

Nanoscopic porous iridium/iridium dioxide superstructures (15 nm): Synthesis and thermal conversion by *in-situ* transmission electron microscopy

Kevin Pappert,¹⁺ Kateryna Loza,¹⁺ Meital Shviro,² Ulrich Hagemann,³ Marc Heggen,⁴ Rafal E. Dunin-Borkowski,⁴ Roland Schierholz,⁵ Takuya Maeda,⁶
Kenji Kaneko⁶ and Matthias Eppe^{1,*}

¹ Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (CeNIDE),
University of Duisburg-Essen, Universitätsstr. 5-7, 45117 Essen, Germany

² Institute of Energy and Climate Research, Electrochemical Process Engineering
(IEK-3), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

³ Interdisciplinary Center for Analytics on the Nanoscale (ICAN) and Center for
Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen,
Carl-Benz-Strasse 199, 47057 Duisburg, Germany

⁴ Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons,
Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

⁵ Institute of Energy and Climate Research, Fundamental Electrochemistry (IEK-
9), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

⁶ Department of Materials Science and Engineering, Kyushu University, 744,
Motooka, Nishi, Fukuoka, 819-0395, Japan

* Corresponding author, e-mail: matthias.eppe@uni-due.de

+ Both authors share first authorship

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Abstract

Porous particle superstructures of about 15 nm diameter that consist of ultrasmall nanoparticles of iridium and iridium dioxide were prepared by reduction of sodium hexachloridoiridate(+IV) with sodium citrate/sodium borohydride in water. The water-dispersible porous particles contained about 20 wt% poly(N-vinylpyrrolidone) (PVP) that was added for colloidal stabilization. High-resolution transmission electron microscopy confirmed the presence of both iridium and iridium dioxide primary particles (1-2 nm) in each porous superstructure. The internal porosity (about 58 vol%) was demonstrated by electron tomography. *In-situ* transmission electron microscopy up to 1000 °C under oxygen, nitrogen, argon/hydrogen (all at 1 bar), and vacuum showed that the porous particles underwent sintering and subsequent compaction upon heating, a process that started around 250 °C and was completed around 800 °C. Finally, well-crystalline iridium dioxide was obtained under all four environments. The catalytic activity of the as-prepared porous superstructures in electrochemical water splitting (oxygen evolution reaction; OER) was considerably reduced by heating due to sintering of the pores and loss of internal surface area.

Introduction

The platinum group metal iridium is one of the rarest non-radioactive metals on earth. Nevertheless, iridium nanoparticles are of high interest in current materials science due to their promising electrochemical properties, mainly as electrode for water-splitting,^[1] oxygen reduction in fuel cells,^[2] or as catalytic sensors,^[3] where a high specific surface area is always beneficial.

However, the synthesis of well-faceted nanostructures of iridium is difficult. This can be ascribed to the comparatively low energy barrier of a homogeneous nucleation compared to a heterogeneous nucleation in the case of iridium. Newly formed iridium atoms will tend to self-nucleate which results in small branched particles rather than well-defined faceted structures.^[4] Consequently, only small quasi-spherical or branched structures are obtained by various synthetic routes.^[5] In general, iridium nanoparticles can be synthesized by different reaction pathways. If the synthesis is performed in water, a strong reducing agent is required because the commonly used precursor complex hexachloridoiridate(+IV), $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$, has comparatively strong Ir-Cl bonds. Several approaches were described to reduce this iridium complex to iridium nanoparticles, *e.g.* by superhydride (lithium triethylborohydride)^[5a] or in imidazolium-based ionic liquids.^[5c] Iridium nanoparticles can also be synthesized by the polyol process where a polyalcohol serves both as solvent and as reducing agent.^[5b]

Porous nanoparticles are of particularly high interest in heterogeneous catalysis due to their high specific surface area which is associated with the inner surface.^[6] Han *et al.* reported a significantly improved oxygen reduction activity of hollow Pd-Pt alloy nanocrystals in comparison to core-shell nanoparticles and to a commercial Pt/C catalyst.^[7] Xia *et al.* found that gold-based nanocages are more efficient than nanoboxes and solid nanoparticles due to the availability of both internal and external active sites.^[8] However, an ideal catalyst not only needs a high activity but also a sufficient durability under operating conditions. Thus, it is important to evaluate the stability of particles subjected to thermal stress under a gaseous environment (*in-situ* or *operando*). Most iridium-based heterogeneous catalytic reactions occur at elevated temperature, *i.e.* between 60 and 400 °C.^[9] Here, we present a polyol-based synthesis of porous iridium/iridium dioxide nanoparticles and their in-depth structural analysis by X-ray diffraction, electron tomography, and X-ray photoelectron spectroscopy. Their thermal stability was

assessed by *in-situ* high-resolution transmission electron microscopy (HRTEM) under dynamic gaseous environment at atmospheric pressure.

Results and discussion

Porous nanoparticles with high specific surface area and high colloidal stability in water were obtained by reduction of $\text{Na}_2[\text{IrCl}_6]$ by sodium citrate/sodium borohydride in the presence of poly(N-vinylpyrrolidone) (PVP). Figure 1 shows representative HRTEM and fast Fourier transform (FFT) images. The mostly spherical particles had diameters between 10-50 nm and an average diameter around 15 nm. A higher magnification showed small primary crystallites with a size between 1 and 3 nm, forming a porous superstructure. The FFT image of such a porous superstructure showed the (020), (112), and (231) diffraction rings of iridium dioxide and the (200) diffraction ring of metallic iridium. This indicates that an intimate composite structure of metallic iridium and iridium dioxide constitutes the larger porous superstructures. The superstructures were stable under ultrasonication and well dispersible in water. The primary particles appear to be intergrown, but have different crystallographic orientations. Note that the particles were prepared in the presence of PVP which is still present on their external and also internal surface (see below). In the following, we will refer to the large spherical particles as "porous iridium superstructures" and to the constituting crystals as "primary crystals".

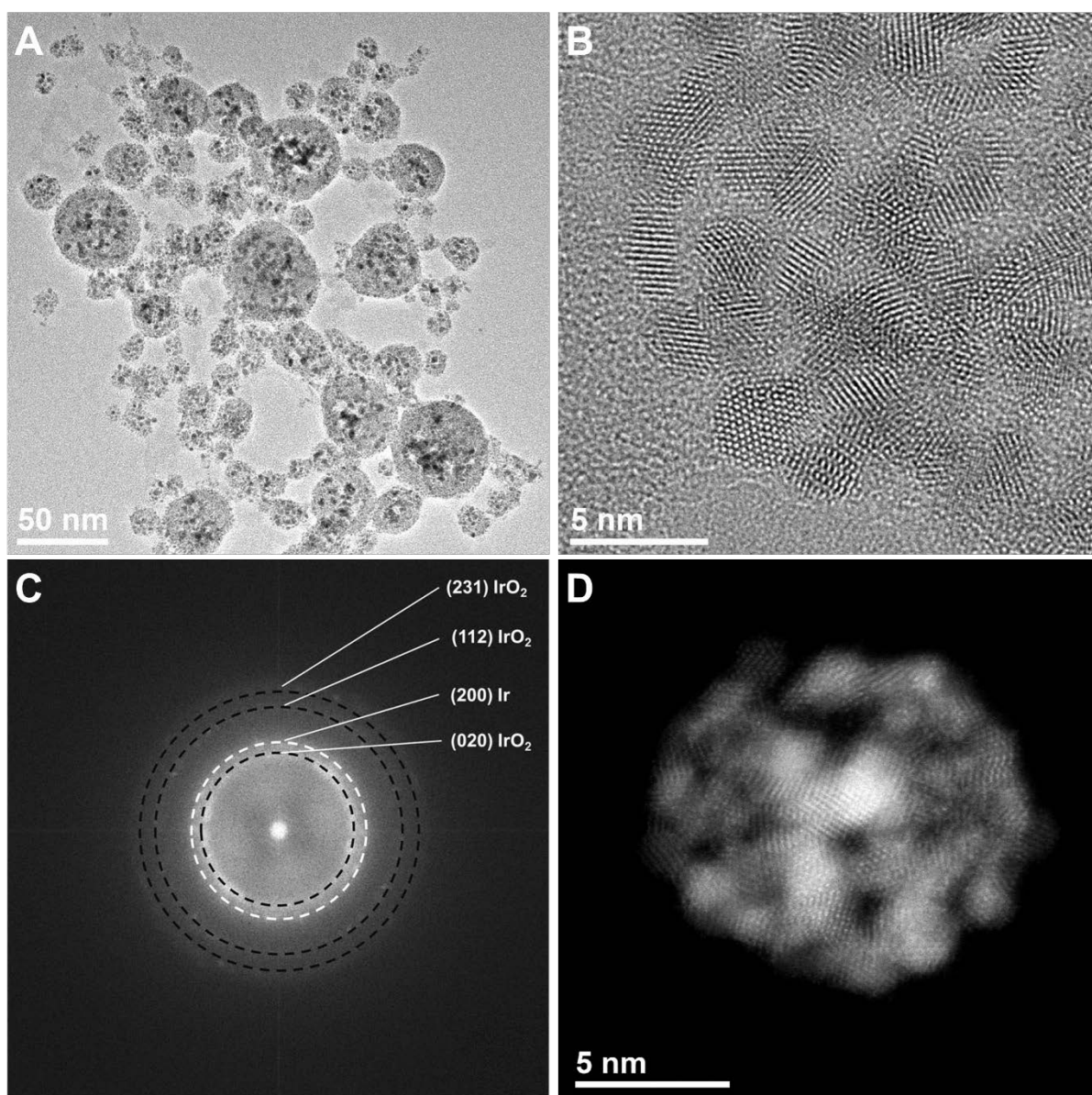


Figure 1: TEM overview, HRTEM, and corresponding FFT images of porous iridium superstructures (10 to 50 nm), consisting of small primary crystals (1 to 3 nm) (A-C); HAADF-STEM image of a single porous superstructure, showing both pores and crystalline domains of primary particles (D).

To visualize the three-dimensional organization of the primary nanoparticles inside the spherical superstructure, high-angle annular dark-field (HAADF) STEM tomography was performed. Isosurface rendering of a volumetric dataset showed internal voids within the superstructure, probably filled with organic material (PVP), and confirmed its porous nature (Figure 2). By setting the

rendering parameters to full opacity and low intensity (**A**), only the exterior of the surface contour was exposed. By decreasing the opacity and increasing the intensity of the surface contour (**B-F**), the internal contours of the primary particles become distinguishable. Volumetric integration led to a porosity of about 58 vol%.

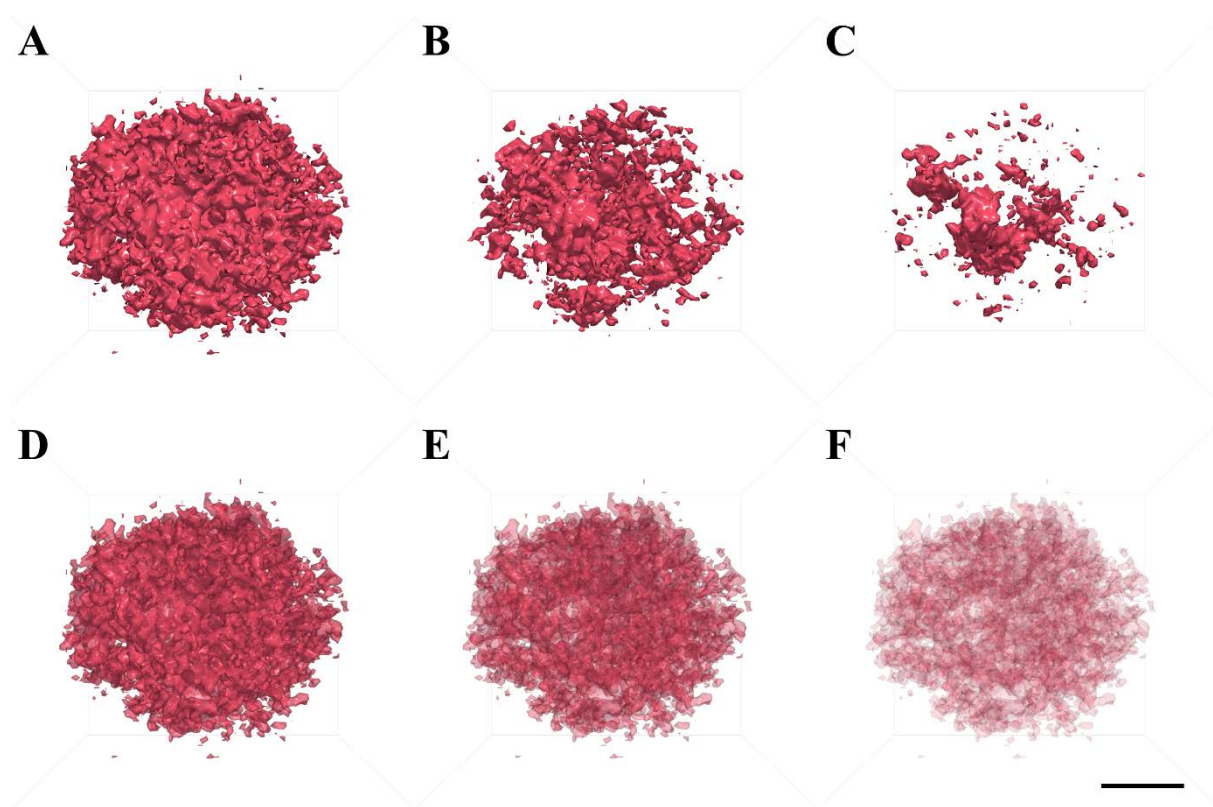


Figure 2: Visualization of a tomographic reconstruction of a porous iridium superstructure (diameter 20 nm). Opacity and intensity of the particle isosurface were varied to elucidate the interior of the nanoparticle: Intensity 2, opacity 1.0 (**A**), intensity 2.5, opacity 1.0 (**B**), intensity 3, opacity 1.0 (**C**), intensity 2, opacity 0.5 (**D**), intensity 2, opacity 0.25 (**E**), intensity 2, opacity 0.1 (**F**). Scale bar 5 nm.

X-ray powder diffraction together with Rietveld refinement gave the overall crystallographic properties of a sample containing more particles than investigated in the electron microscopic study (Figure 3). The refinement showed

a two-phase system with peaks of iridium (fcc lattice) as well as iridium dioxide (tetragonal rutile structure), confirming the FFT data from HRTEM. A strong peak broadening was caused by the small size of the primary crystals. Rietveld refinement gave average crystallite sizes of 1.0 ± 0.1 nm for iridium and 0.7 ± 0.1 nm for iridium dioxide, in good agreement with the HRTEM results. The measured lattice constant of metallic iridium of $a = 3.820\pm0.007$ Å is smaller than in bulk iridium metal (3.839 Å), an observation that is not uncommon for ultrasmall metal nanoparticles.^[10] The lattice constants for iridium dioxide could not be reliably determined due to the very broad diffraction peaks. However, a phase analysis by Rietveld refinement gave an approximate molar ratio of 28% iridium to 72% iridium dioxide (see Table 2).

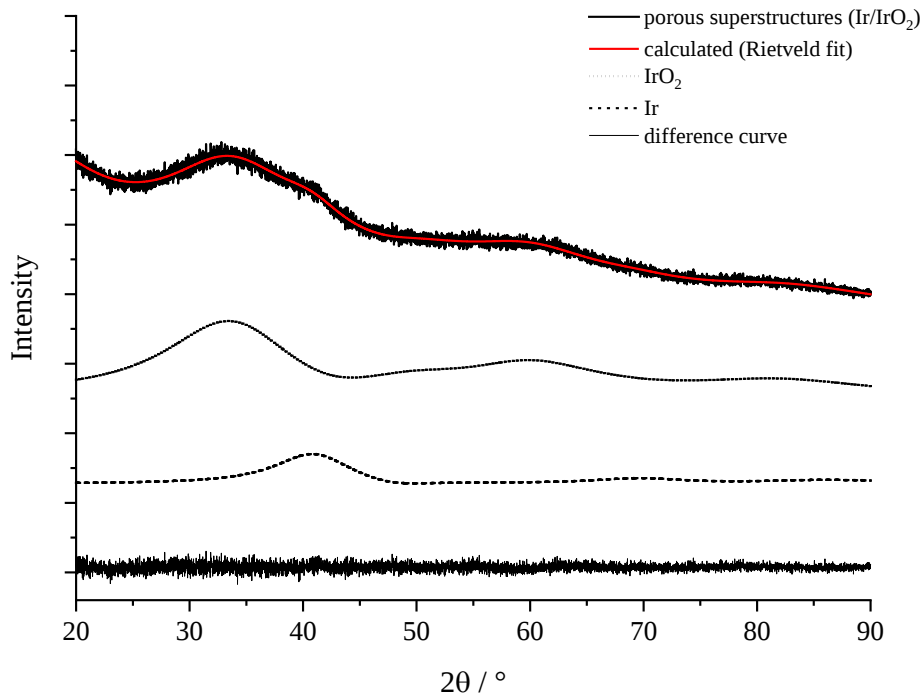


Figure 3: Rietveld refinement of the X-ray diffraction pattern of the porous iridium superstructures. Both iridium and iridium dioxide can be detected, but the peaks are very broad due to the small size of the primary crystals (one nm or less).

X-ray photoelectron spectroscopy (XPS) confirmed the presence of both metallic iridium and iridium dioxide. However, the presence of about 20 wt% PVP (see the thermogravimetric results below) strongly attenuated the iridium signals. The cumulative peak profile showed two maxima at 61.7 eV and 64.5 eV (Figure 4). The observed energies were modelled by peaks of the $4f_{5/2}$ and $4f_{7/2}$ binding energies of iridium(0) and iridium oxide(+IV) as well as traces of the 2s binding energy of sodium(+I). The atomic ratio of iridium(+IV) to Ir(0) was about 2:1, in good agreement with the XRD data.

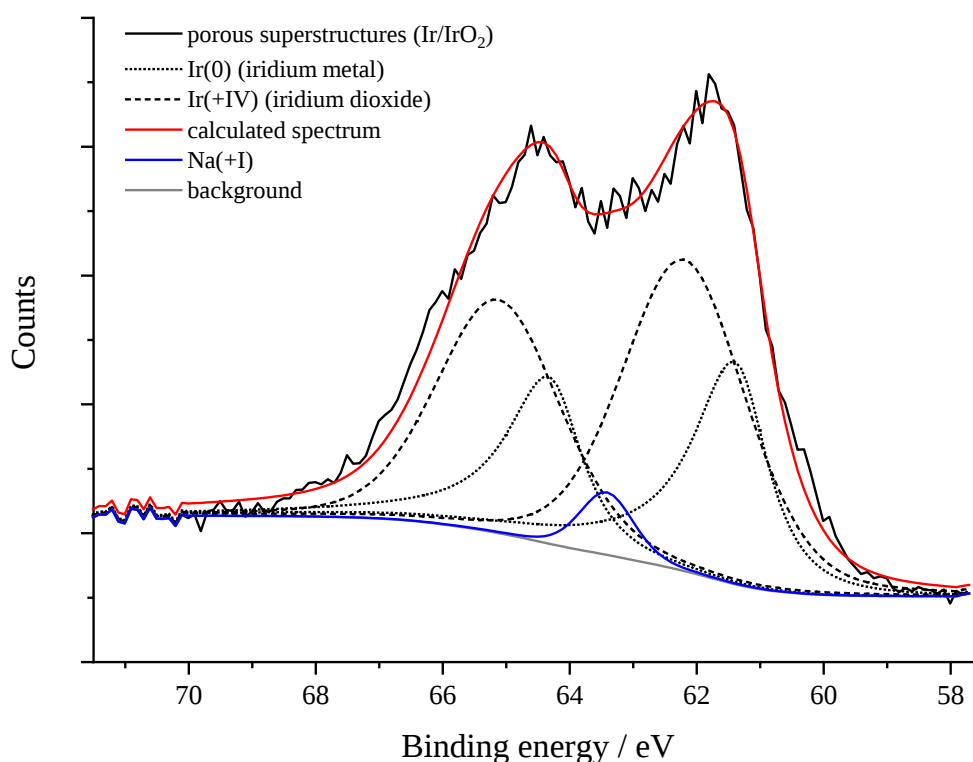


Figure 4: XPS data of the porous iridium superstructures. The spectrum shows 4f peaks of metallic iridium(0) and of iridium dioxide(+IV) as well traces of sodium(+I) (2s peaks).

The traces of sodium are probably due to remaining sodium ions from the reducing agents sodium citrate and sodium borohydride that were adsorbed to the

particles, probably inside the PVP. The fitted peaks positions and hence the binding energies of the $4f_{7/2}$ and $4f_{5/2}$ are slightly higher than the literature values (Table 1). The shift of the iridium binding energies is 0.3 eV whereas the shift for iridium oxide is 0.6 eV. Surface modifications or adsorption of organic molecules can lead to a shift of binding energies. The coating of the particles with PVP is a reasonable explanation for this deviation.

Table 1: XPS binding energies computed from the cumulative peaks and the corresponding peaks of iridium(0) and iridium(+IV) in comparison to literature data.

Sample	Peak	Binding energy / eV
Porous iridium superstructure	1	61.7
	2	64.5
Ir metal (measured)	$4f_{7/2}$	61.4
	$4f_{5/2}$	64.4
IrO ₂ (measured)	$4f_{7/2}$	62.2
	$4f_{5/2}$	65.2
Ir metal ^[11]	$4f_{7/2}$	60.8
	$4f_{5/2}$	63.8
IrO ₂ (anhydrous) ^[11]	$4f_{7/2}$	61.9
	$4f_{5/2}$	64.9
IrO ₂ (hydrated) ^[11]	$4f_{7/2}$	62.5
	$4f_{5/2}$	65.5

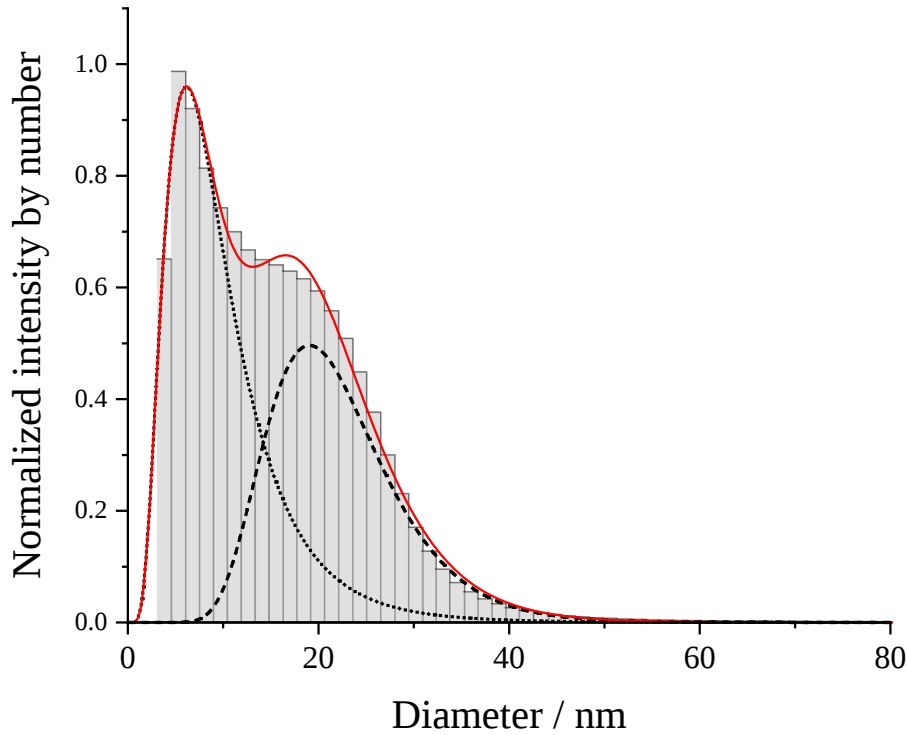


Figure 5: DCS measurement of water-dispersed porous iridium superstructures. The bimodal size distribution was fitted by two independent Gaussians.

The porous iridium superstructures were colloidally stable which is important for the deposition on a substrate like an electrode. Differential centrifugal sedimentation (DCS) of water-dispersed particles gave a broad size distribution that was fitted by two Gaussians with maxima at 8 ± 4 nm and 20 ± 6 nm (Figure 5). Note that there is a systematic underestimation of the particle diameter by DCS, especially for porous nanoparticles. In DCS, the bulk density of the base material is used to calculate the particle size. However, porous particles have a lower effective density (which is basically unknown), hence they sediment more slowly than compact particles of the same size and the particles appear smaller than they actually are.^[12]

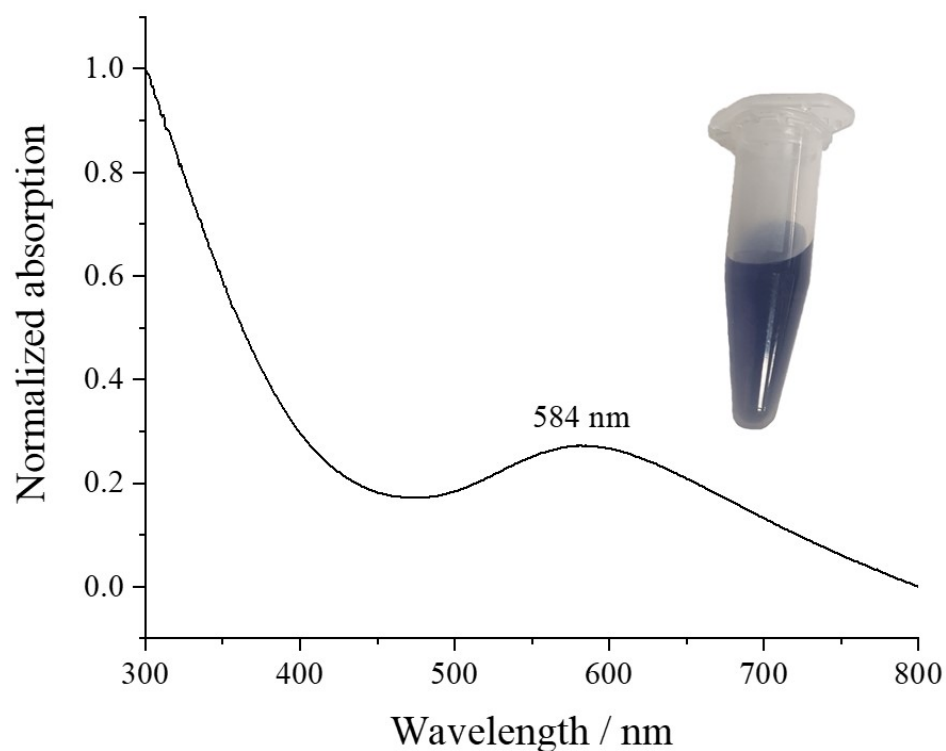


Figure 6: UV/Vis spectrum of water-dispersed porous iridium superstructures, together with an image of the water-dispersed particles that show a characteristic blue-grey color.

The UV/Vis spectrum of water-dispersed porous superstructures showed a broad absorption band at 584 nm and a steep increase in absorption below 400 nm (Figure 6). This kind of absorption is typical for IrO_2 nanoparticles in dispersion.^[13]

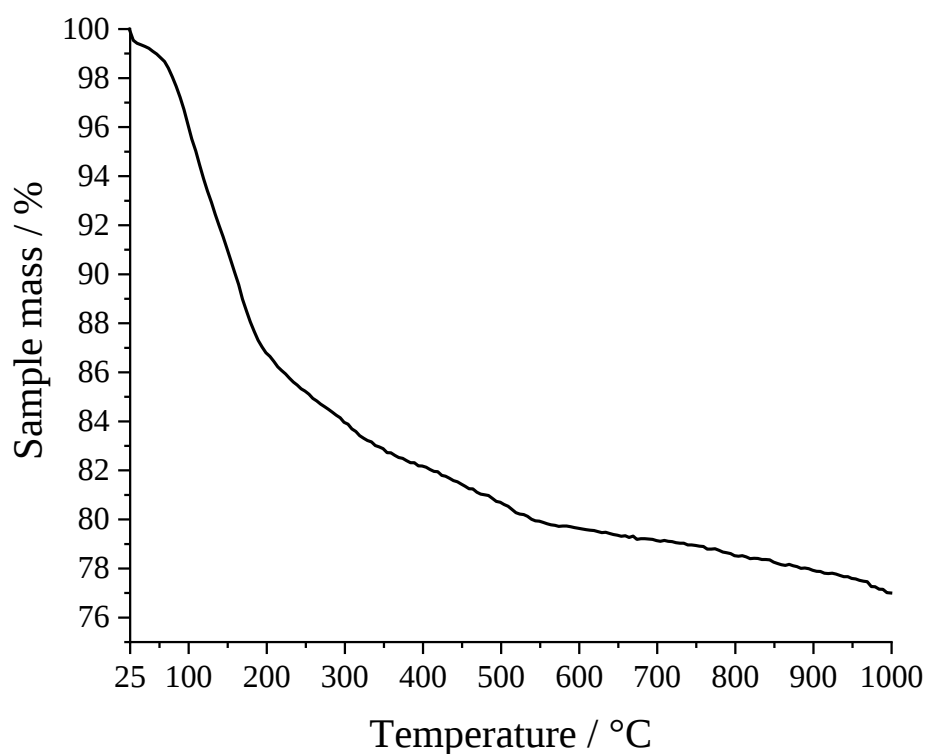


Figure 7: Thermogravimetric analysis of porous iridium superstructures under dynamic oxygen atmosphere. The mass loss is due to traces of water and an oxidation of PVP (about 20 wt%).

Thermogravimetry under oxygen showed the presence of about 20 wt% volatile/combustible material (*i.e.* PVP and traces of water) (Figure 7).

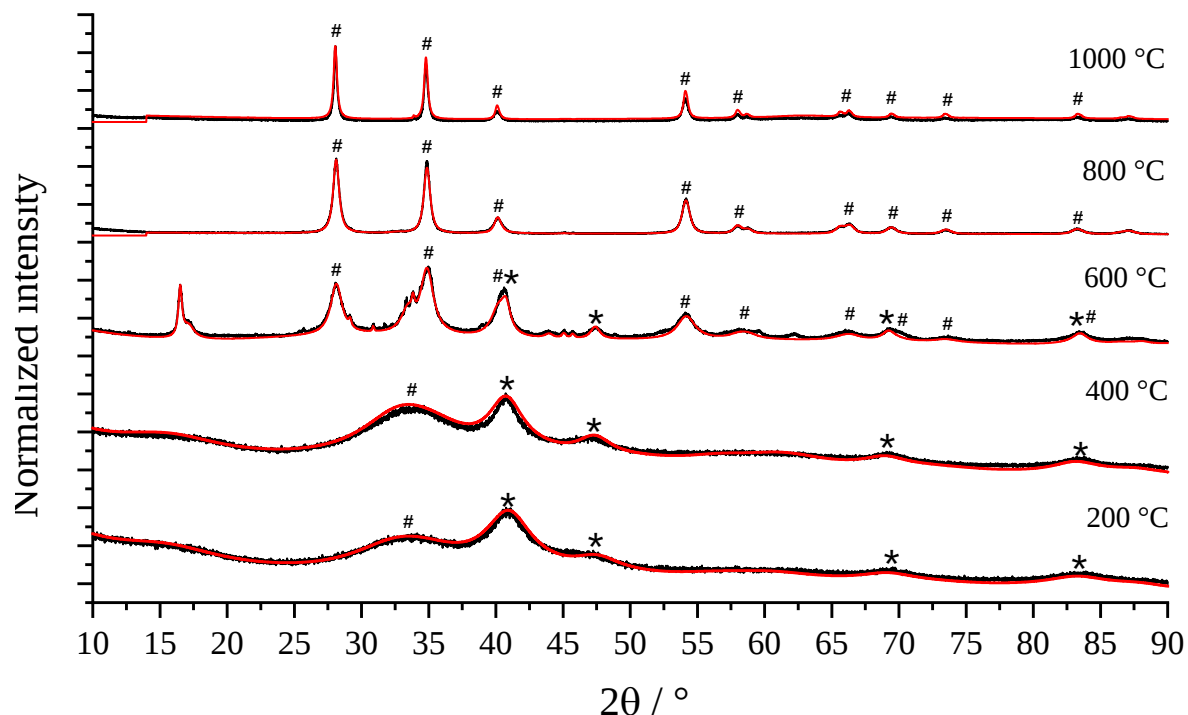


Figure 8: *Ex-situ* X-ray powder diffraction data of porous iridium superstructures after heating under oxygen to the indicated temperature. The particles showed an increase in crystallite size as indicated by the narrowing diffraction peaks. The oxidation of metallic iridium leads to IrO₂ after heating to 800 °C. Black: Original data; red: Rietveld refinement. Peaks of iridium are labelled with an asterisk (*) and peaks of IrO₂ are labelled with a hash (#).

To elucidate the crystallographic phase composition of the sample during the heating process, batches of the porous iridium superstructures were subjected to annealing that was carried out in the thermobalance for optimum temperature control. In five different measurements, they were heated to the final temperatures 200, 400, 600, 800, and 1000 °C, respectively, and then rapidly cooled down to room temperature (free cooling). Then, the samples were analyzed *ex-situ* by X-ray powder diffraction (Figure 8). The atmosphere was Ar/O₂ = 50:50 = vol:vol, *i.e.* oxidizing. A marked increase in crystallinity (narrower peaks) between 400 and 600 °C was observed that can be ascribed to sintering/coalescing of the primary iridium dioxide particles. The diffraction peaks of iridium eventually

vanished, either due to oxidation (less likely) or due to the absence of sintering, leading to their disappearance among the increased iridium peaks. The derived crystallographic parameters are summarized in Table 2.

Table 2: Calculated lattice parameters, crystallite sizes and compositions after heating the porous iridium superstructures to different temperatures. All data were obtained by Rietveld refinement. CS crystallite size.

Temperature	$a(\text{Ir})$ / Å	CS(Ir) / nm	$a(\text{IrO}_2)$ / Å	$c(\text{IrO}_2)$ / Å	CS(IrO_2) / nm	$x(\text{Ir})$ / at%	$x(\text{IrO}_2)$ / at%
initial sample	3.820(7)	1.0(1)	-	-	0.7(1)	28	72
200 °C (O_2)	3.8296(6)	2.9(1)	-	-	1.1(1)	35	65
400 °C (O_2)	3.8375(6)	3.4(1)	-	-	1.1(1)	24	76
600 °C (O_2)	3.8421(3)	10.6(2)	4.4906(5)	3.1509(8)	10.6(3)	20	80
800 °C (O_2)	-	-	4.4964(1)	3.1416(1)	22.5(3)	0	100
1000 °C (O_2)	-	-	4.4999(2)	3.1510(2)	63.9(13)	0	100
bulk phases (lit.)	3.8394 ^[14]	-	4.5051 ^[15]	3.1586 ^[15]	-	-	-

The structural details of the thermal transition of the porous iridium superstructures were further elucidated by *in-situ* transmission electron microscopy. Since oxidizing or reducing conditions can change the surface properties of a nanoparticle that may be used as catalyst, it is important to verify the actual impact of the real operating conditions on the structure of metallic nanoparticles. As iridium/iridium dioxide have potential applications in heterogeneous catalysis and the porosity appears especially promising, we have focused on the susceptibility of the porous iridium superstructures to sintering. A nanoreactor setup permitted the observation of the particle evolution in real time under precise temperature and gas control at atomic resolution. We followed the morphological and crystallographic changes in dynamic chemical environments (oxygen, nitrogen, argon/4% hydrogen, all at 1 bar, respectively, and in vacuum) up to 1000 °C.

Bright-field *in-situ* TEM and *ex-situ* HAADF-STEM images demonstrated the structural evolution of the porous iridium superstructures under different environmental conditions (Figures 9 to 12). In all cases, primary particle growth was observed between 250 and 500 °C. At 750 °C, all porous iridium superstructures had transformed into solid (non-porous) objects with some volume contraction. This process was completed at about 800 to 850 °C (see Supplementary Information). At 1000 °C, the particles were compact and consisted of only few large domains. The initial porous superstructure consisting of small primary crystals had vanished. This structural evolution is thermodynamically favorable due to the decrease of the free surface energy. Neither disintegration nor generation of smaller particles were observed. It is reasonable to assume that at 1000 °C, the organic component PVP has completely burned under oxygen or underwent pyrolysis under vacuum, inert gas or reducing conditions.

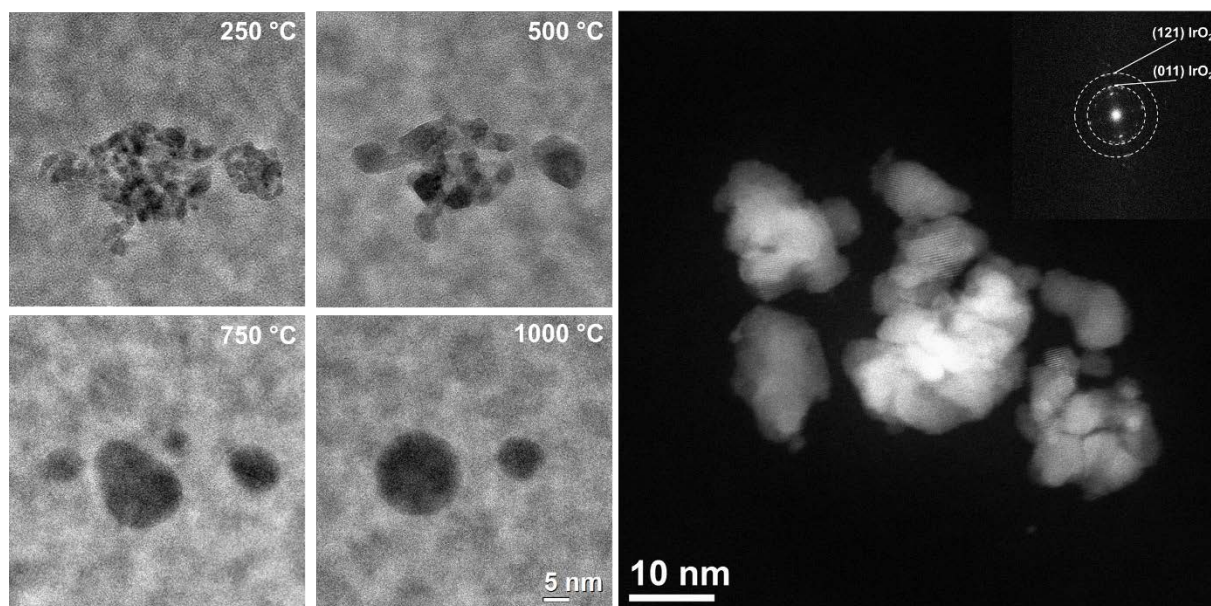


Figure 9: *In-situ* TEM heating under oxygen flow at 1 bar (250, 500, 750 and 1000 °C), and *ex-situ* HAADF-STEM image at 1000 °C and corresponding FFT inset (a time-resolved *in-situ* TEM sequence is available in the Supplementary Information). At 1000 °C, the sample consists of sintered iridium dioxide.

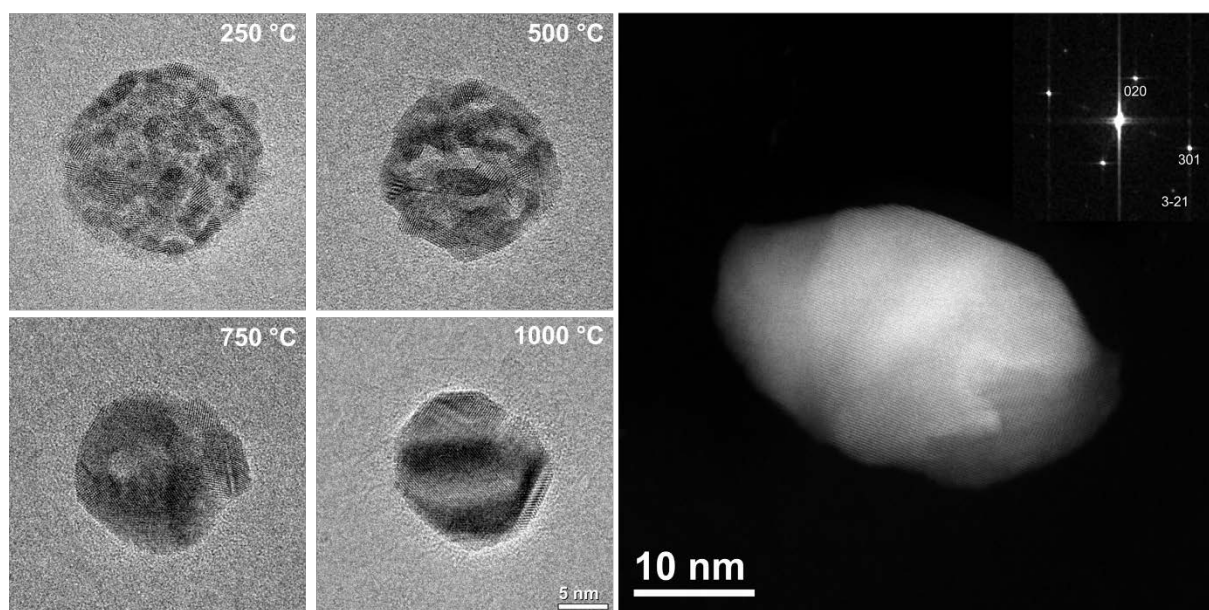


Figure 10: *In-situ* TEM heating in vacuum (250, 500, 750 and 1000 °C), and *ex-situ* HAADF-STEM image after 1000 °C and corresponding FFT inset (a time-resolved *in-situ* TEM sequence is available in the Supplementary Information). At 1000 °C, the sample consists of sintered iridium dioxide.

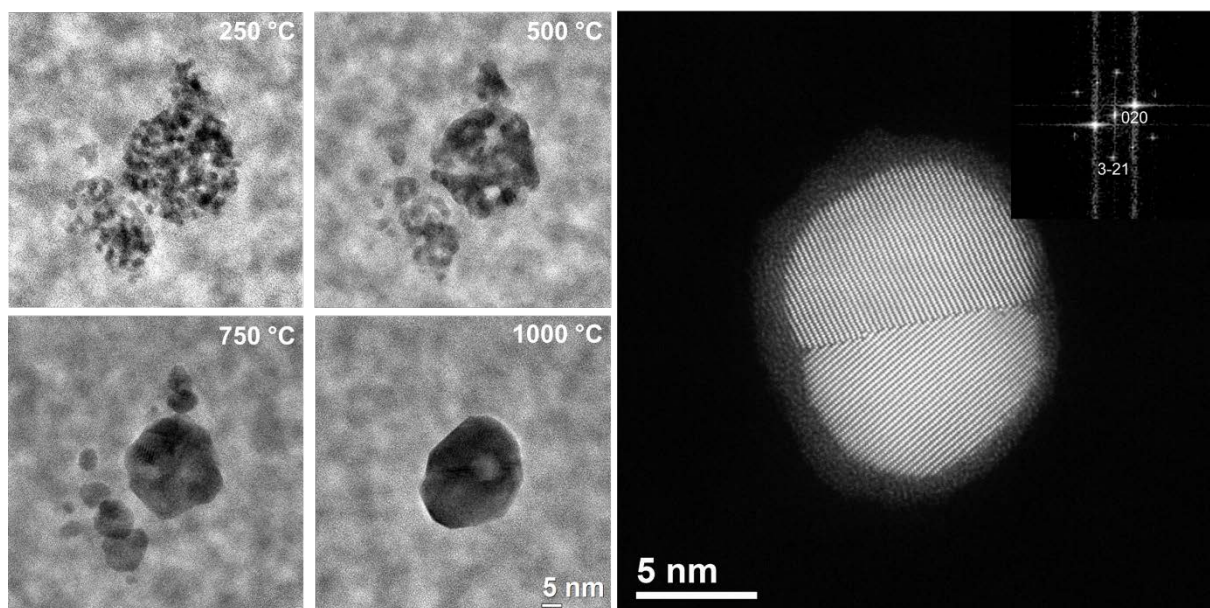


Figure 11: *In-situ* TEM heating under nitrogen flow at 1 bar (250, 500, 750 and 1000 °C), and *ex-situ* HAADF-STEM image after 1000 °C and corresponding FFT inset (a time-resolved *in-situ* TEM sequence is available in the Supplementary Information). At 1000 °C, the sample consists of sintered iridium dioxide.

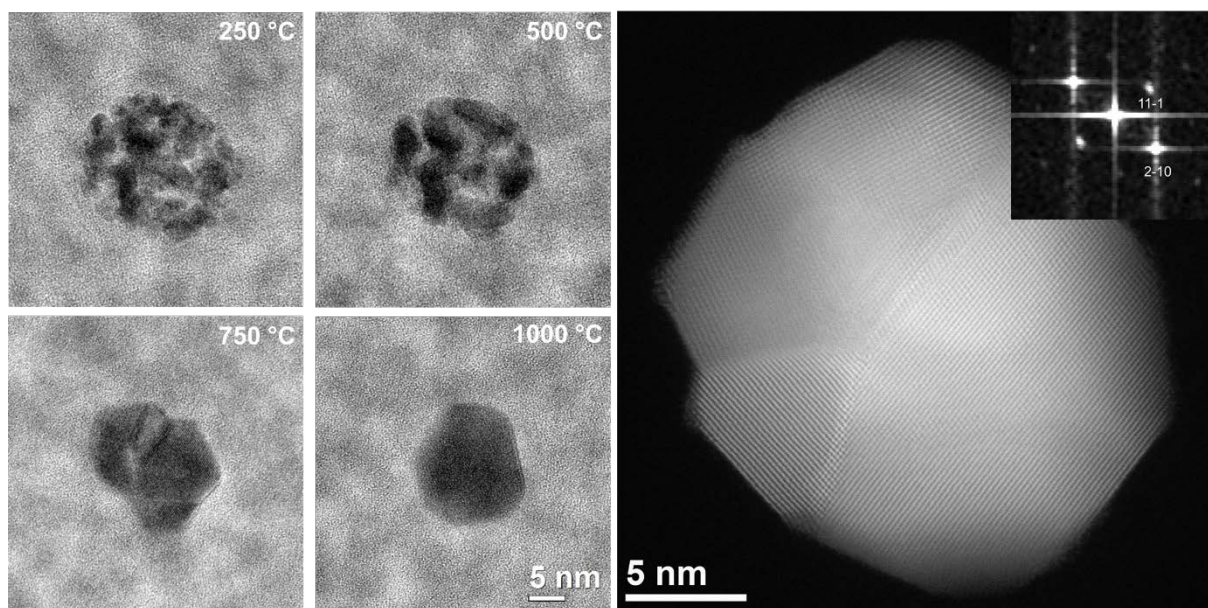


Figure 12: *In-situ* TEM heating under argon/4% hydrogen flow at 1 bar (250, 500, 750 and 1000 °C), and *ex-situ* HAADF-STEM image after 1000 °C and corresponding FFT inset (a time-resolved *in-situ* TEM sequence is available in the Supplementary Information). At 1000 °C, the sample consists of sintered iridium dioxide.

The particles had a round and compact shape after heating to 1000 °C. FFT analysis confirmed the presence of crystalline IrO_2 in all cases, hence the initially present iridium dioxide did not decompose and was not reduced under these conditions, but simply recrystallized. Note that the potential formation of iridium nitride can be excluded in nitrogen atmosphere under these conditions.^[16] It should also be noted that IrO_2 is oxidized in air to volatile IrO_3 only above 1200 °C, *i.e.* well above the highest temperature in our experimental setup.^[17]

So far, only few investigations on the thermal behavior of porous nanostructures were performed by *in-situ* HRTEM. Wang *et al.* reported a gas-induced change in the surface facets of palladium nanoparticles,^[18] including a surface modification by the "inert gas" nitrogen.^[18b] Edge truncation during reduction and oxidation of palladium nanocubes were detected by *in-situ* TEM.^[18a] With a similar setup, Gao *et al.* showed a significant change of the surface contact area

between metal and support.^[19] Xia *et al.* reported the thermal stability of faceted Pt-based nanocages under vacuum.^[20] Recently published results of Altantzis *et al.* showed a quantitative refaceting of Pt nanoparticles in oxygen-hydrogen cycles.^[21] In a reducing environment a more faceted surface was observed. The presence of H₂ and O₂ molecules can result in the promotion or the destabilization of certain facets because the surface energy is affected by gas molecule adsorption.^[21-22]

Besides metallic iridium, biphasic systems of iridium and iridium dioxide have a high potential in heterogeneous catalysis. Investigations of iridium/iridium dioxide composites by Xu *et al.* showed a higher electrocatalytic activity compared to the single-phase materials Ir and IrO₂.^[13a] In general, the mixed oxidation state of iridium shows higher activities in the oxygen evolution reaction (OER) than iridium metal and rutile-type IrO₂ alone.^[23] These biphasic materials have several applications like stimulating electrodes,^[24] electrodes in water splitting,^[1a, 2a] or catalytic sensor systems.^[3a] Iridium oxide fulfills the conditions for an operation in a corrosive environment. Therefore, it is an important oxygen evolution reaction catalyst because of its high activity and stability.^[25]

We tested the porous iridium superstructures in two different states as catalysts for the oxygen evolution reaction (OER): As-prepared and argon-treated (1000 °C), *i.e.* sintered. TEM images of the samples used in catalysis showed randomly oriented porous nanoparticles (as-prepared) and dense particles with well-developed facets (1000 °C) (Figure 13). By STEM-EDX we confirmed that the two samples heated to 1000 °C consisted mainly of iridium dioxide (Figure 14). It was not possible to record meaningful EDX spectra for the as-prepared sample due to the presence of PVP (high amounts of carbon, oxygen, and nitrogen). This led to an overall oxygen signal that could not be assigned to oxygen from iridium dioxide.

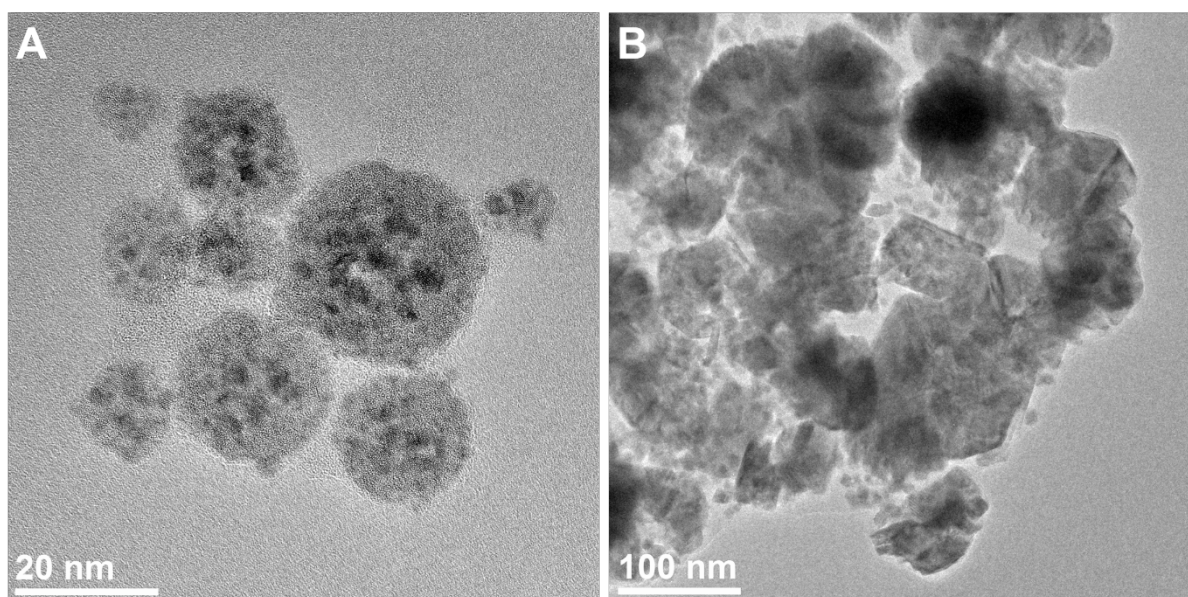


Figure 13: HRTEM images of porous iridium superstructures before OER tests. The samples were as-prepared (**A**) and after heating to 1000 °C in argon (**B**). Sample **A** consists of a mixture of iridium and iridium dioxide, sample **B** consists mainly of iridium dioxide.

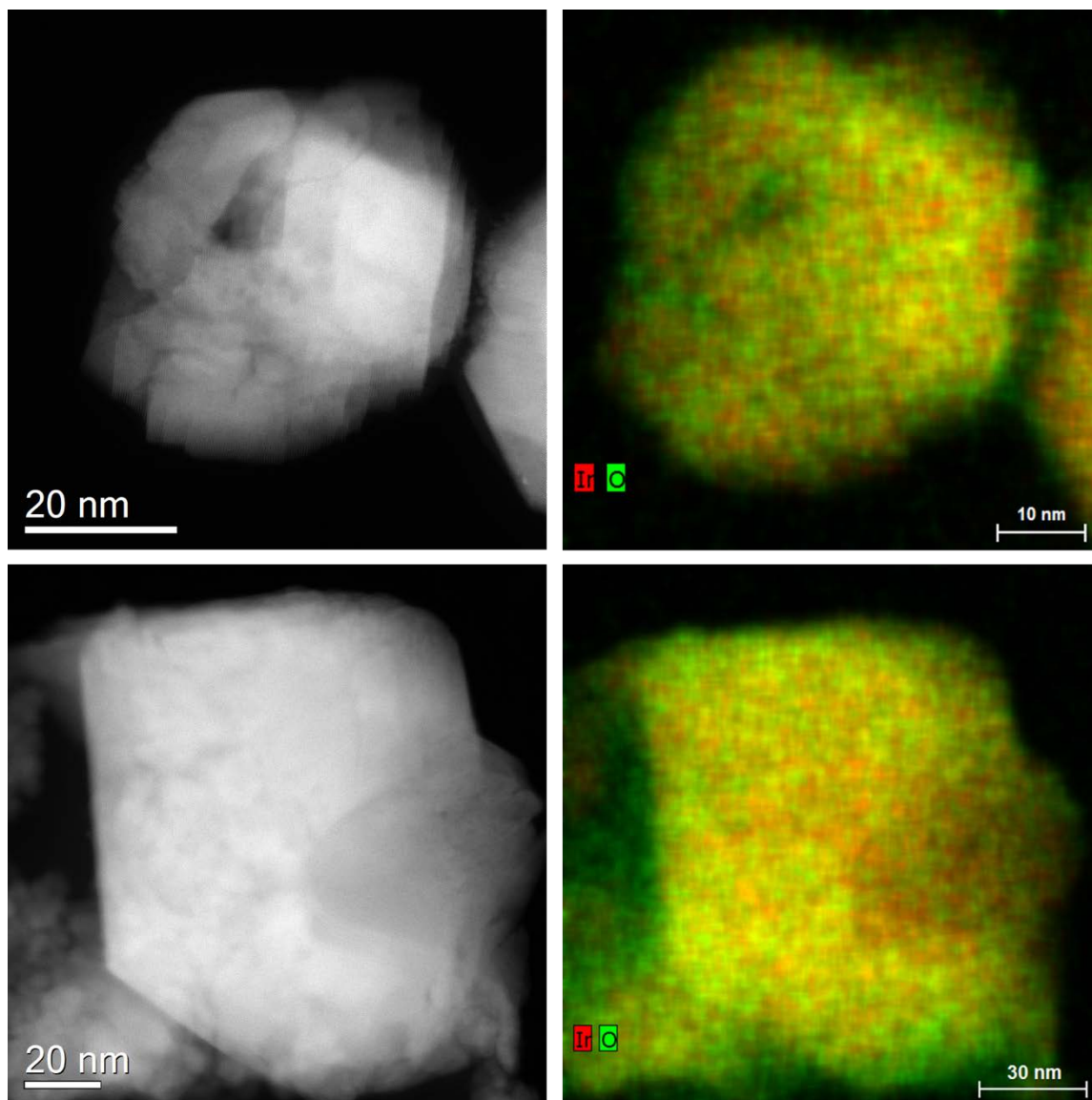


Figure 14: High-angle annular dark field STEM image (**left**) and EDX map (**right**) of porous iridium superstructures before OER tests. The as-prepared samples were heated up to 1000 °C in argon (**top**), and (for comparison) in oxygen (**bottom**). The samples consist mainly of iridium dioxide as shown by the high content of oxygen.

Voltammetry showed an increase of the current density for the as-prepared porous superstructures. The previously annealed catalyst (1000 °C) showed a much lower performance, probably due to the increase in crystallite size, and particle sintering/compaction. The higher activity of the porous iridium superstructures can thus be explained by the specific surface area (mainly internal surface areas)

that is available for the OER reaction. This is especially remarkable because the as-prepared porous structures still contain PVP that is probably filling the nanopores.

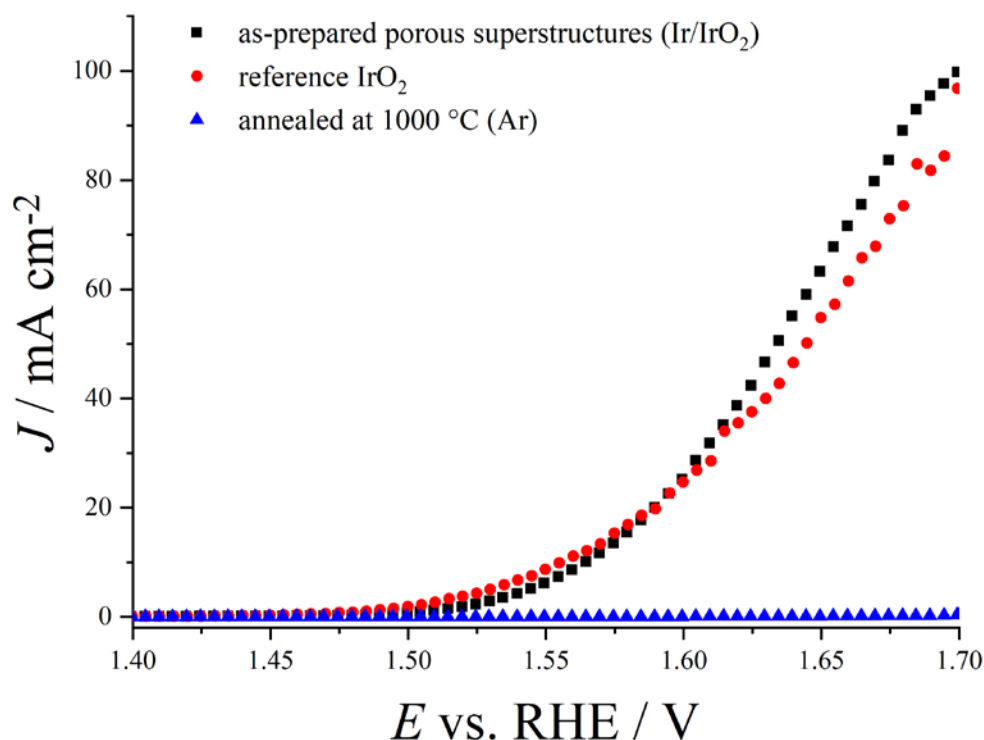


Figure 15: Electrocatalytic oxygen evolution reaction (OER) activities of porous Ir/IrO₂ porous superstructures as-prepared and after heat treatment at 1000 °C in argon. As control, commercially available iridium dioxide was used.

Conclusions

The thermal stability of porous iridium superstructures, consisting of small nanoparticles of metallic iridium and of iridium dioxide, was systematically assessed in different gases (vacuum, oxygen, nitrogen, argon/4% hydrogen) at ambient pressure (1 atm). The porous architecture was stable up to 250 °C for all tested gas mixtures. At higher temperature, the particles underwent compacting and further faceting which was completed at about 750 °C. Under oxygen,

vacuum, nitrogen, and argon/hydrogen, nanocrystalline iridium dioxide was formed at 1000 °C. The as-prepared porous superstructures were catalytically active in the oxygen evolution reaction, but this property was lost after calcination in argon (1000 °C). We conclude that the high inner porosity of the as-prepared superstructure, associated with a high specific surface area, led to the pronounced catalytic activity.

Materials and Methods

Chemicals

For the nanoparticle syntheses, we used poly(N-vinyl pyrrolidone) (PVP K 30, Povidon 30; Fluka, $M = 40,000 \text{ g mol}^{-1}$), sodium borohydride (Sigma-Aldrich, $\geq 96 \%$, p.a.), and trisodium citrate (Acros, anhydrous 98 %). Sodium hexachloridoiridate(+IV), $\text{Na}_2[\text{Ir}^{\text{IV}}\text{Cl}_6]$, was obtained from Sigma-Aldrich (p.a.). Ultrapure water (Purelab ultra instrument from ELGA) was used in all experiments. Before use, all glassware was cleaned with boiling *aqua regia*.

Synthesis of nanoparticles

In a typical synthesis, 0.02 mmol sodium hexachloridoiridate(+IV), $\text{Na}_2[\text{IrCl}_6]$, were dissolved in 6.35 mL water (metal content 0.719 g L^{-1} , in total 4.57 mg Ir) that was neutralized with 20 μL 1 M sodium hydroxide solution. The solution was then diluted to 250 mL with water and heated to 100 °C under reflux. Then, 35 mg trisodium citrate were added as solid. Then, a solution of 150 mg sodium borohydride dissolved in 10 mL cold water (4 °C) was rapidly added. After 1 min, a solution of 120 mg poly-(N-vinylpyrrolidone) (PVP, $M_w = 40,000 \text{ g mol}^{-1}$) in 10 mL water was added. The mixture was stirred for 35 minutes under reflux and turned slightly brown. After this period, another 150 mg sodium borohydride dissolved in 10 mL cold water (4 °C) were rapidly added. Heating under reflux was continued for another 55 min. Thereafter, the mixture was rapidly quenched to room temperature with an ice bath. The dispersion was stirred for another 48 h

at room temperature. The volume of the resulting blue-black dispersion was reduced by vacuum application to 50 mL. The particles were isolated by fourfold ultracentrifugation at 29,400 g (20,000 rpm; 30 min centrifugation time; Sorvall WX Ultra Series instrument), followed by redispersion in water under ultrasonication.

Characterization

Analytical disc centrifugation (differential centrifugal sedimentation; DCS) was performed with a CPS Instruments DC 24000 disc centrifuge (24,000 rpm). Two sucrose solutions (8 wt% and 24 wt%) formed a density gradient which was capped with 0.5 mL dodecane as a stabilizing agent. The calibration standard was a poly(vinyl chloride) (PVC) latex in water with a particle size of 483 nm provided by CPS Instruments. The calibration was carried out prior to each run. A sample volume of 100 μ L was used. Ultraviolet-visible spectroscopy (UV-Vis) was performed with a Varian Cary 300 instrument from 200 to 800 nm with background correction. Suprasil[®] cuvettes with a sample volume of 750 μ L were used. Freeze-drying (lyophilization) was done with a Christ Alpha 2-4 LSC instrument. Thermogravimetric analyses and annealing experiments were performed with a Netzsch TG 449 F3 Jupiter instrument. All measurements were carried out in dynamic gas atmosphere (25 mL min⁻¹) or in vacuum with a heating rate of 5 K min⁻¹ in open alumina crucibles. X-ray photoelectron spectrometry (XPS) was performed with a Physical Electronics PHI 5000 Versaprobe II using aluminum radiation at an energy of 1486.8 eV. A freeze-dried sample was prepared and put onto the sample holder. X-ray powder diffraction (XRPD) was performed on a Bruker D8 Advance diffractometer with Cu K α radiation (1.54184 Å) in Bragg-Brentano geometry. A freeze-dried sample was applied to a single-crystal silicon sample holder. Rietveld refinement was performed with the program Topas 5.0 (Bruker). Lorentzian peak profiles were used. Sample displacement error, zero-point error, and instrumental aberrations were all

corrected by the addition of LaB₆ (NIST; National Institute of Standards and Technology; SRM 660b; $a(\text{LaB}_6) = 4.15689 \text{ \AA}$) as internal standard.^[26]

The electrochemical characterization in the oxygen evolution reaction (OER) was performed in an RDE half-cell containing 0.5 M sulfuric acid and equipped with a polished polycrystalline gold working electrode, a platinum counter electrode, and a reversible hydrogen electrode (RHE) connected to the electrochemical cell. The working electrode rotation was controlled with a modulated speed rotator (Pine Instruments), and the electrochemical measurements were recorded with a VMP3 potentiostat (Bio-Logic Science Instruments). The iridium dioxide reference was obtained from Alfa Aesar (IrO₂ powder, 99%) with a primary particle size (from TEM) of $6.5 \pm 5.3 \text{ nm}$.

HAADF-STEM tomography was performed with a JEOL JEM-ARM200F Cs-corrected S/TEM. For an unobstructed field of view for tomographic data collection a high tilt angle holder was used. The tilt range was from $+66^\circ$ to -80° with increments of 2° . The sample hydrocarbon contamination was mitigated by a beam shower.^[27] Data alignment by cross-correlation, reconstruction with the weighted backprojection algorithm and visualization were performed with the *tomviz* software package.^[28]

Scanning transmission electron microscopy (STEM) was performed with an FEI Titan microscope, equipped with a Cs-probe corrector (CEOS Company) and a high-angle annular dark field (HAADF) detector. Z-contrast conditions were achieved at a probe semi-angle of 25 mrad and an inner collection angle of the detector of 70 mrad.^[29] The FFT analysis was performed with *CrysTBox* (Crystallographic Toolbox).^[30] The elemental mapping by energy-dispersive X-ray spectroscopy (EDX) was conducted on a probe-corrected FEI Titan 80-200 "ChemiSTEM" electron microscope equipped with four symmetrical SDD detectors.^[29]

For *in-situ* electron microscopy, a closed gas cell TEM holder (Climate, DENSSolutions Company) was used. This nanoreactor consisted of two chips with

silicon nitride electron-transparent windows. The bottom chip was equipped with a Pt heater, gas inlet and outlet. For *in-situ* heating experiments in vacuum, a TEM heating holder (Wildfire, DENSsolutions Company) and the nano-chip with carbon support were used. All *in-situ* TEM investigations were performed with an aberration-corrected FEI Titan transmission electron microscope equipped with a Cs-probe corrector (CEOS Company), operated at 300 kV.^[31] For the *in-situ* TEM studies, about 12-15 superstructure particles were in the area of interest, but for clarity, only one is shown. The displayed particles are representative for the whole set of particles in the area of interest.

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