

Electronic Supplementary Information

Ozone: an effective tool for simultaneous activation and dealloying of Pt based nanocatalyst

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HGS synthesis: The details about the synthesis of the Hollow Graphitic Spheres (HGS) can be found in our previous publication¹. Briefly, the carbon support is produced via a nanocasting route using a silica template made of a non-porous core and a mesoporous shell (SiO₂@mSiO₂). The template is impregnated with a Fe(NO₃)₃ solution, acting as the graphitization catalyst, and with divinylbenzene as the carbon source; after the carbonization both iron and the silica are leached out to obtain a hollow-shell carbon nanostructure.

PtNi@HGS synthesis: An impregnation-reduction-annealing route was applied to embed the metals inside the pores of the HGS. The metal precursors were simultaneously introduced in the pores of the carbon support through an ultrasound assisted incipient wetness impregnation. Typically, to prepare 125 mg of 20 wt% PtNi@HGS catalyst (Pt:Ni 1:1 atomic/atomic), two aqueous solutions containing the metal precursors (1.08 M of H₂PtCl₆ · xH₂O, Pt wt% = 39% ± 1% and 2.77 M NiCl₂ · 6H₂O) are mixed according to the appropriate metal ratio. The total volume of the resulting solution is thereafter adjusted with deionized ultrapure water to reach the total pore volume (TPV) of the carbon material. For 100 mg of HGS (TPV = 2.0 cm³/g), 90.7 µL of Pt solution, 35.6 µL of Ni solution and 78.8 µL of H₂O are used. The Pt-Ni solution is subsequently used to impregnate the HGS, and the wet powder is ultra-sonicated for 30 min to ensure an optimal mixing of the metals inside the carbon pores. The solvent is removed, holding the wet material under Ar for 30 min at 120 °C (heating rate = 3 °C/min). The reduction is performed with a H₂/Ar gas mixture (15 vol% H₂) at 200 °C for 1.5 h. After this step the hydrogen flow is switched off and the sample is cooled down naturally to room temperature. The alloying treatment is carried out at 850 °C for 7 hours (heating rate = 5 °C/min) under Ar atmosphere.

Half Cell Electrochemical Measurements: All electrochemical measurements were performed at room temperature in a three-compartment, three electrode Teflon cell. The catalyst ink consisted of 6.36 mg of catalyst powder dispersed in 5 ml of ultrapure water; a 20 µL droplet of the suspension was then deposited onto a Teflon tip containing the carbon disk of 0.196 cm² geometric surface area. The catalyst loadings employed for activity and stability investigations were respectively, 10 and 20 µg_{Pt} cm⁻². The Teflon tip was then connected to a rotating disk electrode (Radiometer Analytical, France), which served as the working electrode. Both the counter electrode, a graphite rod, and the reference electrode, a saturated Ag/AgCl electrode (Metrohm), were housed in separate compartments. The reference electrode compartment was further separated from the main compartment by a Nafion membrane in order to avoid chloride contamination². A Gamry reference 600 potentiostat was employed and controlled in combination with the rotator and the gas system with an in-house-developed LabVIEW software³. The electrolyte employed throughout the study was 0.1 M HClO₄, which was prepared with ultrapure water (18 MΩ, Millipore) and concentrated HClO₄ (Merck, Suprapur). The Ohmic drop was compensated accordingly by positive feedback⁴. All potentials are given with respect to the reversible hydrogen electrode (RHE) potential, which was determined for each experiment individually. All activities were extracted from CVs recorded in O₂-saturated electrolyte at 1600 rpm and at 0.9 V_{RHE} with 50 mV/s scan rate. The stability test consisted in 10800 degradation cycles between 0.4 and 1.0 V_{RHE} with 1 V s⁻¹. The degradation tests were performed without rotation. In order to monitor the electrochemical surface area (ECSA) evolution during the degradation CO-stripping was used to measure the real active area after 0, 360, 1080, 2160, 3600, 5400, 7200 and 10800 potential cycles. In order to simulate the effect of ozone on the surface potential of a catalyst in suspension, we performed a parallel electrochemical experiment with the catalyst

immobilized on a conducting electrode. The measurement of the Open Circuit Potential (OCP) was carried out in a standard three compartment electrochemical cell; utilizing a potentiostat in galvanostatic mode. The working electrode was a glassy carbon tip with a catalyst film deposited on top, just as in standard thin-film rotating disc studies. By fixing the current to 0 A it was, thus, possible to follow the potential evolution during purging with different gases, which reflects the surface potential of the catalyst if it would be dispersed in solution under the same conditions. Note, that the same behavior of the OCP was observed also in comparable experiments on a polycrystalline Pt disc as WE.

Ozone treatment: Both acid leaching treatments (HCl and HClO₄) and all the ozone experiments were applied to the catalyst (PtNi@HGS) after the alloying treatment (850°C, 7h under Ar). For all the acid leaching treatments, 30mg of catalyst was dispersed in 60 mL of acid solution (0.5 M, ultrapure water) and the suspension was continuously stirred at 25°C for about 12h. At the end of treatment, the powder was abundantly rinsed with deionized water, collected via filtration and dried at 75°C in air. For the ozone experiments, a 250 ml round bottom flask was used to disperse 100 mg of catalyst in 75mL of 0.5 M HClO₄ (ultrapure water). After 2-3 min of ultrasonication, the flask was sealed with a rubber septum and ozone was bubbled in the suspension through the use of a Teflon tube inserted through the septum. A similar tube was used to vent the flask thus avoiding overpressures. During the treatment the suspension was continuously stirred. Ozone was provided by an ozone generator (Argentox, Ozone Generator G1) equipped with an O₂ gas bottle. The applied voltage and the gas flow rate were set at 3.7 V and 0.5 L/min, respectively. The resulting measured O₃ concentration was 48 g O₃/Nm³, which corresponds to 40 L O₃/h ($\rho_{O_3} = 2.14 \text{ g/cm}^3$). Ozone was bubbled for different times: 15, 30, 60 and 90 min. At the end of the treatment, the suspension was immediately filtered and abundantly rinsed with deionized water to ensure the complete rapid removal of O₃ dissolved in the electrolyte. Finally, the powder was dried in air at 75°C. In order to reduce the Pt-O layer formed on the NPs surface, the ozone treatment was followed by a gas-phase reduction step in H₂. This treatment (50°C, 1.5 h) was carried out (with the dry powder) in a tubular furnace using a H₂/Ar (15%) gas mixture. Following the reductive step in gas phase, the catalyst was further washed in an acidic medium. The procedure selected for this purpose includes an overnight acid washing in 0.1M HClO₄ at room temperature.

ICP-MS quantification: In order to measure the progress of dealloying, the investigation included a quantitative analysis by means Inductively Coupled Plasma- Mass Spectrometer (ICP-MS, NexION 300X, Perkin Elmer). For the samples after O₃-H₂ activation protocol 1 mg of the catalyst was weighted by means of Microbalance and then dissolved in 6 ml of boiling aqua regia (the solution was prepared from Merck, Suprapur acids). The resulting solution was then diluted and fed to the ICP-MS in steady-state detection mode. For the samples after acid washing, the followed procedure was slightly different as 20 μL from a 20 $\mu\text{g/cm}^2$ catalyst suspension were pipetted and then dissolved in 2 ml aqua regia. To control the reproducibility of the measurement the test was repeated three times for the as-received materials and for every ozone treatment time.

TEM characterization: For TEM investigations the catalyst suspension was diluted by a factor of 1:10 with ultrapure water. About 7 μL of the diluted solution was deposited on a TEM gold finder grid (NH7) coated with a Lacey carbon film and then dried in air. High resolution STEM was performed with a JEOL 2200FS operated at a 200kV acceleration voltage.

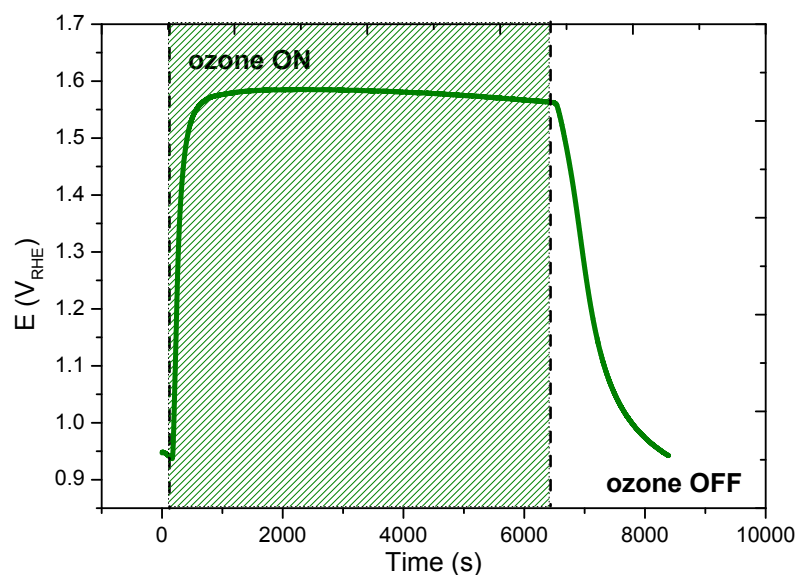


Figure S1: OCP evolution versus time under O_3 exposure. The measurement was carried out following the potential in galvanostatic mode in the RDE three compartment cell described in the above experimental part, with 150 mL 0.1M $HClO_4$ as electrolyte and a catalyst film deposited onto a glassy-carbon disk as working electrode. Once introduced ozone, the OCP rapidly reaches values around 1.6 V_{RHE} and it keeps constant as long as the ozone flow is maintained. Once the ozonizer is switched off, the OCP gradually decreases to the values expected for an O_2 -saturated solution. The concentration of the ozone flow was measured at the outlet of the ozonizer and was fixed at 50 g/Nm^3 throughout all the experiments.

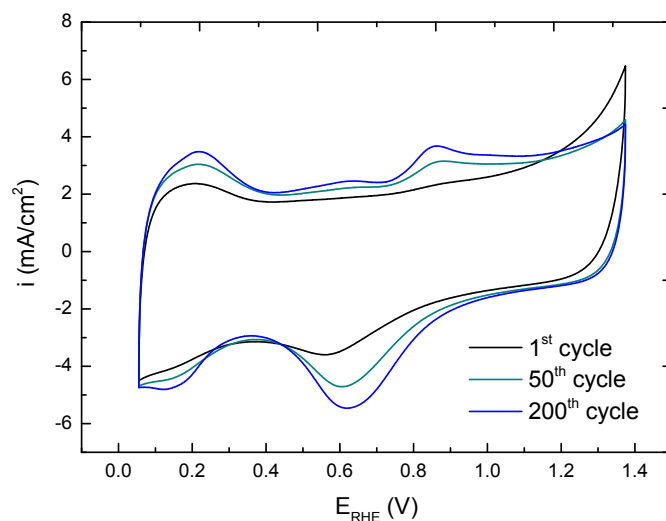


Figure S2: Evolution of the PtNi@HGS Pt features during electrochemical activation. The EC activation protocol included 200 cycles between 0.05 and 1.4 V_{RHE} at 0.2 V/s scan rate.

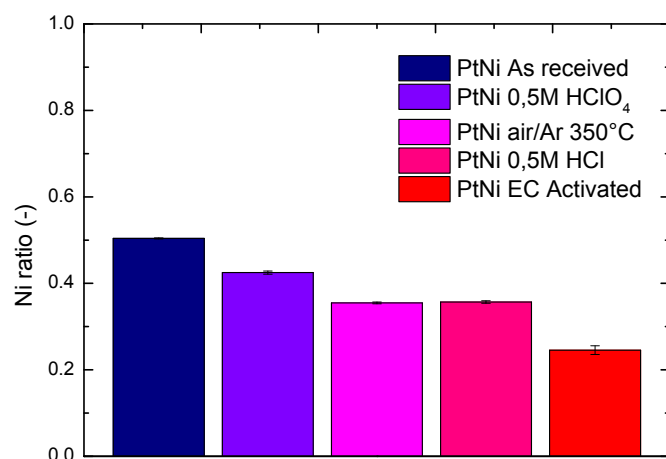


Fig.S3: Ni ratio after the different post-synthesis treatments. None of the reported conventional post-synthesis treatments were able to dealloy the PtNi@HGS as efficiently as electrochemical cycling, as shown by the far higher measured Ni molar ratio. It is reasonable to assume that simple acid washing and mild annealing in air (followed by acid washing in 0.5M perchloric acid) are not sufficient to remove the protective NiC layer, producing in the best case a partially activated catalyst.

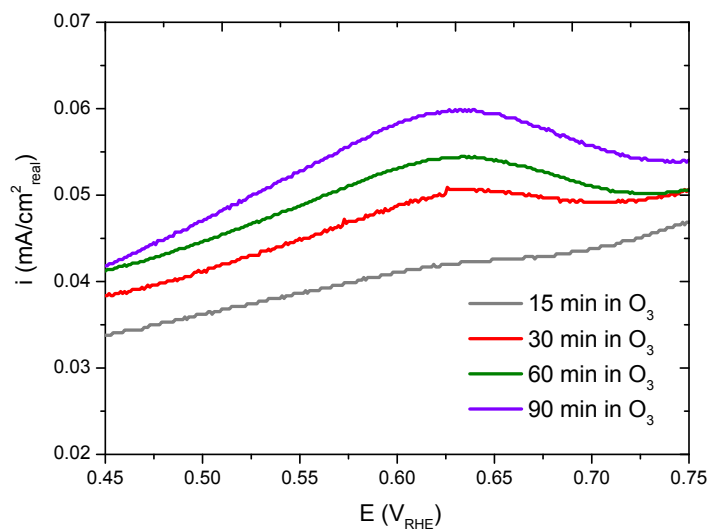


Fig.S4: Growth of the hydroquinone-quinone peak with ozonization time. The CVs were taken at 0.05 V/s at room temperature in 0.1M HClO₄ and the currents were normalized to the active surface area measured by CO-stripping.

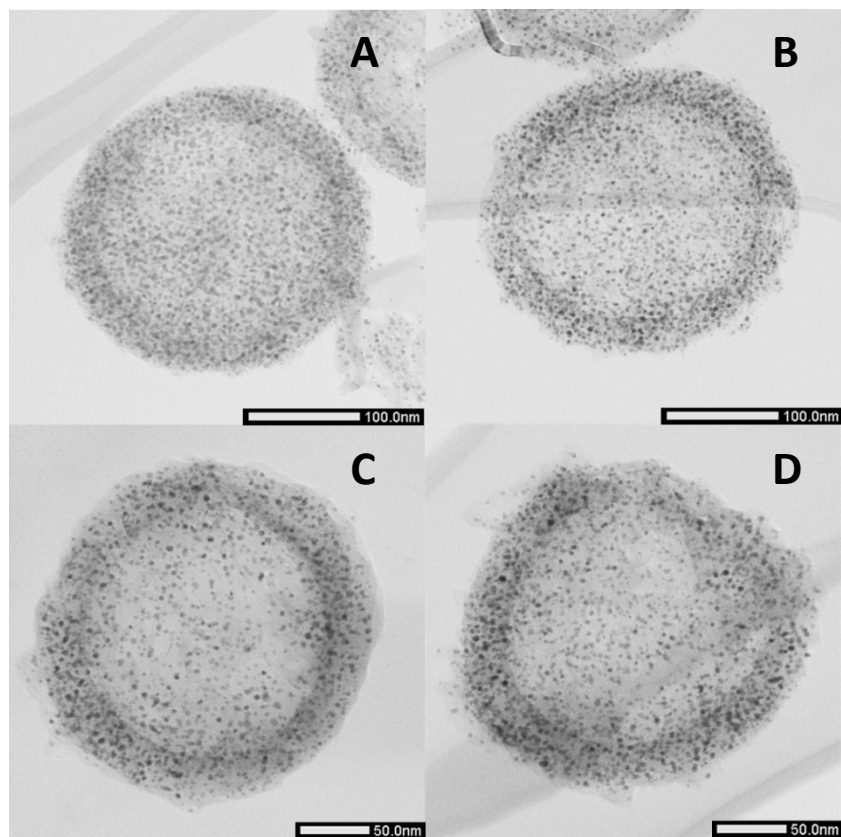


Fig.S5: High magnification BF-STEM images of PtNi@HGS for the different ozone treatment times, 15 (A), 30 (B), 60 (C) and 90 (D) minutes.

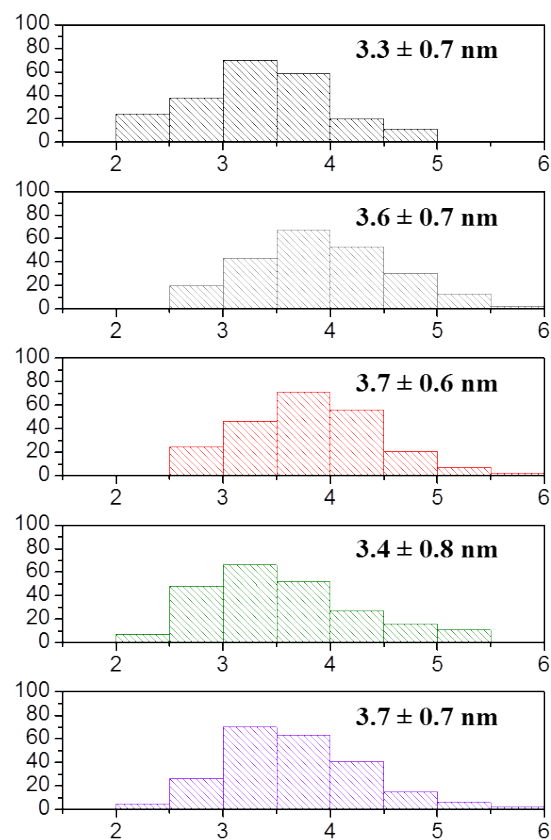


Fig.S6: Particle Size Distribution and average diameter for the as-received (black) and ozone treated for 15 min (grey), 30 min (red), 60 min (green), 90 min (violet) PtNi@HGS.

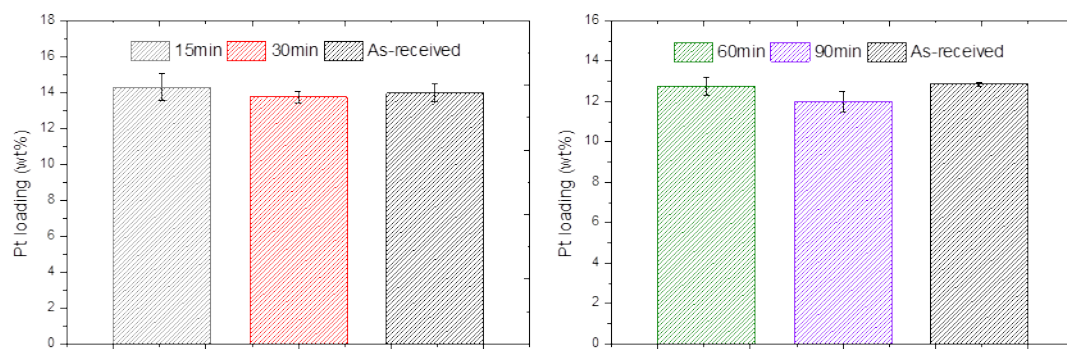


Fig.S7: Platinum loading measured by ICP-MS for the different ozone treatment times. The samples treated for 60 and 90 minutes belong to a different batch of PtNi@HGS than the materials treated for 15 and 30 minutes. Thus, as the measured Pt loading for the as-received materials slightly differs between the two batches, the different O₃ treatment times are displayed in two separate groups.

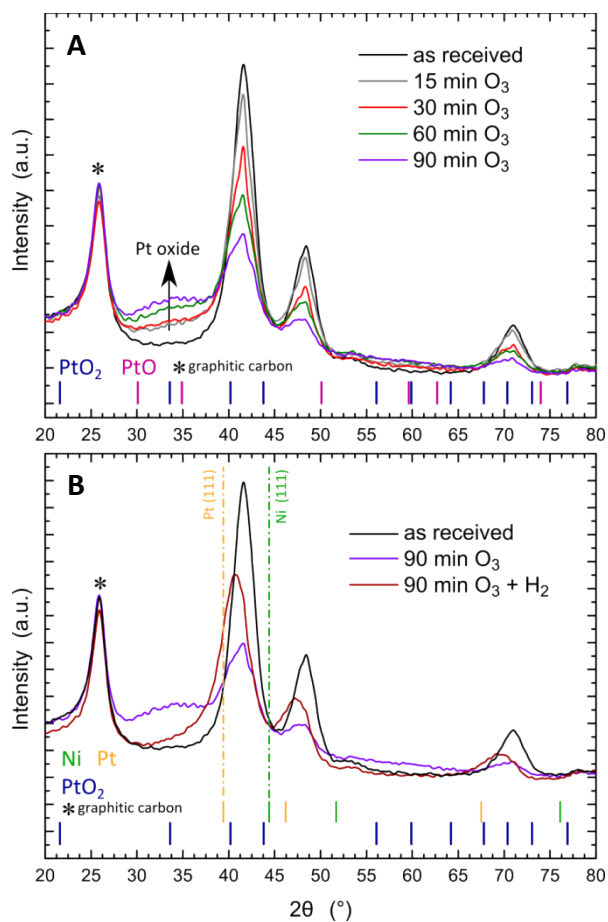


Fig.S8: (A) XRD patterns measured after different ozone treatment time. (B) Comparison between the XRD patterns recorded after the synthesis (as received), after 90 min of O₃ treatment and after the subsequent H₂ gas-phase reduction.

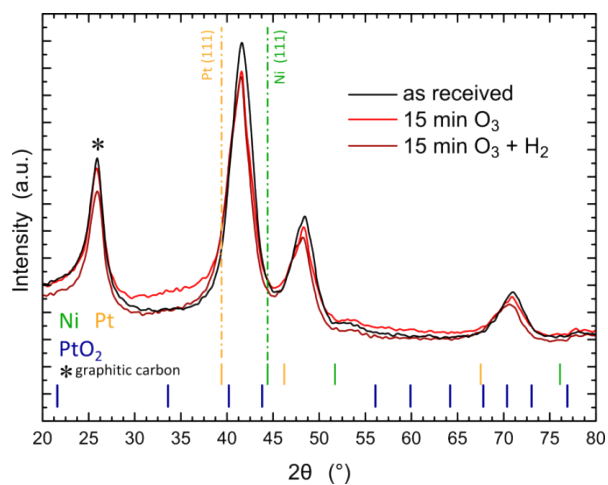


Fig.S9: Comparison between the XRD patterns recorded after the synthesis (as received), after 15 min of O₃ treatment and after the subsequent H₂ gas-phase reduction.

References

1. C. Galeano, J. C. Meier, V. Peinecke, H. Bongard, I. Katsounaros, A. A. Topalov, A. Lu, K. J. J. Mayrhofer and F. Schüth, *Journal of the American Chemical Society*, **134**, 20457-20465.
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4. D. van der Vliet, D. S. Strmcnik, C. Wang, V. R. Stamenkovic, N. M. Markovic and M. T. M. Koper, *Journal of Electroanalytical Chemistry*, 2010, **647**, 29-34.