integrated water splitting device combining PV and PEC technology offers possibilities of splitting water by solar energy without an external bias.

4 Experimental

4.1 Chemicals and methods

All manipulations of air and moisture sensitive materials were carried out under nitrogen using all glass assemblies. NMR spectra were recorded on a Bruker Avance II spectrometer operating at ¹H: 300.1 MHz; ¹³C: 75.5 MHz; ¹⁹F: 282.4 MHz, chemical shifts δ are given in part per million (ppm) relative to TMS (¹H, ¹³C) and CFCl₃ (¹⁹F) and coupling constants (*J*) are given in Hz. NMR spectra have been plotted by Bruker TopSpin 3.5 pl7 [43] software. Mass spectra were recorded on a Finnigan MAT 95 (EI, 70 eV) in m/z (intensity in %). Data collection for Xray structure elucidation was performed on a STOE IPDS II diffractometer using monochromated Mo–K_α radiation (λ = 0.71071 Å). The programs used in this work are STOE's X-Area [44] and the WINGX suite of programs [45], including SIR-92 [46], SHELX & SHELXL [47] and PLATON [48] for structure solution and refinement. H-atoms were calculated geometrically and a riding model was applied during the refinement process. TG measurements were performed on a TGA/DSC1 (METTLER-TOLEDO GmbH, Germany) apparatus.

4.2 Precursor synthesis

1-Ethoxy-4,4,4-trifluorobut-1-en-3-on (ETFB, 1) was prepared by dissolving 2.9 mL (30 mmol, 1.0 equiv.) ethyl vinyl ether and 12.1 mL (150 mmol, 5.0 equiv.) pyridine were dissolved in 80 mL DCM. This solution was cooled to 0 °C under stirring. Over the course of 30 min 4.3 mL (30 mmol, 3.0 equiv.) trifluoroacetic acid anhydride was added dropwise. This solution was left to stir overnight at rt. Afterwards 300 mL of 3% Na₂CO_{3(aq)} were added. The mixture was extracted with EtOAc (4 × 200 mL). The organic phase was washed with 4 × 100 mL brine and the solvent was removed under reduced pressure. The crude product was purified by vacuum distillation (40 °C, 10^{-3} mbar) and was obtained as a yellow oil **1** that was used in further synthesis of compound **2**. Yield: 69% (3.48 g). ¹H NMR (300.1 MHz, 298 K, CDCl₃) δ [ppm]: 7.84 (d, 1H, 2-H, ³*J*_{H,H} = 12 Hz), 5.80 (d, 1H, 3-H, ³*J*_{H,H} = 12 Hz), 4.06 (q, 2H, 6-H), 1.39 (t, 3H, 7-H). ¹⁹F NMR (282.4 MHz, 298 K, CDCl₃) δ [ppm]: -78.8 (¹*J*_{FC} = 284 Hz, ²*J*_{FC} = 32 Hz).

N-(4,4,4-Trifluorobut-1-en-3-on)-6,6,6-trifluoroethylamin (HTFB-TFEA, 2) 5.04 g (30 mmol, 1.0 equiv.) of compound 1 was dissolved in 80 ml toluene and was cooled to 0 °C under stirring. Over the course of 30 min 2.4 mL (30 mmol, 1.0 equiv.) 2,2,2-trifluoroethylamine was added dropwise. This solution was left to stir for 1 h. A solid was crystallized from the reaction mixture, washed with *n*-pentane and recrystallized in a 1:1 toluene/*n*-pentane mixture, yielding a colorless solid **2**. Yield: 84% (5.57 g). ¹H NMR (300.1 MHz, 298 K, CDCl₃) δ [ppm]: 9.99 (s, 1H, NH); 7.05 (dd, ³*J*_{H,H} = 8 Hz, 1H, 4-H); 5.54 (d, ³*J*_{H,H} = 8 Hz, 1H, 2-H); 3.82 (m, 2H, 5-H). ¹⁹F NMR (282.4 MHz, 298 K, CDCl₃) δ [ppm]: -73.2 (6-F); -77.4 (4-F). Elemental Analysis calc. for C₆H₄F₆NO: C 34.44, H 3.30, N 5.74 found: C 34.12, H 2.88, N 6.51.

Sodium salt of bidentate ligand (NaTFB-TFEA (2b)) was prepared by reacting with NaOEt. Therefore 0.023 g (1.0 mmol, 1.0 equiv.) of sodium were added to 10 mL of ethanol. After stirring for 30 min 1.0 mmol (1.0 equiv.) of bidentate ligand (2) were added to the solution. After removal of the excess solvent, an off-white solid (2b) was obtained. Yield: (1.0 mmol, >99%). ¹H NMR (300.1 MHz, 298 K, CDCl₃) δ [ppm]: 7.57 (m, 1H, 4-H); 5.12 (d, ³J_{H,H} = 5 Hz, 1H, 3-H); 3.74 (m, 1H, 5-H). ¹⁹F NMR (282.4 MHz, 298 K, CDCl₃) δ [ppm]: -72.8 (6-F); -76.7 (4-F).

[(COD)IrCl]₂ (3) was prepared following a modified procedure described by Tani et al. [49] To a stirred solution of 0.441 g (NH₄)₂[IrCl₆] (1.0 mmol, 1.0 equiv.) in a 2:1 mixture of H₂O and isopropyl alcohol (15 mL) 0.98 mL cycloocta-1,5-diene (COD) (8.0 mmol, 8.0 equiv.) was slowly added. The resulting solution was heated to reflux for 12 h when a red-orange solid precipitated out. After cooling to rt the reaction mixture was evaporated to dryness and the crude product was extracted with 20 mL of *n*-pentane. After decanting and removal of the excess solvent, a red-orange solid (3) was obtained. Yield: 0.470 g (0.70 mmol, 70%), ¹H NMR (300.1 MHz, 298 K, CDCl₃) δ [ppm]: 4.24-4.23 (m, 4H, 1-H); 2.29–2.24 (m, 4H, 2-H); 1.57–1.49 (m, 4H, 2-H). ¹³C NMR (75.5 MHz, 298 K, CDCl₃) δ [ppm]: 62.4 (C1); 31.9 (C2). Elemental Analysis calc. for C₁₆H₂₄Cl₂Ir₂: C 28.61, H 3.60 found: C 29.12, H 2.98.

[(CO)₂Ir(TFB-TFEA)] (5) 1.5 mmol (2.1 equiv.) of the sodium salt of bidentate ligand **2** (**2b**) was placed in a flask. Afterwards 0.470 g (0.7 mmol, 1.0 equiv.) of [(COD)IrCl]₂ (**3**) dissolved in 30 mL anhydrous THF were added to the sodium compound (**2b**). The mixture was stirred for 4 h at room temperature. Afterwards CO was vigorously bubbled through the reaction mixture for 10 min. The solvent was removed under reduced pressure and the crude product was sublimed (45 °C, 10^{-3} mbar) in dynamic vacuum to afford red crystals **5**. Yield: 0.402 g (0.86 mmol, 86%), ¹H NMR (300.1 MHz, 298 K, CDCl₃) δ [ppm]: 7.91 (d, ³J_{H,H} = 8 Hz, 1H, 6-H); 6.04 (d, ³J_{H,H} = 8 Hz, 1H, 5-H); 4.66 (m, 2H, 7-H). ¹³C NMR (75.5 MHz, 298 K, CDCl₃) δ [ppm]: 171.6 (C1); 169.5 (C2); 163.8 (C6); 95.4 (C5); 68.7 (C7). ¹⁹F NMR (282.4 MHz, 298 K, CDCl₃) δ [ppm]: -70.9 (6-F); -73.3 (4-F). EI-MS (70 eV, 30 °C): *m/z* (intensity) = 468 (100%) [M]^{+•}, 412 (64%) [M-2 CO]^{+•}, 18 (66%) [H₂O]^{+•}. Elemental Analysis calc. for C₈H₄F₆NO₃Ir: C 20.52, H 0.86, N 2.99 found: C 20.73, H 1.07, N 3.17.

4.3 CVD experiments

Thin film deposition was performed in a horizontal cold-wall MOCVD reactor equipped with an inductive field heating. The substrates (1.3 cm \times 1.3 cm) were heated through graphite susceptor. The molecular precursor was introduced to the reactor through a glass flange by applying a dynamic vacuum (10⁻³ mbar) and heating the precursor reservoir to the desired temperature. No carrier or reactive gases were used [50]. Also thin films were deposited by radio frequency PECVD onto FTO, Au and Au@Cu substrates using precursor **5** as iridium source and pure O₂ gas as additional oxygen source. The as-grown films were amorphous IrO_x and were annealed for 5 h in air at 750 °C to obtain crystalline IrO₂ as reported elsewhere [27].

4.4 Materials characterization

Room-temperature powder X-ray diffraction (XRD) was obtained on a STOE-STADI MP diffractometer operating in the reflection mode using Cu–K_α (λ = 1.5406 Å) radiation. The microstructures of the samples were examined using field-emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 430, see supporting information). Water splitting measurements were carried out in a two electrode setup with a 1 M KOH electrolyte using a "Oriel LCS-100, Newport, model

94011A" to simulate the solar spectrum and data was collected with "Gamry Reference 600 Potentiostat". As current-voltage source a thin film silicon solar cell (a-Si:H/a-Si:H/ μ c-Si:H) equipped with platinum as hydrogen evolution catalyst has been used in an in-house produced cell that has been invented at Forschungszentrum Jülich GmbH [39, 40]. As OER iridium containing films have been deposited on different kind of substrates (see above) at University of Cologne.

5 Supporting information available

NMR, EI mass spectra and XRD pattern are presented in SI. X-ray crystallographic data files (CCDC 1908527) in CIF format are available free of charge via the Internet.

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