Synthesis concepts for metal nanoparticles in different shapes and their pyrene-supported linkage to SWCNTs

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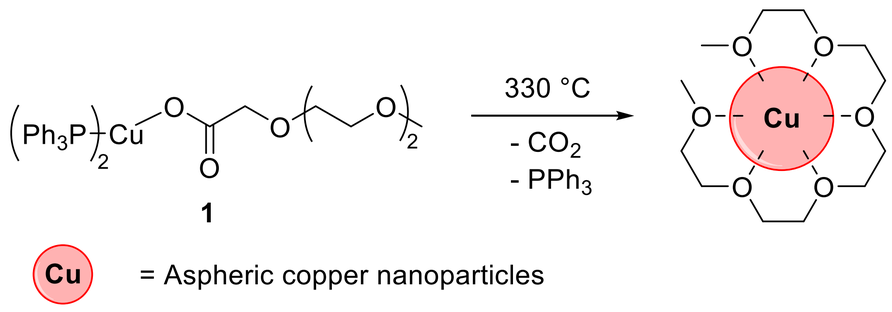
Motivation

Metal nanoparticles attached to carbon-based nanostructured materials enable new applications in electrochemical energy storage (*e.g.* fuel cells) [1] as well as chemical detection [1,2,3] and optical sensing [2,3,4]. Requirements for electronic sensors are appropriate and versatile nanoelectronic transducers, the design of which can comprise the modification of the channel material of a nanoelectronic field-effect transistor, e.g. made from semiconducting single-walled carbon nanotubes (s-SWCNTs). In the ideal case, this component can be functionalized with nanoscopic building blocks in a modular manner that allows a selective response and tuning of the sensitivity. Field-effect transistors (FETs) using individualized SWCNTs have been proposed for this case as FET channel material with special properties regarding sensitivity and selectivity of resulting sensor devices [5,6].

Recently, we presented a scalable on-chip functionalization approach for SWCNTs between palladium electrodes in the geometry of a field-effect transistor with preformed gold nanoparticles [5]. This method is wafer-level compatible and comprises two stages of flow chemistry. In a new chemical approach, we are using pyrenylalkylthioates as linker molecules for non covalent functionalization of SWCNTs with metal nanoparticles which also enable debundling of CNT agglomerates.

Preparation of aspheric copper nanoparticles



Cu = Aspheric copper nanoparticles

*Scheme 1: Synthesis of copper nanoparticles by thermolysis of copper(I) carboxylate **1** [7].*

- Preparation of copper nanoparticles by thermal decomposition of compound **1** in *1*-hexadecylamine (precursor concentration: 10 mM, ϑ = 330 °C, t = 10 min)

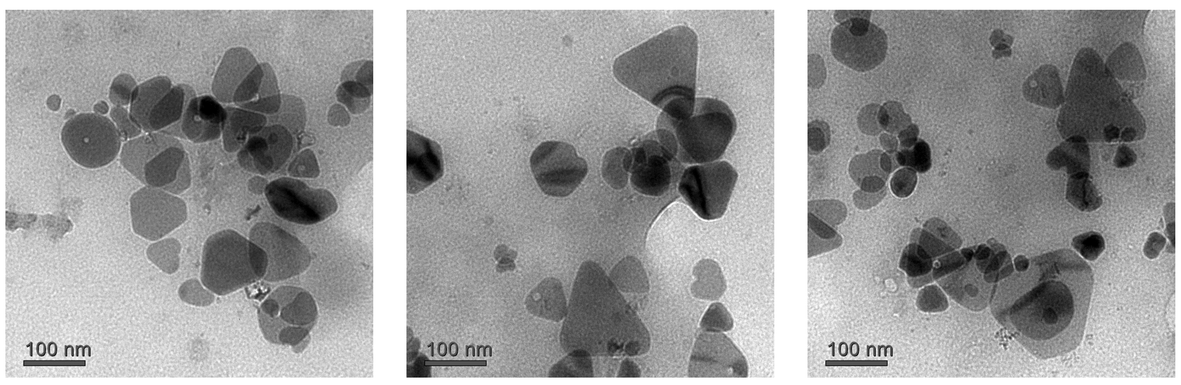


Figure 1: TEM images of aspheric copper nanoparticles.

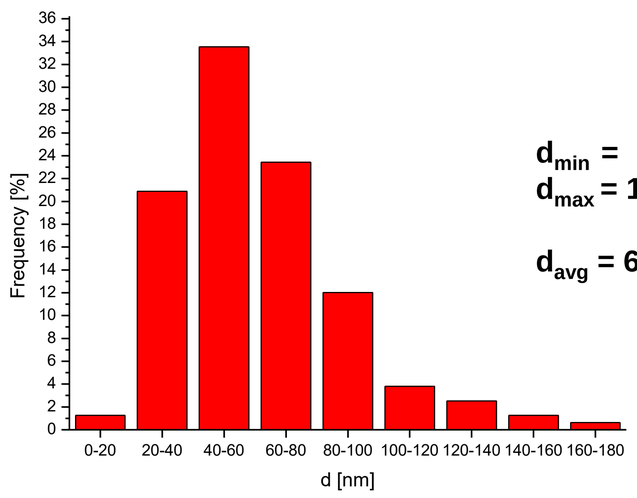
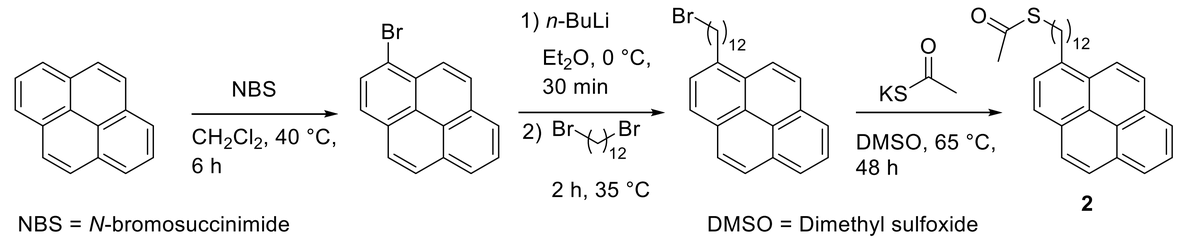


Figure 2: Particle size distribution from TEM of aspheric copper nanoparticles.

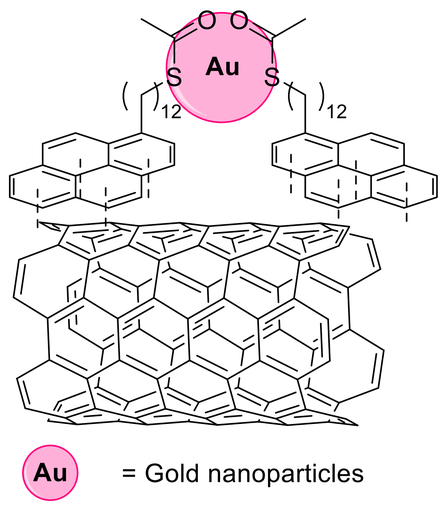
Summary

- **Preparation of aspheric copper nanoparticles by thermal decomposition of copper(I) carboxylates**
  → Different shape (spheres, triangles, hexagons and ellipses) & size (19 to 162 nm size)
- **Template supported synthesis of gold nanoparticles by thermal decomposition of copper(I) carboxylates in the presence of $HAuCl_4$**
  → Different shape (spheres, triangles and ellipses) & size (13 to 75 nm size)
- **Pyrene derivatives with long alkyl chains and terminal thioacetate functionalization can be used for linkage of nanoparticles to CNTs by *π-π*-stacking and also enable debundling of CNT agglomerates.**

Linkage to CNTs



*Scheme 2: Synthesis protocol for the preparation of functionalized pyrene derivative **2**.*



Scheme 3: Representation of linkage between the pyrene derivative and CNTs by π-π-stacking.

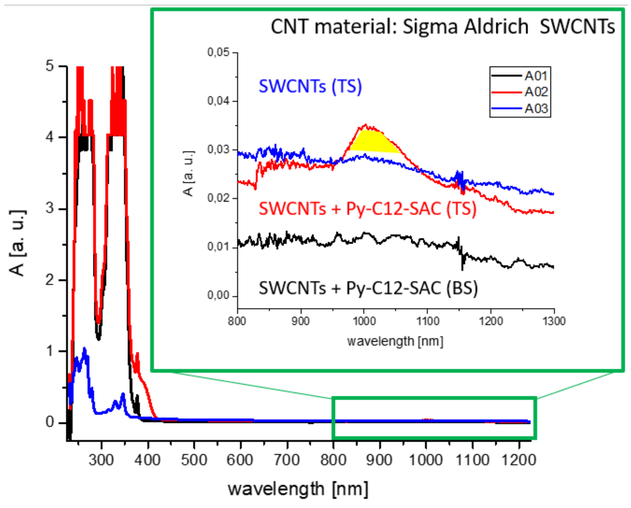
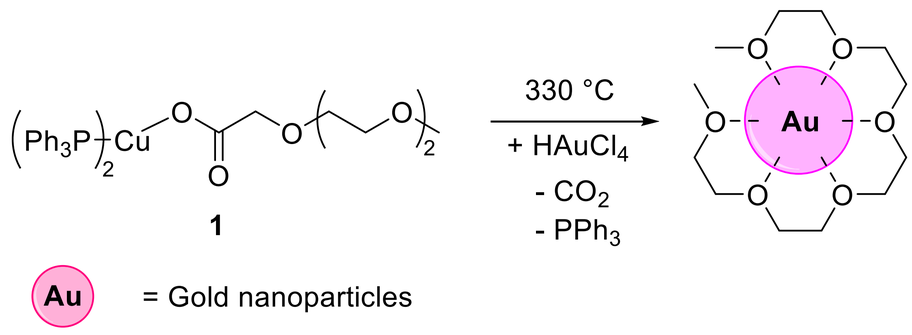


*Figure 3: UV-Vis-NIR spectrum of pyrene derivative **2** and SWCNTs.*

Preparation of gold nanoparticles



*Scheme 4: Synthesis of gold nanoparticles by thermolysis of copper(I) carboxylate **1** in the presence of $HAuCl_4$.*

- Preparation of gold nanoparticles by thermal decomposition of compound **1** in *1*-hexadecylamine in the presence of $HAuCl_4$ (precursor and Au^{3+} concentration: 10 mM, ϑ = 330 °C, t = 10 min)

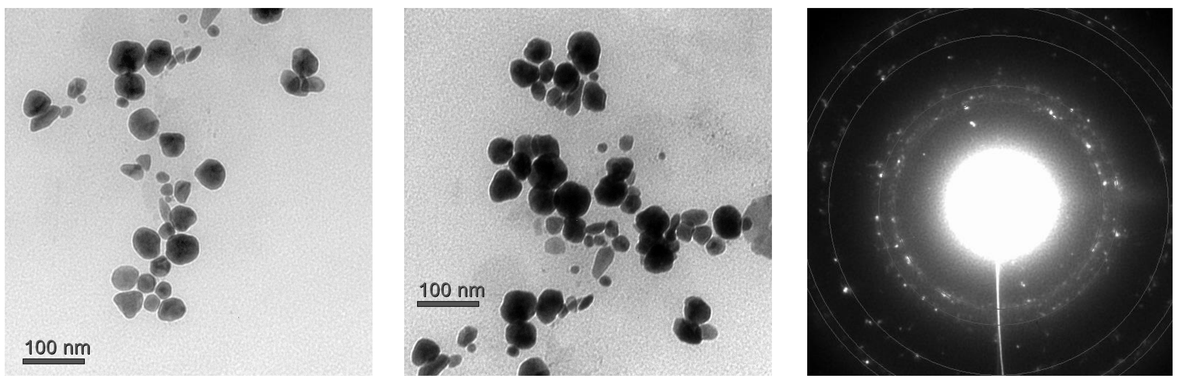


Figure 4: TEM images (left, center) and electron diffraction pattern (right) of gold nanoparticles.

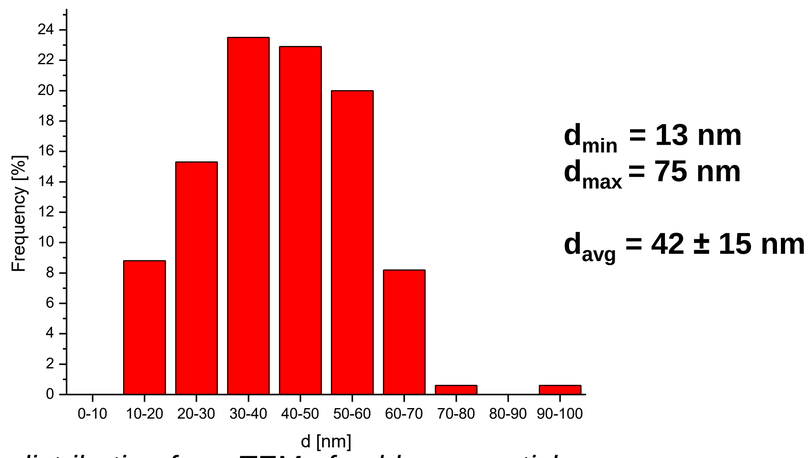


Figure 5: Particle size distribution from TEM of gold nanoparticles.

Acknowledgments

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References

[1] I. Capek, *Adv. Colloid Interface Sci.* **2009**, *150*, 63–89. [2] K. Yoshimura, C. Langhammer, B. Dam, *Mat. Res. Soc. Bull.* **2013**, *38*, 495–503. [3] R. D. Rodriguez, T. Blaudeck, J. Kalbacova, E. Sheremet, S. Schulze, D. Adner, S. Hermann, M. Hietschold, H. Lang, S. E. Schulz, D. R. T. Zahn, *RSC Adv.* **2016**, *6*, 15753–15758. [4] C.J. Zhou, S. Wang, J.L. Sun, N. Wie, L.-J. Yang, Z.Y. Zhang, J.H. Liao, L.-M. Peng, *Appl. Phys. Lett.* **2013**, *102*, 1031021–1031025. [5] T. Blaudeck, D. Adner, S. Hermann, H. Lang, T. Gessner, S. E. Schulz, *Microelectron. Eng.* **2015**, *137*, 135–140. [6] S. Mubeen, T. Zhang, B.Y. Yoo, M.A. Deshusses, N.V. Myung, *J. Phys. Chem. C* **2007**, *111*, 6321–6327. [7] D. Adner, M. Korb, S. Schulze, M. Hietschold, H. Lang, *Chem. Commun.* **2013**, *49*, 6855–6857.