SYNTHESIS OF BIMETALLIC NANOPARTICLES WITH TAILORED SIZE AND COMPOSITION

A novel recipe based on atomic layer deposition has been established for the fully-tailored synthesis of supported Pt-In bimetallic nanoparticles. The combination of *in situ* X-ray diffraction and *in situ* grazing-incidence small-angle X-ray scattering measurements revealed the mechanism of bimetallic nanoparticle formation.

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Bimetallic nanoparticles play a pivotal role in optical, magnetic and electronic applications, and are true workhorses during the catalytic transformation of chemicals. In particular, supported Pt nanoparticles alloyed with In, Ga or Sn are highly selective catalysts for the dehydrogenation of propane to propylene. It is well established that the size and composition of the nanoparticles strongly impact the catalytic properties and performance. Yet, conventional synthesis strategies lack proper control over the nanoparticle morphology and composition.

We report a new procedure for the tailored synthesis of bimetallic nanoparticles containing a non-noble metal next to a noble metal, here exemplified for nanoalloys containing In as non-noble and Pt as noble metal. The recipe is based on the use of atomic layer deposition (ALD), a vapour phase deposition method that is characterised by alternating exposure of the sample to chemical precursors **[1]**. ALD ensures that the amount of deposited material can be controlled at the monolayer level and enables conformal depositions on 3D substrates. **Figure 1a** schematically describes the steps involved in the fabrication process of the Pt-In bimetallic nanoparticles. Thin layers of In_2O_3 and Pt are sequentially deposited by ALD, yielding a Pt/In_2O_3 bilayer structure. These bilayers are then subjected to a temperature programmed reduction (TPR) in hydrogen to induce the formation of Pt-In nanoalloys.

Using *in situ* X-ray diffraction (XRD) at UGent and *in situ* grazing-incidence small-angle X-ray scattering (GISAXS) at beamline **BM26** (Dubble CRG), the mechanism of bimetallic particle formation was studied in detail. **Figure 1b** shows the structural evolution of a Pt/In_2O_3 bilayer during TPR in hydrogen as measured with XRD. Initially, the pattern shows diffractions from In_2O_3 (222) and metallic Pt (111). The disappearance of the In_2O_3 (222) peak around 330°C is indicative of complete reduction of the In_2O_3 layer. The In_2O_3 reduction is accompanied by a shift of the Pt (111) diffraction towards lower 2θ angle, implying expansion of the Pt fcc lattice due to insertion of In into the Pt structure. The stabilisation of the shifted diffraction peak indicates the formation of an $InPt_3$ fcc alloy. The evolution of the nanoscale morphology of the sample during TPR was monitored with *in situ* GISAXS. The temporal evolution of the main scattering feature is visible in the 2D colour plot in **Figure 1c**. A stable scattering pattern is observed up to 300°C, followed by a gradual peak shift to lower q_y-values until 450°C. These results indicate that the insertion of In in the Pt fcc lattice, as monitored by XRD, is accompanied by the migration and redistribution of Pt atoms across the surface, as schematically illustrated in **Figure 1d**.

The composition of the formed bimetallic alloys can be tuned by controlling the ratio of the deposited thickness of Pt to the thickness of In_2O_3. **Figure 2a** presents the relation between the as-deposited Pt/(Pt+In) atomic ratio and the alloy phase(s) obtained after TPR. These phases were found to be independent of the total deposited thickness of the as-deposited bilayer. Four different phase-pure alloys are achievable, with wide Pt/(Pt+In) atomic ratio windows for $InPt_3$, In_9Pt_{13} and In_2Pt, and only a small window for $In_{48}Pt_{52}$. For Pt/(Pt+In) atomic ratios below 20%, metallic In is observed next to the most In-rich phase, In_7Pt_3. In addition, our method enables tuning of the particle size with high precision in a range from 1 to 30 nm by changing the total

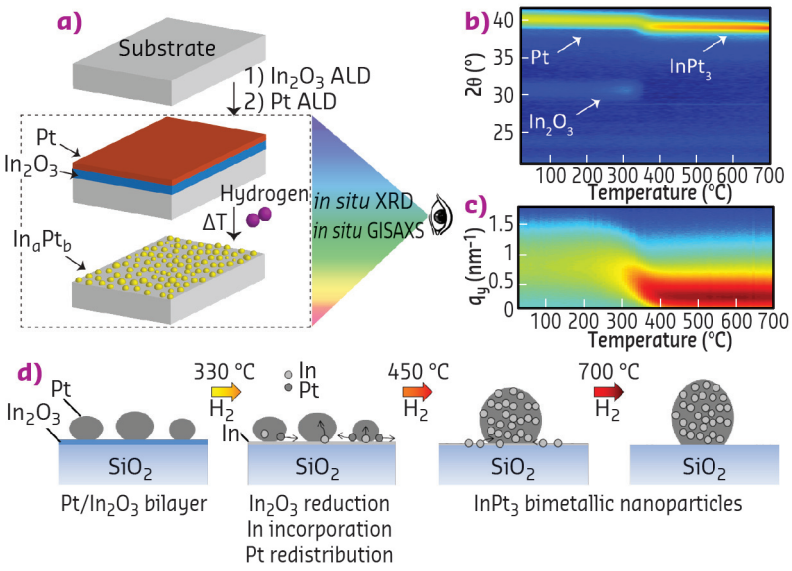

Fig. 1: *a*) ALD-based Pt-In bimetallic nanoparticle synthesis. *b*) *In situ* XRD patterns measured during TPR in hydrogen. *c*) *In situ* GISAXS line profiles measured during TPR in hydrogen. *d*) Bimetallic nanoparticle formation mechanism as interpreted from *in situ* XRD and GISAXS.

thickness of the ALD-grown Pt/In_2O_3 bilayer (**Figure 2b**). Tuning of the particle size while keeping the composition the same can thus be achieved by scaling the layer thicknesses of the Pt and In_2O_3 layers while keeping the Pt/(Pt+In) atomic ratio constant.

Finally, successful bimetallic nanoparticle synthesis was achieved on mesoporous silica, resulting in high surface area nanocatalysts which showed promising high activity for propane dehydrogenation.

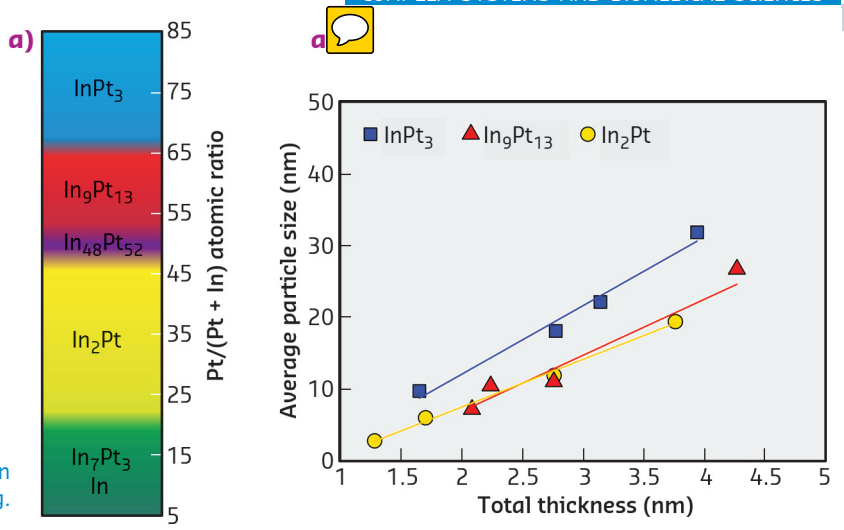

Fig. 2: a) Colour bar demonstrating composition tuning. b) Graph demonstrating size tuning.

PRINCIPAL PUBLICATION AND AUTHORS

Atomic layer deposition route to tailor nanoalloys of noble and non-noble metals, R.K. Ramachandran (a), J. Dendooven (a), M. Filez (b), V.V. Galvita (b), H. Poelman (b), E. Solano (a), M.M. Minjauw (a), K. Devloo-Casier (a), E. Fonda (c), D. Hermida-Merino (d), W. Bras (d), G.B. Marin (b) and C. Detavernier (a), *ACS Nano* **10**, 8770-8777 (2016); doi: 10.1021/acsnano.6b04464.
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MEDICAL APPLICATION OF SYNCHROTRON RADIATION: TOWARDS A NEW NON-INVASIVE METHOD TO SUPPRESS EPILEPTIC SEIZURES

For about a third of patients with epilepsy, current medication is ineffective and, in some cases, surgical resection is the only possible solution. However, this invasive procedure is risky and can only be achieved if the lesion is accessible. Synchrotron microbeam irradiation could offer an interesting alternative for these drug-resistant patients.

At **ID17,** the biomedical beamline, we have developed a new method using microbeams of a few tens of microns that allow the accurate irradiation of specific areas of the brain. Crossing these microbeams at the target region can deposit a sufficient radiation dose for the destruction of certain cells without opening the skull. Previous studies have shown the tolerance of biological tissues to this type of radiosurgery, *i.e.* the absence of lesions in the immediate vicinity of the microbeam and very few side effects, a significant advantage over current techniques that often present "collateral" damage. The development of the micro beam approach is possible due to the exceptional physical properties of the X-rays produced by the ESRF.

We have demonstrated the possibility of using microbeams to treat some forms of epilepsy during preclinical research. After an initial proof of concept performed on rats **[1]**, we have shown that microbeam irradiation, applied at four different levels of the somatosensory cortex (which generates seizures in this model), has beneficial effects for more than nine weeks (**Figure 1**).

The non-invasive 200 micron wide transections reduce the neuronal connections in the target area, with a resulting reduction in the synchronising capability of neurons, which is monitored by local field potentials. Between radiation zones, magnetic resonance imaging and histological analyses showed that the tissue is not altered and behavioural tests have shown that animals retain normal locomotion and motor coordination. **Figure 2** shows the irradiation geometries, a lateral dose profile, MRI images together with histological sections using various staining techniques.