Gold Nanoparticles Generated by Thermolysis of Gold(I) Carboxylates

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Introduction

Transition metal 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 production process of the gold NP depends on different conditions like stabilizer amount, 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.

Synthetic aspects

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 gold NP formed.
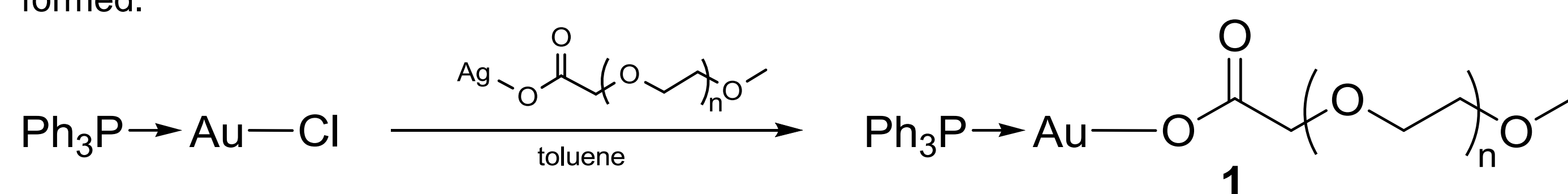
The new gold compounds **1** are accessible by treatment of commercially available triphenylphosphinogold(I)chloride and the corresponding silvercarboxylate (n = 0 − 5).

Thermal behavior

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

$$Ph_3P \rightarrow Au\text{—}O \cdots \xrightarrow{\triangle T} Au^0 + PPh_3 + CO_2 + C_xH_yO_z \ (x \geq 2)$$
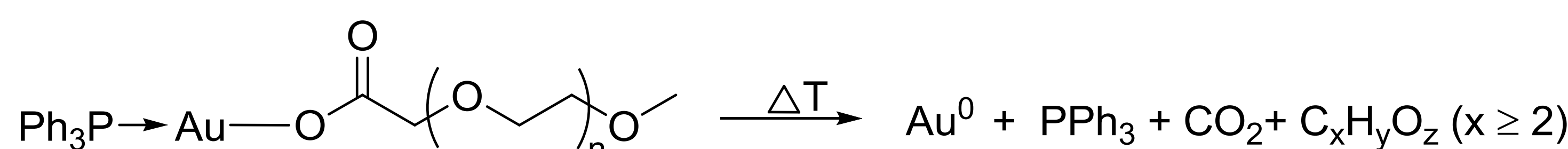
For investigations compound **1** with n = 2 was used. In a typical experiment a 6.3×10^{-3} M solution in p-xylene was prepared and heated to reflux (138 °C) for 1 h. The color of the solution turned from colorless to intensive purple which indicates the formation of gold NP. For investigations of a 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 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 is depending on the temperature, while a low temperature gives a sharp size distribution.
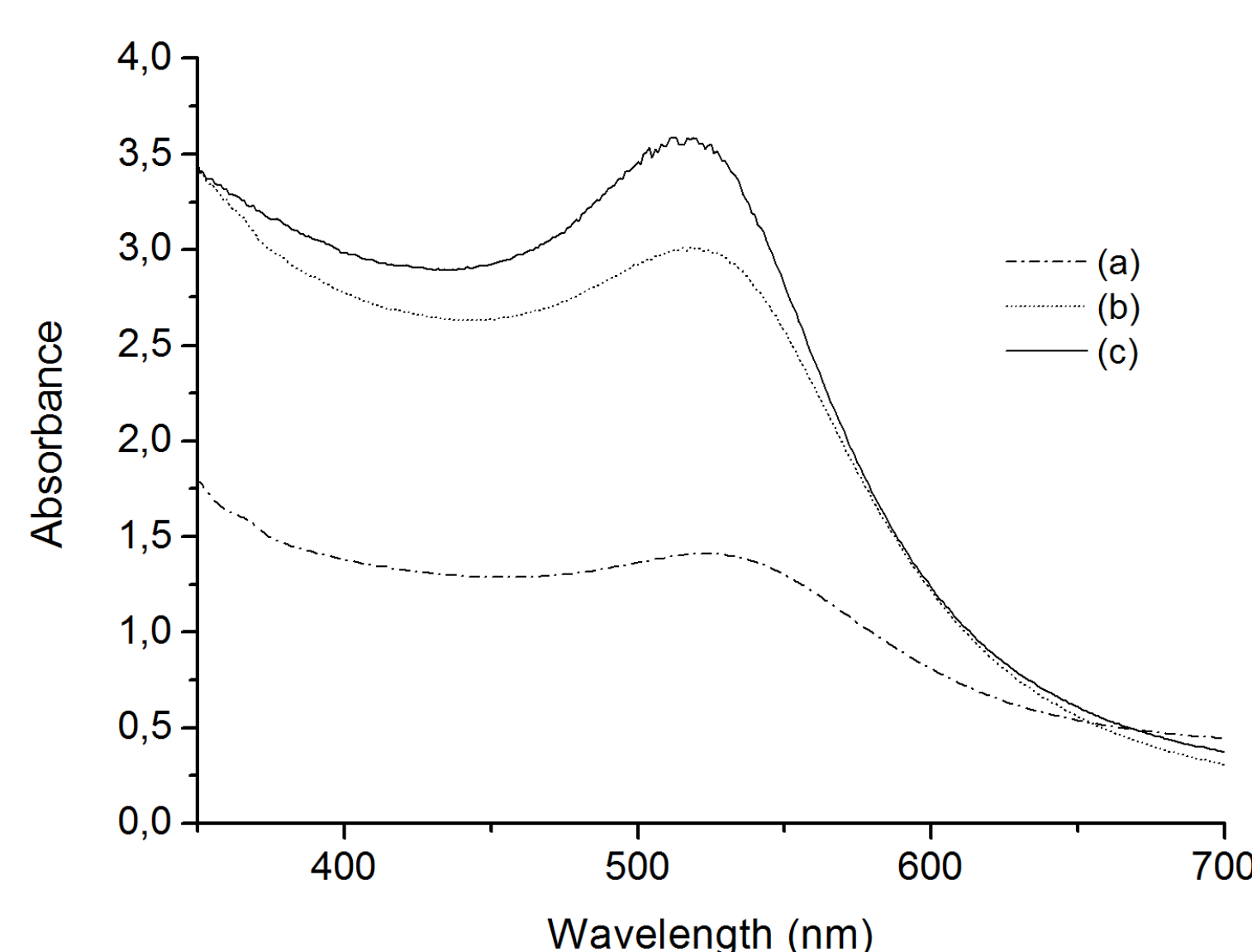

Fig. 1: UV-Vis spectra of Au colloids obtained by thermolysis of **1** (n = 2, c = 6.3×10^{-3} M) in boiling mesitylene (a), p-xylene (b), and toluene (c).
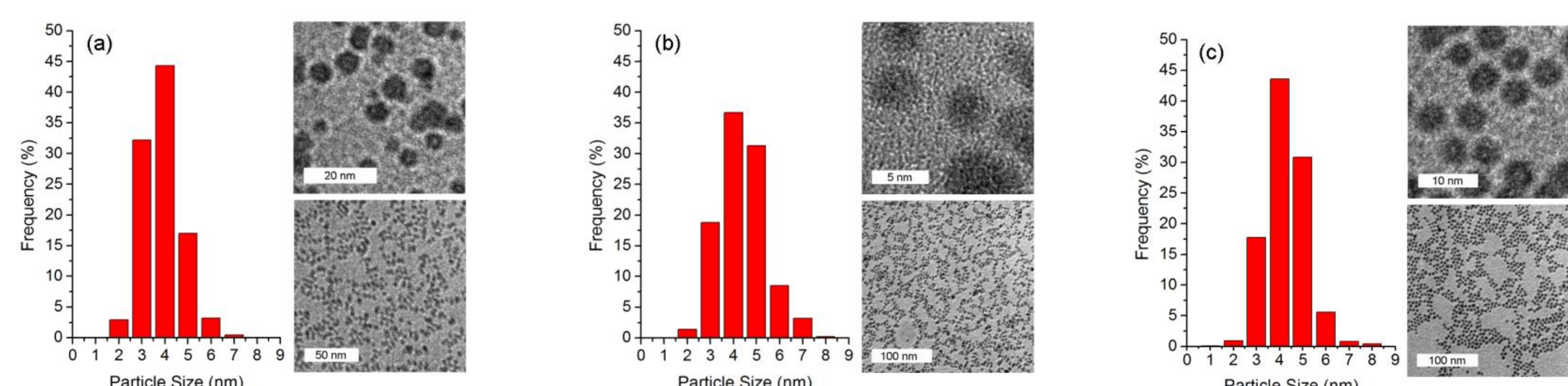

Fig. 2: TEM images and size distribution of Au-NPs derived from **3** generated in boiling (a) mesitylene, (b) p-xylene and (c) toluene.

NP generation depending on the chain length

The influence of the chain length on the NP size distribution and the average size was investigated. Therefore precursor molecule **1** was synthesized with different chain length from n = 0 to n = 5. For n = 0 or 1 no NP could be received 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.
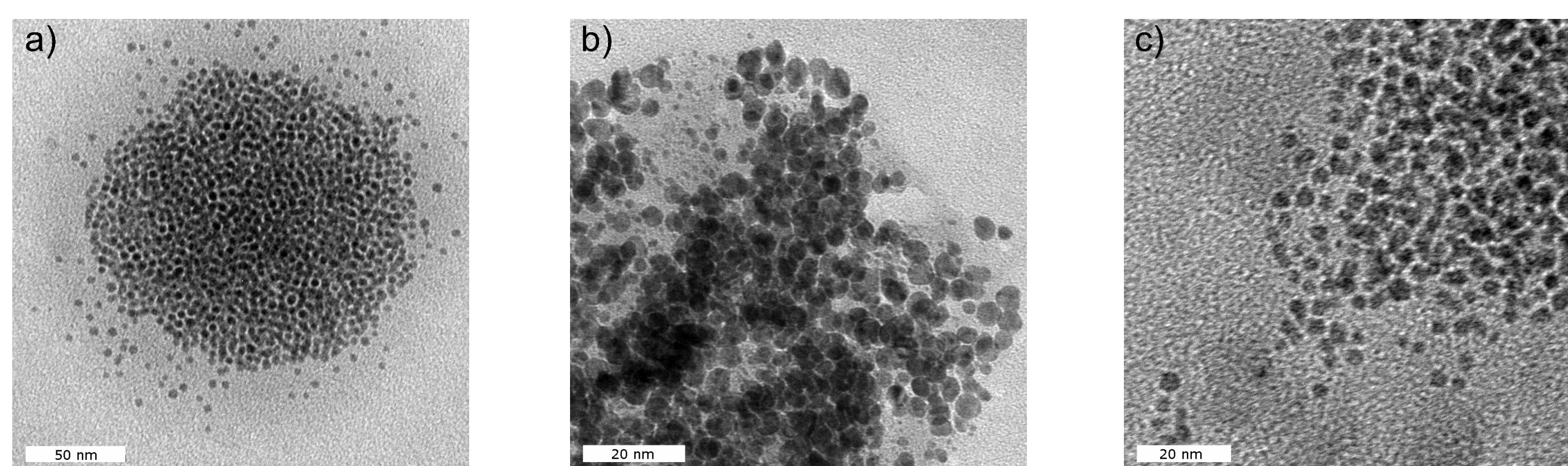

Fig. 3: TEM images of Au-NP derived from **1** depending on the chain length n after 1h thermolysis in p-xylene (a) n = 3, (b) n = 4, and (c) n = 5.

Time-depending studies

For this study compound **1** with n = 4 was used and an UV-Vis spectrum was taken 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.
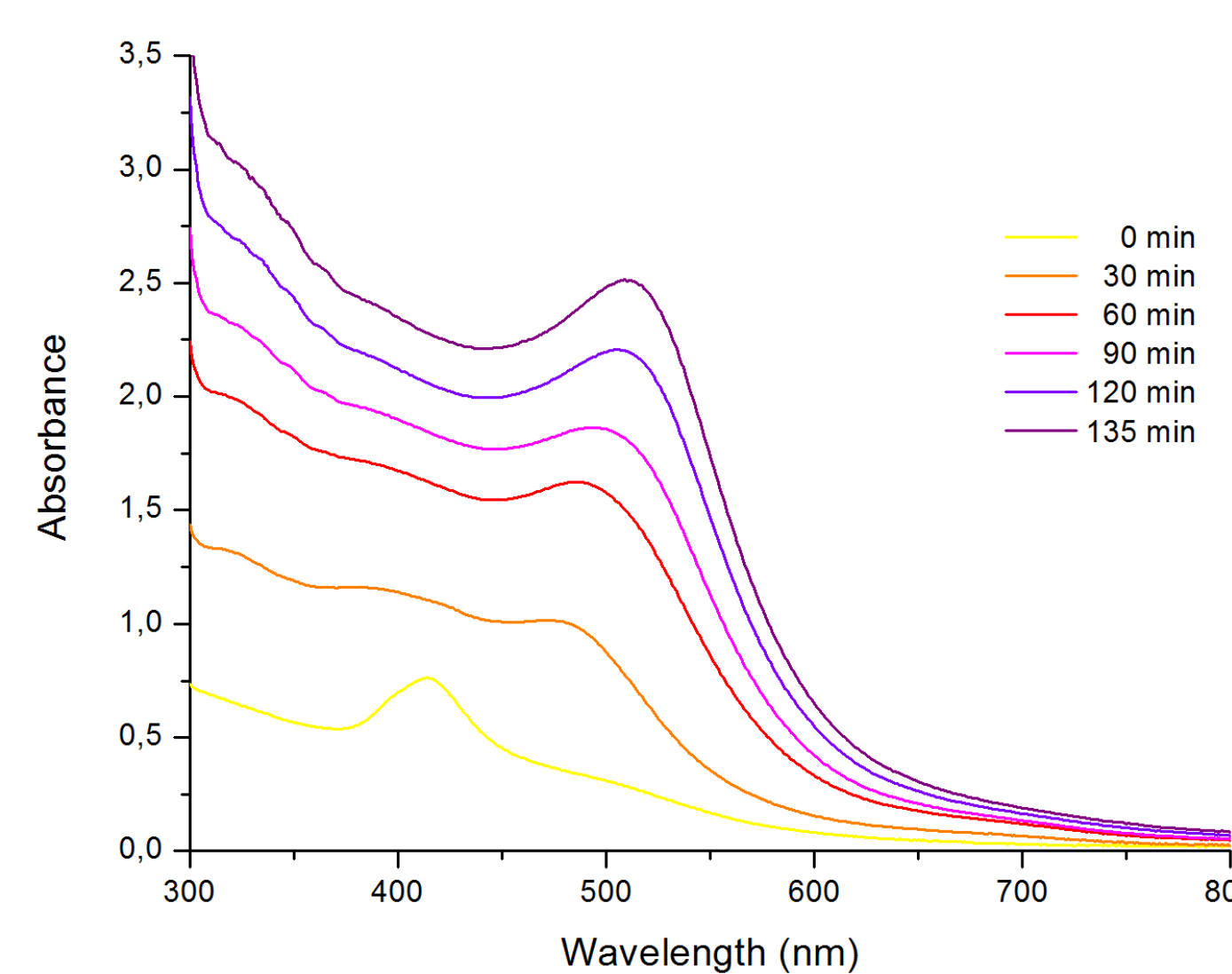

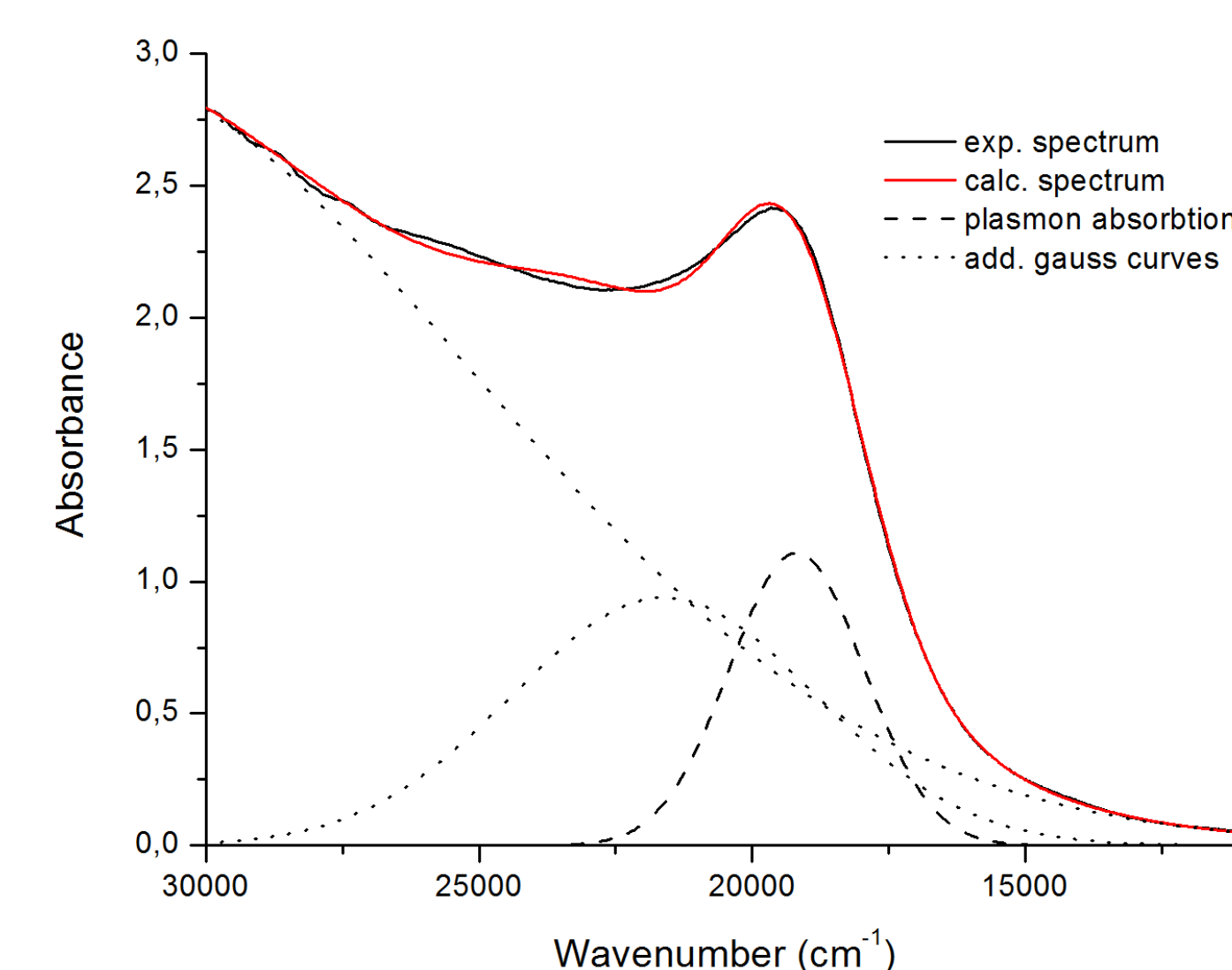Fig. 4: UV-Vis spectra of the increasing plasmon absorbtion of **1** with n = 4.

Fig. 5: Exemplary deconvolution plot of the UV-Vis spectrum at 135 min of **1** with n = 4.

The time-depending plasmon shift of the maxima is shown in Fig. 6, which is caused by a size increase of the forming NP. For the intensity of the plasmon band a maximum is found at a reaction time of 145 min (Fig. 7). In the beginning a lot of NP are formed which agglomerate to bigger particles. After 145 min a level of UV-Vis inactivity is reached due to the particle size. The plot of the plasmon half width confirms this increase of the particle size. In our opinion this phenomena is connected with an energy-time uncertainty.
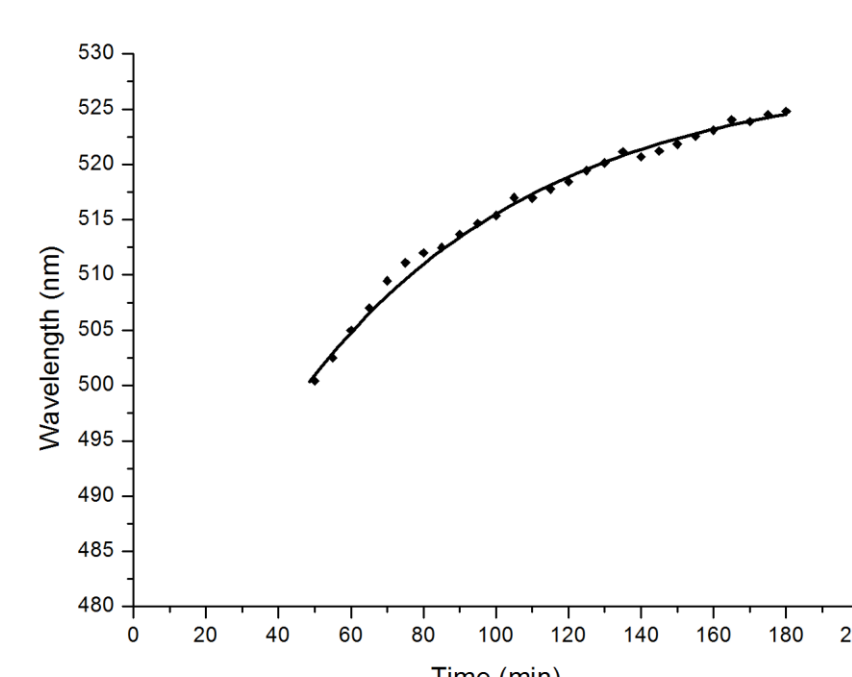

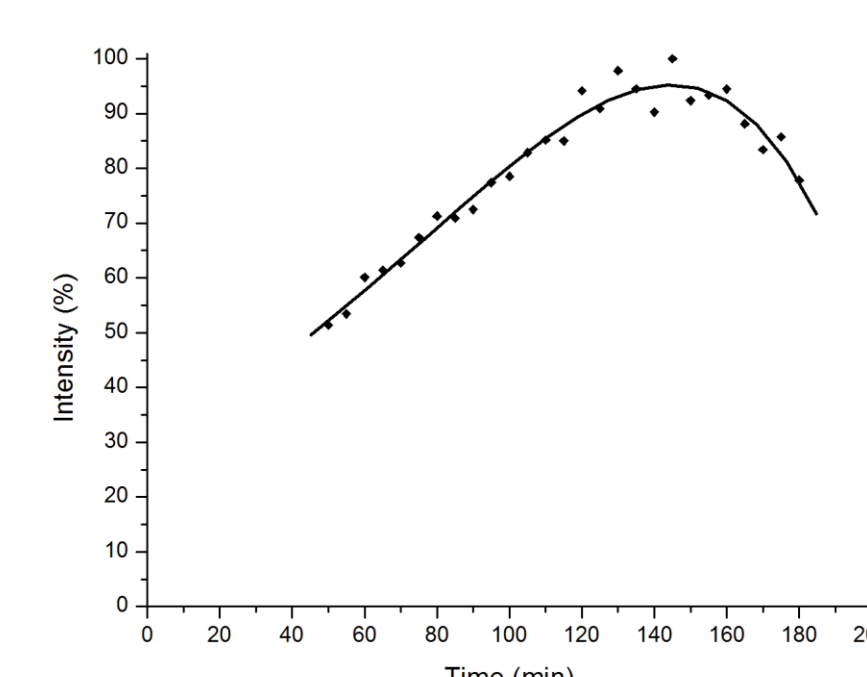Fig. 6: Time depending plasmon maxima shift of **1** with n = 4.

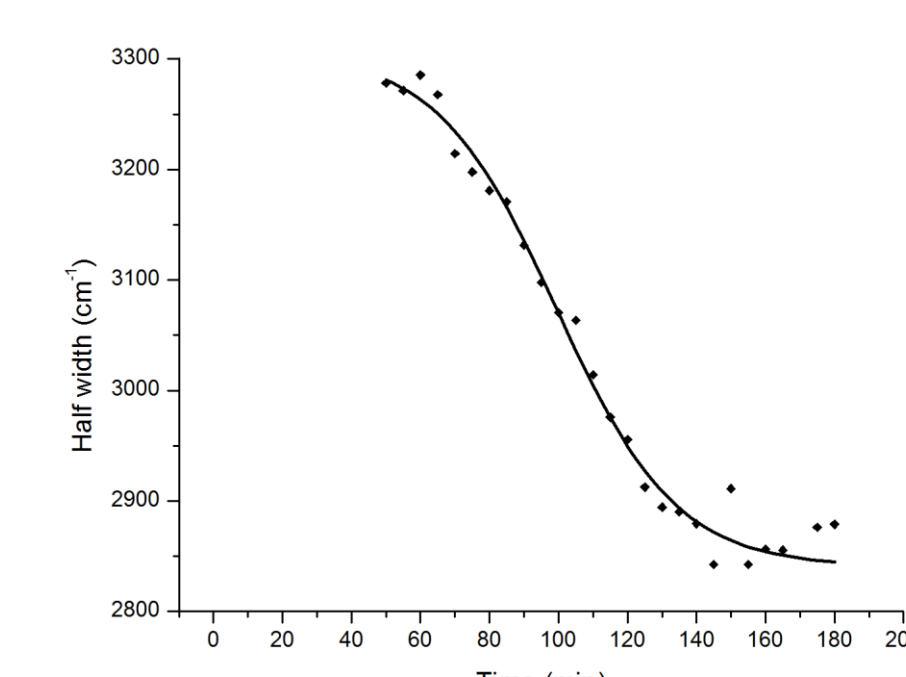Fig. 7: Time depending plasmon intensity of **1** with n = 4.

Fig. 8: Time depending plasmon half width of **1** with n = 4.

Conclusion

The behavior of new gold precursors containing a stabilizer and a reducing agent in one compound for the formation of gold NP by thermolysis is discussed. We showed successfully that gold NP can be formed by thermolysis of these precursors. At different temperatures NP with an average size diameter of ca 4 nm and a small size distribution were observed. The narrowest size distribution was obtained at low temperatures (111 °C) with a diameter of 3.9 nm.

The chain length of the oligoethyleneglycol chain in the precursor did not show a significant influence on the particle size and size distribution of the formed NP. In general a size diameter between 3.3 and 4.0 nm was found.

In summary a very simple way was shown to generate gold NP with a very narrow size distribution and a size diameter in the range of 3.3 to 4.0 nm out of one precursor without any additional stabilizer and reducing agent.

References

[1] S-A. Dong, S-P. Zhou, *Mater. Sci. Eng., B*, **2007**, *140*, 153. [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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