Gold Nanoparticles with Covalently Attached Polymer Chains[**]

Stefan Nuß, Henrik Böttcher, Hellmuth Wurm,
and Manfred L. Hallensleben*

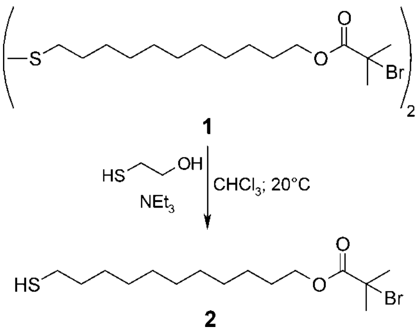
Over recent years thiol-stabilized gold nanoparticles (Au-NPs) have attracted increasing interest[1] because of their potential in divergent fields such as nanoelectronics and -optics as well as DNA diagnostics.[2]

Alkanethiolate-stabilized Au-NPs of narrow size distribution are easy to synthesize and of relatively high stability.[3] The shell of these organic–inorganic hybrid materials can be functionalized by site-exchange reactions thus allowing the controlled change of the properties of the particles and the adjustment of the surface for further reactions.[4]

Au-NPs modified with polymer chains covalently bound to the surface by a "grafting from" reaction have been described in only two examples.[5] "Grafting from" by the use of the so-called "living"/controlled radical polymerization in accord with the mechanism of atom transfer radical polymerization (ATRP), which was first described in 1995,[6] is promising but has not been applied to Au-NPs yet. It has, however, been shown that ATRP is a suitable method for preparing polymer layers covalently bound to the surface of different solid materials and even for the generation of block copolymer grafts.[7]

A polymer shell is interesting for the control of surface properties, for an increase in chemical and/or thermal stability, and, if functional monomers are used, for the provision of functional groups in the bound polymer chains for further modification. Herein we show that ATR grafting from polymerization is an efficient synthetic route to attach polymer chains covalently to nanoparticles.

The $C_{12}S$ residues on dodecanethiol-stabilized Au-NPs are replaced by the thiol **2** by means of site-exchange reactions. Compound **2** is synthesized starting from the known compound **1**[7d] (Scheme 1) by cleavage of the disulfide bond. Compound **2** contains a thiol group, which serves as an anchor to bind **2** to the surface of the Au-NPs, and a α-bromoester moiety, which is suitable as an initiator group for the ATR Polymerization. Thus the site-exchange reaction leads to Au-NPs functionalized on the surface with initiator moieties for a "living"/controlled radical polymerization. The ratio of **2** to surface-bound dodecanethiol can be varied within narrow ranges and be confirmed by ^{1}H NMR spectroscopy. In combination with thermogravimetic analysis (TGA) measurements the number of initiator groups per mg Au-NP can be calculated, which allows the preselection of a defined initiator/catalyst ratio for the polymerization.



Scheme 1. Synthesis of thiol initiator **2**. This molecule can be attached to a gold surface by the thiol functionality and contains a α-bromoester moiety as an initiator unit for ATR polymerization.

ATR polymerization starting from initiator-modified Au-NPs was carried out with Cu^IBr/Me_6tren (Me_6tren = tris(2-dimethylaminoethyl)amine) (Figure 1). This catalytic system allows the polymerization of *n*-butylacrylate at room temperature.[8] Dynamic processes at the surface such as desorption of initiator molecules or thermal initiation of the monomer are suppressed to a large extent under these reaction conditions. The organic part of this new organic–inorganic hybrid can be as much as 90% w/w (TGA) after the polymerization. The ^{1}H NMR spectrum and glass transition temperature of the surface-bound polymer chains (determined by dynamic difference calorimetry) are almost identical with those obtained from investigations on free poly(*n*-butylacrylate).

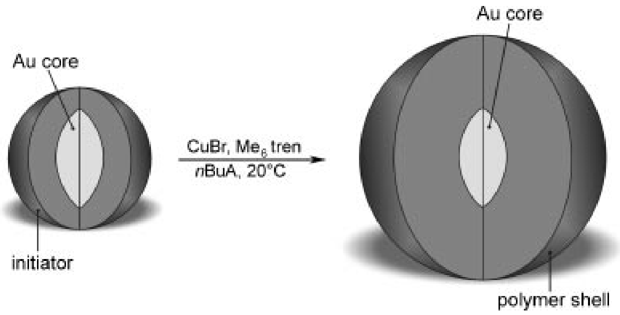


Figure 1. Generation of a polymer shell around the Au-NPs; *n*BuA = *n*-butylacrylate.

Transmission electron microscopy (TEM) investigations reveal that the Au-NPs are still individual particles after the graft polymerization (Figure 2). The size distribution of the Au-NPs is unaffected by the grafting process; the average diameter is about 2 nm.

The high energy impact during TEM measurements almost completely destroys the attached polymer. However, scanning force microscopy (SFM) investigations convincingly demonstrate the successful grafting of the Au-NPs (Figure 3). The gold cores are depicted by the white protrusions in the SFM images; the polymer chains are shown in gray. Figures 3a

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[*] Prof. Dr. M. L. Hallensleben, Dipl.-Chem. S. Nuß,
Dipl.-Chem. H. Böttcher, Dr. H. Wurm
Institut für Makromolekulare Chemie
Universität Hannover
Am Kleinen Felde 30, 30167 Hannover (Germany)
Fax: (+49) 511-762-4996
E-mail: hallensleben@mbox.imc.uni-hannover.de

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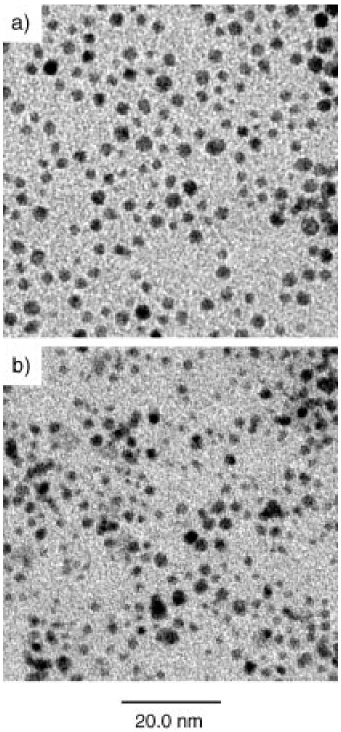

Figure 2. TEM images of a) dodecanethiol-stabilized, and b) polymer-coated Au-NPs.

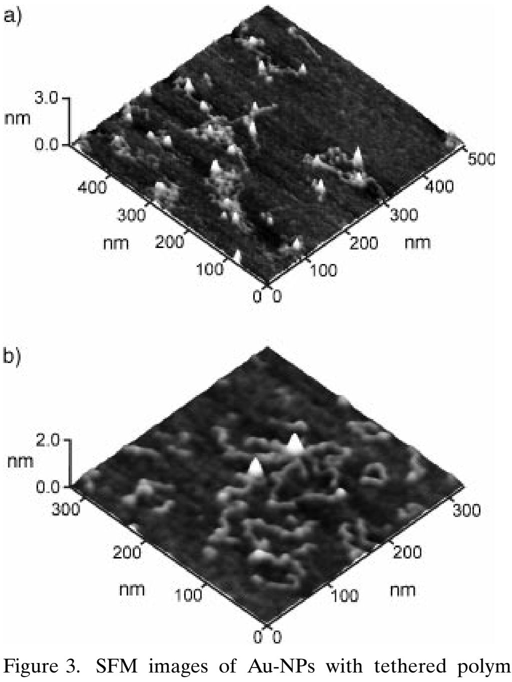

Figure 3. SFM images of Au-NPs with tethered polymer chains spin-casted onto mica from a) $CHCl_3$, and b) THF solution.

and b clearly demonstrate that the polymer chains are bound to the gold cores, which confirms the success of the ATR grafting-from polymerization. Figure 3b also shows that different numbers of chains of varying lengths are attached to the Au-NP and that even unbound chains are present.

The different number of chains on the surface may be the result of the statistical site-exchange reaction of dodecanethiol against compound **2**, but may also be caused by the size distribution of the Au-NP itself. This finding from the SFM investigation is in good agreement with GPC results (Figure 4). The polymer-grafted Au-NPs give a relatively broad distribution (chromatogram A, polydispersity index (PDI) = 1.63) compared to that for the cleaved polymer (chromatogram B, PDI = 1.25), showing that the single polymer chains undergo controlled growth also on the surface. The monomodal distribution of trace A can be regarded as proof for the interpretation that the "free" polymer chains in Figure 3b are a result of the spin-casting process during the preparation of the SFM probes.

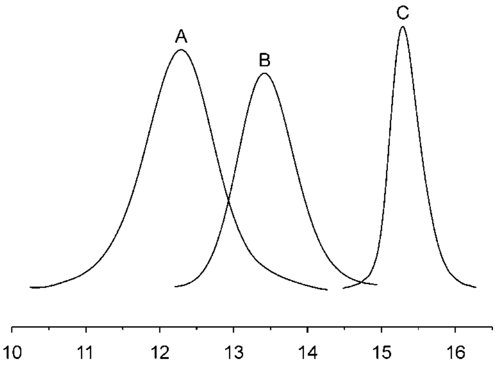

Figure 4. GP chromatograms of A) polymer-grafted Au-NP ($\bar{M}_n$ = 206000 g mol^{-1}, PDI = 1.63), B) cleaved polymer ($\bar{M}_n$ = 75000 g mol^{-1}, PDI = 1.25), and C) dodecanethiol-stabilized Au-NPs ($\bar{M}_n$ = 4700 g mol^{-1}, PDI = 1.14); molecular mass relative to polystyrene standard; V_e = elution volume.

The GPC traces can be compared only qualitatively, since although calibrations were carried out with a polystyrene standard, the chemical structure of the materials is different. However, the polymer-grafted Au-NPs (chromatogram A) show a much shorter elution time than the dodecanethiol-stabilized Au-NPs (chromatogram C) and the detached polymer chains (chromatogram B). This is due to an increase of the hydrodynamic radii and of the molecular weight as a result of the grafting reaction. From the molecular weights one can estimate an average degree of grafting of three polymer chains per gold core, which is in full agreement with the results of SFM investigations (see Figure 3).

We have shown that Au-NPs can be grafted with polymer chains by the ATRP mechanism in a simple sequence of reactions. No free polymer chains are formed during the grafting reaction and the Au-NPs remain unchanged in size and size distribution.

Experimental Section

Dodecanethiol-protected gold colloids were prepared according to the method in reference [3]. The synthesis was carried out at room temperature with a threefold molar excess of dodecanethiol to tetrachloroauric acid. Compound **1** was synthesized according to the method in reference [7d].

2: Thioethanol (12 mL, 0.14 mol) and triethylamine (0.6 mL, 4.3 mmol) were added to a solution of **1** (1.69 g, 2.4 mmol) in degassed chloroform (40 mL). After stirring overnight at room temperature the solution was extracted repeatedly with water, dried over sodium sulfate, concentrated in vacuo, and filtered over silica gel with petroleum ether/ethyl acetate (20:1 v/v) to give **2** as a colorless liquid; yield: 1.02 g (2.9 mmol, 60 %). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.17$ (t, $J = 7$ Hz, 2H; $OCOCH_2$), 2.52 (q, $J = 7$ Hz, 2H; $HSCH_2$), 1.94 (s, 6H; CH_3), 1.70 – 1.57 (m, 4H; CH_2), 1.40 – 1.24 (m, 14H; CH_2); ^{13}C NMR ($CDCl_3$, APT, 100 MHz): $\delta = 171.72$, 66.12, 55.99, 34.01, 30.78, 29.43, 29.42, 29.41, 29.12, 29.03, 28.34, 28.32, 25.75, 24.62; MS: m/z (%): 354 (2) [M^+], 87 (100).

Site-exchange process: C_{12} colloid (385 mg) and thiol initiator **2** (69 mg, 0.2 mmol) were dissolved in toluene (190 mL) and stirred for 24 h at room temperature. The solution was evaporated to dryness in vacuo and the crude product intensively washed with ethanol to give initiator-functionalized Au-NPs (390 mg).

Tris(2-dimethylaminoethyl)amine (Me_6Tren) was synthesized according to the method given in reference [9].

ATR polymerization and cleavage of the grafted polymer chains: Initiator-functionalized Au-NPs (66 mg) were dissolved in toluene (1 mL) and n-butylacrylate (2 mL, 14.0 mmol), and CuBr (3.8 mg, 26 µmol) and Me_6Tren (7.0 mg, 30 µmol) were dissolved in n-butylacrylate (3 mL, 20.9 mmol). Both solutions were degassed with argon and combined. After the mixture had been stirred for 24 h at room temperature, the product precipitated in methanol, yielding a dark brown, viscous substance. The supernatant liquid was decanted, the residue was repeatedly washed with methanol and dried in vacuo to give the product (527 mg). The polymer-coated Au-NPs (38 mg) were dissolved in toluene (20 mL), and n-butanol (2 mL) and p-toluenesulfonic acid (20 mg) were added. Heating overnight under reflux, filtration over silica gel, and drying in vacuo gave the cleaved polymer.

TEM images were recorded on a Philips CM-300 microscope working at 300 kV. SFM measurements were performed on a Digital Instruments Multimode SPM with a Nanoscope IIIa controller in the tapping mode. The resonance frequency dependent on the Si-cantilever ($K \cong 42$ N m^{-1}, Nanosensors) was set to about 330 kHz. Samples were prepared by spin casting of a dilute $CHCl_3$ or THF solution with a concentration of 0.01 mg mL^{-1} at 2000 rpm on mica as a substrate. GP chromatograms were recorded on a Spectra-Physics SP 8100 (polystyrene calibration). Thermogravimetric measurements were carried out on a Netzsch TG 209.

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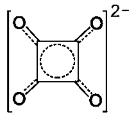
Solvothermal Synthesis of a 24-Nuclear, Cube-Shaped Squarato-oxovanadium(IV) Framework: $[N(nBu)_4]_8[V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}]$

Johann Spandl, Irene Brüdgam, and Hans Hartl*

Polyoxometalates with organic oxygen donor groups show an impressive structural and electronic diversity. As a result, extensive synthetic research has been carried out in this field in the past few years, with the aim of synthesizing compounds with interesting magnetic or catalytic properties,[1] as well as precursors for metal oxides of high purity.[2] Notable successes were achieved in synthesizing polyoxo-alkoxo-metalates with chelating trisalkoxy ligands.[3] Polyoxometalate fragments that are otherwise usually unstable can be stabilized by using suitable, highly symmetrical polydentate coligands such as oxalate and squarate. The high symmetry of the bis-bidentate squarato group **1**, as well as the suitable spacing of the four oxygen donor atoms favors the interconnection of small polyoxo-alkoxo-vanadate units to highly symmetric supermolecular polyoxometalate derivatives. Until now, suprisingly few squarato-oxovanadium compounds have been structurally characterized. In the anions $[V_2O_2(C_4O_4)_2(OH)(H_2O)_3]^-$,[4, 5] $[V_2O_3(C_4O_4)_2(H_2O)_3]^-$,[5] $[V_2O_2(C_4O_4)_2F_4]^{4-}$,[4] $[V_3O_3(C_4O_4)_3F_4]^{4-}$,[6] and $[V_4O_6(C_4O_4)_5(H_2O)_4]^{4-}$,[5] the squarato group is a μ_2-bridging ligand; only in the polymeric compounds $^2_\infty[V(OH)(C_4O_4)]$ and $^3_\infty[V(OH)(C_4O_4)(H_2O)]$,[7] is the squarato ligand found to be μ_3- and μ_4-bridging, respectively.[7] Herein, we report the solvothermal synthesis and structure of the cube-shaped 24-nuclear oxo-alkoxo-squarato complex $[N(nBu)_4]_8[V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}]$ (**2**) (Figure 1), which is an astonishing example of a compound with μ_4-bridged oxo-alkoxo-vanadium fragments.



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Vanadium(V) oxytrialkoxides prove to be auspicious starting materials for the synthesis of new polyoxometalates.[8] In

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[*] Prof. Dr. H. Hartl, Dipl.-Chem. J. Spandl, I. Brüdgam
Freie Universität Berlin
Institut für Chemie/Anorganische und Analytische Chemie
Fabeckstrasse 34 – 36, 14195 Berlin (Germany)
Fax: (+49) 30-83854003
E-mail: hartl@chemie.fu-berlin.de