Electronic Supplementary Information

Size Characterisation of Au Nanoparticles by ICP-MS Coupling Techniques

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Experimental

Instrumentation

ICP-MS

All measurements were carried out with a quadrupole ICP-MS (ELAN 5000, Perkin-Elmer SCIEX, Überlingen, Germany). The experimental parameters are given in Table 1 and are daily optimised by a 10 $\mu g \cdot L^{-1}$ solution of Li, Y and Tl (Merck, Darmstadt, Germany). The raw data were further processed using Chromafile MS software (Perkin-Elmer, LabControl, Cologne, Germany).

Coupling of HPLC and GE to ICP-MS

Delivery of the mobile phase (0.5 $mL \cdot min^{-1}$) was carried out by a S1121 Solvent Delivery System Pump (Sykam, Fürstenfeldbruck, Germany) and a S8110 gradient mixer (Sykam). Samples were filtered through 0.2 µm filters (membraPure, Membrex 18 PET unsterile diameter 18 mm) and introduced by a metal-free Rheodyne 9725i injection valve (Phenomenex) equipped with a 20 µL PEEK sample loop (Phenomenex). All connections were made of PEEK in order to minimise the blank values. The detailed working conditions are summarised in Table 2.

The principal set-up of the GE-ICP-MS system is described elsewhere [1]. The parameters used throughout this work are given in Table 2.

Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM)

For comparative measurements of the NP sizes two independent methods were applied. The dynamic light scattering (DLS) measurements were carried out at the University of Mainz (Prof. M. Schmidt, D. Störkle) using a Uniphase He/Ne laser (λ = 632.8 nm, 22 mW), a ALV-SP 86 Goniometer (ALV, Langen, Germany), a ALV/High QE APD-Avalanche photodiode with fiber optic detection, a ALV3000 correlator, and

a Lauda RC-6 thermostatization unit (Lauda GmbH, Lauda-Königshofen, Germany). Data evaluation followed standard procedures applying cumulate analysis and simplex-algorithm. Prior to measurement the solutions were filtered through 20 nm (in the case of the 5 nm Au colloids) and 100 nm pore size (for Au NPs of bigger size) Anotop filters (Whatman International Ltd, Madestone, UK), respectively.

TEM images were taken with a Philips EM420 electron microscope (Philips Electron Optics, The Netherlands) at the University of Mainz (Institute of Physical Chemistry, Dr. Ute Kolb). Data was analysed using standard procedures.

Reagents

SeaKem®LE agarose was obtained from Biozym (Hessisch Oldendorf, Germany). Hydrogentetrachloroaurate ($HAuCl_4 \cdot 3H_2O$, 99%), citric acid trisodium salt, sodium dodecyl sulphate (SDS) for molecular biology, min. 98.5% (GC), were received from Sigma (Deisenhofen, Germany). Gold colloid solutions with different particle sizes (nominal 20 nm, mean particle size 17-23 nm (monodisperse, according to the producer); nominal 10 nm, mean particle size 8-12 nm (monodisperse); nominal 5 nm, mean particle size 3.5-6.5 nm (monodisperse)) were purchased from Sigma as well. For their analysis, these solutions were diluted to 1:100 with water. Sodium borohydride (98%), DL-mercapto succinic acid (MSA, 99%) and methanol (ECD grade, >99.8%) were purchased from Acros Organics (Geel, Belgium). Sodium dihydrogenphosphate and disodium hydrogenphosphate (both p.a.) was from Merck (Darmstadt, Germany). All solutions were prepared in Milli-Q water (> 18.0 MΩ · cm) (Milli-Pore, Schwalbach, Germany).

Preparation of Au nanoparticles

Preparation of citrate reduced Au nanoparticles (Citrate method)

The citrate reduced Au nanoparticles were prepared according to the method developed by Turkevich et al. [2]. Therefore, 10 mL of an aqueous $2.5 \cdot 10^{-4}$ mol·L^{-1} $HAuCl_4 \cdot 3H_2O$ solution was heated to 95 °C. Then 417 µL of a 20 mmol·L^{-1} trisodium citrate solution was added at once under vigorous stirring, subsequently the solution changed slowly its colour to red. The solution was kept near the boiling point for 15 min and allowed to cool down. In the following this sample is called 'sample 1', with Au/citrate ratio of 0.3. Another sample (sample 2) was synthesised adding 312 µL of the 20 mmol·L^{-1} trisodium citrate solution (Au/citrate ratio of 0.4). These given ratios give a certain control of the resulting size of the NPs.

Preparation of the Au nanoparticles modified with mercaptosuccinic acid (MSA method)

A procedure based on the work of Brust et al. was used to prepare MSA-modified Au nanoparticles [3]. 8.04 mL of a 12.5 mmol·L^{-1} solution of MSA in methanol was added to a deep yellow solution of hydrogentetrachloroaurate (31.7 mg) in methanol (17 mL). After mixing the colour faded slightly away to give a pale yellowish transparent solution. A freshly prepared aqueous sodium borohydride solution (22.4 mg in 1.5 mL water) was then added drop by drop during 5 min. The solution turned dark-brown and after stirring for one hour the solution was filled in a centrifugal tube and centrifuged for 30 min at 4000 rpm. The precipitate was washed twice with a 20% (v/v) water/methanol solution and twice with pure methanol. Thereafter, the precipitate was decanted and re-dispersed in the washing solution in an ultrasonic bath (15 min). After the last washing step the precipitate was dried under vacuum at room temperature. Due to the chosen Au/MSA ratio (0.8), the

resulting NPs should have a size between 1.28 nm and 1.94 nm as reported in the literature [4].

Table 1: Instrumental operating of ICP-MS

ICP System	
Instrument	ELAN 5000 (Perkin-Elmer SCIEX)
RF power	1300 W
Plasma gas flow	15.5 L min^{-1}
Auxiliary gas flow	1.1 L min^{-1}
Nebuliser gas flow	1.2 L min^{-1}
Sampler cone	Ni, 1.0 mm orifice
Skimmer cone	Ni, 0.7 mm orifice
Dwell time	250 ms
Monitored isotopes	^{103}Rh, ^{197}Au
Sample introduction	
Nebuliser	Cross-flow nebuliser (AHF Feuerbacher, Tübingen, Germany)
Spray chamber	Scott-type (AHF Feuerbacher)
Flow rate	0.5 mL min^{-1} (for HPLC separations)
	0.3 mL·min^{-1} (for GE separations)

Table 2: Instrumental operating of HPLC and GE

HPLC system	
Column	Nucleosil 7 µm particle size, C18, 1000 Å pore size, 250x2 mm (Phenomenex, Aschaffenburg, Germany)
Flow rate	0.5 $mL \cdot min^{-1}$
Mobile phase	10 $mmol \cdot L^{-1}$ SDS, 1 $mmol \cdot L^{-1}$ NaH_2PO_4, 1 $mmol \cdot L^{-1}$ Na_2HPO_4
Injection volume	20 µL
GE system	
Gel dimensions	80 mm length, 1.2 mm ID
Gel composition	2 - 2.4 % (w/w) SeaKem®LE agarose
Voltage	400 V
Flow rate of elution buffer	0.3 $mL \cdot min^{-1}$
Injection volume	1 µL
Electrode buffers	10 $mmol \cdot L^{-1}$ SDS, 1 $mmol \cdot L^{-1}$ NaH_2PO_4, 1 $mmol \cdot L^{-1}$ Na_2HPO_4
Elution buffer	electrode buffers + 10 $\mu g \cdot g^{-1}$ Rh as internal standard

References

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