Integration of covalent and non-covalent functionalized SWCNTs in FETs

A. Kossmann[1], D. Adner[1], S. Schulze[2], T. Blaudeck[3,4], S. Hermann[3,4], C. Tegenkamp[2], S. E. Schulz[3,4] and H. Lang[1]*

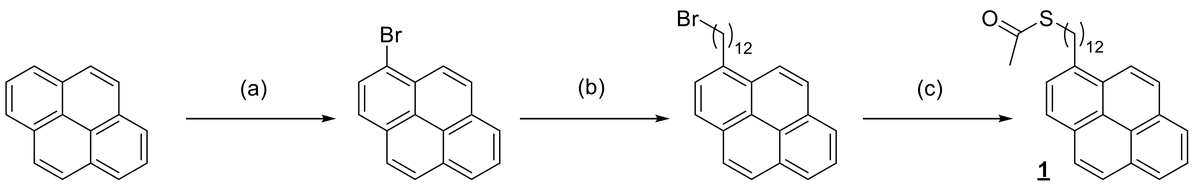
[1]Technische Universität Chemnitz, Institute of Chemistry, Inorganic Chemistry, Germany
[2]Technische Universität Chemnitz, Institute of Physics, Solid Surfaces Analysis, Germany
[3]Technische Universität Chemnitz, Center for Microtechnologies (ZfM), Germany
[4]Fraunhofer Institute for Electronic Nano Systems (ENAS), Chemnitz, Germany

Motivation

Metal nanoparticles (M-NPs) attached to carbon-based nanostructured materials enable new nanoelectronic solutions for, e.g. energy storage, such as fuel cells or supercapacitors [1] and also for chemical, biochemical [1,2,4] and optical sensors [2,3,4]. A requirement for electronic sensors is the design of a versatile nanoelectronic transducer. In the ideal case, such a component can be functionalized with nanoscopic building blocks in a modular manner that allows selective response and tuning of the sensitivity of the device. Nanoelectronic field-effect transistors (FETs) using individualized single-walled carbon nanotubes (SWCNTs) have been proposed as a FET channel material [5,6].

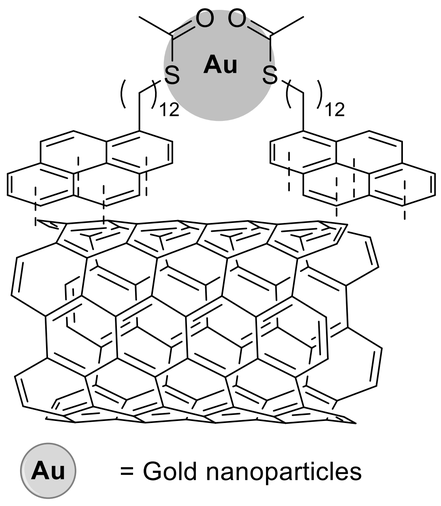
Recently, we presented a scalable on-chip functionalization approach for SWCNTs between palladium electrodes in the geometry of a FET with preformed Au-NPs based on the Hirsch-functionalization of SWCNTs [5]. This method is wafer-level compatible and comprises two stages of flow chemistry. In a new chemical approach, we propose the deposition of dispersed SWCNTs by using alkylthioate functionalized pyrene which allows selective attachment of M-NPs.

Non-covalent functionalization



(a) *N*-bromosuccinimide, CH_2Cl_2, 6 h, RT; (b) *n*-BuLi, Et_2O, 30 min, 0°C; Br-$(CH_2)_{12}$-Br, 2 h, 35 °C; (c) Potassium thioacetate, Me_2SO, 48 h, 60 °C

***Scheme 1**: Synthesis protocol for the preparation of **1**.*



Au = Gold nanoparticles

***Scheme 2**: Schematic representation of a possible linkage between **1** and CNTs by π-π-stacking.*

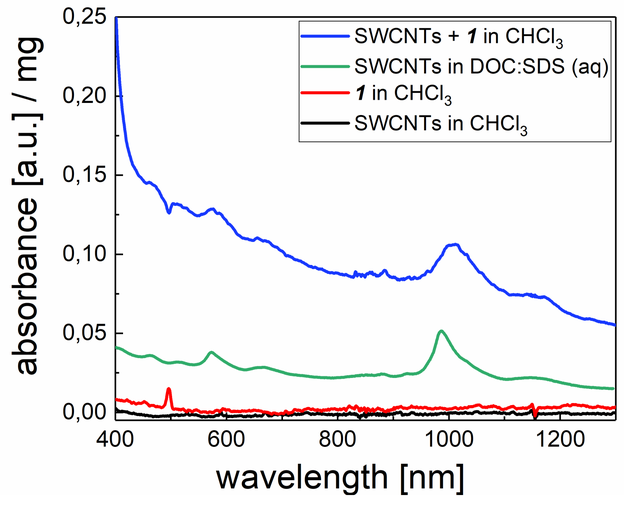


***Figure 1**: UV-Vis/NIR spectra of **1** and SWCNTs (Reference system: SWCNTs dispersed with SDS).*

- Preparation of SWCNT dispersions (Sigma Aldrich *(6,5)*-SWCNTs, 80 % purity) in a $CHCl_3$-solution of **1**
- No debundling of SWCNTs by using ultrasonic bath sonication (BS, *Fig. 1*, blue line)
- Absorption band at 1000 nm for tip sonication (TS, *Fig. 1*, green line) → Indication of CNT debundling (S_{11} transition of semiconducting SWCNTs)

Summary & Outlook

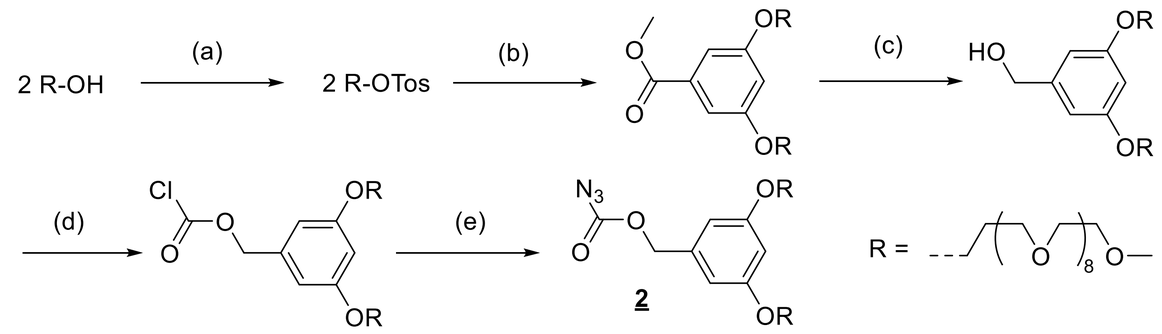
Summary:

- **Debundling of SWCNTs in organic solvents supported by alkylthioate functionalized pyrene through non-covalent interaction**
  → Access to stable SWCNTs dispersions for integration in FETs
- **Au-NP functionalization of SWCNTs by usage of azidobenzyl formiates**
  → Interaction of Au-NPs with ethylene glycol chains
- **Formation of hexagonal gold agglomerates by redoxchemical reactions in water dispersion of Cu-NPs**
  → Scalable synthesis of hexagonal Au nanostructures

Outlook:

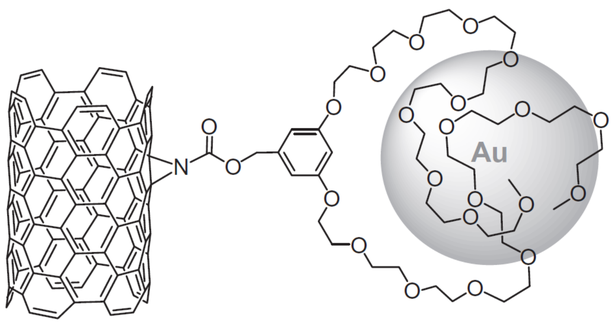
- **Selective attachment of Au-NPs by usage of alkylthioate functionalized pyrene on SWCNTs and integration on wafer-level**
  → Take advantage of thiophilic behavior of Au-NPs

Covalent functionalization



(a) TosCl, NaOH, H_2O/THF, 25 °C, 2 h; (b) *3,5*-dihydroxybenzoic acid methyl ester, K_2CO_3, Me_2CO, 56 °C, 72 h; (c) $LiAlH_4$, THF, 25 °C, 15 h; (d) Cl_2CO, toluene, 25 °C, 3 h; (e) NaN_3, THF, 25 °C, 96 h.

***Scheme 3**: Synthesis protocol for the preparation of **2** [5,7].*



***Scheme 4**: Schematic representation of linkage between **2** and CNTs by [2+1]-cycloaddition [7].*

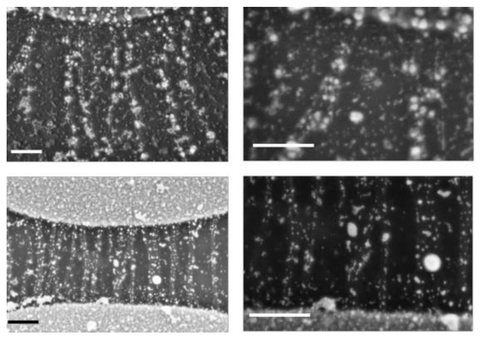
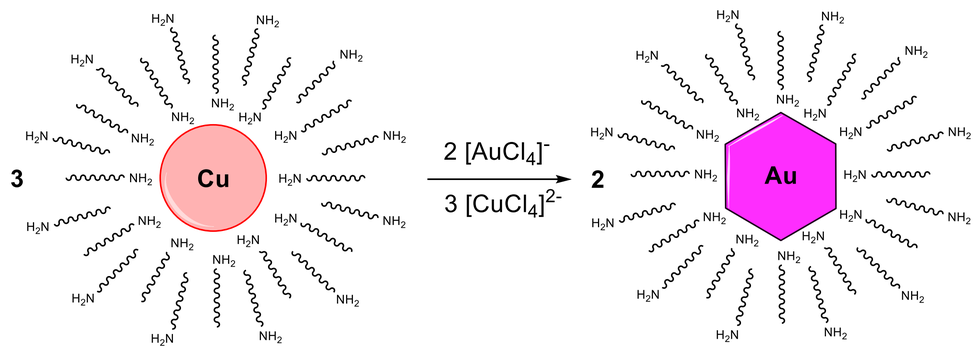


***Figure 2**: REM images (scale bar: 200 nm) of Au-NP decorated CNTs functionalized at 23 °C (top) and 40 °C (bottom) [7].*

- No resolution of SWCNTs and ethylene glycol chains by REM (Fig. 2)
- Linear alignment of Au-NPs is observable at 23 °C and 40 °C → Indication of successful CNT functionalization
- Partial agglomeration of Au-NPs

Synthesis of hexagonal gold nanoparticles



***Scheme 5**: Representation of gold nanoparticle formation in aqueous Cu-NP dispersion.*

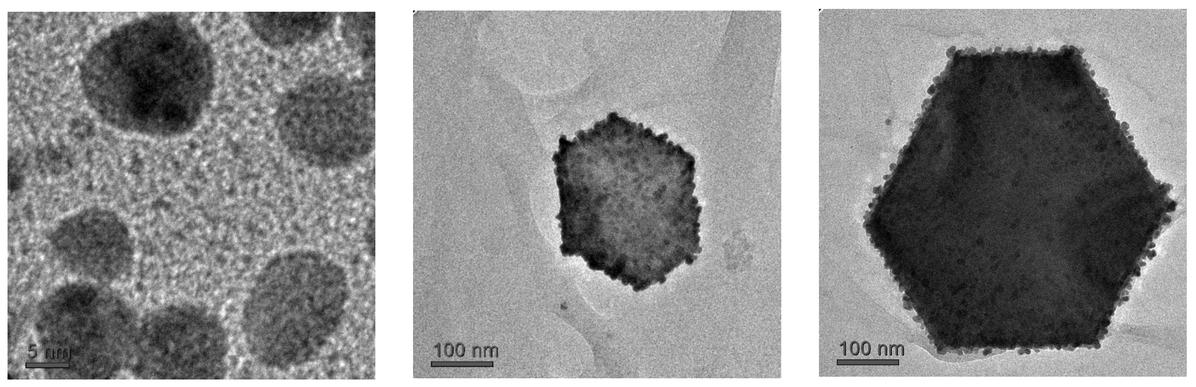


***Figure 3**: Au-NPs synthesized by redox-chemistry in aqueous Cu-NP dispersions at various Au^{3+} concentrations (left to right: 0.05/0.50/5.00 mmol·L^{-1}).*

- Formation of spherical Au-NPs at lower Au^{3+} concentrations (5–10 nm)
- Hexagonal agglomerates from Au-NPs at higher Au^{3+} concentrations (150–500 nm)

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