A continuous and contamination-free process chain to a laser-synthesized heterogeneous catalyst

Sebastian Kohsakowski1,2, Stephan Barcikowski2, Thomas Vinnay3, Galina Marzun2,3

1University of Duisburg-Essen, Technical Chemistry I and Center of Nanointegration Duisburg-Essen (CENIDE), Universitätsstraße 7, 45141 Essen.

2NETZ-NanoEnergieTechnikZentrum, Carl-Benz-Straße 199, 47057 Duisburg

3Carl-Padberg Zentrifugenbau GmbH, Geroldsecker Vorstadt 60, 77933 Lahr.

For catalyst preparation, the usage of stabilizers and ligands is a major disadvantage of conventional methods for nanoparticle synthesis such as chemical reduction of precursors [1]. Ligands and stabilizers have to be removed by calcination and additives may cause catalysts poisoning. Characterization of active sites proves to be elusive. Furthermore, upscaling is not trivial and synthesis parameters are often difficult to transfer to other materials.

To circumvent these drawbacks, we used pulsed laser ablation in liquids (PLAL) for the synthesis of ligand-free nanoparticles, which can be deposited on carrier materials to realize an impurity-free heterogenous catalyst [2]. Even though several approaches for size control of laser-synthesized NPs are established (adding a salt [3], re-irradiation [4], centrifugation [5]), the main challenge is to up-scale the synthesis by ensuring the purity of the catalyst. Therefore, our projects aims to laser synthesize NPs and optimize their size in a continuous process in a tubular bowl centrifugation. By using an exchangeable plastic insert in the centrifuge, a clean size separation can be realized, since no ion release is expected from the walls. After the continuous contamination-free centrifugation, the small NPs can be directly transferred in a static mixer for particle adsorption. Good reproducibility and a linear up-scaling of nanoparticle generation was achieved by a continuous flow synthesis using a high-power picosecond laser system consisting of a 500W ps-laser source and a laser scanner with scanning speeds of up to 500m/s. Productivities of up to 4 g/h colloidal nanoparticles were achieved (step 1 in Fig. 1) [6]. State of the art to separate the different nanoparticle size fractions is a discontinuous centrifugation, which is limited by a small volume. To process a high volume of colloid and enable a continuous process chain (Fig 1.), we realized the size-classification and separation in a continuous tubular bowl centrifuge (step 2).

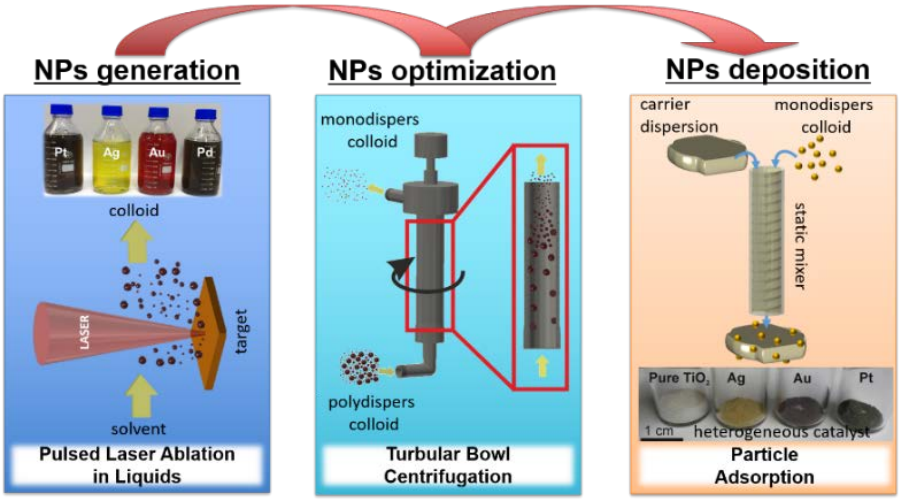

Figure 1: Schematically scheme of the continuous process chain from laser-generated NPs and size selection to a heterogeneous catalyst.

With this centrifuge a sharp separation at a cut-off threshold under 15 nm could be reached for laser-generated Au- and Pt-NPs. The centrifuged colloids have a high monodispersity with a narrow size distribution, as can be seen for laser-generated platinum NPs in Fig. 2. Downstream fabrication of heterogeneous catalysts is driven by electrostatic attraction to the support in a continuous process, with a quantitative yield (step 3 Fig. 1) [5]. Moreover, the use of the here investigated disposal inserts within the tube centrifuge, presents a promising approach to be applied for medical purposes (e.g. lateral flow assays) since contamination-free nanoparticles can be produced. Therefore, the application of the bowl centrifuge enables us to transfer the process chain on a complete continuous level.

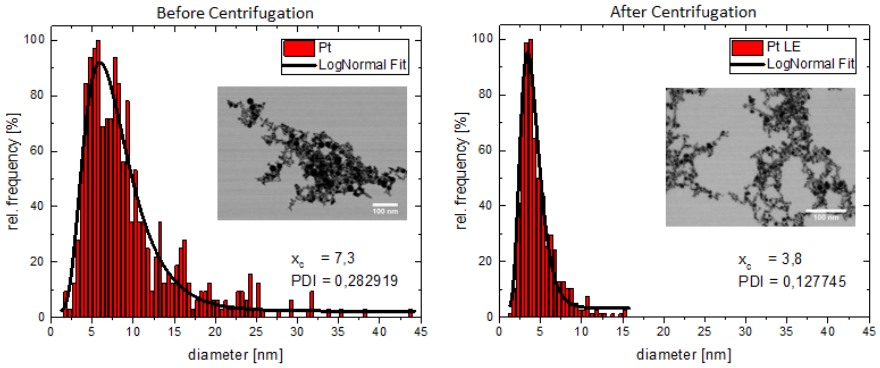

Figure 2: TEM-images and size distributions for laser-generated Pt-NPs before (left) and after (right) centrifugation in the tubular bowl centrifuge

[1] Turkevich et al.; *Discussions of the faraday Society*,11, (1951), 55.

[2] Marzun et al., *Langmuir*, 30, (2014), 11928.

[3] Merk et al., *Langmuir*, 5, (2013), 4213.

[4] Lau et al., Chemical Physics Letters, 610-611, (2014), 256.

[5] Gu et al., *Catalysis Letters,* 145 (5), (2015), 1105.

[6] Streubel et al., *Nanotechnology,* 27 (20), (2016), 205602.