

Investigations on Platinum Group Metal Nanoparticle Separation with Magnetic Beads

Christine Ruffert*, Nadja C. Bigall**, Lutz Rissing*

*Leibniz Universität Hannover, Institute for Micro Production Technology, GERMANY

**Leibniz Universität Hannover, Institute for Physical Chemistry and Electrochemistry, GERMANY

We propose an approach for the magnetic bead-based capture and release of metallic nanoparticles of the platinum group, which can be interesting for many small-scale synthesis reactions e.g. in the area of fine chemical production. For example, Pd is used as catalyst for Suzuki coupling, which is an important reaction for drug synthesis, or C-N coupling methods like BUCHWALD coupling. Furthermore, the reversible attachment of metals might be relevant in the area of water purification. Industrial and pharmaceutical processes comprise solvent extraction, nanofiltration, chemical precipitation, and adsorption [1]. Magnetic beads are small (typically 1, 2.8 or 5.5. μm) microspheres consisting of a non-magnetic matrix e.g. made of silica or polystyrene with embedded ferromagnetic nanoparticles. Due to the size of the magnetic particles, the microspheres feature superparamagnetic properties. This allows for a manipulation with magnetic forces, but avoids agglomeration of the beads without a field. Such beads have been well established for example in biotechnology or biomedical applications for the manipulation of biomolecules such as proteins, cells or bacteria [2, 3]. The application of magnetic beads for the capture and manipulation of metallic nanoparticles has hardly been under investigation so far. The development of a microfluidic magnetic bead-based separation system might allow for a re-use of the Pd catalyst, which would be of high industrial impact. The investigations described here can be used for both, Pd and Pt particles featuring similar chemical properties.

To transfer the experiments from the *in-vitro* level to a microfluidic approach, a chip design is proposed allowing for the realization of the sample preparation and incubation with the surface-functionalized magnetic beads as well as particle recovery on one single chip. The chips are fabricated by soft lithography with an SU-8™ master mold, patterned by standard UV photolithography on a 4-in Si wafer, followed by molding in PDMS (Sylgard®184 Silicone Elastomer kit). Here, Pt nanoparticles synthesized in an aqueous solution were used [4]. The as-prepared nanoparticles of approximately 5 nm in diameter were bound to commercial avidin functionalized magnetic beads via an avidin-biotin bond, a common approach for biomolecule manipulation by magnetic forces [2]. To do so, Pt particles were biotinylated using biotin-functionalized polyethylene glycol (*Biotin-PEG-thiol* from Nanocs). Magnetic beads from the *BcMag™ Monomer Avidin Kit* (by Bioclone Inc.) were prepared following the available protocol. The Pt nanoparticles were taken from a 10^{-9} molar aqueous solution. Four mixing ratios of Pt nanoparticles to Biotin-PEG-thiol molecules were applied, namely 1:10, 1:100, 1:1 000, and 1:10 000. To evaluate the bonding efficiency or the most suitable ratio, inductively-coupled plasma optical emission spectroscopy (ICP-OES) measurements were carried out quantifying the platinum content in the respective supernatant. Biotinylated Pt particles and avidin-coated beads were incubated for 1h at room temperature with gentle vortexing. Subsequently, the beads were separated by a permanent magnet. It could be observed that within 1min the cloudy suspension became colorless clear, while the magnetic material assembled close to the magnet, confirming a successful attachment of Pt nanoparticles to the avidin-coated beads. This was proven by EDX analysis and ICP-OES measurements. Commonly, the sample is discarded after detection and quantification. However, there are potential applications, where a recycling of the bound sample is significant such as catalyst recovery. Therefore, our further goal is to recover the Pt (or platinum group member, respectively) particles from the beads. Investigations on cracking the avidin-biotin bond to recycle the Pt particles employ four different approaches: (a) Adding an excess of free biotin to elute the target particle; (b) heating the sample to denature the avidin and hence break the avidin-biotin bond, (c) exposing the sample to UV light, and (d) adding elution buffer from the *BcMag™ Monomer Avidin Kit* designed for sample release. A successful detachment of the nanoparticles would enable to recycle them for further catalytic reactions without the need to completely dissolve the Pt in aggressive acids as reported for metallic gold [5]. After incubation of the avidin-coated magnetic beads with the biotinylated Pt nanoparticles, TEM measurements were carried out and combined with an EDX mapping to validate the binding process.

Fig. 1 exemplarily shows an avidin-coated magnetic bead after incubation with biotinylated Pt nanoparticles. An enlargement of the surface area allows an identification of the bulk material of the bead SiO_2 , crystalline magnetite nanoparticles giving the bead the superparamagnetic properties, and finally the bound 5 nm Pt nanoparticles. Table 1 gives an overview of the material composition for the magnetic bead shown in Fig. 1.

Zeta potential measurements were performed to verify the surface functionalization steps. The measurements were carried out on a Zetasizer-Nano instrument (Malvern Instruments GmbH) equipped with a HeNe laser ($\lambda = 633 \text{ nm}$, $p = 4 \text{ mW}$) and an avalanche photodiode detector.

The determination of the zeta potential was done in deionized water at 20°C. First, the pure Pt particles and avidin-coated magnetic beads were characterized separately. The Pt nanoparticles featured a zeta potential of about -74 mV, the avidin beads in de-ionized water had a potential of -10 mV. The zeta potential for Pt and beads after incubation, this means Pt attached to the beads, delivered a zeta potential of (-37.5 ± 0.5) mV (see Fig. 2a).

The samples exposed to heat, UV light, and elution buffer had a zeta potential in the range of -32 mV to -38 mV. This is comparable to the sample after incubation of Pt and beads. Contrarily, the sample incubated with a surplus of free biotin resulted in a positive zeta potential of +7.6 mV (see Fig. 2b). This indicates the release of Pt nanoparticles from the beads. An outstanding task is to determine the exact location of the separation within the avidin bead-Biotin-PEG-thiol-Pt molecule chain and the purification of the recycled Pt nanoparticles. Ongoing experiments will focus on the validation of the first results and the quantification of bound and recovered nanoparticles, respectively, by TEM and ICP-OES measurements. A stable process will then be transferred from the vial to microfluidic chip level.

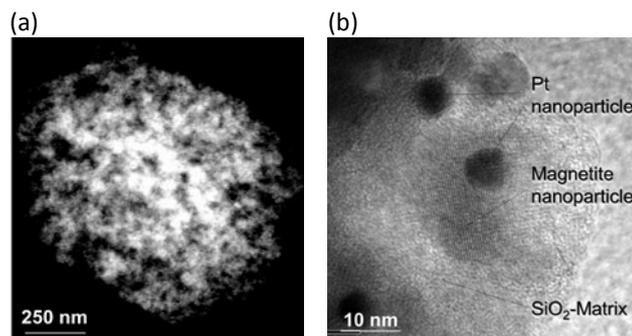
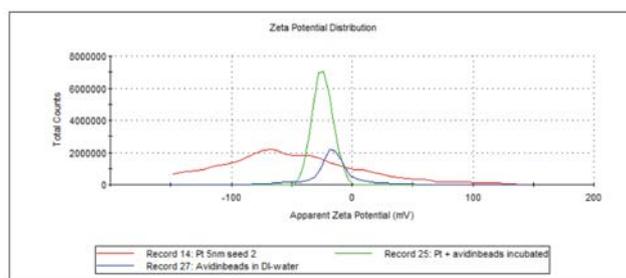


Figure 1. Magnetic bead with Pt nanoparticles bound to the surface (a) complete bead, (b) enlargement

Table 1: EDX analysis result for an avidin-coated magnetic bead after incubation with biotinylated Pt nanoparticles

Element	Content [at.- %]
O	60,38
Si	17,69
Fe	20,14
Pt	1,79
Sum	100,00

(a)



(b)

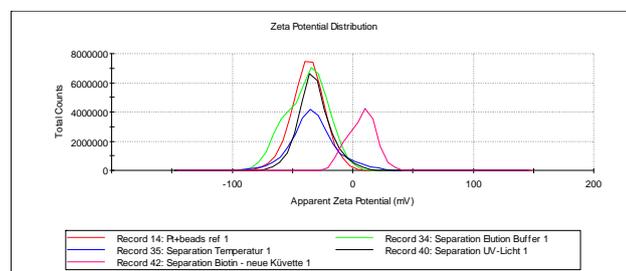


Figure 2. Zeta potential measurement results for (a) Pt, avidin-coated magnetic beads, and Pt bound to magnetic beads and (b) samples after separation compared to Pt bound to beads (total counts)

REFERENCES:

1. "Improved Methods for Catalyst Recovery in Biopharmaceutical Production," J. Fisher, J. Hurry, Pharma Manufacturing Sep 22, 2010 www.pharmamanufacturing.com/articles/2010/134.html
2. "Magnetic bead handling on-chip: new opportunities for analytical applications," M.A.M. Gijs, Microfluid Nano-fluid, **1**, 22–40, 2004
3. "Microfluidic applications of magnetic particles for biological analysis and catalysis", M.A.M. Gijs, F. Lacharme, U. Lehmann, Chem. Rev. **110**, 1518–1563, 2010
4. "Monodisperse Platinum Nanospheres with Adjustable Diameters from 10 to 100 nm: Synthesis and Distinct Optical Properties," N.C. Bigall, Th. Härtling, M. Klose, P. Simon, L.M. Eng, A. Eychmüller, Nanoletters, **8**, No. 12, 4588–4592, 2008
5. "Energy-Efficient Noble Metal Recovery by the Use of Acid-Stable Nanomagnets," M. Rossier, F.M. Koehler, E.K. Athanassiou, R.N. Grass, M. Waelle, K. Birbaum, D. Günther, W.J. Stark, Ind. Eng. Chem. Res., **49**, 9355–9362 (2010)

Acknowledgment

The authors would like to thank Heide Kühn from the Material Testing Institute for Materials and Manufacturing Engineering (MPA) Hannover, Armin Feldhoff from the Institute for Physical Chemistry and Electrochemistry (PCI) and the Institute of Materials Science (IW) of the Leibniz Universität Hannover for their kind support.