Metal- and Metal Oxid Nanoparticles

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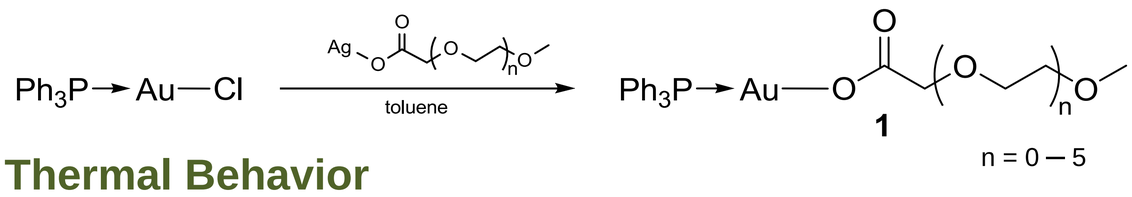
Introduction

Transition metal and metal oxide nanoparticles (= NP) are of high interest in many applications due to their unique optical, electrical, magnetical and catalytical properties depending on their size, shape and size distribution. [1] An established pathway for the metal NP synthesis is the chemical reduction of metal ions in aqueous or organic solvents. [2] As stabilizing components mostly polymers, co-polymers or dendrimers with donating functionalities including N, P, S, and O donor atoms are used. [3] The formation process of NPs depend on different conditions like stabilizer amount, type of reducing agent, and temperature. [4] A precursor which combines stabilizer and reducing agent will simplify the generation process. Here we report on the synthesis, thermal behavior and the ability to form gold NP by thermolysis of such precursors as well as the synthesis, characterisation and the magnetic properties of Fe_3O_4 NP.

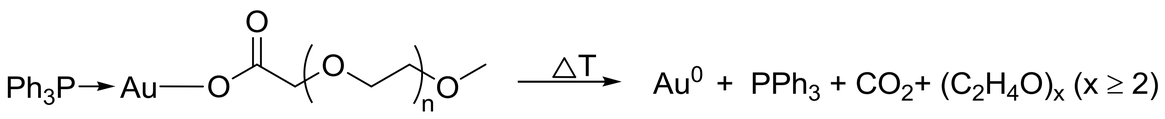
Gold NP Precursors

Gold NP are typically synthesized from the commercially available $HAuCl_4$ precursor. For the synthesis a reducing agent (*e.g.* sodium citrate or $NaBH_4$) in the presence of a stabilizer is necessary, whereas polyethyleneglycol is used most commonly. [5]
We designed a series of new precursors that consist of a carboxylic functionality, which is able to reduce the Au(I) center to Au(0) and an oligoethyleneglycol moiety for the stabilization of the formed gold NP.



Thermal Behavior

TG-MS studies of the gold compounds show the formation of triphenylphosphine, CO_2 and oligoethyleneglycol chains with different chain length. The CO_2 formed indicates the reduction of the gold. The detected oligoethyleneglycol chains confirms the release of the stabilizer.



For investigations compound **1** with n = 2 was used. In a typical experiment a 6.3 x 10^{-3} M solution in *p*-xylene was prepared and heated to reflux (138 °C) for 1 h. The color of the solution turned from colorless to intensive purple which indicates the formation of gold NP. For investigations of a temperature dependence, the experiments where carried out additionally in toluene (111 °C, 24 h) and mesitylene (165 °C, 10 min). TEM studies show that the most narrow size distribution could be obtained at 111 °C with an average size diameter of 3.9 nm. At 138 and 165 °C a broader distribution was found. At these temperatures NP with an average diameter of 4.0 nm were obtained. It pointed out that the influence of the temperature on the NP size is very small. However the size distribution depends on the temperature, while a low temperature gives a narrow size distribution.

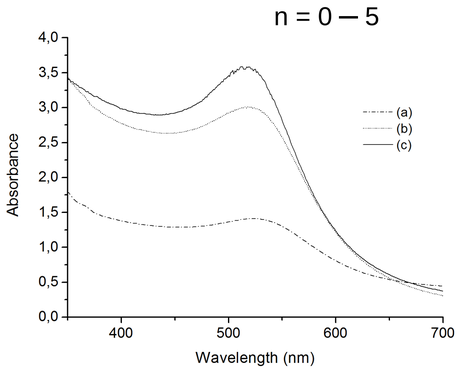


*Fig. 1: UV-Vis spectra of Au colloids obtained by thermolysis of **1** (n = 2, c = 6.3 x 10^{-3} M) in boiling mesitylene (a), p-xylene (b), and toluene (c).*

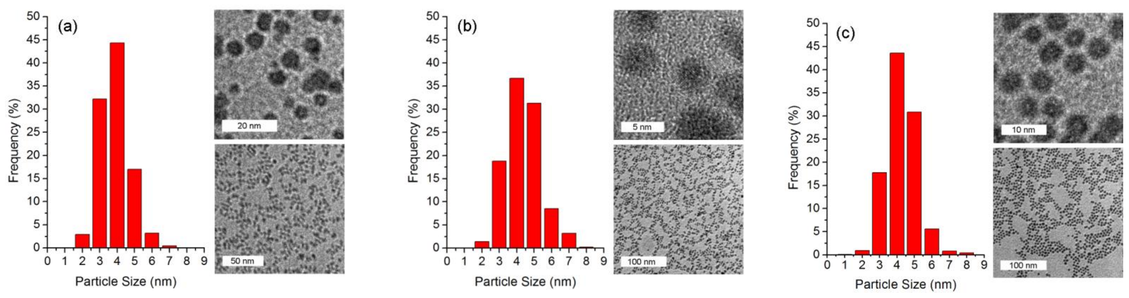


*Fig. 2: TEM images and size distribution of Au NPs derived from **1** generated in boiling (a) mesitylene, (b) p-xylene, and (c) toluene.*

Au NP Generation Depending on the Chain Length

The influence of the chain length on the NP size distribution and on the average size was investigated. Precursor molecule **1** was synthesized with different chain lengths from n = 0 to n = 5. For n = 0 or 1 no NP could be achieved caused by the very short glycol “chains” which are unable to stabilize NP. In contrast precursors with n = 2 – 5 form NP. TEM analyses show a size distribution between 2 and 6 nm and an average size diameter in range of 3.3 to 3.9 nm. Out of this results no significant influence of the chain length was found.

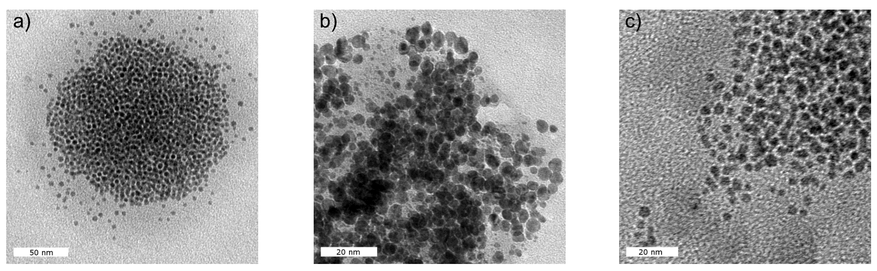


*Fig. 3: TEM images of Au NP derived from **1** depending on the chain length n after 1h thermolysis in p-xylene (a) n = 3, (b) n = 4, and (c) n = 5.*

Time-Depending Studies

For this study compound **1** with n = 4 in *p*-xylene (6.3 x 10^{-3} M; 138 °C) was used and an UV-Vis spectrum was recorded every 5 min to monitor the NP formation. The characteristic plasmon band and an increase of its absorption could be observed time-dependently (Fig. 4). The investigation of the plasmon band requires a deconvolution of each spectrum. In further investigations the time-depending plasmon shift was studied.

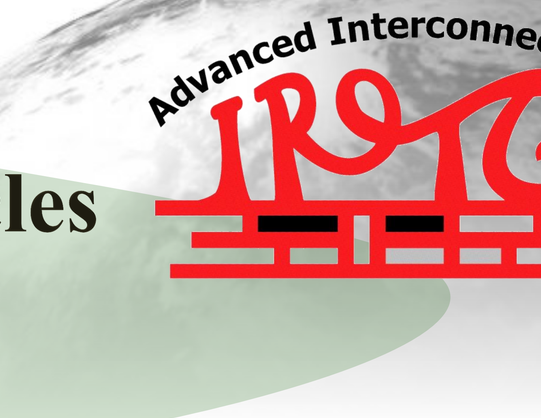
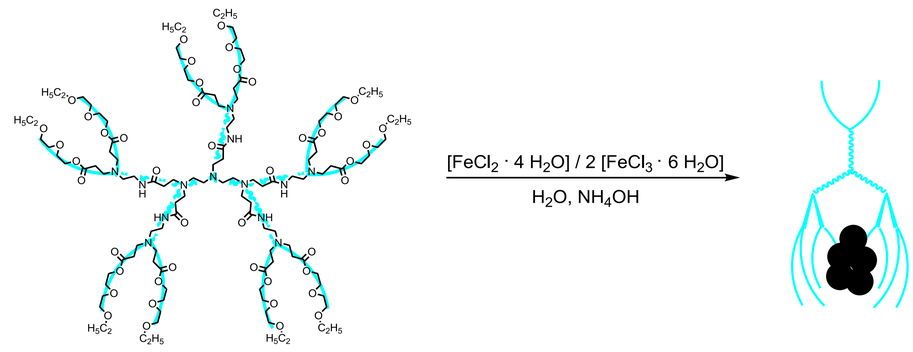


*Fig. 4: UV-Vis spectra of the increasing plasmon absorption of **1** with n = 4.*

Iron Oxide (Fe_3O_4) NP Synthesis

Stable magnetic Fe_3O_4-NP (magnetite) have been synthesized using the chemical co-precipitation method of ferrous (Fe^{2+})/ferric (Fe^{3+}) mixed aqueous salt-solutions in presence (*in-situ*) of novel amidoamine-based, di(ethylene glycol) grafted dendrimers as stabilizers to prevent agglomeration and to embed the NP in a biocompatible organic matrix. The dendritic stabilizers were synthesized by a consecutive divergent synthesis methodology including addition and amidation cycles and characterized thoroughly by FTIR, ^1H NMR, $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry.



Characterisation and Properties of the Fe_3O_4 NP

The identity of the formed magnetite NP was proved via FTIR, X-Ray Powder Diffraction (XRD) analysis and Vibrating-Sample Magnetometry (VSM) exhibiting superparamagnetic behavior as depicted in Fig. 5.

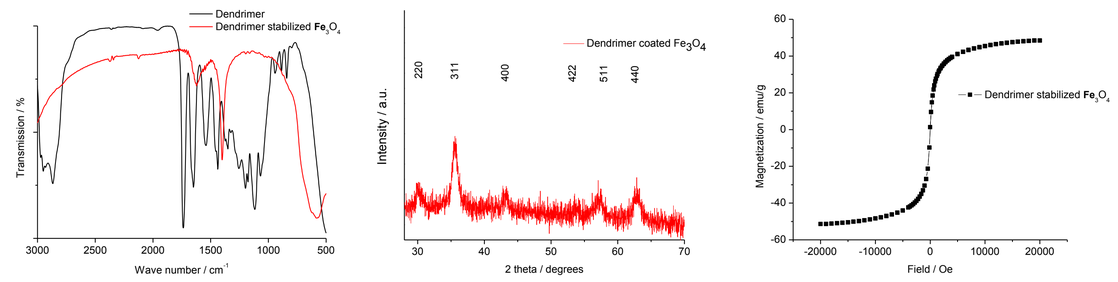


Fig. 5: IR spectra (left), XRD (middle) and vibrating sample magnetometry (right) of Fe_3O_4 NP.

The morphology of the dendrimer coated Fe_3O_4 NP was analyzed by TEM investigations. Images of the magnetite NPs are shown in Fig. 6. The evaluation of the TEM measurements indicates a monodispersity and a narrow size distribution with an average diameter in the range of 7.4 nm (± 1.5 nm) (Fig. 6).

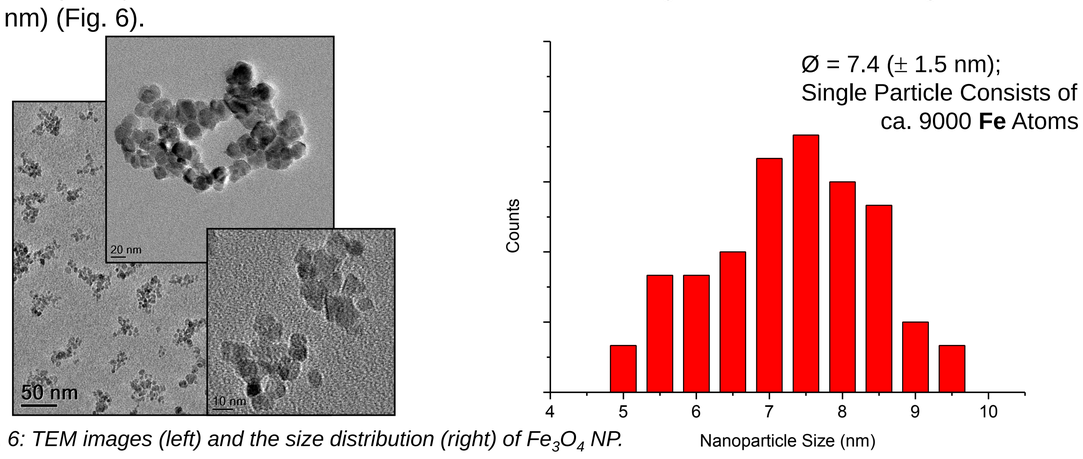


Fig. 6: TEM images (left) and the size distribution (right) of Fe_3O_4 NP.

References

[1] (a) S-A. Dong, S-P. Zhou, *Mater. Sci. Eng., B*, **2007**, *140*, 153; (b) A.-H. Lu, E. L. Salabas, F. Schüth, *Angew. Chem. Int. Ed.* **2007**, *46*, 1222. [2] G. Schmid, B. Corain, *Eur. J. Inorg. Chem.,* **2003**, 3081. [3] (a) E. Boisselier, A. K. Diallo, L. Salmon, C. Ornelas, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2010**, *132*, 2729; (b) J. Zhou, J. Ralston, R. Sedev, D. A. Beattie, *J. Colloid Interface Sci.*, **2009**, *331*, 251; (c) F. Bonet, V. Delmas, S. Grugeon, R. Herrera Urbina, P-Y. Silvert, K. Tekaia-Elhsissen, *Nanostruct. Mater.*, **1999**, *11(8)*, 1277. [4] (a) M. Hostetler, J. Wingate, C. Zhong, J. Harris, R. Vachet, N. Evans, R. Murray, *Langmuir*, **1998**, *14*, 17; (b) N. Toshima, T. Yonezawa, *New J. Chem.*, **1998**, *22*, 1179. [5] (a) J. Turkevitch, P.C. Stevenson, J. Hillier, *Discuss. Faraday Soc.,* **1951,** *11,* 55; (b) G. Frens, *Nature (London), Phys. Sci.,* **1973**, *241*, 20; (c) C-H. Wang, C-J. Liu, C-L. Wang, T.-E. Hua, J. M. Obliosca, K. H. Lee, Y Hwu, C-S. Yang, R-S. Liu, H-M. Lin, J-H. Je, G. Margaritondo, *J. Phys. D: Appl. Phys.*, **2008**, *41*, 1.

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