Efficient, low cost synthesis of sodium platinum bronze $Na_xPt_3O_4$.

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Supporting information

I-Synthesis

The platinum oxide (PtO_y) thin films were synthesized by magnetron sputtering in pure oxygen at a pressure of 4 Pa. The platinum target with a chemical composition better than 99.9 at% was sputtered with a medium frequency supply (Advanced Energy Pinnacle+) by applying an average discharge current of 1 A at a frequency of 350 kHz. The target to substrate distance was fixed to 5 cm. The films deposited on soda lime glass (SLG) and silicon wafer pieces were subsequently annealed in air for 2 hours at different temperatures.

II-Chemical analysis

Energy dispersive X-ray spectroscopy (EDX) measurements were performed at different positions between the film/substrate interface and the film surface within the JEOL JEM-2100F transmission electron microscope . Secondary ion mass spectroscopy Na/Pt depth profiles were collected by using a cesium ion gun. The profile measured on the sample annealed in air at 570°C is shown in Figure 1. As the EDX measurements stated a Na/Pt atomic ratio of 1.5 at the film substrate interface (600 nm from the film surface), this SIMS profile represents the evolution of the Na/Pt atomic ratio.

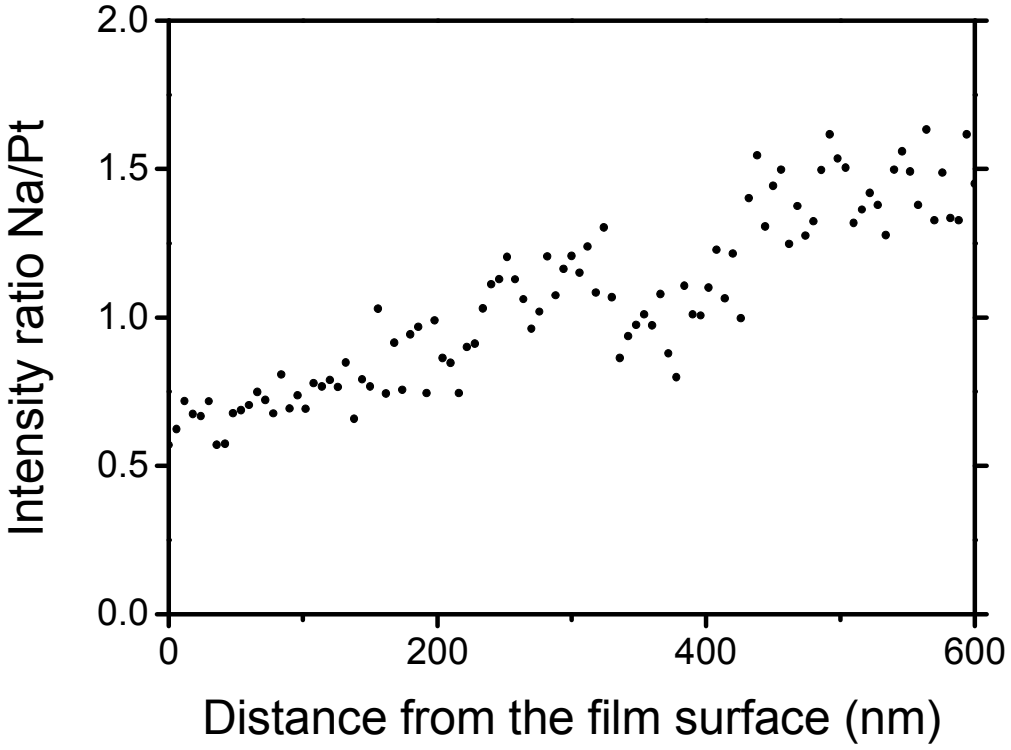

Figure 1: SIMS depth profile of the Na/Pt intensity ratio for the sample annealed at 570°C.

The electronic stucture of the films at the Pt-L_3 edge was probed by X-ray absorption near edge structure (XANES) using the synchrotron radiation of the KMC2 beamline of the BESSY 2 synchrotron at the Helmoltz Zentrum Berlin. The bulk-sensitive fluorescence yield (FLY) procedure was used under quasi-normal excitation and take off at 45° from the sample surface. The oxydation state of platinum has been calculated by taking into account the contribution of a single 5 d empty state of metallic platinum to the area of the X-ray absorption resonance. This contribution has been extracted from the X-ray absorption signal of the Platinum foil. Details of the procedure can be found in [1] for platinum compounds and similarly in [2] for gold compounds.

III-Structural analysis

The X-ray diffraction signal was collected with λ-k_{α}Co=0.179 nm using an INEL diffractometer with an incident angle of 4°. Figure 2 presents the diffractogramm of the sample annealed in air at 570°C after background removal and the corresponding Rietveld refinement. The structural parameters of the $NaPt_3O_4$ phase used for the calculation are listed in Table 1 and caption.

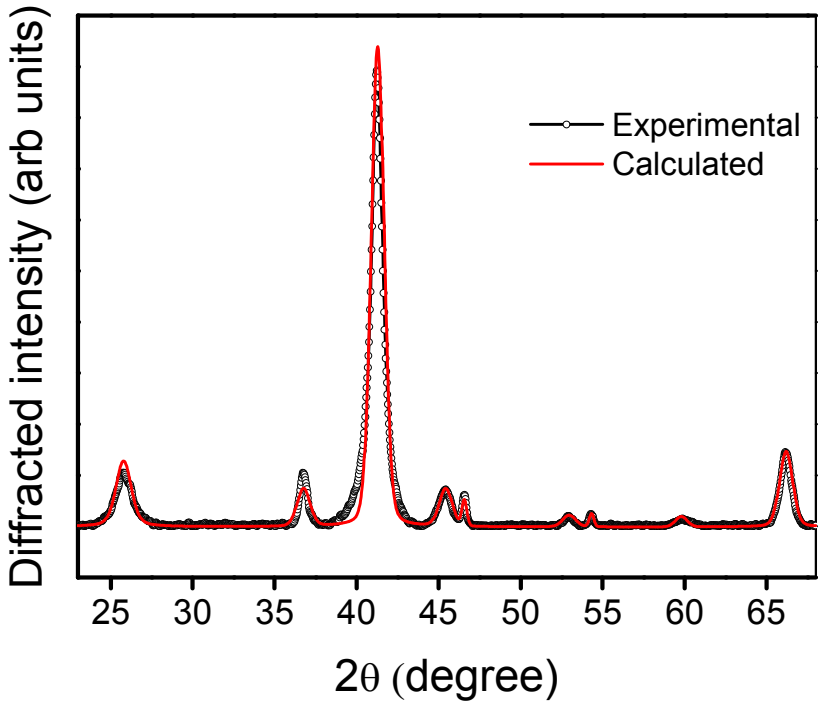

Figure 2: X-ray diffractogramm and corresponding Rietveld refinement of the sample annealed at 570°C

Atom	Wickoff	x	y	z	Occ
Na	2a	0.0	0.0	0.0	1
Pt	6c	0.25	0.0	0.50	1
O	8e	0.25	0.25	0.25	1

Table 1: Structural parameters for the $NaPt_3O_4$ phase at 25°C: Pm3n (No. 223) with a=5.674 Å.

Raman analyses were performed on the film annealed at 570°C using a Horiba LabRAM HR confocal microscope equiped with a 532 nm laser beam. The laser power was limited to approx. 2 mW. Figure 3 shows a spectrum characteristic for the analysed sample. It presents two main contributions peaking at 186 and 683 cm^{-1}, which are representative of the vibrational signature of the $Na_xPt_3O_4$ structure [3].

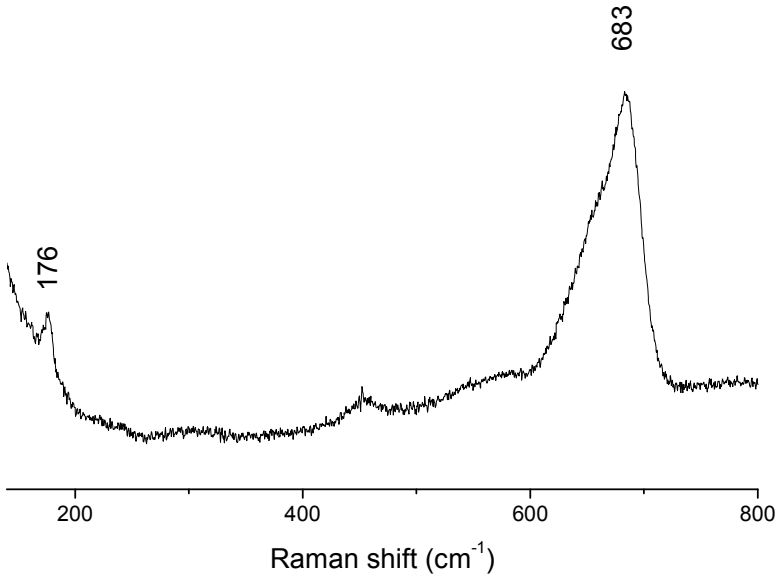

Figure 3: Raman spectrum collected on the sample annealed at 570°C.

High resolution transmission electron microscopy (HRTEM) was performed with a JEOL JEM-2100F. Samples were prepared in a focused ion beam (FIB)/scanning electron microscope (SEM) dual beam system (FEI Strata DB235) by using the "in-situ" lift-out technique. Thinning of the foil was done with an acceleration voltage of 30 kV at the beginning and with 5 kV at the end to minimize any possible preparation artifact.

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[2] Hlil, E.K.; Baudoing-Savois, R.; Moraweck, B.; Renouprez, A.J. *J. Phys. Chem.* **1996,** *100,* 3102.

[3] Graham, G.W.; Weber, W.H.; McBride, J.R.; Peters, C.R. *J. Raman Spectrosc.* **1991,** *22,* 1.